

**Near-Infrared Emission in Low-Dimensional Halide
Perovskite Derivatives: Cs_2MX_6 (M: Mo/W/Sn; X:
Cl/Br) and $(\text{C}_8\text{H}_{12}\text{N})_2\text{PbBr}_4$ with Doping**

विद्या वाचस्पति की उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis

*submitted in partial fulfilment of the requirements of the degree of
Doctor of Philosophy*

द्वारा / By

बर्णाली मण्डल /

Barnali Mondal

पंजीकरण सं. / Registration No.: 20193681

शोध प्रबंध मार्गदर्शक / Thesis Guide:

प्रोफेसर अंशुमन नाग / Prof. Angshuman Nag



भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे
Indian Institute of Science Education and Research Pune

November 2024

Dedicated to

My Elder Sister Gouri Mondal,

Parents Atul Kumar Mondal and Shova Rani Mondal...

Declaration by Student

Name of Student: Barnali Mondal

Reg. No.: 20193681

Thesis Supervisor(s): Prof. Angshuman Nag

Department: Chemistry

Date of joining program: 1st August, 2019.

Date of Pre-Synopsis Seminar: September, 2024.

Title of Thesis: Near-Infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs_2MX_6 (M: Mo/W/Sn; X: Cl/Br) and $(\text{C}_8\text{H}_{12}\text{N})_2\text{PbBr}_4$ with Doping

I declare that this written submission represents my idea in my own words and where others' ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this thesis is the original work done by me under the guidance of

Dr./Prof. Angshuman Nag

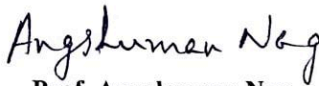
Date: 15th November, 2024

Signature of the student Barnali Mondal

Certificate

I certify that the work incorporated in the thesis entitled “**Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs_2MX_6 (M: Mo/W/Sn; X: Cl/Br) and $(\text{C}_8\text{H}_{12}\text{N})_2\text{PbBr}_4$ with Doping**” submitted by Ms. Barnali Mondal was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institute. For the completion of the thesis, a few results are taken from collaborators after their permissions and are clearly mentioned in the thesis.

Dated: 15th November, 2024.


Prof. Angshuman Nag

(Research Guide)

Acknowledgements

The last stair of my student life, has undoubtedly become one of the most important parts so far. The prolonged five years' journey couldn't constrain it to a professional boundary, rather it transformed me to a reflective individual, better thinker, an altogether better version of my own-self. For being so, there are people, places, objects, I am indebted to, my heartfelt gratitude remains for each and everyone.

The first person who comes to my mind is Prof. Angshuman Nag, my PhD guide. The first conversation with him about owning up the work and ideas, being empowered and sincere, importantly being disciplined in the unstructured PhD-life: touched my heart. His profound knowledge and teaching, his effort and dedication towards research always encouraged me. His approach and critical thinking towards a problem or an experimental result have directed me to shape the thought-process. His frequent sayings to me of not being rush, to seat, be steady and think: are the pivotal to me for becoming a thinker and an individual researcher. I wish to gain the magical power of writing and story-telling he possesses; that transforms an ordinary piece of writing attractive and a good read. I am blessed to be his student, would always cherish those thoughtful conversations, and advices towards life and science for becoming a better researcher as well as a good and responsible human being. In a word, depending on various factors, my PhD might be considered as moderate to good, but irrespective of every parameter, he is the best guide I could ever have for my PhD journey.

I am grateful to my research advisory committee members, Prof. Pramod Pillai from IISER Pune and Prof. Santosh K. Haram, from University of Pune; their valuable comments and suggestions during the meetings were helpful for proceeding our work.

I would heartily thank my collaborators: Prof. Prasenjit Ghosh and Ms. Riteeka Tanwar of IISER Pune; and Prof. K.V. Adarsh and Dr. Ajay K. Poonia of IISER Bhopal. On the one hand, working with them gave me the opportunity to come across with new ideas and learn new things, one the other hand their work completed our findings. I am truly grateful to Prof. DD Sarma, IISc Bangalore; Prof. Pralay Santra, CeNS, Bangalore for valuable discussion and help during data analysis. I cordially thank Prof. Sameer Sapra, IIT Delhi for providing the infrastructure of XPS experiment. I also acknowledge SAIF at IIT Bombay for ICP-MS measurements.

I am thankful to IISER Pune for giving me an opportunity to carry out my doctoral studies here along with the outstanding research facility, and academic environment. Thanks to all the faculty members of Department of Chemistry, IISER Pune. I am grateful to the labs of Prof. Nirmalya Ballav, Prof. Pramod Pillai, Prof. Pankaj Mandal, Prof. Partha Hazra and Prof. Sujit K. Ghosh for the co-operation in performing various experiments. Thanks to the non-teaching staffs and instrument operators of IISER Pune; with their active support and assistance, many things become easier, even without our knowledge.

I would thank the funding agencies (DST, DST-FIST, SERB India) of my research. I heartily acknowledge Council of Scientific & Industrial Research (CSIR) for providing me the fellowship.

I am grateful and blessed with my Physics teacher Goutam Ghosh, love for science originated with your outstanding teaching in my school-life. I wish I could meet you once again, thanks a lot Sir. I acknowledge my Physical Chemistry teachers: Prof. Arijit De, Krishnath College and Prof. Mohammad Qureshi, Prof. Uttam Manna, Dibyangana Di and Nirban Dada from IIT Guwahati, for educating the basic chemistry and research that help to pursue my doctoral studies.

I heartily extend my gratitude to the past and present lab-mates for teaching, assistance and wonderful working environment. Thank you, Anuraj Bhaiya, Vikash Bhaiya for guiding with experimental techniques in the very beginning. Thanks a lot, Athunya for being in my starting. I am truly grateful to Tariq Bhaiya, your way of teaching and problem solving is commendable, learnt a lot. Thanks Rayanda, for those insightful discussions in the first half of my PhD, learnt many concepts from you. I am grateful to Habib Bhaiya, starting from minute details of carrying out experiments to the analysis; I'm enriched with your guidance. Thanks a lot Parikshit, I had never thought of a co-operative lab-mate like you. Thank you Sajid, your hard-work is inspirational. Thanks to Taniya and Srijita for those endless tea-times with scientific and non-scientific discussions, those outings or dinner parties: would remain in my memories. Urmila, Animesh, Ajinkya, Manmayuri, Ujjal, Vijay and everyone: thank you and best wishes for your future. From research to cooking to travelling, I enjoyed a lot and would love to be in touch with you all.

Specially thanks to Tea and MDP, the front garden of main building for energizing me to think and write. The songs: Sedin Dujone, Ferari Mon, Bhalobashar Morshum, Aarambh, Unstoppable and Photograph for boosting me every time I need; I am beholden to their creators.

Whole-heartedly thankful to all my friends: Sneha, Chumki, Julekha, Nilufa, Ankita, Moinul, Modasser and Preeti. Though I never had a circle, but wherever I go, school or college or IIT or IISER, I always have these dots who complete my journey.

Grateful to Ritam Pal for providing me invaluable time and assistance whenever I need.

Last and undoubtedly the most, I am indebted to my family: my elder-sister Gouri Mondal and parents Atul Kumar Mondal and Shova Rani Mondal. My Didi has been a witness of my small to smaller achievements and failures. She has the patience and intellectual mind to listen all my concerns: doesn't matter whether it's chemical or personal; she always has the best possible solution. I am blessed to have my parents with their open-minded thinking and unwavering support and belief on me. Without my family nothing could have been ever possible.

.

List of abbreviations

0D: Zero dimensional

1D: One dimensional

2D: Two dimensional

3D: Three dimensional

AFM: Atomic force microscopy

DOS: Density of states

PEA: Phenylethylammonium

EPR: Electron paramagnetic resonance

EQE: External quantum efficiency

FA: Formamidinium

FIR: Far-infrared

FESEM: Field emission scanning electron microscopy

FWHM: Full width at half maximum

GOD: Goodness of fit

ICP-MS: Inductively coupled plasma mass spectroscopy

IRF: Instrument response function

IR: Infrared

JDOS: Joint density of states

LED: Light-emitting diode

MA: Methylammonium

MIR: Mid-infrared

NIR: Near-infrared

PCE: Power conversion efficiency

List of abbreviations

- pc-LED:** Phosphor converted LED
- PDOS:** Projected density of states
- PL:** Photoluminescence
- PLE:** Photoluminescence excitation
- PL QY:** Photoluminescence quantum yield
- PMMA:** poly (methyl methacrylate)
- PTFE:** Polytetrafluoroethylene
- PXRD:** Powder X-ray diffraction
- SAED:** Selected area electron diffraction
- SOC:** Spin-orbit coupling
- STE:** Self-trapped exciton
- SCXRD:** Single-crystal X-ray diffraction
- SWIR:** Short-wave infrared
- TCSPC:** Time-correlated single-photon counting
- TEM:** Transmission electron microscopy
- TGA:** Thermogravimetric analysis
- UV:** Ultraviolet
- VIS:** Visible
- XPS:** X-ray photoelectron spectroscopy

Lead halide perovskites (APbX_3 , A: monovalent cation, X: Cl, Br, I) have been widely explored since last fifteen years due to their extraordinary optoelectronic properties. If the connectivity between metal-halide octahedra is lifted, the electronic dimensionality reduces successively from 3D to 2D, 1D and 0D. This thesis focuses on such low-dimensional (0D and 2D) perovskite derivatives which emit in the near-infrared (NIR) region (900 – 1300 nm) through $d-d$ and $f-f$ electronic transitions.

NIR emissions have several applications like non-invasive bio-imaging, food processing and therapy. NIR emissions are typically obtained from epitaxially grown III-V semiconductors, or colloidal PbS nanocrystals, or filament-based incandescent lamps. They have their own pros and cons. An alternative approach is to develop NIR emitting phosphors by Cr^{3+} ($d-d$ transition) or lanthanides ($f-f$ transitions) in halide or oxide-based hosts. But in that case, the excitation is high energy UV/blue light leading to thermalization losses. To address the issue, in chapter 2, we have shown all inorganic 0D perovskite derivatives Cs_2MX_6 (M: Mo/W; X: Cl/Br) have both excitation and emission in far-red (787 nm) and NIR (986 nm) region. By employing low-temperature (8 K) photoluminescence study, we found out that the excitation and emission happens through vibronically coupled $d-d$ transitions. Then in order to dilute the NIR luminescent centers reducing concentration quenching, we doped W^{4+} / Mo^{4+} in another 0D system Cs_2SnCl_6 , as discussed in Chapter 3. As a proof of concept, phosphor-converted light emitting diodes (pc-LED) were fabricated by coating these NIR phosphors on both 730 nm and 400 nm commercial LED chips. In Chapter 4, we explored the possibility of colloidal synthesis of Yb^{3+} doped phenylethylammonium lead bromide ($\text{PEA}_2\text{PbBr}_4$) 2D perovskites showing NIR emission at 997 nm because of $f-f$ transition of Yb^{3+} .

This thesis includes five chapters, all are briefly discussed in this section.

Chapter 1: Introduction

This chapter discusses briefly about the research direction of this thesis and explains the motivation to pursue that direction. It starts with the introduction of three-dimensional (3D) halide perovskite structure and how the structure evolves from 3D to lower dimensional perovskites (2D, 1D and 0D). After that, it discusses about near-infrared (NIR) emission and the ranges. What are the importances of NIR emission and NIR LEDs, that is presented here, along with the illustration of a few important terms of LEDs. The possible NIR emitters starting from III-V semiconductors to

quantum dots, the alternatives doped halide perovskites and transition metal complexes are presented here. Though the traditional semiconductors are efficient and commercialized, but they include expensive synthesis methodology. On the other, the doped perovskites require high energy excitation and suffers from thermalization loss. Therefore, to address that, we present another alternative set of 0D perovskite derivatives Cs_2MX_6 ($\text{M} = \text{Mo/W}$, $\text{X} = \text{Cl/Br}$) which can absorb (787 nm) and emit (986 nm) in the NIR region through $d-d$ transition of M^{4+} ; this fact results decreased Stokes shift and a 730 nm pc-LED with less input power. Moreover, we introduce M^{4+} doping in a 0D host Cs_2SnCl_6 to decrease concentration quenching; we also explore the possible solution processibility of 2D perovskites. All these are presented in the scope of the thesis.

Chapter 2: Vibronically coupled near-infrared (NIR) emission and excitation from $d-d$ transitions of Cs_2MX_6 ($\text{M} = \text{Mo/W}$, $\text{X} = \text{Cl/Br}$)

Near-infrared emission in halide perovskite or perovskite derivatives is obtained from transition metal ion or lanthanide dopants. In most of the cases, high energy UV or blue excitation energy is used to obtain NIR emission. This causes a large thermalization loss. Therefore, getting a phosphor with excitation and emission from same pair of electronic states with reduced Stokes shift and thermalization loss is highly desired. In this chapter, we have shown Cs_2MX_6 ($\text{M} = \text{Mo/W}$, $\text{X} = \text{Cl/Br}$) can effectively absorb (787 nm) and emit (986 nm) in the NIR region through $d-d$ transitions of M^{4+} (d^2) involving same pair of electronic states. Tanabe-Sugano diagram of d^2 electronic configuration in octahedral environment explains the excitation and emission processes. Low temperature photoluminescence (at 8 K) data show unique mirror-image like vibronically coupled excitation – emission spectra which is rare for an undoped compound. Moreover, phosphor-converted light emitting diode (pc-LED) has been fabricated with far-red (730 nm) LED chip which can be operated at a nominal voltage of 1.8 V. This kind of pc-LEDs with lower input power can be important for obtaining higher wall-plug efficiency in NIR pc-LED applications.

Chapter 3A: W^{4+} -doped Cs_2SnCl_6 for near-infrared emission

Vacancy-ordered double perovskites like Cs_2SnCl_6 , offers enhanced stability and non-toxicity compared to traditional lead halide perovskites, though they typically exhibit poor optical properties. This chapter explores the incorporation of dopant into the octahedral coordination sites of this material to achieve near-infrared (NIR) emission. Specifically, we study the doping of W^{4+}

ions into Cs_2SnCl_6 lattice, utilizing a modified hydrothermal synthesis method. All four doped compounds show significant sub-band absorption due to $d-d$ transitions of W^{4+} ($5d^2$) in octahedral crystal field and NIR emission in 800 – 1300 nm with maxima at 965 nm. The optimized doping percentage was 3.3%, further enhancement resulted concentration quenching, while the optimized doping minimizes this effect, therefore enhances emission intensity and radiative recombination. Temperature-dependent photoluminescence studies (7-300 K) elucidate the excitation and emission mechanisms. Additionally, a proof-of-concept phosphor-converted light-emitting diode (pc-LED) with 400 nm LED using the optimized W^{4+} -doped Cs_2SnCl_6 has been fabricated. The pc-LED produces reasonable NIR output power of 10.3 mW at 401 mA, implying the potential application possibility of these materials in solid-state lighting.

Chapter 3B: Mo^{4+} -doped Cs_2SnCl_6 for near-infrared emission

The second part of chapter 3 explores Mo^{4+} doping in octahedral lattice site of Cs_2SnCl_6 . Unlike W^{4+} doping, Mo^{4+} -doped Cs_2SnCl_6 crystals show dual emissions covering the entire NIR-I and NIR-II regions (peaks are at 980 nm and 1350 nm respectively). Both the peaks have different lifetimes at room temperature which suggest that they might have different emission origins. Moreover, low temperature PL at 7 K shows multiple splitting of both the peaks. However, we could not understand the actual reason of this usual PL though the result is well reproducible.

Chapter 4: Yb^{3+} -doped (phenylethylammonium) $_2\text{PbBr}_4$ 2D layered hybrid perovskite for NIR emission

Doping metal ions into two-dimensional layered hybrid perovskites has gained researchers' interest due to the unique structure and optical properties of 2D perovskites. The repeating quantum well formation with lead-halide octahedra and insulating organic cations, result quantum and dielectric confinement effects that might influence exciton-dopant interactions. Though Mn^{2+} -doping in these materials was well-explored, but NIR emission was not achieved in 2D perovskites. This chapter studies the doping of lanthanide ion, Yb^{3+} , in 2D layered hybrid perovskite $(\text{PEA})_2\text{PbBr}_4$ to achieve near-infrared emission. Micrometer-sized crystals of undoped and Yb^{3+} -doped $(\text{PEA})_2\text{PbBr}_4$ have been synthesized. Moreover, ~ 3.5 nm thick nanoplatelets are also obtained after sonication. Both undoped and doped samples show sharp excitonic absorption at 407 nm and emission at 414 nm. For doped ones, a part of excited energy is transferred to Yb^{3+} .

Notably, de-excitation of this leads to the NIR emission at ~ 997 nm, attributed to $f-f$ transition of Yb^{3+} dopant.

Chapter 5: Thesis summary and future outlook

This chapter summarizes the whole thesis work mentioning its key aspects and based on that along with the prior literatures, it discusses about some possibilities which could be pursued in the future.

Table of contents

Chapter 1: Introduction

1.1 Halide perovskites	1
1.2 Dimensionality reduction in halide perovskites	2
1.3 What is near-infrared (NIR) emission?	3
1.4 Advantages of NIR emission (900 – 1300 nm) and NIR phosphor converted LEDs (pc-LEDs)	3
1.5 Important parameters of NIR LEDs	4
1.6 What are the NIR emission origins?	7
1.6.1 Incandescent lamp	7
1.6.2 Organic NIR LEDs	8
1.6.3 Colloidal quantum dots and commercialized semiconductors	8
1.7 An alternate way-out with metal ion dopants	11
1.8 NIR emissive d^2 transition metal complexes	12
1.9 Drawbacks of metal complexes	15
1.10 Scope of the thesis	16
1.11 References	18

Chapter 2: Vibronically coupled near-infrared (NIR) emission and excitation from $d-d$ transitions of Cs_2MX_6 ($M = Mo/W$, $X = Cl/Br$)

Abstract	29
Graphical abstract	29
2.1 Introduction	30
2.2 Methodology section	31
2.2.1 Chemicals	31
2.2.2 Synthesis of Cs_2MoCl_6 single crystals	31
2.2.3 Synthesis of Cs_2MoBr_6 single crystals	32
2.2.4 Synthesis of Cs_2WCl_6 single crystals	32
2.2.5 Structural characterization	32
2.2.6 Optical properties	33
2.2.7 Phosphor converted light emitting diodes (pc-LEDs)	33

Table of contents

2.3 Results and discussion.....	34
2.3.1 Synthesis, structure and stability of Cs ₂ MoCl ₆	34
2.3.2 Optical characterization and Tanabe-Sugano diagram of Cs ₂ MoCl ₆	41
2.3.3 Vibronically coupled electronic excitation and emission and structural rigidity of Cs ₂ MoCl ₆	46
2.3.4 Variation of crystal field in Cs ₂ MoCl ₆ , Cs ₂ MoBr ₆ and Cs ₂ WCl ₆	53
2.3.5 NIR pc-LEDs.....	63
2.4 Conclusions.....	66
2.5 References.....	67

Chapter 3A: W⁴⁺-doped Cs₂SnCl₆ for near-infrared emission

Abstract.....	74
Graphical abstract.....	74
3A.1 Introduction.....	75
3A.2 Methodology section.....	76
3A.2.1 Chemicals.....	76
3A.2.2 Synthesis of undoped Cs ₂ SnCl ₆ crystals.....	76
3A.2.3 Synthesis of W ⁴⁺ doped Cs ₂ SnCl ₆ crystals.....	76
3A.2.4 Synthesis of Cs ₂ WCl ₆ crystals.....	76
3A.2.5 Structural and optical characterization.....	77
3A.2.6 Phosphor converted light emitting diodes (pc-LEDs).....	78
3A.3 Results and discussion.....	78
3A.3.1 Synthesis and structural characterization.....	78
3A.3.2 Room-temperature optical properties.....	84
3A.3.3 Temperature-dependent photoluminescence and structure.....	86
3A.3.4 NIR pc-LED of 3.3% W ⁴⁺ doped Cs ₂ SnCl ₆	91
3A.4 Conclusions.....	93
3A.5 References.....	94

Table of contents

Chapter 3B: Mo⁴⁺-doped Cs₂SnCl₆ for near-infrared emission

Abstract	99
Graphical abstract.....	99
3B.1 Introduction	100
3B.2 Methodology section	100
3B.2.1 Chemicals.....	100
3B.2.2 Synthesis of undoped Cs ₂ SnCl ₆ crystals.....	101
3B.2.3 Synthesis of Mo ⁴⁺ doped Cs ₂ SnCl ₆ crystals.....	101
3B.2.4 Structural and optical characterization.....	101
3B.3 Results and discussion	102
3B.3.1 Synthesis and structural characterization.....	102
3B.3.2 Room-temperature optical properties	103
3B.3.3 Temperature-dependent photoluminescence and structure	104
3B.4 Conclusions	107
3B.5 References	107

Chapter 4: Yb³⁺-doped (Phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

Abstract	110
Graphical abstract.....	110
4.1 Introduction	111
4.2 Methodology section.....	112
4.2.1 Chemicals	112
4.2.2 Synthesis of undoped (PEA) ₂ PbBr ₄	112
4.2.3 Synthesis of Yb ³⁺ - doped (PEA) ₂ PbBr ₄	113
4.2.4 Structural characterization and optical properties	113
4.3 Results and discussion.....	114
4.3.1 Synthesis, structure, morphology	114
4.3.2 Optical properties	117

Table of contents

4.4 Conclusions	121
4.5 References	122
 <i>Chapter 5: Thesis summary and future outlook</i>	
5.1 Thesis summary	128
5.2 Future outlook	130
5.3 References	131
 <i>List of publications</i>	 133
<i>Copyrights and permissions</i>	134

Chapter 1

Introduction

1.1 Halide perovskites

The materials having a crystal structure same as CsTiO_3 ¹ and general formula AMX_3 with A being a monovalent cation, M a divalent cation and X as halide anion are termed as halide perovskites. Figure 1.1 shows the schematic representation of a typical three-dimensional (3D) halide perovskite structure, where, larger green sphere is monovalent A-site cation, grey spheres are divalent M-site cations and smaller blue spheres are halide anions X. The M-X-M network in the corner-shared metal halide octahedra forms a three-dimensional connectivity and cuboctahedron void that accommodates the A-site cation.²⁻⁴

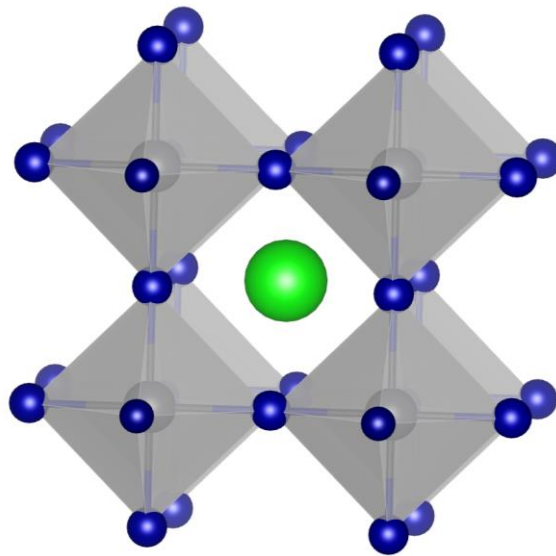


Figure 1.1: Schematic representation of a halide perovskite structure having generalized formula AMX_3 . Here, the larger green sphere is monovalent A-site cation, grey spheres with octahedral coordination are divalent M-site cations and the smaller blue spheres are halide anions termed as X.

Victor Moritz Goldschmidt found that the stability of a perovskite structure is dependent on the ionic radii of the constituent ions. The formation probability of such structure is determined by Goldschmidt tolerance factor (t).

$$t = \frac{r_A + r_X}{\sqrt{2}(r_M + r_X)} \dots\dots (1)$$

Here, r_A and r_M are the ionic radii of cations A^+ and M^{2+} respectively and r_X is the ionic radius of anion X^- .^{5, 6} Stable cubic perovskites should have the tolerance factor (t) range of 0.8-1.0.^{2, 7} In

case of halide perovskites, with respect to size, A-site cations like cesium (Cs^+), methylammonium (CH_3NH_3^+ ; MA^+), formamidinium ($\text{NH}_2\text{CHNH}_2^+$; FA^+); B-site cations like Pb^{2+} , Sn^{2+} , Ge^{2+} etc. result the formation of stable perovskite structure maintaining appropriate ‘ t ’ value.^{3, 7, 8}

Among these, lead halide perovskites (APbX_3) are the most widely explored for their extraordinary properties, like, solution processibility, high absorption coefficient (in order of $\sim 10^5 \text{ cm}^{-1}$), near unity photoluminescence quantum yield (PL QY), narrow full width half maxima (FWHM) and high charge carrier mobility.^{4, 9-11} Depending on those, they have become potential optoelectronic device materials in last 15 years.³ For example, lead halide perovskite-based solar cell has achieved power conversion efficiency (PCE) of $\sim 26\%$.¹² Besides, the external quantum efficiency (EQE) of perovskite-based light-emitting diodes (LED) has crossed 20% making them interesting for lighting applications.¹³

1.2 Dimensionality reduction in halide perovskites

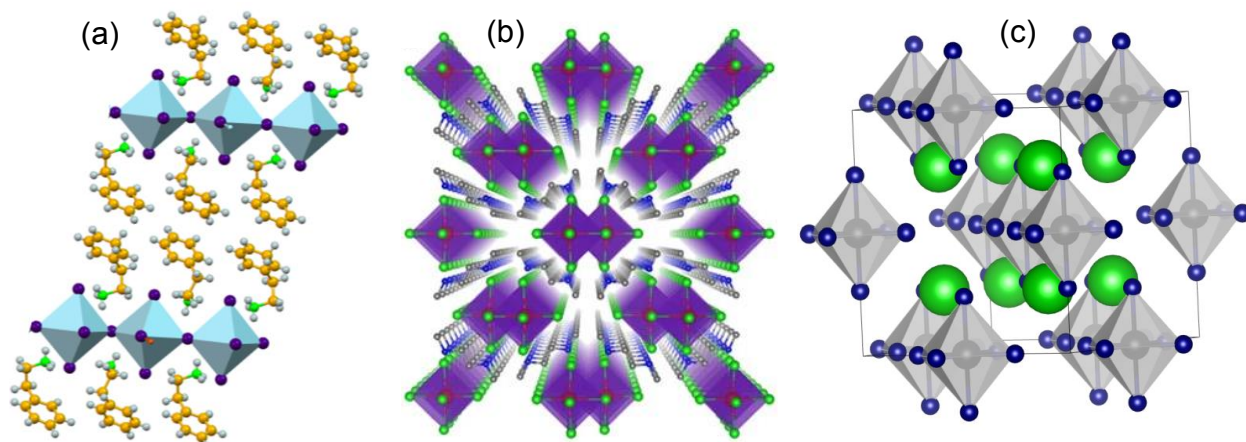


Figure 1.2: Schematic representation of (a) 2D, (b) 1D and (c) 0D perovskite derivative structures. The figure (b) is reprinted from reference [14] with permission. Copyright © 2017, The Author(s).

Now, if the connectivity between metal-halide octahedra is lifted, structural dimensionality reduces from 3D to 2D, 1D and 0D. These are called lower-dimensional (2D, 1D and 0D) perovskites¹⁴⁻¹⁶ or perovskite derivatives.¹⁷ Figure 1.2 represents them schematically, however, morphologically all of these are three-dimensional. Here, it is important to note that the dimensionality refers to electronic dimensionality or in terms of electronic connectivity. For example, if the octahedra are connected through two dimensions then the electrons can travel in a plane, but vertically they are

disconnected by large A-site cations, these compounds are called 2D. If the connectivity is in one dimension, then they are called 1D. And when all the octahedra are separated from each other; then the compounds are sometimes called electronically 0D (Figure 1.2c). Though the extended polyhedral connectivity is absent, but the electronic band structure shows little dispersion of the bands resulting weak interaction between the octahedra. Therefore, more precisely these are called vacancy-ordered perovskite/ double-perovskite structure.^{17, 18}

Unlike 3D, the lower-dimensional compounds offer some intriguing properties, like quantum and dielectric confinement in bulk compounds, high exciton binding energy, exciton self-trapping etc.¹⁴⁻¹⁶ Therefore, their photo-physical properties are quite interesting to look into. But due to reduced dimensionality, the charge transport property is poor which is not favorable for optoelectronic applications. This thesis focuses on such low-dimensional (0D and 2D) perovskite derivatives which emit in the near-infrared (NIR) region (900 – 1300 nm) through *d-d* and *f-f* electronic transitions.

1.3 What is near-infrared (NIR) emission?

The infrared (IR) region lies in the range of around 700 – 10⁶ nm (0.7 – 1000 μ m) of electromagnetic radiation. The whole IR region is divided into several parts. Initial part is known as near-infrared (NIR) region. This part is sub-divided: the ranges of ~700 – 900 nm is termed as NIR-I and ~1000 – 1700 nm is termed as NIR-II region.¹⁹⁻²¹ Another more generalized term is short-wave infrared (SWIR) region. This usually includes the range of 1000 – 2500 nm of the electromagnetic radiation.²² The latter value varies since it corresponds to the band gap of InGaAs detectors, the most important detectors in this particular range. After that, the range of 3000 – 5000 nm is referred as mid-wave infrared region (MWIR) and 8000 – 12000 nm is known as long-wave infrared region (LWIR). Rest of the part belongs to far-wave infrared (FWIR) region, this FWIR overlaps with the terahertz range. In this thesis, mostly the range of 900 – 1300 nm would be discussed and is termed as NIR region.

1.4 Advantages of NIR emission (900 – 1300 nm) and NIR phosphor converted LEDs (pc-LEDs)

Why should we be interested in NIR emission of 900 – 1300 nm? There are certain organic bonds, namely, O-H, N-H and C-H. The 2nd overtones of the stretching frequency of these bonds lie in the

above mentioned NIR region (shown in Table 1.1). Therefore, they can absorb NIR radiation of this region efficiently. Utilizing this property, the materials which emit light in this range can be applied to detect the freshness of a fruit or food item. For instance, Saikia et al. has explained that NIR emissive (peaking around 1000 nm) phosphors can be used to inspect the freshness of fruits.²³ Under the illumination of NIR light, by NIR camera, they observed darker spots on an apple where rotting has started in comparison with the other apple. Whereas in visible light, that part was looking absolutely fine. This is because of more water content of the rotten part, where greater amount of NIR light has been absorbed and eventually this has created the contrast to the NIR detector.

Table 1.1: Some organic bonds with 2nd overtone (in nm) of their stretching frequency (in cm⁻¹)

Organic bonds	Stretching frequency (cm ⁻¹)	2 nd overtone (nm)
O-H	3500	995
N-H	3300	1000
C-H	3000	1100

Besides, comparatively lower wavelength of 900 – 1300 nm NIR light has less amount of heat energy, this causes minimal damage of living cell, therefore, this is used in non-invasive bioimaging.^{24, 25} Another important application of this lower wavelength NIR light is pain relief therapy or wound healing process.^{26, 27} Exposure of body to low level of IR light, gentle penetration and going to deeper layers of body promote vasodilatory effect, i.e., increase blood flow and oxygen flow in affected area and sooth the pain. This aids body's natural recovery process. Also, the NIR therapy is useful for arthritis, muscle pain and post injury recovery.

1.5 Important parameters of NIR LEDs

All the above-mentioned applications need NIR light emitting sources. Though the sources like sunlight, tungsten-halogen lamps are there, one important NIR emitting source is NIR LED. Now, electroluminescent NIR LEDs mostly have lower efficiency and/or higher cost in comparison with

the visible ones.²⁸⁻³² One alternate strategy is to fabricate all inorganic NIR pc-LEDs, where the phosphor is some inorganic material doped with NIR emitter.³³⁻³⁸ This phosphor is coated on top of a commercial LED chip and after providing the bias to the LED chip, both the emissions from LED and phosphor are obtained. Schematic representation of a typical pc-LED is shown in Figure 1.3.

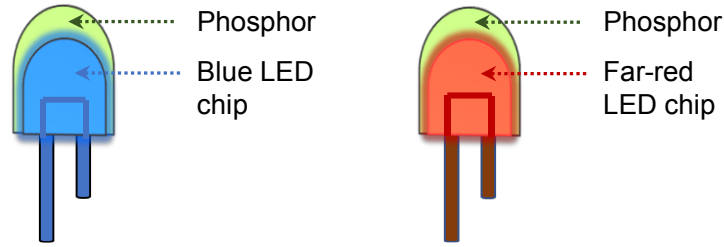


Figure 1.3: Schematic representation of pc-LEDs with different LED chips. Here, blue and red colored LEDs imply the commercial chips emitting at 400 nm and 730 nm respectively. Outer green colored layer signifies the coated phosphor on top of the chips.

For understanding the performance of these pc-LEDs, we need to learn a few parameters. They explain and evaluate the working efficiency of a pc-LED. Those are discussed below:

(1) Radiant flux or radiant power: Radiant flux is the total amount of radiant energy (i.e., electromagnetic radiation or energy) that is emitted from a source per unit time.^{34, 39} This is usually expressed in W, μ W or mW units and is considered as an important parameter for evaluating the performance of LED devices.

(2) Luminous flux or luminous power and luminous intensity: Luminous flux is defined as the total power of visible light that is emitted from a source per unit time. But this differs from radiant flux which includes whole electromagnetic radiation. On the other hand, luminous flux considers human eye sensitivity to various wavelength.^{40, 41} For instance, a green light achieves higher luminous power than that of a blue light of same power. Because human eye perceives green light better than blue light. The SI (International System of Units) unit of luminous flux is lumen (lm).

One lm is the luminous power that is generated from a source that emits one candela (cd) of luminous intensity over a solid angle of one steradian (sr).⁴⁰

$$\text{lm} = \text{cd} \times \text{sr} \quad \dots\dots(2)$$

Luminous intensity (SI unit cd) is not to be confused with luminous flux. Luminous flux is the total perceived power in all directions whereas luminous intensity is the perceived power per unit steradian. A lamp with 1 lm bulb and the light focused evenly into a 1 sr beam, would have the luminous intensity of 1 cd. If the optics are changed to concentrate the beam to $\frac{1}{2}$ sr, the luminous intensity would be 2 cd, i.e., narrower, brighter with same 1 lm of luminous flux. Candela comes from the Latin word ‘candle’. A common candle emits around 1 cd of luminous intensity.⁴⁰

(3) Luminous efficacy or power efficiency: Luminous efficacy is the measure of how well a source produces visible light, i.e., how well input power is being converted to electromagnetic radiation and detected by eye.

$$\text{Luminous efficacy} = \frac{\text{Luminous flux}}{\text{Input power}} \quad \dots\dots(3)^{42}$$

SI unit is lm/W, i.e., it is the luminous flux produced by a light source per unit input power.⁴³⁻⁴⁶

This is a key parameter signifying that increased luminous efficacy implies lower energy consumption for a given source.

(4) Photoluminescence quantum efficiency: This is a significant property of the phosphor, but not the quantum efficiency of LED. It is of two types: internal quantum efficiency (η_{int}) and external quantum efficiency (η_{ext}). These are defined as:^{44, 47}

$$\eta_{int} = \frac{N_{em}}{N_{abs}} \quad \dots\dots(4)$$

$$\eta_{ext} = \frac{N_{em}}{N_{in}} \quad \dots\dots(5)$$

$$\eta_{ext} = \eta_{int} \times A \quad \dots\dots(6)$$

Where, N_{em} , N_{abs} and N_{in} are number of emitted, absorbed and incident photon respectively.

$$A = \text{absorbed fraction} = \frac{N_{abs}}{N_{in}}$$

(5) Optical-to-optical and electricity-to-optical power conversion efficiencies: These are two significant parameters for measuring the efficiency of a pc-LED. Optical-to-optical power conversion efficiency (η_{o-o}) is the measure of how much power of a commercial LED is being converted to phosphor’s output power. That is⁴⁸

$$\eta_{O-O} = \frac{\text{Output power of phosphor's emission}}{\text{Output power of commercial LED}} \quad \dots\dots(7)$$

Electricity-to-optical power conversion efficiency (η_{El-O}) is the measure of how much electricity is being converted to the output power of phosphor's emission.⁴⁸⁻⁵⁰

$$\eta_{El-O} = \frac{\text{Output power of phosphor's emission}}{\text{Input power of pc-LED}} \quad \dots\dots(8)$$

Electricity-to-optical power conversion efficiency (η_{El-O}) is also termed as wall-plug efficiency,⁴⁷ and considered as an important parameter to know pc-LED's efficiency.⁵¹

1.6 What are the NIR emission origins?

There are several kinds of NIR emitters for application in various fields. They are divided into three parts and briefly discussed in this section.

1.6.1 Incandescent lamp

Among the incandescent lamps, the modern version of **tungsten-halogen lamp** is the important one. 85% of its emitted light falls in IR region, rest are UV and visible (Figure 1.4).⁵²

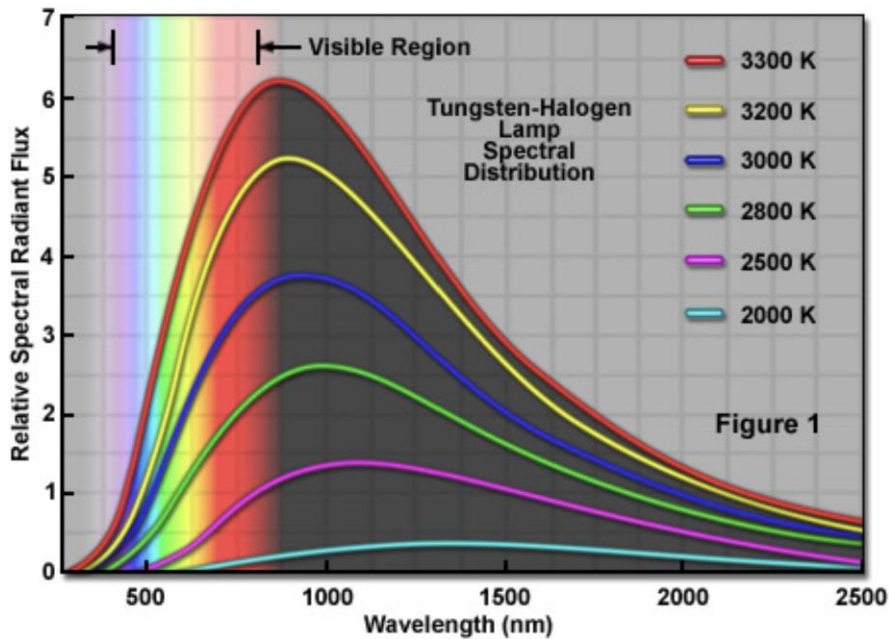


Figure 1.4: Spectral distribution of tungsten-halogen lamp. The figure is adapted from reference [52] with permission. Copyright, The Author.

Tungsten-halogen lamp is used in optical microscopy. Moreover, in UV-Vis-NIR spectrophotometer, it is used as an infrared light source. These are comparatively inexpensive with reasonably good illumination and easy to replace. But the high input power makes it energy inefficient. Besides, though halogen regenerative cycle is there, but due to excessive heating effect, thinner part of the filament breaks and lifetime comes to an end.

1.6.2 Organic NIR LEDs

There are many organic molecules which emit in the NIR region and works as active material in organic LED. For example, many of the Pt complex-based organic NIR LEDs are there, but the EQE could not exceed 10% for above 800 nm emission.⁵³⁻⁵⁵ Besides, some host-guest based organic systems are there; with ~9.6% EQE for emission at 800 nm.⁵⁶ But as of now, there are no electroluminescent organic NIR LED which emit significantly beyond 1000 nm with an EQE > 1%.⁵⁷ The reason behind this inefficiency is emission quenching due to vibrational overtone of C-H, O-H etc. bonds and non-radiative recombination due to smaller energy gap and aggregation of the organic molecules.

1.6.3 Colloidal quantum dots and commercialized semiconductors

Another important class of NIR emitters is colloidal quantum dots. There are II-VI, III-V, IV-VI nanocrystals, for example HgTe, InAs, PbS etc.⁵⁸ They have tunable NIR emission depending on their crystallite size due to quantum confinement effect, i.e., increase of band gap with decreasing size if the nanocrystals' size is smaller than their exciton Bohr diameter. Among the vast numbers of these traditional semiconducting nanocrystals, a few representative compounds emitting in the NIR region are discussed here. For instance, in 1999, Rogach et al has reported the first synthesis of colloidal HgTe nanocrystals (II-VI semiconductor) having emission in the range of 800 – 1400 nm with a maximum around 1080 nm.⁵⁹ The nanocrystals have appreciably high photoluminescence quantum yield of 48%. In 2000, Banin and coworker has grown several II-VI and III-V shells (for example, CdSe, ZnSe, GaAs, InP) on InAs core nanocrystals and obtained better photostability and stability towards oxidation.⁶⁰ For InAs/CdSe and InAs/ZnSe core/shell nanocrystals, PLQY of ~20% has been obtained for emission peaking at ~1300 nm. PbS nanocrystals have been first synthesized with water-based routes in 1985.^{61, 62} Though, they have size quantization property, but are non-emissive. Later, PbS nanocrystals have been synthesized in

diverse media and methods. In 2003, Scholes and co-worker have synthesized colloidal PbS nanocrystals following the synthesis of cadmium chalcogenides⁶³ and PbSe⁶⁴ utilizing hot-injection method.⁶⁵ Interestingly the nanocrystals have size tunable bandgap from 800 – 1800 nm due to strong quantum confinement effect (Figure 1.5a). Band-edge absorption and emission of nanocrystals with 6.5 nm diameter are shown in Figure 1.5b. The emission has a quantum yield of ~20% in comparison with the standard NIR dye IR125.

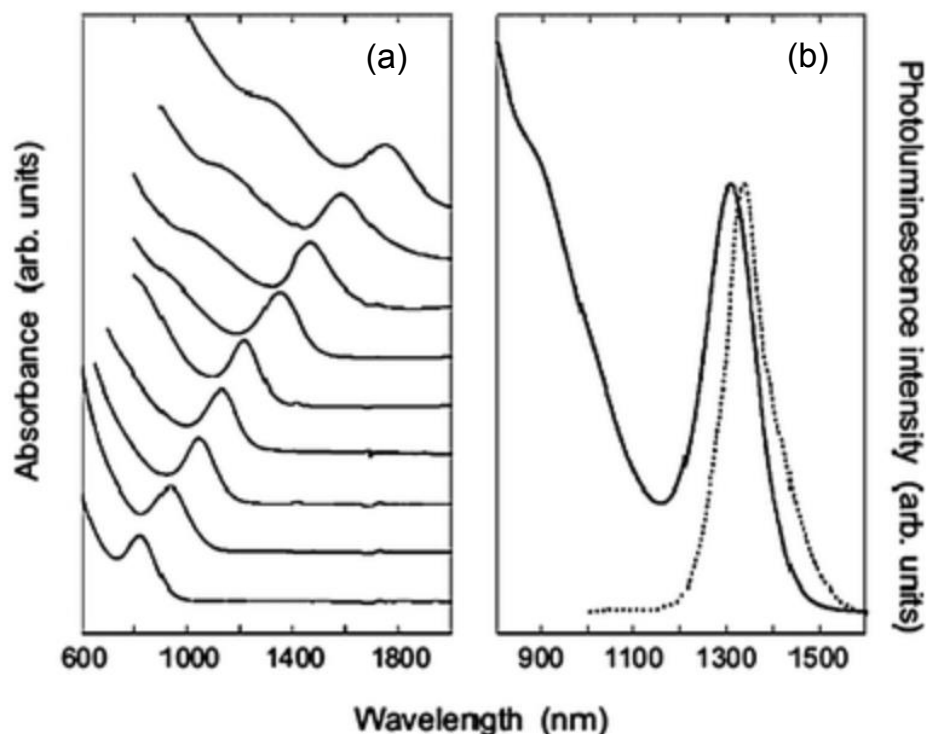


Figure 1.5: Optical properties of PbS nanocrystals at room temperature. (a) Absorption spectra due to tunable sizes leading to tunable band gaps in the range of 800 – 1800 nm. (b) Excitonic absorption and emission of nanocrystals with diameter 6.5 nm. Adapted from reference [65] with permission. Copyright © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

PbS nanocrystals have been synthesized with various media like organic and aqueous solvents, glass, polymer matrices; and different approaches such as hot-injection, sonochemical and electrochemical techniques.⁶⁶⁻⁷⁰ However, with respect to size distribution and emission properties, hot-injection method has produced the best quality lead chalcogenide nanocrystalline materials.⁵⁸

After these important earlier works, the field has evolved a lot with time. Recently, Talapin and coworkers have developed a novel high temperature molten salt colloidal synthesis method for the synthesis of colloidal III-V semiconductor which were inaccessible earlier.⁷¹ For example, GaAs

nanocrystals synthesized in this method in the temperature between 425 – 500 °C has tunable emission with the peak positions of 617 – 759 nm. Moreover, quantum dot-based electroluminescent LEDs have been improved a lot. Konstantatos and coworkers have reported PbS-based electroluminescent LED with 1550 nm emission and an efficiency of 18.6%.⁷²

But in a large number of traditional semiconducting nanocrystals, toxic elements like Pb, Cd, Hg and As are involved; which causes an obstacle towards the way of their commercialization. Besides, the emission can be quenched for self-absorption and high frequency vibration of different organic bonds (like C-H, O-H and N-H) in the nanocrystalline systems or surroundings.

Apart from these, another class of environmentally benign NIR emitter is CuInS₂ (CIS) nanocrystals.⁷³ They emit in the broad NIR range of 800 - 1400 nm (peak at 967 nm). Lie et al. has introduced a passivation strategy with ZnI₂ chemical additive and obtained an enhancement of PL QY from 7.4% to 21.1% (Figure 1.6).⁷³ They have also fabricated NIR electroluminescent LED with 4.3% external quantum efficiency. In this case of CuInS₂, though the compound is comprised of non-toxic elements, but mostly the efficiency has been compromised.

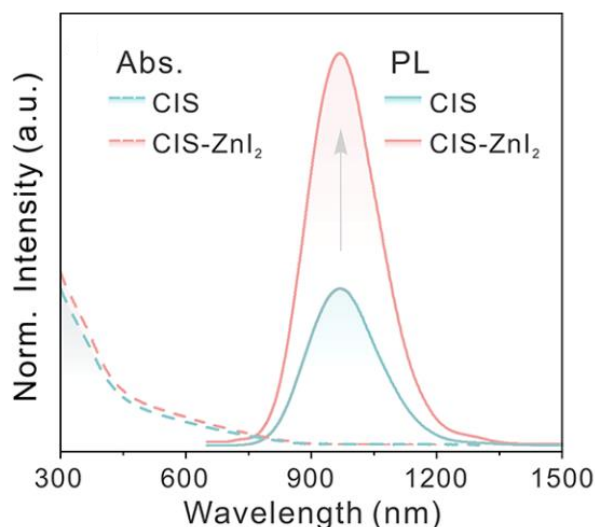


Figure 1.6: Optical absorption and emission of CuInS₂ (CIS) and CIS-ZnI₂ nanocrystals at room temperature. Adapted from reference [73] with permission. Copyright © 2024, American Chemical Society.

On the other hand, there are epitaxially grown III-V quantum wells like, GaAs, InGaAsP, AlGaAs which are commercialized and working pretty well in different NIR electroluminescent LED applications.⁷⁴ But due to their expensive synthesis procedure, these are quite costly.

1.7 An alternate way-out with metal ion dopants

An alternative approach is to develop NIR phosphors by incorporating Cr^{3+} ($d-d$ transition) or lanthanides ($f-f$ transition) into halide or oxide-based hosts.^{23, 35, 75-79} Some of the examples of such NIR emissions from $d-d$ and $f-f$ transitions of metal ions are discussed here.

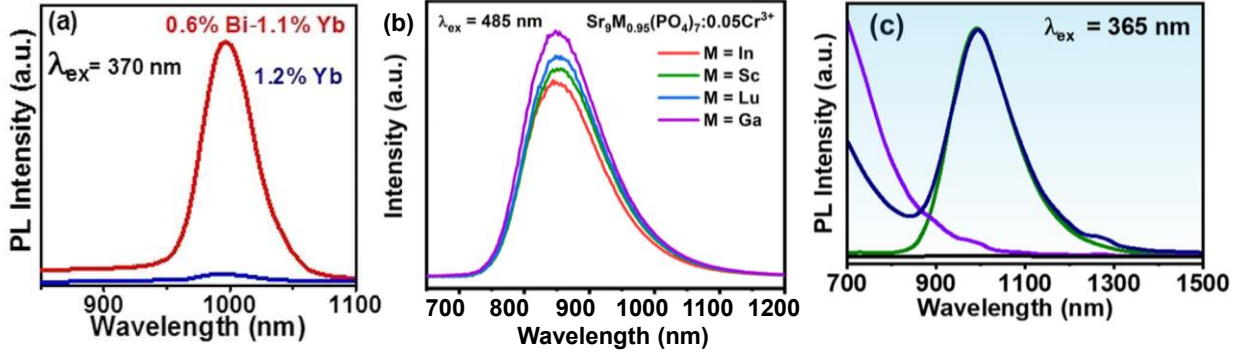


Figure 1.7: Near-infrared emission through $d-d$ and $f-f$ transitions of metal ion dopants. (a) PL emission spectra of Yb^{3+} -doped (blue) and Bi^{3+} - Yb^{3+} codoped (maroon) $\text{Cs}_2\text{AgInCl}_6$ double perovskites showing emission at 994 nm due to $f-f$ electronic transition of Yb^{3+} . (b) NIR emission at 850 nm from $\text{Sr}_9\text{M}_{0.95}(\text{PO}_4)_7:0.05\text{Cr}^{3+}$ ($\text{M} = \text{Ga}, \text{Sc}, \text{In}, \text{and Lu}$) due to the $d-d$ transition of Cr^{3+} . (c) PL spectra of undoped (black), Cr^{3+} -doped (green) and Cr^{3+} - Bi^{3+} codoped (blue) double perovskite $\text{Cs}_2\text{Ag}_{0.6}\text{Na}_{0.4}\text{InCl}_6$. Emission at 1000 nm arises from $d-d$ transition of Cr^{3+} . Figure (a) is adapted from reference [75] with permission. Copyright © 2020, Wiley. The figure (b) is reprinted from reference [37] with permission. Copyright © 2016, American Chemical Society. (c) is adapted from reference [23] with permission. Copyright © 2009, Wiley.

Figure 1.7a presents the emission spectra of Yb^{3+} -doped (blue) and Bi^{3+} - Yb^{3+} codoped (maroon) $\text{Cs}_2\text{AgInCl}_6$ after excitation of UV light 370 nm.⁷⁵ Both show sharp NIR emission peaking at 994 nm resulting from the Laporte forbidden transition $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ originating from inner-core f -electrons of Yb^{3+} . The codoped sample has enhanced emission due to sensitization with Bi^{3+} . Figure 1.7b shows the PL spectra of $\text{Sr}_9\text{M}_{0.95}(\text{PO}_4)_7:0.05\text{Cr}^{3+}$ ($\text{M} = \text{Ga}, \text{Sc}, \text{In}, \text{and Lu}$) phosphor upon excitation with 485 nm light.³⁷ All the samples are showing NIR emission around 850 nm due to $d-d$ transition of Cr^{3+} with d^3 electronic configuration in octahedral crystal environment. The broad emission comes from spin-allowed $^4\text{T}_2 (^4\text{F}) \rightarrow ^4\text{A}_2$ electronic transition at Dq/B value of 2.24 for the compound $\text{Sr}_9\text{Ga}(\text{PO}_4)_7:\text{Cr}^{3+}$. On the other hand, Figure 1.7c presents Cr^{3+} doping in a halide double perovskite host $\text{Cs}_2\text{Ag}_{0.6}\text{Na}_{0.4}\text{InCl}_6$.²³ Here, 2% Cr^{3+} -doping (green) and 2% Cr^{3+} -0.5% Bi^{3+} cooping (blue) have been discussed. In the NIR region, both the samples show similar broad near-infrared emission peaking at 1000 nm. This broad emission again originates

from the spin-allowed transition ${}^4T_2 \rightarrow {}^4A_2$ of Cr^{3+} (d^3) in a weak crystal-field ($Dq/B \approx 2.2$). Interestingly, if Cr^{3+} doping is done in a strong crystal field, then it can produce a sharp emission in NIR region.⁸⁰ Here, the emission is due spin-forbidden ${}^4E \rightarrow {}^4A_2$ transition with a longer millisecond lifetime. There are some other NIR emissive phosphors, like Ni^{2+} -doped $MgTa_2O_6$ ⁸¹ and $Mg_3Ga_2GeO_8$ ⁸² phosphors; Mn^{4+} -doped $LaAlO_3$ ⁸³ and $Ba_3Ca_4(BO_3)_3(SiO_4)Cl$ ⁸⁴ phosphors. Some of these are presented in Figure 1.8.

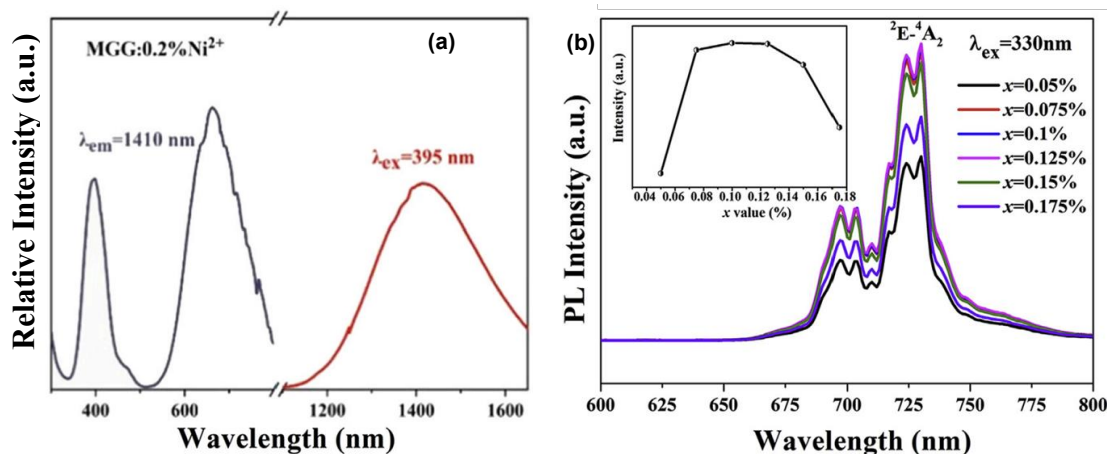


Figure 1.8: Near-infrared emission through $d-d$ transitions of Ni^{2+} and Mn^{4+} dopants. (a) PL emission spectrum of Ni^{2+} -doped (red) $Mg_3Ga_2GeO_8$ with emission at 1410 nm. (b) NIR emission at 730 nm from Mn^{4+} -doped $LaAlO_3$. Figure (a) is adapted from reference [82] with permission. Copyright © 2017, Wiley. The figure (b) is reprinted from reference [83] with permission. Copyright © 2016, American Chemical Society.

Figure 1.8a presents broad NIR emission (red spectrum) peaking at 1410 nm (excitation 395 nm) from another transition metal ion dopant Ni^{2+} in the oxide host $Mg_3Ga_2GeO_8$.⁸² It also shows the PL excitation spectrum (black) showing different absorption bands due to $d-d$ transitions of Ni^{2+} (d^8 , in octahedral crystal field). Figure 1.8b shows emission at 730 nm from Mn^{4+} , doped in $LaAlO_3$ host lattice.⁸³ Inset shows emission intensity with different percentages of Mn^{4+} dopant. The emission is due to ${}^2E \rightarrow {}^4A_2$ transition originating from Mn^{4+} (d^3 , in octahedral crystal field). All these phosphors show reasonably good NIR emission, but they need to be excited with high energy UV/ blue light, therefore power consumption would be high for pc-LED applications.

1.8 NIR emissive d^2 transition metal complexes

Apart from these widely explored d^3 systems with NIR emission, in some 90s reports, there are

certain transition metal complexes with Mo^{4+} , W^{4+} , Re^{5+} or Os^{6+} metal ions, they possess d^2 electronic configuration and emit in NIR region in octahedral crystal environment.⁸⁵⁻⁸⁸ Some of such complexes with Re^{5+} , Os^{6+} and W^{4+} having different organic ligands like ethylenediamine, oxalate, 1,2-bis(dimethylphosphino)ethane (dmpe) and (CH) are shown in Figure 1.9.

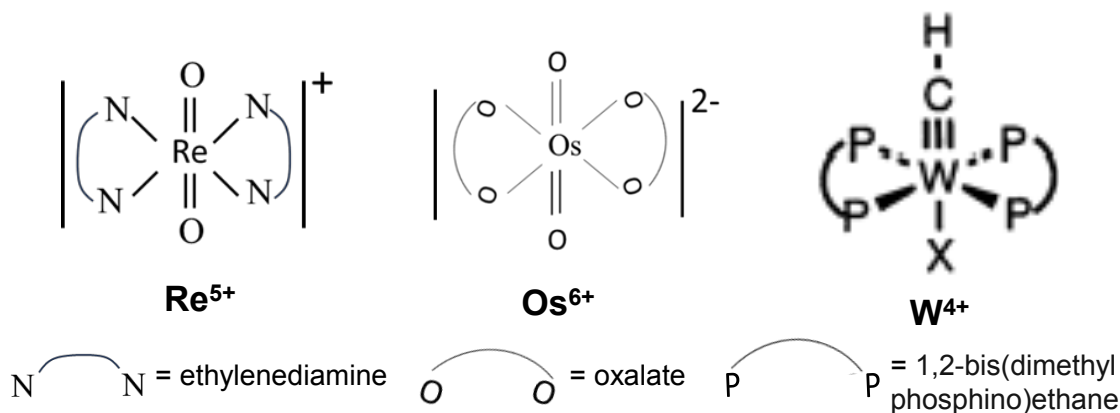


Figure 1.9: Some transition metal complexes with Re^{5+} , Os^{6+} and W^{4+} with organic ligands like ethylenediamine, oxalate and 1,2-bis(dimethylphosphino)ethane (dmpe) and (CH) respectively. Third panel is adapted from reference [88]

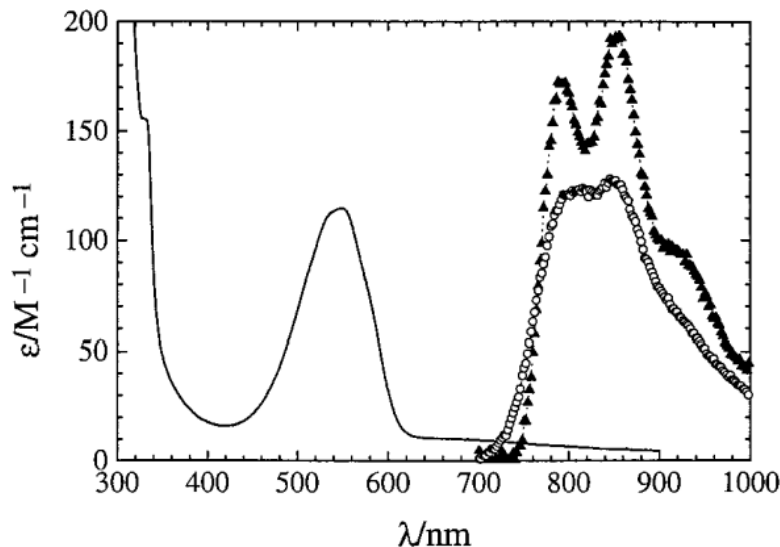


Figure 1.10: Mirror-image like optical absorption (solid line, at 300 K) and emission (white circle, at 300 K) of $[\text{MoOCl}(\text{CN-t-Bu})_4][\text{BPh}_4]$ complex. The spectrum with black triangle is PL at 77 K showing vibronic transition with split peaks. Adapted from reference [85] with permission.

These molecular crystals usually show vibronic $d-d$ transition at cryogenic temperatures with mirror-image like absorption and emission spectra. Figure 1.10 shows such absorption and

phosphorescence spectra with vibronic transitions at 77 K for $[\text{MoOCl}(\text{CN-t-Bu})_4][\text{BPh}_4]$ complex, which has Mo in +4 oxidation state.⁸⁵ It is important to note, Mo^{5+} with d^1 configuration, exhibits spin-allowed $d-d$ transition for PL with a lifetime of a few tens to 100 ns, whereas Mo^{6+} , with d^0 configuration, is not expected to show any $d-d$ transition.^{85, 89} For understanding vibronic transitions, let us very briefly discuss about Frank-Condon principle (shown in Figure 1.11).

Franck-Condon principle states that electronic transitions would be vertical that allow the bond length to remain constant during the transition. Therefore, for different excitation and emission from ground state (G.S.) to first excited state (E.S.) and vice versa, an imaginary absorption – emission spectra would look like a mirror image with vibronic lines (right side of Figure 1.11).

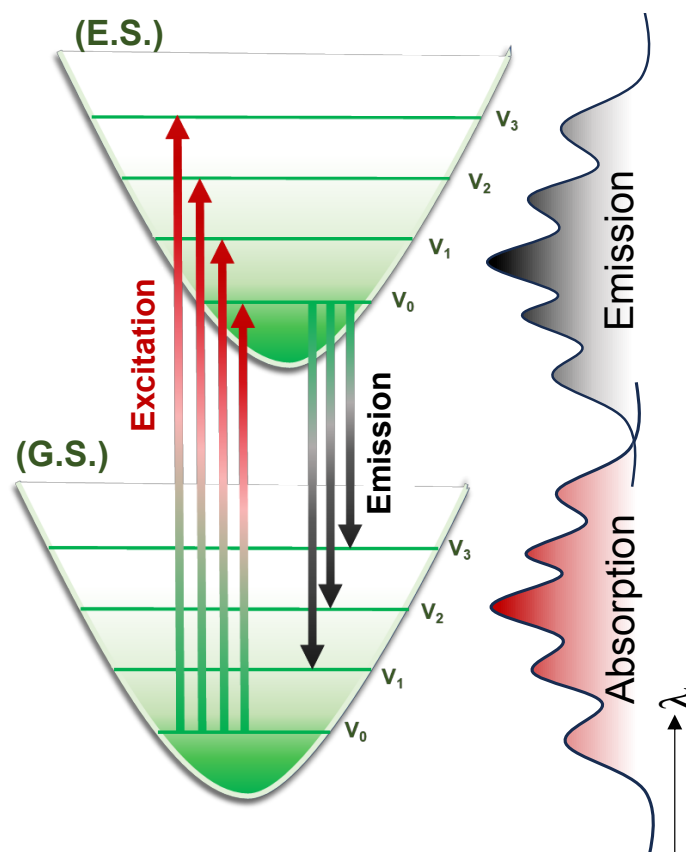


Figure 1.11: Schematic representation of Franck-Condon principle. The G.S. and E.S. correspond to electronic ground and excited states respectively. Horizontal lines named as ‘v’ are different vibrational levels of respective electronic states. Red and black arrows signify excitation and emission processes. Right side shows imaginary absorption and emission spectra.

This principle is typical for any molecule and explains the mirror-image absorption and emission of previously discussed molecular complexes with d^2 transition metals.

1.9 Drawbacks of metal complexes

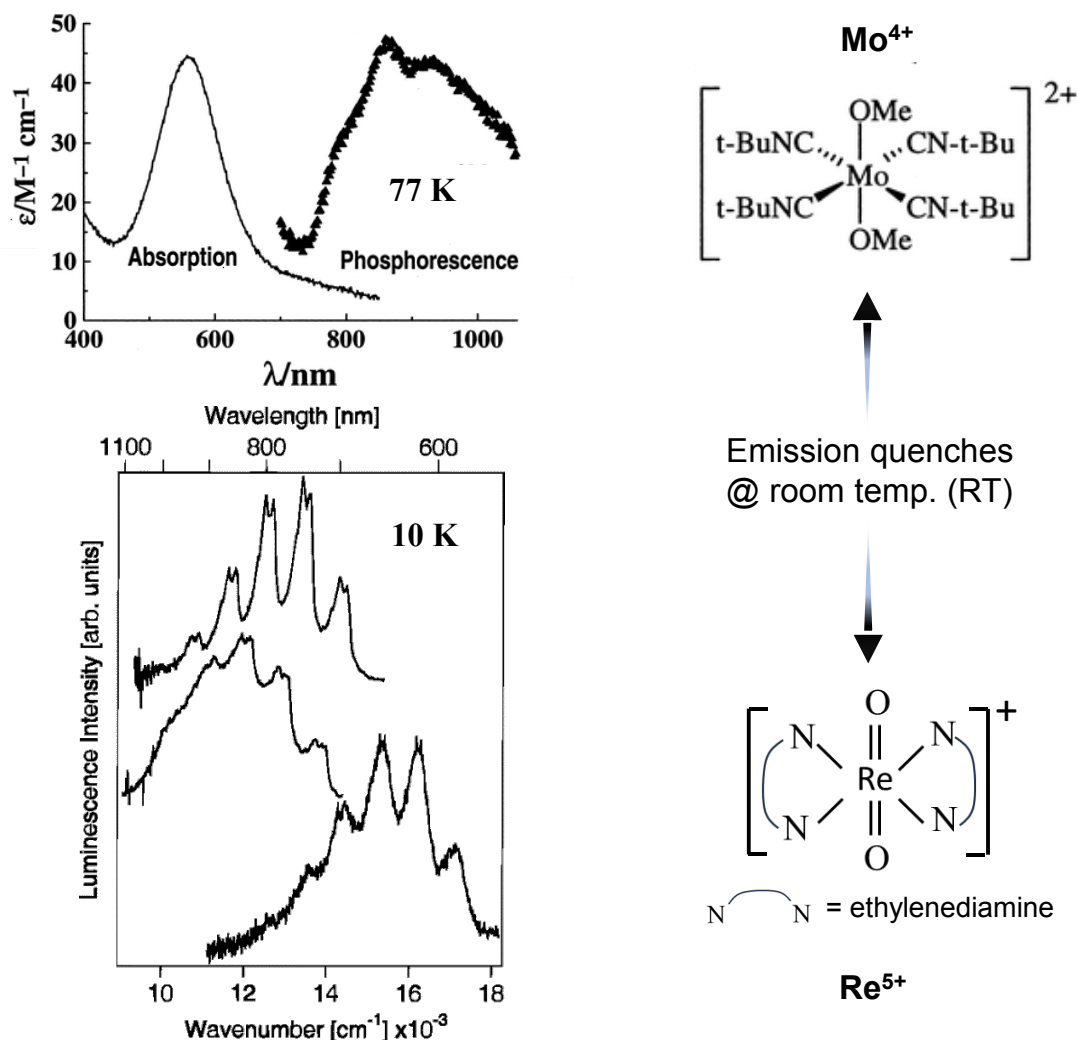


Figure 1.12: Upper panel shows mirror-image like optical absorption and phosphorescence of $[\text{Mo}(\text{OCH}_3)_2(\text{CN-t-Bu})_4][\text{PF}_6]_2$ complex along with the structure of complex cation. Lower panel presents PL spectra of *trans*- $\text{ReO}_2(\text{tmen})_2\text{Cl}$ (bottom trace), *trans*- $\text{ReO}_2(\text{en})_2\text{Cl}$ (middle trace), and *trans*- $\text{ReO}_2(1\text{-vinylimidazole})_4\text{I}$ (top trace) along with the structure of one of the complexes. The ligands *N, N, N', N'*-tetramethylethylenediamine and ethylenediamine are abbreviated as tmen and en. All emissions are shown at cryogenic temperatures with vibronic transition and split peaks. But the emission quenches significantly at room temperature. Upper and lower panels are adapted from reference [85] and [86] with permission. Copyright © 1998 and 2000 respectively, American Chemical Society.

Though all these d^2 transition metal complexes emit in NIR region, but they have certain constraints too. All these complexes have organic ligands containing bonds like O-H, N-H and C-H. These bonds have high frequency vibration and the 2nd overtone of those overlaps well with the

NIR region (discussed in section 1.4 and Table 1.1). Therefore, presence of these organic moieties and non-radiative recombination quench photoluminescence significantly at room temperature, though they emit quite well at cryogenic temperatures. Figure 1.12 shows such Mo^{4+} and Re^{5+} based complexes, which emit in NIR region with vibronic coupling, but emission quenches at room temperature.^{85, 86} This inhibits these organic metal complexes from practical applications.

1.10 Scope of the thesis

If we summarize the possibilities and drawbacks of above-discussed NIR emitters (section 1.6 to 1.9), there exist two issues which need to be addressed: (1) excitation with high energy UV/ blue light and emission at NIR region leading to thermalization loss; (2) non-radiative recombination and photoluminescence quenching at room temperature due to high frequency vibration of organic parts present in certain systems or surroundings.

In a recent article, it is shown that Cs_2MoCl_6 and Cs_2WCl_6 (with $\text{Mo}^{4+}/\text{W}^{4+}$) emit in NIR (900–1300 nm) region with high PL QY (26%) at room temperature.⁹⁰ But the emission is assigned as self-trapped excitonic (STE) emission with 1.8 eV red-shift from excitation (400 nm). In contrast, there are many more d^2 transition metal complexes with NIR emission through $d-d$ electronic transitions (section 1.8).⁸⁵⁻⁸⁸

In backdrop of these diverging prior reports and in order to address the two issues discussed above, in Chapter 2 of this thesis, we hypothesized that all inorganic Cs_2MX_6 ($\text{M} = \text{Mo}/\text{W}$; $\text{X} = \text{Cl}/\text{Br}$) 0D perovskite derivatives can fulfill the criteria of decreased Stokes shift and emit NIR radiation efficiently. They have both the excitation and emission in far-red (787 nm) and NIR (986 nm) regions which involve same pair of electronic states. Applying temperature dependent photoluminescence spectroscopy (300 – 8 K), we determined the mechanism as $d-d$ transitions (not STE) of M^{4+} (d^2 , octahedral environment) producing vibronically coupled mirror-image like PL excitation and emission spectra at cryogenic temperatures (schematically shown in Figure 1.13, top panel).

In Cs_2MX_6 crystals all are luminescent centers (Figure 1.13, middle panel), therefore, the emission could be quenched due to non-radiative energy transfer between these $[\text{MX}_6]^{2-}$ centers. In order to decrease this concentration quenching,⁹¹⁻⁹³ in Chapter 3, we dope W^{4+} or Mo^{4+} in another 0D host

Cs_2SnCl_6 . Right-side diagram of middle panel (Figure 1.13) presents the doped structure with diluted emission centers. The ionic radii of Sn^{4+} , W^{4+} and Mo^{4+} in octahedral environment are similar with values of 69, 66 and 65 picometer, respectively.⁹⁴ This makes the host appropriate for doping. Further as a proof of concept, we utilize these phosphors to fabricate NIR pc-LEDs, by coating them on top of 730 nm (far-red) and 400 nm (blue) commercial LED chips.

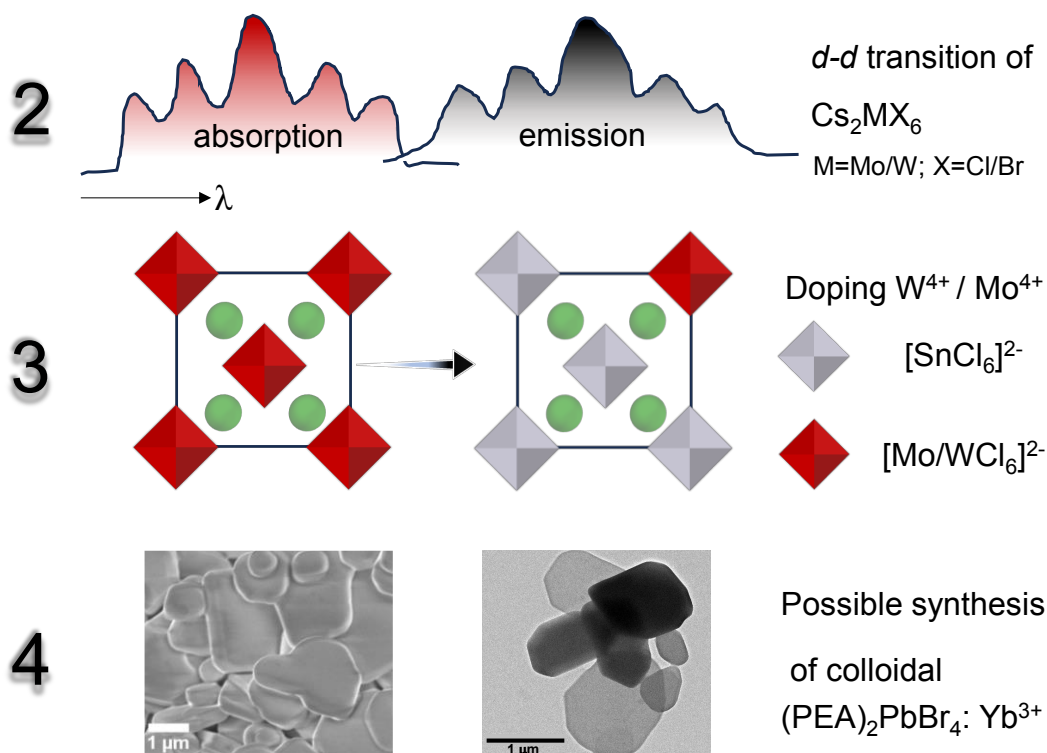


Figure 1.13: Schematic representation of the scope of this thesis. Chapter 2 (top panel) describes the NIR excitation and emission mechanisms through $d-d$ transition for Cs_2MX_6 ($\text{M} = \text{Mo}/\text{W}$; $\text{X} = \text{Cl}/\text{Br}$) kind of 0D perovskite derivatives. That is graphically shown here with mirror-image like absorption (red) and emission (black) spectra. In order to decrease the luminescent centers and eventually concentration quenching, Chapter 3 (middle panel) discusses doping of W^{4+} or Mo^{4+} in another 0D matrix Cs_2SnCl_6 . Left-side diagram with red octahedra (depict $[\text{MoCl}_6]^{2-}$ or $[\text{WCl}_6]^{2-}$) stands for the structure of Cs_2MoCl_6 or Cs_2WCl_6 (green spheres are Cs^+ , Cl^- are not shown for simplicity); here all are emission centers. Right-side diagram with grey ($[\text{SnCl}_6]^{2-}$) and red octahedra (depict $[\text{MoCl}_6]^{2-}$ or $[\text{WCl}_6]^{2-}$) represent W^{4+} or Mo^{4+} -doped Cs_2SnCl_6 structure with diluted emission centers. Chapter 4 (bottom panel) shows microplatelets (left image) and nanoplatelets (right image) of $(\text{PEA})_2\text{PbBr}_4$ and explores the possible colloidal synthesis of Yb^{3+} -doped $\text{PEA}_2\text{PbBr}_4$ 2D perovskites.

All the compounds of Chapter 2 and 3 are microcrystalline solids and are difficult to achieve solution processibility. Therefore, in Chapter 4 we explore possible colloidal synthesis of Yb^{3+}

doped phenylethylammonium lead bromide (PEA₂PbBr₄) 2D perovskites for NIR emission. Bottom panel of Figure 1.13 shows the microplatelets and nanoplatelets of (PEA)₂PbBr₄. We could obtain weak NIR emission (at 997 nm) from the doped sample because of *f-f* transition of Yb³⁺ along with poor solution processibility through the nanoplates. All these comprehensive studies of the thesis involve material design and synthesis, detailed photo-physical characterization with optical spectroscopy and fabrication of possible pc-LEDs applying the NIR phosphors.

1.11 References

1. Graef, M. D.; McHenry, M. E. Structure of Materials: An Introduction to Crystallography, Diffraction and Symmetry. *Cambridge University Press*, **2012**.
2. Li, C.; Lu, X.; Ding, W.; Feng, L.; Gao, Y.; Guo, Z. Formability of ABX₃ (X = F, Cl, Br, I) Halide Perovskites. *Acta Cryst. B* **2008**, *64* (6), 702-707.
3. Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. *Chem. Rev.* **2019**, *119* (5), 3036-3103.
4. Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X.-G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C.-J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Seró, I. M.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Prieto, J. P.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roeffaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Buschbaum, P. M.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L., State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775-10981.
5. Goldschmidt, V. M. Die Gesetze der Krystallochemie. *Naturwissenschaften* **1926**, *14* (21), 477-485.
6. Bartel, C. J.; Sutton, C.; Goldsmith, B. R.; Ouyang, R.; Musgrave, C. B.; Ghiringhelli, L. M.; Scheffler, M. New Tolerance Factor to Predict the Stability of Perovskite Oxides and Halides. *Sci. Adv.* **2019**, *5* (2), eaav0693.

7. Li, Z.; Yang, M.; Park, J.-S.; Wei, S.-H.; Berry, J. J.; Zhu, K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chem. Mater.* **2016**, 28 (1), 284-292.
8. Huang, L.-Y.; Lambrecht, W. R. L. Electronic Band Structure Trends of Perovskite Halides: Beyond Pb and Sn to Ge and Si. *Phys. Rev. B* **2016**, 93 (19), 195211.
9. Shohl, W. A. D.; Zhou, Y.; Padture, N. P.; Mitzi, D. B. Synthetic Approaches for Halide Perovskite Thin Films. *Chem. Rev.* **2019**, 119 (5), 3193-3295.
10. Shamsi, J.; Urban, A. S.; Imran, M.; Trizio, L. D.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, 119 (5), 3296-3348.
11. Roo, J. D.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Driessche, I. V.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, 10 (2), 2071-2081.
12. Park, J.; Kim, J.; Yun, H.-S.; Paik, M. J.; Noh, E.; Mun, H. J.; Kim, M. G.; Shin, T. J.; Seok, S. I. Controlled Growth of Perovskite Layers with Volatile Alkylammonium Chlorides. *Nature* **2023**, 616 (7958), 724-730.
13. Chiba, T.; Hayashi, Y.; Ebe, H.; Hoshi, K.; Sato, J.; Sato, S.; Pu, Y.-J.; Ohisa, S.; Kido, J. Anion-Exchange Red Perovskite Quantum Dots with Ammonium Iodine Salts for Highly Efficient Light-Emitting Devices. *Nat. Photonics* **2018**, 12 (11), 681-687.
14. Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; Burgt, L. J. V. D.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. One-Dimensional Organic Lead Halide Perovskites with Efficient Bluish White-Light Emission. *Nat. Commun.* **2017**, 8 (1), 14051.
15. Saparov, B.; Mitzi, D. B. Organic-Inorganic Perovskites: Structural Versatility for Functional Materials Design. *Chem. Rev.* **2016**, 116 (7), 4558-4596.
16. Katan, C.; Mercier, N.; Even, J. Quantum and Dielectric Confinement Effects in Lower-Dimensional Hybrid Perovskite Semiconductors. *Chem. Rev.* **2019**, 119 (5), 3140-3192.
17. Maughan, A. E.; Ganose, A. M.; Scanlon, D. O.; Neilson, J. R. Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors. *Chem. Mater.* **2019**, 31 (4), 1184-1195.

18. Morgan, E. E.; Kent, G. T.; Zohar, A.; O'Dea, A.; Wu, G.; Cheetham, A. K.; Seshadri, R. Hybrid and Inorganic Vacancy-Ordered Double Perovskites A_2WCl_6 . *Chem. Mater.* **2023**, *35* (17), 7032-7038.
19. Zhu, S.; Yung, B. C.; Chandra, S.; Niu, G.; Antaris, A. L.; Chen, X. Near-Infrared-II (NIR-II) Bioimaging via Off-Peak NIR-I Fluorescence Emission. *Theranostics* **2018**, *8* (15), 4141-4151.
20. Lu, L.; Li, B.; Ding, S.; Fan, Y.; Wang, S.; Sun, C.; Zhao, M.; Zhao, C.-X.; Zhang, F. NIR-II Bioluminescence for in Vivo High Contrast Imaging and in Situ ATP-Mediated Metastases Tracing. *Nat. Commun.* **2020**, *11* (1), 4192.
21. Zhao, M.; Li, B.; Zhang, H.; Zhang, F. Activatable Fluorescence Sensors for in Vivo Bio-Detection in the Second Near-Infrared Window. *Chem. Sci.* **2021**, *12* (10), 3448-3459.
22. Gréboval, C.; Chu, A.; Goubet, N.; Livache, C.; Ithurria, S.; Lhuillier, E. Mercury Chalcogenide Quantum Dots: Material Perspective for Device Integration. *Chem. Rev.* **2021**, *121* (7), 3627-3700.
23. Saikia, S.; Ghosh, A.; Nag, A. Broad Dual Emission by Codoping Cr^{3+} ($d \rightarrow d$) and Bi^{3+} ($s \rightarrow p$) in $Cs_2Ag_{0.6}Na_{0.4}InCl_6$ Double Perovskite. *Angew. Chem. Int. Ed.* **2023**, *62* (33), e202307689.
24. Li, B.; Zhao, M.; Feng, L.; Dou, C.; Ding, S.; Zhou, G.; Lu, L.; Zhang, H.; Chen, F.; Li, X.; Li, G.; Zhao, S.; Jiang, C.; Wang, Y.; Zhao, D.; Cheng, Y.; Zhang, F. Organic NIR-II Molecule with Long Blood Half-Life for in Vivo Dynamic Vascular Imaging. *Nat. Commun.* **2020**, *11* (1), 3102.
25. Kim, B.; Kim, H.; Kim, S.; Hwang, Y.-R. A Brief Review of Non-Invasive Brain Imaging Technologies and the Near-Infrared Optical Bioimaging. *Appl. Microsc.* **2021**, *51* (1), 9.
26. Graça, M. F. P.; Moreira, A. F.; Correia, I. J. Application of Near-Infrared Light Responsive Biomaterials for Improving the Wound Healing Process: A Review. *J. Drug Del. Sci. Tech.* **2024**, *93*, 105409.
27. Desmet, K. D.; Paz, D. A.; Corry, J. J.; Eells, J. T.; Riley, M. T. T. W.; Henry, M. M.; Buchmann, E. V.; Connelly, M. P.; Dovi, J. V.; Liang, H. L.; Henshel, D. S.; Yeager, R. L.; Millsap, D. S.; Lim, J.; Gould, L. J.; Das, R.; Jett, M.; Hodgson, B. D.; Margolis, D.; Whelan, H. T. Clinical and Experimental Applications of NIR-LED Photobiomodulation. *Photomed. Laser Surg.* **2006**, *24* (2), 121-128.

28. Supran, G. J.; Song, K. W.; Hwang, G. W.; Correa, R. E.; Scherer, J.; Dauler, E. A.; Shirasaki, Y.; Bawendi, M. G.; Bulović, V. High-Performance Shortwave-Infrared Light-Emitting Devices Using Core–Shell (PbS–CdS) Colloidal Quantum Dots. *Adv. Mater.* **2015**, 27 (8), 1437-1442.
29. Hong, W.-L.; Huang, Y.-C.; Chang, C.-Y.; Zhang, Z.-C.; Tsai, H.-R.; Chang, N.-Y.; Chao, Y.-C. Efficient Low-Temperature Solution-Processed Lead-Free Perovskite Infrared Light-Emitting Diodes. *Adv. Mater.* **2016**, 28 (36), 8029-8036.
30. Qu, J.; Rastogi, P.; Gréboval, C.; Lagarde, D.; Chu, A.; Dabard, C.; Khalili, A.; Cruguel, H.; Robert, C.; Xu, X. Z.; Ithurria, S.; Silly, M. G.; Ferré, S.; Marie, X.; Lhuillier, E. Electroluminescence from HgTe Nanocrystals and Its Use for Active Imaging. *Nano Lett.* **2020**, 20 (8), 6185-6190.
31. Vasilopoulou, M.; Kim, H. P.; Kim, B. S.; Papadakis, M.; Gavim, A. E. X.; Macedo, A. G.; Silva, W. J. D.; Schneider, F. K.; Teridi, M. A. M.; Coutsolelos, A. G.; Yusoff, A. R. B. M., Efficient Colloidal Quantum Dot Light-Emitting Diodes Operating in the Second Near-Infrared Biological Window. *Nat. Photonics* **2020**, 14 (1), 50-56.
32. Franco, M. D.; Zhu, D.; Asaithambi, A.; Prato, M.; Charalampous, E.; Christodoulou, S.; Kriegel, I.; Trizio, L. D; Manna, L.; Jalali, H. B.; Stasio, F. D. Near-Infrared Light-Emitting Diodes Based on RoHS-Compliant InAs/ZnSe Colloidal Quantum Dots. *ACS Energy Lett.* **2022**, 7 (11), 3788-3790.
33. Wang, S.; Pang, R.; Tan, T.; Wu, H.; Wang, Q.; Li, C.; Zhang, S.; Tan, T.; You, H.; Zhang, H. Achieving High Quantum Efficiency Broadband NIR $\text{Mg}_4\text{Ta}_2\text{O}_9\text{:Cr}^{3+}$ Phosphor Through Lithium-Ion Compensation. *Adv. Mater.* **2023**, 35 (22), 2300124.
34. Rajendran, V.; Fang, M.-H.; Guzman, G. N. D.; Lesniewski, T.; Mahlik, S.; Grinberg, M.; Leniec, G.; Kaczmarek, S. M.; Lin, Y.-S.; Lu, K.-M.; Lin, C.-M.; Chang, H.; Hu, S.-F.; Liu, R.-S. Super Broadband Near-Infrared Phosphors with High Radiant Flux as Future Light Sources for Spectroscopy Applications. *ACS Energy Lett.* **2018**, 3 (11), 2679-2684.
35. Gan, W.; Cao, L.; Gu, S.; Lian, H.; Xia, Z.; Wang, J. Broad-Band Sensitization in $\text{Cr}^{3+}\text{--Er}^{3+}$ Co-Doped $\text{Cs}_2\text{AgInCl}_6$ Double Perovskites with 1.5 μm Near-Infrared Emission. *Chem. Mater.* **2023**, 35 (14), 5291-5299.
36. Zhang, Y.; Miao, S.; Liang, Y.; Liang, C.; Chen, D.; Shan, X.; Sun, K.; Wang, X.-J. Blue LED-Pumped Intense Short-Wave Infrared Luminescence Based on $\text{Cr}^{3+}\text{--Yb}^{3+}\text{--Co}$ -Doped Phosphors. *Light Sci. Appl.* **2022**, 11 (1), 136.

37. Zhao, F.; Cai, H.; Song, Z.; Liu, Q. Structural Confinement for Cr^{3+} Activators toward Efficient Near-Infrared Phosphors with Suppressed Concentration Quenching. *Chem. Mater.* **2021**, *33* (10), 3621-3630.
38. Song, E.; Ming, H.; Zhou, Y.; He, F.; Wu, J.; Xia, Z.; Zhang, Q. Cr^{3+} -Doped Sc-Based Fluoride Enabling Highly Efficient Near Infrared Luminescence: A Case Study of $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$. *Laser Photonics Rev.* **2021**, *15* (2), 2000410.
39. Rajendran, V.; Lesniewski, T.; Mahlik, S.; Grinberg, M.; Leniec, G.; Kaczmarek, S. M.; Pang, W.-K.; Lin, Y.-S.; Lu, K.-M.; Lin, C.-M.; Chang, H.; Hu, S.-F.; Liu, R.-S. Ultra-Broadband Phosphors Converted Near-Infrared Light Emitting Diode with Efficient Radiant Power for Spectroscopy Applications. *ACS Photonics* **2019**, *6* (12), 3215-3224.
40. Choudhury, A. K. R. 1 - Characteristics of Light Sources. In *Principles of Colour and Appearance Measurement*, Ed. Woodhead Publishing: **2014**, pp 1-52.
41. Smith, N. A., 21 - Lighting. In *Electrical Engineer's Reference Book (Sixteenth Edition)*, Laughton, M. A.; Warne, D. J., Eds. Newnes: Oxford, **2003**, pp 21-1-21-31.
42. Luo, D.; Wang, L.; Or, S. W.; Zhang, H.; Xie, R.-J. Realizing Superior White LEDs with Both High R9 and Luminous Efficacy by Using Dual Red Phosphors. *RSC Adv.* **2017**, *7* (42), 25964-25968.
43. Rea, M. S.; Bierman, A. A New Rationale for Setting Light Source Luminous Efficacy Requirements. *Lighting Research & Technology* **2016**, *50* (3), 340-359.
44. Joos, J. J.; Botterman, J.; Smet, P. F. Evaluating the Use of Blue Phosphors in White LEDs: the Case of $\text{Sr}_{0.25}\text{Ba}_{0.75}\text{Si}_2\text{O}_7\text{N}_2:\text{Eu}^{2+}$. *J. Solid State Light.* **2014**, *1* (1), 6.
45. Murphy, T. W., Jr. Maximum Spectral Luminous Efficacy of White Light. *J. Appl. Phys.* **2012**, *111* (10), 104909.
46. Wu, S.-F.; Li, S.-H.; Wang, Y.-K.; Huang, C.-C.; Sun, Q.; Liang, J.-J.; Liao, L.-S.; Fung, M.-K. White Organic LED with A Luminous Efficacy Exceeding 100 lm W^{-1} without Light Out-Coupling Enhancement Techniques. *Adv. Funct. Mater.* **2017**, *27* (31), 1701314.
47. Panigrahi, K.; Nag, A. Challenges and Strategies to Design Phosphors for Future White Light Emitting Diodes. *J. Phys. Chem. C* **2022**, *126* (20), 8553-8564.
48. Fang, L.; Zhang, L.; Wu, H.; Wu, H.; Pan, G.; Hao, Z.; Liu, F.; Zhang, J. Efficient Broadband Near-Infrared $\text{CaMgGe}_2\text{O}_6:\text{Cr}^{3+}$ Phosphor for pc-LED. *Inorg. Chem.* **2022**, *61* (23), 8815-8822.

49. Mach, R. M.; Mueller, G. O.; Krames, M. R.; Trottier, T. High-Power Phosphor-Converted Light-Emitting Diodes Based on III-Nitrides. *IEEE J. Sel. Top. Quant.* **2002**, *8* (2), 339-345.
50. Zurfi, A.; Zhang, J. Model Identification and Wall-Plug Efficiency Measurement of White LED Modules. *American Journal of Engineering and Applied Sciences* **2016**, *9* (2).
51. Smet, P. F.; Parmentier, A. B.; Poelman, D. Selecting Conversion Phosphors for White Light-Emitting Diodes. *J. Electrochem. Soc.* **2011**, *158* (6), R37.
52. Davidson, M. W. Tungsten-Halogen Incandescent Lamps. <https://zeiss-campus.magnet.fsu.edu/print/lightsources/tungstenhalogen-print.html>.
53. Wang, S.-F.; Su, B.-K.; Wang, X.-Q.; Wei, Y.-C.; Kuo, K.-H.; Wang, C.-H.; Liu, S.-H.; Liao, L.-S.; Hung, W.-Y.; Fu, L.-W.; Chuang, W.-T.; Qin, M.; Lu, X.; You, C.; Chi, Y.; Chou, P.-T. Polyatomic Molecules with Emission Quantum Yields >20% Enable Efficient Organic Light-Emitting Diodes in the NIR(II) Window. *Nat. Photonics* **2022**, *16* (12), 843-850.
54. Cao, L.; Li, J.; Zhu, Z.-Q.; Huang, L.; Li, J. Stable and Efficient Near-Infrared Organic Light-Emitting Diodes Employing A Platinum(II) Porphyrin Complex. *ACS Appl. Mater. Interfaces* **2021**, *13* (50), 60261-60268.
55. Wang, S. F.; Yuan, Y.; Wei, Y.-C.; Chan, W.-H.; Fu, L.-W.; Su, B.-K.; Chen, I. Y.; Chou, K.-J.; Chen, P.-T.; Hsu, H.-F.; Ko, C.-L.; Hung, W.-Y.; Lee, C.-S.; Chou, P.-T.; Chi, Y. Highly Efficient Near-Infrared Electroluminescence up to 800 nm Using Platinum(II) Phosphors. *Adv. Funct. Mater.* **2020**, *30* (30), 2002173.
56. Cho, H.-H.; Gorgon, S.; Londi, G.; Giannini, S.; Cho, C.; Ghosh, P.; Tonnelé, C.; Casanova, D.; Olivier, Y.; Baikie, T. K.; Li, F.; Beljonne, D.; Greenham, N. C.; Friend, R. H.; Evans, E. W. Efficient Near-Infrared Organic Light-Emitting Diodes with Emission from Spin Doublet Excitons. *Nat. Photonics* **2024**, *18* (9), 905-912.
57. Santos, P. L. D.; Stachelek, P.; Takeda, Y.; Pander, P. Recent Advances in Highly-Efficient Near Infrared OLED Emitters. *Mater. Chem. Front.* **2024**, *8* (7), 1731-1766.
58. Rogach, A. L.; Eychmüller, A.; Hickey, S. G.; Kershaw, S. V. Infrared-Emitting Colloidal Nanocrystals: Synthesis, Assembly, Spectroscopy, and Applications. *Small* **2007**, *3* (4), 536-557.
59. Rogach, A.; Kershaw, S. V.; Burt, M.; Harrison, M. T.; Kornowski, A.; Eychmüller, A.; Weller, H. Colloidally Prepared HgTe Nanocrystals with Strong Room-Temperature Infrared Luminescence. *Adv. Mater.* **1999**, *11* (7), 552-555.

60. Cao; Banin, U. Growth and Properties of Semiconductor Core/Shell Nanocrystals with InAs Cores. *J. Am. Chem. Soc.* **2000**, *122* (40), 9692-9702.
61. Nenadovic, M. T.; Rajh, T.; Micic, O. I. Size Quantization in Small Semiconductor Particles. *J. Phys. Chem.* **1985**, *89* (3), 397-399.
62. Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. Hybrid Electronic Properties between the Molecular and Solid State Limits: Lead Sulfide and Silver Halide Crystallites. *J. Chem. Phys.* **1985**, *83* (3), 1406-1410.
63. Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706-8715.
64. Murray, C. B.; Sun, S.; Gaschler, W.; Doyle, H.; Betley, T. A.; Kagan, C. R. Colloidal Synthesis of Nanocrystals and Nanocrystal Superlattices. *IBM J. Res. Dev.* **2001**, *45* (1), 47-56.
65. Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, *15* (21), 1844-1849.
66. Dutta, A. K.; Ho, T.; Zhang, L.; Stroeve, P. Nucleation and Growth of Lead Sulfide Nano- and Microcrystallites in Supramolecular Polymer Assemblies. *Chem. Mater.* **2000**, *12* (4), 1042-1048.
67. Bakueva, L.; Gorelikov, I.; Musikhin, S.; Zhao, X. S.; Sargent, E. H.; Kumacheva, E. PbS Quantum Dots with Stable Efficient Luminescence in the Near-IR Spectral Range. *Adv. Mater.* **2004**, *16* (11), 926-929.
68. Chen, S.; Truax, L. A.; Sommers, J. M. Alkanethiolate-Protected PbS Nanoclusters: Synthesis, Spectroscopic and Electrochemical Studies. *Chem. Mater.* **2000**, *12* (12), 3864-3870.
69. Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F.; Zhang, J. Z.; Hyeon, T. Generalized and Facile Synthesis of Semiconducting Metal Sulfide Nanocrystals. *J. Am. Chem. Soc.* **2003**, *125* (36), 11100-11105.
70. Hens, Z.; Vanmaekelbergh, D.; Stoffels, E. J. A. J.; Kempen, H. V. Effects of Crystal Shape on the Energy Levels of Zero-Dimensional PbS Quantum Dots. *Phys. Rev. Lett.* **2002**, *88* (23), 236803.
71. Ondry, J. C.; Zhou, Z.; Lin, K.; Gupta, A.; Chang, J. H.; Wu, H.; Jeong, A.; Hammel, B. F.; Wang, D.; Fry, H. C.; Yazdi, S.; Dukovic, G.; Schaller, R. D.; Rabani, E.; Talapin, D. V. Reductive

Pathways in Molten Inorganic Salts Enable Colloidal Synthesis of III-V Semiconductor Nanocrystals. *Science* **2024**, 386 (6720), 401-407.

72. Pradhan, S.; Dalmases, M.; Taghipour, N.; Kundu, B.; Konstantatos, G. Colloidal Quantum Dot Light Emitting Diodes at Telecom Wavelength with 18% Quantum Efficiency and Over 1 MHz Bandwidth. *Adv. Sci.* **2022**, 9 (20), 2200637.

73. Liu, Z.; Hao, C.; Liu, Y.; Wu, R.; Zhang, J.; Chen, Z.; Wang, F.; Guan, L.; Li, X.; Tang, A.; Chen, O. Short-Wave Infrared Light-Emitting Diodes Using Colloidal CuInS₂ Quantum Dots with ZnI₂ Dual-Passivation. *ACS Nano* **2024**, 18 (32), 21523-21533.

74. THORLABS Single-Color IR LEDs (750 - 1600 nm). https://www.thorlabs.com/newgrouppage9.cfm?objectgroup_id=2814.

75. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Codoped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, 59 (28), 11307-11311.

76. Jia, Z.; Yuan, C.; Liu, Y.; Wang, X.-J.; Sun, P.; Wang, L.; Jiang, H.; Jiang, J. Strategies to Approach High Performance in Cr³⁺-Doped Phosphors for High-Power NIR-LED Light Sources. *Light Sci. Appl.* **2020**, 9 (1), 86.

77. Saikia, S.; Joshi, A.; Arfin, H.; Badola, S.; Saha, S.; Nag, A. Sb³⁺-Er³⁺-Codoped Cs₂NaInCl₆ for Emitting Blue and Short-Wave Infrared Radiation. *Angew. Chem. Int. Ed.* **2022**, 61 (32), e202201628.

78. Arfin, H.; Rathod, R.; Shingote, A. S.; Priolkar, K. R.; Santra, P. K.; Nag, A. Short-Wave Infrared Emissions from Te⁴⁺-Ln³⁺ (Ln: Er, Yb)-Codoped Cs₂NaInCl₆ Double Perovskites. *Chem. Mater.* **2023**, 35 (17), 7133-7143.

79. Rajendran, V.; Chen, K.-C.; Huang, W.-T.; Majewska, N.; Leśniewski, T.; Grzegorzczak, M.; Mahlik, S.; Leniec, G.; Kaczmarek, S. M.; Pang, W. K.; Peterson, V. K.; Lu, K.-M.; Chang, H.; Liu, R.-S. Pentavalent Manganese Luminescence: Designing Narrow-Band Near-Infrared Light-Emitting Diodes as Next-Generation Compact Light Sources. *ACS Energy Lett.* **2023**, 8 (1), 289-295.

80. Hsu, J.-Y.; Chung, R.-J.; Majewska, N.; Kreft, D.; Sheu, H.-S.; Lee, J.-F.; Mahlik, S.; Fang, M.-H. Probing Local Structural Changes by Sharp Luminescent Infrared Nanophosphor for Application in Light-Emitting Diodes. *Chem. Mater.* **2022**, 34 (24), 11093-11100.

81. Zhu, F.; Gao, Y.; Zhu, B.; Huang, L.; Qiu, J. Ni²⁺-Doped MgTa₂O₆ Phosphors Capable of Near-Infrared II and III Emission Under Blue-Light Excitation. *Chem. Eng. J.* **2024**, *479*, 147568.
82. Wang, C.; Lin, J.; Zhang, X.; Dong, H.; Wen, M.; Zhao, S.; Yuan, S.; Zhu, D.; Wu, F.; Mu, Z. Efficient Ultra-Broadband NIR-II Emission Achieved by Multi-Site Occupancy in Mg₃Ga₂GeO₈: Ni²⁺ Phosphor. *J. Alloys Compd* **2023**, *942*, 168893.
83. Li, S.; Zhu, Q.; Li, X.; Sun, X.; Li, J.-G. Near-Infrared Emitting Microspheres of LaAlO₃:Mn⁴⁺: Defects Engineering via Ge⁴⁺ Doping for Greatly Enhanced Luminescence and Improved Afterglow. *J. Alloys Compd* **2020**, *827*, 154365.
84. Wang, J.; Tan, T.; Pang, R.; Li, D.; Li, C.; Zhang, S.; Jiang, L.; Zhang, H. A Novel Broadband Ba₃Ca₄(BO₃)₃(SiO₄)Cl:Mn⁴⁺ Near-Infrared Phosphor with A Special Pseudo-Octahedral Mn⁴⁺ Coordination Structure. *Dalton Trans.* **2023**, *52* (41), 15078-15090.
85. Isovitsch, R. A.; Beadle, A. S.; Fronczek, F. R.; Maverick, A. W. Electronic Absorption Spectra and Phosphorescence of Oxygen-Containing Molybdenum(IV) Complexes. *Inorg. Chem.* **1998**, *37* (17), 4258-4264.
86. Savoie, C.; Reber, C. Coupled Electronic States in Trans-Dioxo Complexes of Rhenium(V) and Osmium(VI) Probed by Near-Infrared and Visible Luminescence Spectroscopy. *J. Am. Chem. Soc.* **2000**, *122* (5), 844-852.
87. Grey, J. K.; Butler, I. S.; Reber, C. Effect of Pressure on Coupled Electronic Ground and Excited States Determined from Luminescence Spectra of Trans-Dioxorhenium(V) Complexes. *J. Am. Chem. Soc.* **2002**, *124* (39), 11699-11708.
88. Re, R. E. D.; Hopkins, M. D. Electronic Spectra and Structures of *d*² Molybdenum–Oxo Complexes. Effects of Structural Distortions on Orbital Energies, Two-Electron Terms, and the Mixing of Singlet and Triplet States. *Inorg. Chem.* **2002**, *41* (26), 6973-6985.
89. Mohammed, A. K.; Maverick, A. W. Solution Fluorescence and Photoredox Reactions of Molybdenum (V) Oxo Complexes. *Inorg. Chem.* **1992**, *31* (22), 4441-4443.
90. Liu, Z.; Qin, X.; Chen, Q.; Chen, Q.; Jing, Y.; Zhou, Z.; Zhao, Y. S.; Chen, J.; Liu, X. Highly Stable Lead-Free Perovskite Single Crystals with NIR Emission Beyond 1100 nm. *Adv. Opt. Mater.* **2022**, *10* (21), 2201254.
91. Ahmed, H. A. A. S.; Swart, H. C.; Bergman, P.; Kroon, R. E. Concentration Quenching of Eu²⁺ Doped Ca₂BO₃Cl. *Mater. Res. Bull.* **2016**, *75*, 47-50.

Chapter 1

Introduction

92. Dexter, D. L.; Schulman, J. H. Theory of Concentration Quenching in Inorganic Phosphors. *J. Chem. Phys.* **1954**, 22 (6), 1063-1070.
93. Shionoya, S.; Yen, W. M.; Yamamoto, H. *Phosphor handbook*. CRC press: **2018**.
94. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst. A* **1976**, 32 (5), 751-767.

Chapter 2

Vibronically coupled near-infrared (NIR) emission and excitation from $d-d$ transitions of Cs_2MX_6 ($\text{M} = \text{Mo/W}$, $\text{X} = \text{Cl/Br}$)

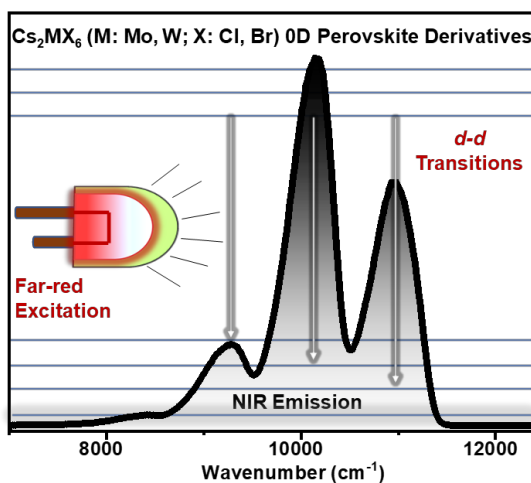
The work of this chapter has been published in the following article:

Mondal, B.; Shinde, A.; Rajput, P. K.; Arfin, H.; Tanwar, R.; Ghosh, P.; Nag, A. Vibronically Coupled Near-Infrared Emission and Excitation from $d-d$ Transitions of Cs_2MX_6 ($\text{M} = \text{Mo/W}$, $\text{X} = \text{Cl/Br}$). *ACS Energy Lett.* **2024**, 9, 819-828.

Copyright permission has been taken for the entire article from the American Chemical Society.

Abstract

In near-infrared (NIR)-emitting phosphors, the emission typically originates from forbidden $d-d$ or $f-f$ electronic transitions of metal ion dopants. But the excitation happens through higher-energy (UV or blue) allowed transitions, resulting in energy loss for this UV- or blue-to-NIR conversion. Here we report Cs₂MX₆ (M = Mo/W, X = Cl/Br) 0D perovskite derivatives with NIR excitation and emission arising from the same pair of d-electronic states, showing small Stokes shifts. The samples show significant optical absorption at 787 nm (12700 cm⁻¹) and emission at 986 nm (10140 cm⁻¹) because of the d^2 electronic configuration of M⁴⁺ in isolated [MX₆]²⁻ octahedra. Interestingly, isolated [MX₆]²⁻ also leads to vibrational fine structures in the electronic excitation and emission spectra at cryogenic temperatures, which are rare for undoped inorganic crystals. Finally, phosphor-converted light-emitting diodes are fabricated by coating Cs₂MoCl₆ on commercial 730 nm LED chips without requiring UV-blue chips.

Graphical abstract

2.1 Introduction

Designing materials for near-infrared (NIR) light-emitting diodes (LEDs) is at the forefront of research because of their various potential applications, including non-invasive bioimaging, night vision, security, and food processing.¹⁻⁸ But electroluminescent NIR LEDs have lower efficiency and/or higher cost compared to visible ones.⁹⁻¹³ The narrow band gap of NIR electroluminescent materials, coupled with overtones of high-frequency vibrations of chemical bonds (such as C–H, N–H, and O–H) in the system or surroundings, leads to quenching of the NIR emission. An alternative approach is to go for phosphor-converted LEDs (pc-LEDs), where the phosphor is a wide-band-gap inorganic material (without high-frequency vibrations) doped with a NIR emitter,¹⁴⁻²⁰ like Cr³⁺-doped Mg₄Ta₂O₉.⁷ But the required excitation energies in such doped phosphors are often too high, falling in the UV-blue region, causing a huge energy loss for this UV-to-NIR or blue-to-NIR optical conversion, even after achieving a high photoluminescence (PL) quantum yield (QY). Therefore, it is desired that the excitation and emission happen through the same pair of electronic states, typically the ground and first excited states of the phosphor, with a small Stokes shift. Colloidal quantum dots like PbS and CuInSe₂ are available options with their own pros and cons.²¹⁻²⁴ Here we show that Cs₂MX₆ (M = Mo/W, X = Cl/Br) zero-dimensional (0D) perovskite derivatives can fulfill the requirement with a unique kind of vibrationally coupled electronic excitation and emission in the NIR region.

Prior reports²⁵⁻²⁷ suggested that some molecular complexes of Mo⁴⁺, Re⁵⁺, and Os⁶⁺ with two d-electrons (*nd*²) showed NIR emission with *d–d* transitions. But their PL QY was not reported to be high at room temperature, probably because of the high-frequency vibrations of organic moieties which quench the PL. In a recent report,²⁸ Cs₂MoCl₆ showed NIR (900–1300 nm) emission with a high PL QY of 26% at room temperature. The emission was assigned to a self-trapped exciton (STE) with a large red-shift of 1.8 eV compared to the excitation. In the backdrop of these somewhat diverging prior reports, we hypothesize that the *d–d* transitions (not a STE) of isolated [MoCl₆]^{2–} octahedra in Cs₂MoCl₆ can lead to NIR emission with a small Stokes shift. The Tanabe–Sugano diagram of the *d*² electronic system suggests that the transition between the ground (³*T*_{1g}) and first excited (³*T*_{1g}–¹*T*_{2g}) state d-electron energy levels can lead to NIR excitation and emission. But the transition is spin- and Laporte-forbidden. So, the excitation will be poor if we dope a few % Mo⁴⁺ into a suitable host. Instead, [MoCl₆]^{2–} octahedra are present thoroughly

out of the undoped Cs₂MoCl₆ crystal, and this high concentration can make the forbidden excitation reasonably strong. Furthermore, the large atomic numbers of Mo⁴⁺ and W⁴⁺ lead to strong spin-orbit coupling (SOC), partially relaxing the spin-selection rules, and the Laporte rule can also be partially relaxed if asymmetric vibrations accompany the electronic excitation/emission process.

To verify this hypothesis, we synthesized Cs₂MX₆ (M = Mo/ W, X = Cl/Br) 0D perovskite derivatives by a facile hydrothermal method and explored their excitation and emission processes in the temperature range of 8–300 K. The absorption spectra showed three *d–d* transitions, namely, $^3T_{1g}-^1T_{2g}/^1E_g$, $^3T_{1g}-^3T_{2g}$, and $^3T_{1g}-^3T_{1g}(P)$, labeled as *E*₁, *E*₂, and *E*₃, respectively. Among those, the spin-forbidden transition *E*₁ has the lowest energy and yields both excitation and emission. The 0D lattice and high rigidity lead to vibrational fine structure in both the excitation and emission spectra, with a small value of the Huang–Rhys parameter (*S* ≈ 2). The high concentration of [MX₆]^{2−} units makes the *E*₁ excitation significantly strong, and that motivated us to fabricate pc-LEDs by coating Cs₂MoCl₆ on commercial 730 nm far-red LED chips, leading to far-red-to-NIR optical conversion.

2.2 Methodology section

2.2.1 Chemicals

Cesium chloride (Sigma Aldrich, CsCl, Reagent plus, 99.9 %), cesium bromide (Sigma Aldrich, CsBr, 99.9%, trace metal basis), molybdenum (V) chloride (thermoscientific, MoCl₅, 99.6%, metal basis), tungsten (IV) chloride (Sigma Aldrich, WCl₄, 95%) and hydrochloric acid (Sigma Aldrich, HCl, 37 wt %, 99.99%), hydrobromic acid (Sigma Aldrich, HBr, 48% w/w in H₂O, 99.9%), poly (methyl methacrylate) (Sigma Aldrich, PMMA), 2-propanol (Rankem), toluene (Sigma Aldrich, anhydrous, 99.8%) and distilled water (Milli-Q).

2.2.2 Synthesis of Cs₂MoCl₆ single crystals

Cs₂MoCl₆ single crystals are synthesized by following a modified hydrothermal method.²⁸ For the synthesis, 168.4 mg (1 mmol) CsCl, 136.6 mg (0.5 mmol) MoCl₅ and 5 mL 10 M HCl (made with 4.2 mL 12 M HCl and 0.8 mL distilled water) are taken in a polytetrafluoroethylene (PTFE) hydrothermal autoclave. The hydrothermal autoclave is heated at 180 °C for 12 hours, then cooled

down to room temperature over a period of 30 hours. Millimeter sized, green colored, crystals are formed. Then the crystals are filtered out, washed several times with 2-propanol and kept in vacuum for drying. These crystals and their powder are used for further characterization and measurements.

2.2.3 Synthesis of Cs_2MoBr_6 single crystals

Cs_2MoBr_6 single crystals are synthesized with the same method followed for Cs_2MoCl_6 crystals. The following are the only differences: instead of CsCl and HCl, 168.4 mg (1 mmol) CsBr and 6 mL 9 M HBr are used and the heating time was 24 hours for this case.

2.2.4 Synthesis of Cs_2WCl_6 single crystals

The synthesis methodology of Cs_2WCl_6 single crystals is same as that of Cs_2MoCl_6 crystals. The only difference is, WCl_4 (0.5 mmol, 162.8 mg) is used to synthesize Cs_2WCl_6 , instead of MoCl_5 .

2.2.5 Structural characterization

Single-crystal X-ray diffraction (SCXRD) measurements are performed using a Bruker Smart Apex Duo diffractometer at room temperature (298 K), equipped with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The frames are integrated with the Bruker SAINT software package by a narrow-frame algorithm. The structures are solved by a direct method and refined by full-matrix least-squares on F² using the SHELXTL software package. Powder X-ray diffraction (PXRD) measurements at room temperature and higher temperatures are carried on Bruker D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation (1.54 $\text{\AA}$). Low temperature PXRD measurements are performed on Malvern Panalytical Empyrean Series 3 X-ray diffractometer with Oxford Cryosystems PheniX which can reach up to 12 K. Chromium-plated copper sample holder is used with the X-ray source of Cu $K\alpha$ radiation (1.54 $\text{\AA}$). Selected area electron diffraction (SAED) patterns are taken by using a UHR FEG-TEM, JEOL JEM 2100F field emission transmission electron microscope which is operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements are carried out using a Kratos Analytical Ltd. (model- Axis Supra) spectrometer featuring monochromatic Al $K\alpha$ as X-ray source. The samples are pressed onto carbon tape and are transferred to the instrument. The samples are non-metallic and suffer from charging during the XPS measurements. To overcome the issue, appropriate charge neutralization is done by using

flood gun. The binding energy values are scaled by fixing the binding energy of C 1s to 284.6 eV. The deconvolution of the experimental core level spectra is performed using the X-ray Photoelectron Spectroscopy Tools (XPST) package in Igor Pro Software. Field emission scanning electron microscopy (FESEM) measurements are carried out using the Zeiss Ultra Plus FESEM instrument. Raman spectra are measured with LM Surelock instrument with an excitation of 633 nm laser.

2.2.6 Optical properties

Optical diffused-reflectance measurements are carried out on Shimadzu UV3600 plus UV-VIS-NIR spectrophotometer. The reflectance data are converted to absorbance by using Kubelka-Munk transformation,²⁹ using the following equation:

$$F(R) = \alpha/S = (1-R)^2/2R \dots\dots (1)$$

where F(R) is the Kubelka-Munk function, R is reflectance, α is absorption coefficient and S is the scattering factor. Steady state photoluminescence (PL) measurements are carried out using FLS 980 (Edinburgh Instruments) using Xe-lamp as excitation source. Time-resolved PL decay profiles are recorded in the same instrument using a microsecond flash lamp as the excitation source (400 nm). All the experimental decay profiles are fitted with mono-exponential decay function:

$$I_t = I_0 + A \exp(-t/\tau) \dots\dots (2)$$

where I_t is PL counts at any variable time = t, I_0 is the offset and τ is the PL lifetime with amplitude A. Temperature-dependent PL measurements are also performed on the FLS980 (Edinburgh Instruments). The substrate (powdered sample is sandwiched between two sapphires) containing the sample is mounted on a gold-plated sample holder attached to a closed cycle He cryostat (Advanced Research Systems) with a temperature controller (Lake Shore Cryotronics) to achieve the desired temperatures.

2.2.7 Phosphor converted light emitting diodes (pc-LEDs)

pc-LEDs are fabricated by coating Cs₂MoCl₆ on commercial LED chips. Finely ground Cs₂MoCl₆ powder (30 mg) is mixed with 25 weight % of PMMA (10 mg) in 100 μ L toluene and heated at 60 °C for 1 hour to obtain a better dispersion. The paste is then drop casted on top of two kinds of

commercial LED chips, one emitting 400 nm light, and the other emitting at 730 nm radiation. The pc-LEDs with 400 nm chip are operated with bias ranging from 2.6 to 3.0 V, the pc-LEDs with 730 nm chip are operated in the range of 1.4 to 1.8 V, achieving NIR emission of varying intensity. The measurements on pc-LEDs are done with Hamamatsu photonic multi-channel analyzer C10028 with Keithley 2450 source meter. A panel of seven Cs_2MoCl_6 NIR pc-LEDs with 730 nm is used as illumination source for imaging fruits in NIR region. The seven pc-LEDs connected in series is operated at 8 V voltage. NIR photography has been done with InGaAs based NIR camera that has sensitivity in the range of 950-1700 nm. A mobile quad camera has been used to take images under room light and described as the visible camera.

2.3 Results and discussion

2.3.1 Synthesis, structure and stability of Cs_2MoCl_6

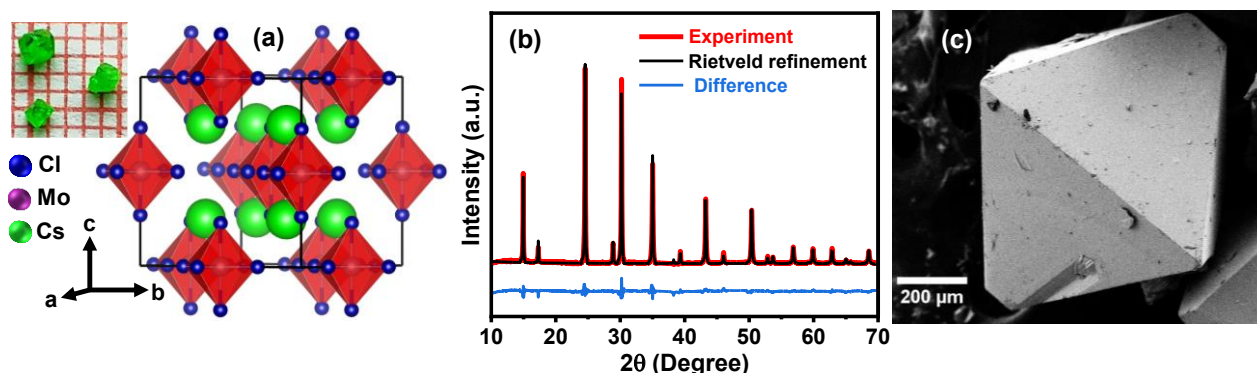


Figure 2.1: (a) Crystal structure of Cs_2MoCl_6 obtained from SCXRD data measured at room temperature. $[\text{MoCl}_6]^{2-}$ octahedra are electronically separated from each other, forming a 0D perovskite derivative structure. The inset shows a digital photograph of the synthesized single crystals (length of 1 box of graph paper = 1 mm). (b) Rietveld refinement (black line) of the PXRD pattern (red line) of Cs_2MoCl_6 . (c) FESEM image of Cs_2MoCl_6 , showing ~ 1 mm sized crystal with octahedral morphology.

Cs_2MoCl_6 single crystals were synthesized by a modified hydrothermal method.²⁸ Stoichiometric amounts of cesium chloride and molybdenum (V) chloride were dissolved in 5 mL of 10 M HCl in a hydrothermal autoclave and heated at 180 °C for 12 h. After the reaction mixture cooled to room temperature at a rate of 5 °C/h, green-colored, millimeter-sized (1–2 mm) single crystals were obtained, as shown in the inset of Figure 2.1a. The crystals were washed with isopropanol,

dried, and stored for further study. Details of their synthesis and characterization are provided in the methodology section.

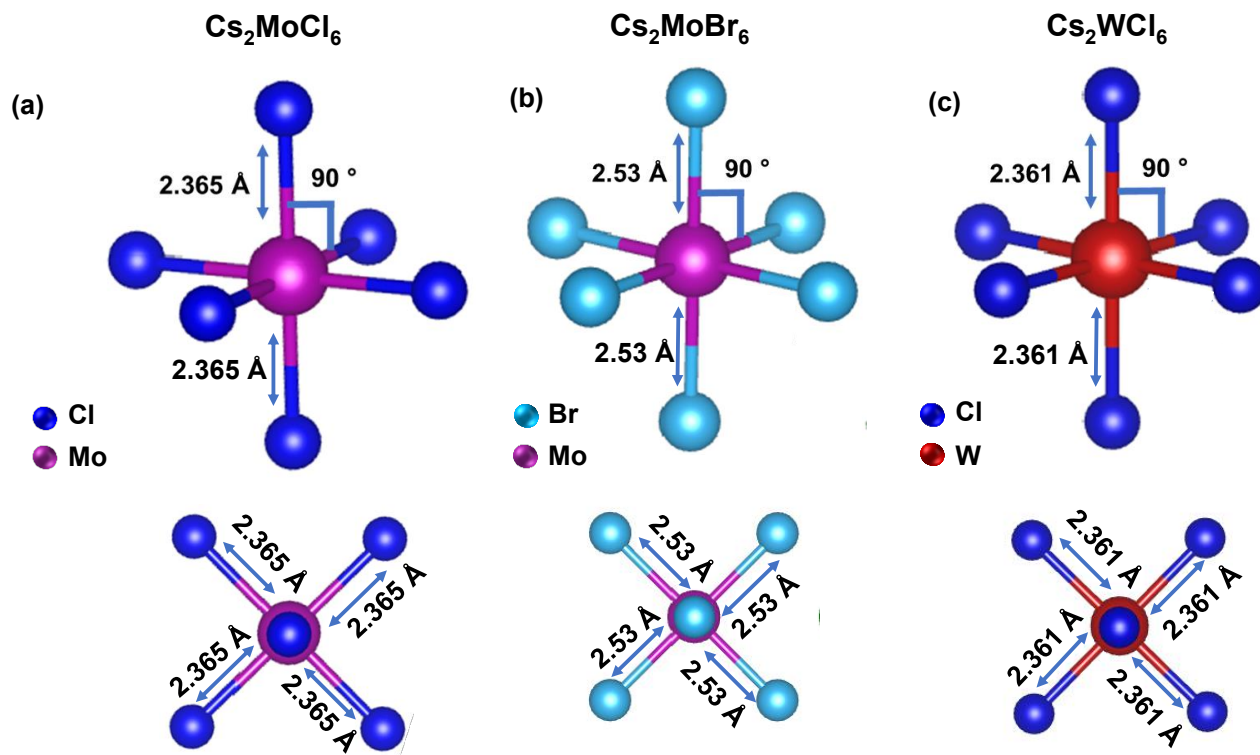


Figure 2.2: Bond length and bond angle representation of (a) $[\text{MoCl}_6]^{2-}$, (b) $[\text{MoBr}_6]^{2-}$ and (c) $[\text{WCl}_6]^{2-}$ octahedra obtained from SCXRD data of Cs_2MoCl_6 , Cs_2MoBr_6 and Cs_2WCl_6 , respectively, at 298 K. Parikshit K. Rajput has helped with the analysis of SCXRD data.

Single-crystal X-ray diffraction (SCXRD) data measured at room temperature show that Cs_2MoCl_6 crystallizes with space group $Fm\bar{3}m$, similar to the prior report.²⁸ The obtained structure is shown in Figure 2.1a. Cs_2MoCl_6 forms a structure where individual $[\text{MoCl}_6]^{2-}$ octahedra are separated from each other by large Cs^+ ions, resulting in the crystal being electronically 0D. Such a structure can be considered as a vacancy-ordered perovskite/double-perovskite structure^{30, 31} and is referred to here as a 0D perovskite derivative. This is a cubic lattice with parameters of $a = b = c = 10.24 \text{ Å}$ and $\alpha = \beta = \gamma = 90^\circ$. More details on structural refinement parameters are provided in Table 2.1. The similarity in Mo-Cl bond lengths (2.365 Å) and Cl-Mo-Cl bond angles (90° and 180°) in Figure 2.2a confirms the octahedral nature of the $[\text{MoCl}_6]^{2-}$ unit. [Figure 2.1b](#)

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo}/\text{W}$, $X = \text{Cl}/\text{Br}$)

shows the powder X-ray diffraction (PXRD) pattern of Cs_2MoCl_6 at room temperature. Structural refinement was done using the Rietveld refinement method, and the parameters are given in Table 2.2. The experimental PXRD pattern is in good agreement with the simulated one obtained from our SCXRD data, having a residual least-squares refinement (R_p) value of 1.9 and a weighted residue (R_{wp}) value of 3.4. This refinement confirms the phase purity of the overall sample in the powder form. Also, the selected area electron diffraction (SAED) pattern (Figure 2.3) of Cs_2MoCl_6 matches with the PXRD pattern. X-ray photoelectron spectroscopy (XPS) data for Mo 3d, Cs 4s, Cs 3d, and Cl 2p core levels of Cs_2MoCl_6 are shown in Figure 2.4. Only one kind of Mo species is observed. Its oxidation state agrees with Mo^{4+} , supporting the formation of Cs_2MoCl_6 . It has to be noted here that the sample is non-conducting in nature and the XPS data need to be recorded after ensuring a proper charge compensation. The field emission scanning electron microscopy (FESEM) image of Cs_2MoCl_6 in Figure 2.1c. shows a single crystal having an octahedral morphology and size of ~ 1 mm, which can be correlated with the digital image of the crystal (inset of Figure 2.1a).

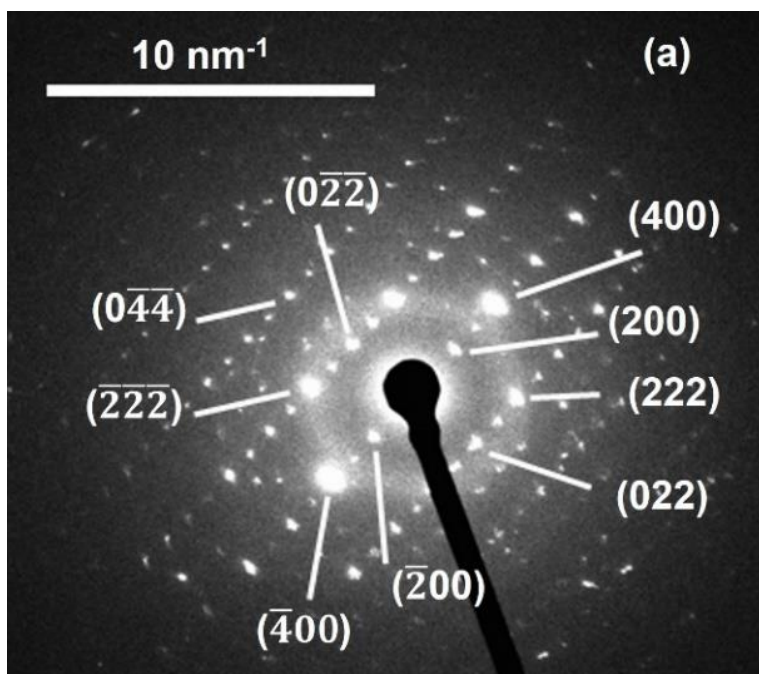


Figure 2.3: SAED pattern of Cs_2MoCl_6 .

Chapter 2

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br)

Table 2.1: Crystal structure refinement of Cs₂MoCl₆, Cs₂MoBr₆ and Cs₂WCl₆, using SCXRD data measured at room temperature (298 K). Parikshit K. Rajput has helped with the analysis of SCXRD data.

Identification code	Cs ₂ MoCl ₆	Cs ₂ MoBr ₆	Cs ₂ WCl ₆
Chemical formula	Cs ₂ MoCl ₆	Cs ₂ MoBr ₆	Cs ₂ WCl ₆
CCDC number	2292099	2292100	2292098
Formula weight	574.46 g/mol	841.22 g/mol	662.37 g/mol
Temperature	298(2) K	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	cubic	cubic	cubic
Space group	F m $\bar{3}$ m	F m $\bar{3}$ m	F m $\bar{3}$ m
Unit cell dimensions	a=b=c= 10.2467(5) Å $\alpha=\beta=\gamma= 90^\circ$	a=b=c= 10.647(4) Å $\alpha=\beta=\gamma= 90^\circ$	a=b=c= 10.2179(13) Å $\alpha=\beta=\gamma= 90^\circ$
Volume	1075.85(16) Å ³	1207.0(13) Å ³	1066.8(4) Å ³
Z	4	4	4
Density (calculated)	3.547 g/cm ³	4.629 g/cm ³	4.124 g/cm ³
Absorption coefficient	9.305 mm ⁻¹	26.830 mm ⁻¹	18.983 mm ⁻¹
F (000)	1016	1448	1144
Theta range (For data collection)	3.44 to 28.06°	3.31 to 24.97°	3.45 to 28.14°
Index ranges	-13<= <i>h</i> <=13 -13<= <i>k</i> <=13 -13<= <i>l</i> <=13	-12<= <i>h</i> <=12 -12<= <i>k</i> <=12 -12<= <i>l</i> <=12	-10<= <i>h</i> <=13 -13<= <i>k</i> <=13 -13<= <i>l</i> <=13
Reflection collected	4278	4681	3311
Independent reflections	96	77	96
Coverage (Independent reflections)	100%	98.7%	100%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Structure solution technique	direct methods	direct methods	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	SHELXT 2014/5 (Sheldrick, 2014)	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²		
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	SHELXL-2018/3 (Sheldrick, 2018)	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	96 / 0 / 7	77 / 6 / 7	96 / 0 / 7
Goodness-of-fit on F²	1.297	1.163	1.936
Final R indices; I>2σ(I)	R1 = 0.0306, wR2 = 0.1308	R1 = 0.0517, wR2 = 0.1328	R1 = 0.0298, wR2 = 0.1969
All data	R1 = 0.0314, wR2 = 0.1335	R1 = 0.0252, wR2 = 0.1338	R1 = 0.0301, wR2 = 0.1973
Weighting scheme	w=1/[σ ² (F _o ²)+(0.1000P) ²] where P=(F _o ² +2F _c ²)/3		

Chapter 2

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br)

Table 2.2: Structural parameters from Rietveld refinement of PXRD data of Cs₂MoCl₆, Cs₂MoBr₆ and Cs₂WCl₆ at room temperature (298 K).

Chemical formula	Cs ₂ MoCl ₆	Cs ₂ MoBr ₆	Cs ₂ WCl ₆
Wavelength	1.5406 Å (Cu Kα)	1.5406 Å (Cu Kα)	1.5406 Å (Cu Kα)
Crystal system	Cubic	Cubic	Cubic
Space group	Fm $\bar{3}$ m	Fm $\bar{3}$ m	Fm $\bar{3}$ m
a = b = c (Å)	10.23(4)	10.639(4)	10.216(3)
α = β = γ (deg)	90.00(1)	90.00(2)	90.000(3)
Unit cell volume (Å ³)	1070.5(6)	1204.21(6)	1066.20(5)
R _p (%)	1.9	5.7	7.3
R _{wp} (%)	3.4	7.6	9.2
R _{exp} (%)	2.5	5.4	7.2
χ ²	3.24	3.61	2.56
GoF	1.8	1.9	1.6

The thermal stability of the sample was determined by measuring high-temperature PXRD patterns and doing thermogravimetric analysis (TGA). The TGA data in Figure 2.5a in the SI show no weight loss up to 573 K. High-temperature PXRD data Figure 2.6 also show the thermally stable crystal phase of the sample. The observation that Cs₂MoCl₆ is stable up to 573 K (300 °C) is encouraging for pc-LED applications.³² The stability of Cs₂MoCl₆ powder has also been checked by storing the sample for 150 days in three different conditions, namely, in air, in a vacuum desiccator, and in the inert environment of nitrogen gas inside a glovebox. In all three cases, the PXRD data shown in Figure 2.7 confirm that the sample remains phase-pure over 150 days. Likewise, the PL spectral features and intensity (Figure 2.8) of Cs₂MoCl₆ also remain largely stable during these 150 days.

Chapter 2

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

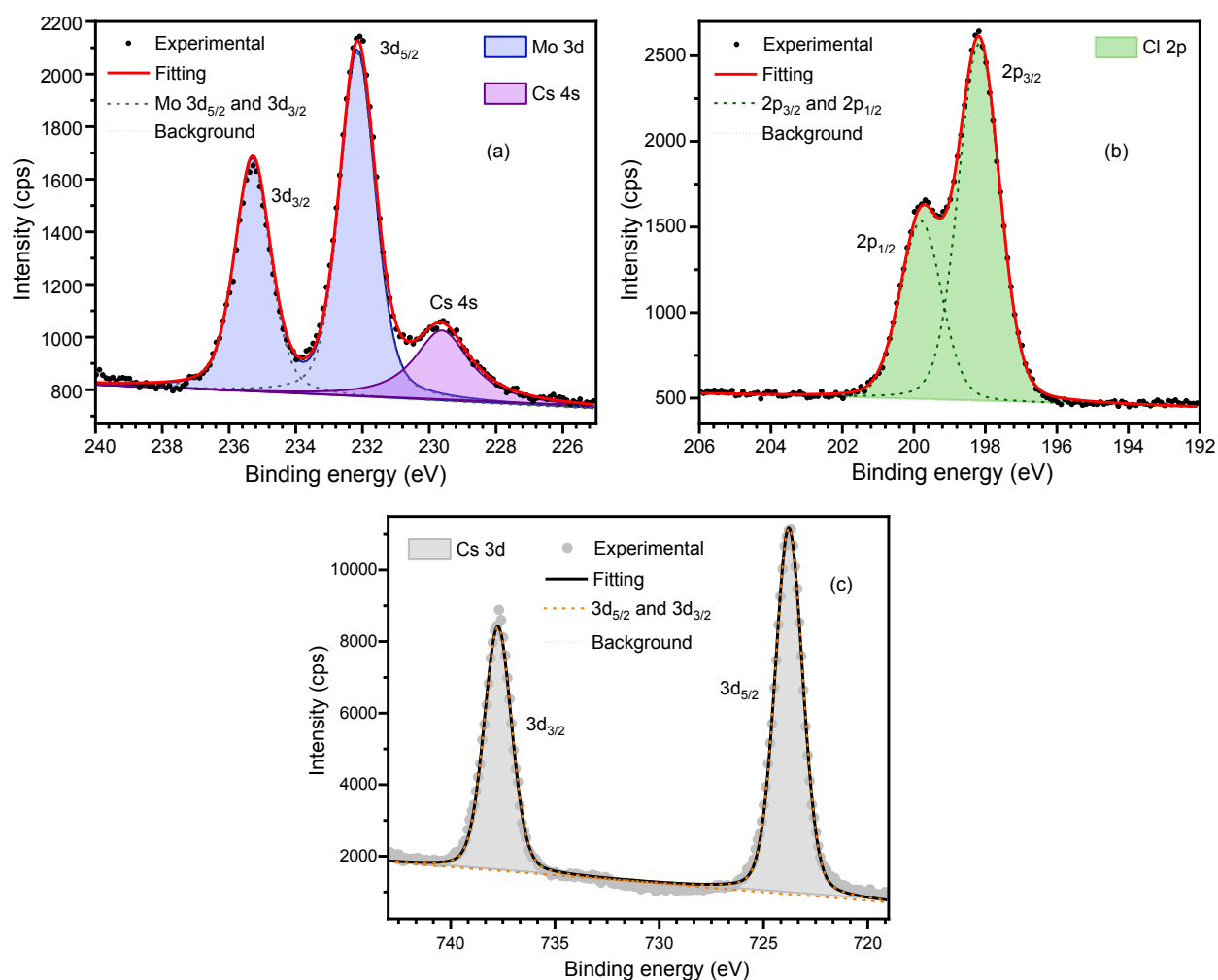


Figure 2.4: XPS core level spectra of Cs_2MoCl_6 : (a) Mo 3d (blue) and Cs 4s (purple) spectra, (b) Cl 2p, and (c) Cs 3d. The spectral deconvolution and overall fitting are shown. The fitting has been done by Prof. Pralay K. Santra, CeNS, Bangalore.

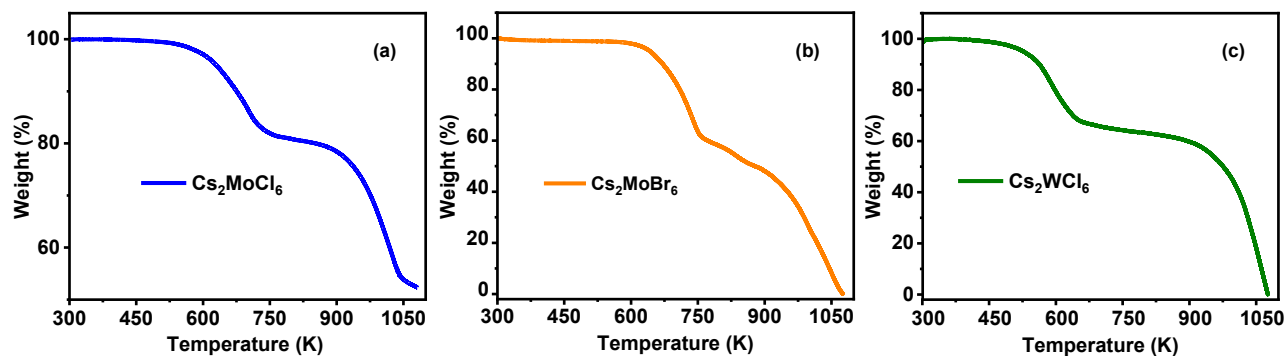


Figure 2.5: Thermogravimetric analysis (TGA) data of (a) Cs_2MoCl_6 , (b) Cs_2MoBr_6 , and (c) Cs_2WCl_6 .

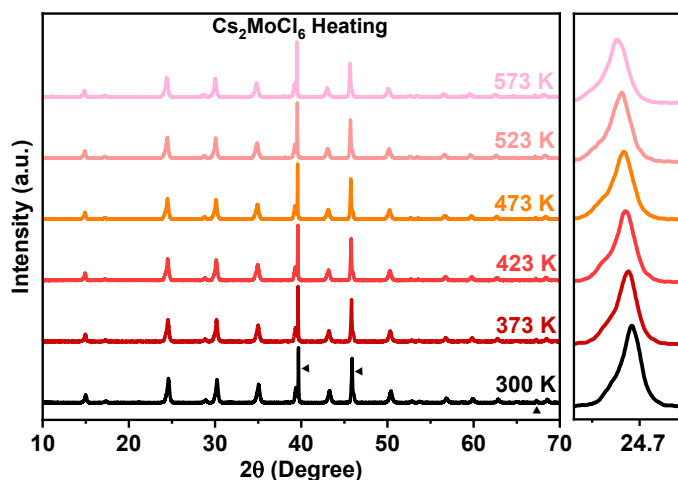


Figure 2.6: High temperature PXRD data of Cs_2MoCl_6 powder while heating the sample from 300 to 573 K. Peaks with triangular mark are due to Pt substrate. Phase purity is maintained in the entire temperature range. Enlarged view of one peak showing lower 2θ shift of the patterns with increasing temperature implies unit cell expansion.

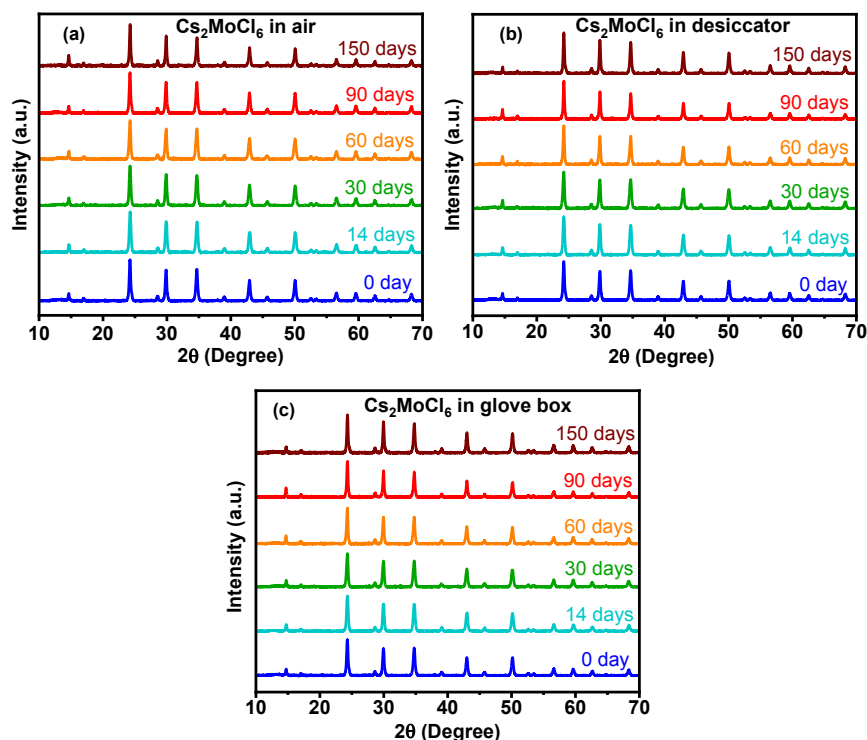


Figure 2.7: PXRD patterns of Cs_2MoCl_6 crystals after storing the sample in (a) air, (b) vacuum desiccator, and (c) nitrogen filled glove box for different time intervals. The patterns suggest phase purity in all three cases above 150 days.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

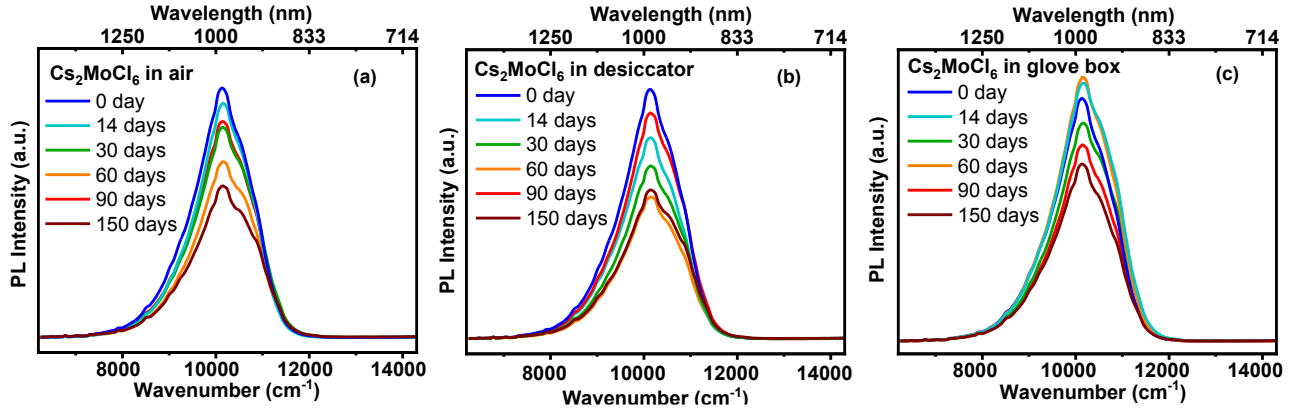


Figure 2.8: PL spectra of Cs_2MoCl_6 after storing the sample in (a) air, (b) vacuum desiccator, and (c) nitrogen filled glovebox for different time intervals. In all spectra, excitation wavenumber is 25000 cm^{-1} (400 nm). Other instrumental parameters are also kept same. Same amount of samples is taken for every measurement. The spectral features do not change with time, but a small decrease in intensity is observed. Overall, the data suggest a reasonable stability of PL over 150 days.

2.3.2 Optical characterization and Tanabe-Sugano diagram of Cs_2MoCl_6

Figure 2.9a shows the UV-visible-NIR absorption spectrum (blue line) and PL spectrum (red line) of Cs_2MoCl_6 powder, recorded at room temperature. The absorption spectrum shows three major features at wavenumbers $E_1 = 12700 \text{ cm}^{-1}$ (787 nm), $E_2 = 22000 \text{ cm}^{-1}$ (455 nm) and $E_3 = 28000 \text{ cm}^{-1}$ (357 nm). Mo^{4+} has an electronic configuration of $[\text{Kr}]4d^2$, where $[\text{Kr}]$ represents the electronic configuration of Kr. Also, the 0D crystal structure of Cs_2MoCl_6 leads to electronic structure dominated by the isolated $[\text{MoCl}_6]^{2-}$ octahedra. In such a situation, the three absorption bands might be attributed to $d-d$ electronic transitions of Mo^{4+} ions in the octahedral environment, following the Tanabe-Sugano diagram³³ shown in Figure 2.9b. The transitions can be assigned to $^3T_{1g} \rightarrow ^1T_{2g}/^1E_g$ (E_1), $^3T_{1g} \rightarrow ^3T_{2g}$ (E_2) and $^3T_{1g} \rightarrow ^3T_{1g}$ (P) (E_3) $d-d$ transitions of Mo^{4+} . Among these, E_1 is spin-forbidden, but the SOC of heavy metal ion Mo^{4+} can partially relax the spin selection rule.³⁴ The experimental ratios of E_2/E_1 and E_3/E_1 match with the obtained ratios from Tanabe-Sugano diagram at Dq/B value of 2.39. The value of B is found to be $\sim 880 \text{ cm}^{-1}$ and the crystal-field splitting energy ($10Dq$) of Cs_2MoCl_6 is $\sim 21000 \text{ cm}^{-1}$. Details of this calculation is presented below.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo}/\text{W}$, $X = \text{Cl}/\text{Br}$)

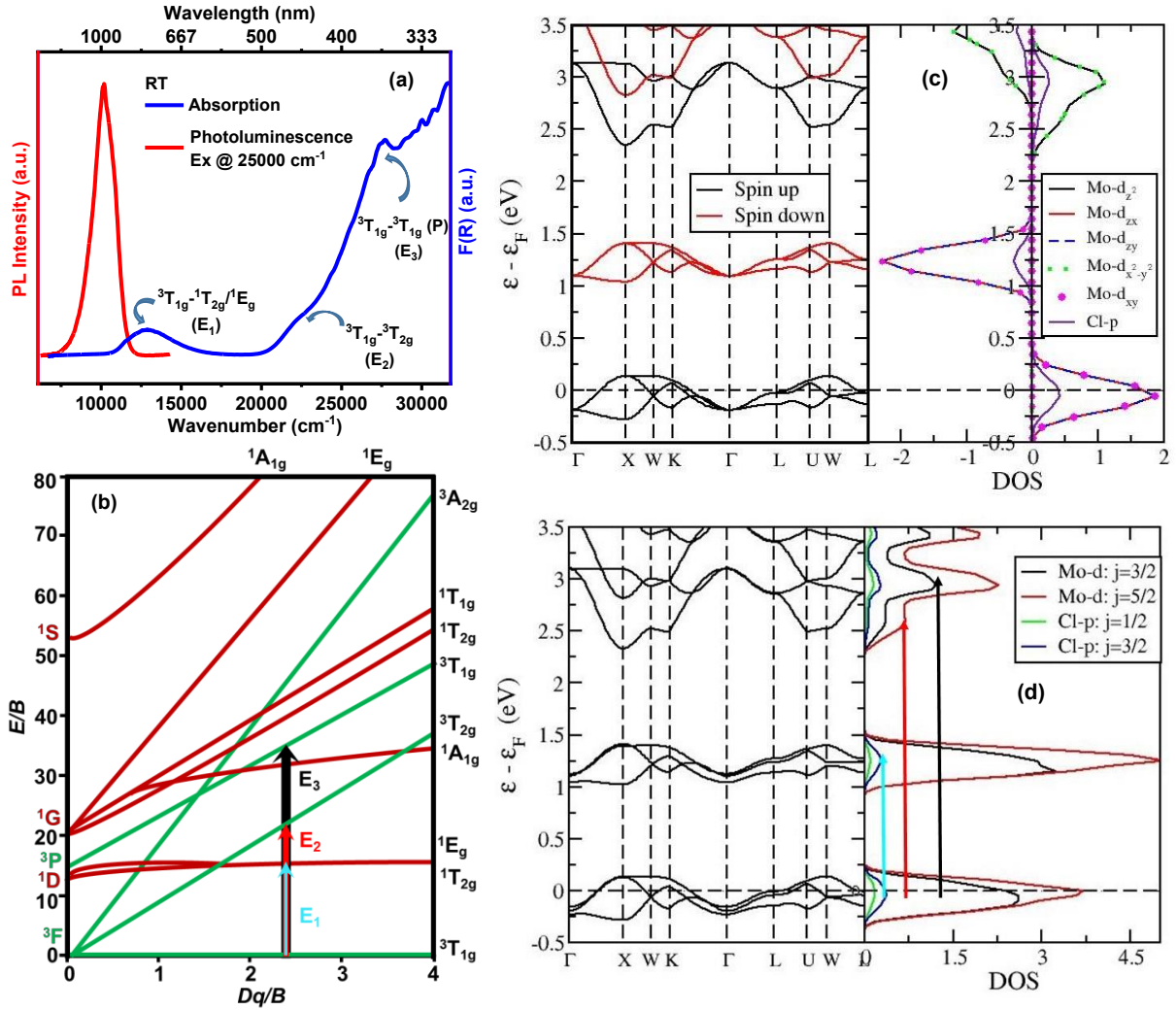


Figure 2.9: (a) UV-visible-NIR absorption spectrum (blue line) and NIR emission spectrum (red line) of Cs_2MoCl_6 powder at room temperature. Here, reflectance (R) data are converted to absorbance by using Kubelka-Munk function, $F(R) = (1-R)^2/2R$.²⁹ (b) Tanabe-Sugano diagram of d^2 electronic configuration in an octahedral crystal environment showing three transitions, E_1 (turquoise arrow), E_2 (red arrow), and E_3 (black arrow), for the Cs_2MoCl_6 crystal at a Dq/B value of 2.39. Dq is the crystal field parameter, B is the Racah parameter, and E represents transition wavenumber. (c) Left panel: spin-resolved band structure of Cs_2MoCl_6 . Right panel: contributions to the density of states (DOS) from the Mo- d orbitals and Cl- p orbitals. (d) Same as (c) but computed with inclusion of spin-orbit coupling interactions. The vertical lines in turquoise, red, and black denote the initial and final states involved in the transitions corresponding to E_1 , E_2 , and E_3 , respectively. The DFT calculations were done by Prof. Prasenjit Ghosh of Physics Department of IISER Pune. The study has been included here for the sake of completion of the work.

Calculation of E , B , Dq and $10Dq$ for Cs₂MoCl₆ comparing experimental data (Figure 2.9a) with Tanabe-Sugano diagram (Figure 2.9b):

Experimental (Figure 2.9a):

$$E_1 = 12700 \text{ cm}^{-1}, E_2 = 22000 \text{ cm}^{-1}, \text{ and } E_3 = 28000 \text{ cm}^{-1}.$$

$$\text{So, } E_2/E_1 = 1.73, E_3/E_1 = 2.20, \text{ and } E_3/E_2 = 1.27$$

Tanabe-Sugano diagram (Figure 2.9b):

$$\text{At } Dq/B = 2.39$$

$$E_1/B = 15, E_2/B = 22.8, \text{ and } E_3/B = 34.7$$

$$\text{So, } E_2/E_1 = 1.52, E_3/E_1 = 2.31, \text{ and } E_3/E_2 = 1.52$$

The ratios obtained from the Tanabe-Sugano diagram match with the experimental ratio.

Averaging the values obtained from all three transitions, $B_{\text{avg}} \approx 880 \text{ cm}^{-1}$.

$$Dq = 2.39 \times B_{\text{avg}} = 2103.2 \text{ cm}^{-1}.$$

Therefore, crystal field splitting energy ($10Dq$) $\approx 21000 \text{ cm}^{-1}$.

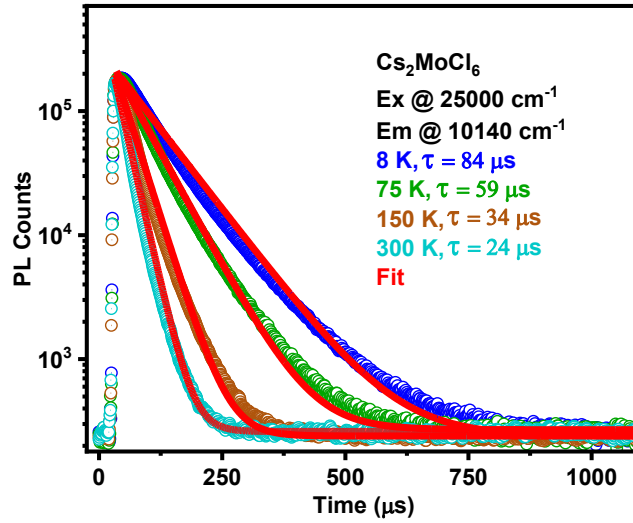


Figure 2.10: PL decay dynamics of Cs₂MoCl₆ at different temperatures, fitted with a mono-exponential decay function shown in eq. 2 of methodology section. Lifetime is indicated by τ .

Along with these absorptions, we observe NIR emission with a peak at 10140 cm^{-1} (986 nm) from Cs₂MoCl₆ at room temperature, as shown in Figure 2.9a. The emission overlaps with the absorption band with a peak at $E_1 = 12700 \text{ cm}^{-1}$ with a Stokes shift of 2560 cm^{-1} . The PL lifetime at 10140 cm^{-1} is found to be $24 \text{ } \mu\text{s}$ at 300 K, as shown in Figure 2.10. The long lifetime agrees with a

Chapter 2

Vibronically coupled near-infrared emission and excitation from $d-d$ transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

(partially relaxed) spin-forbidden $d-d$ transition, which is also Laporte-forbidden. Note that Mo^{5+} , with d^1 electronic configuration, is known to exhibit a spin-allowed $d-d$ transition for PL with a lifetime of a few tens to 100 ns, whereas Mo^{6+} , with d^0 configuration, is not expected to show any $d-d$ transition.²⁵ Based on the energy and lifetime, we assign the emission as de-excitation of E_I , i.e., $^1T_{2g}/^1E_g \rightarrow ^3T_{1g}$ transitions of Mo^{4+} ions. We note that our assignment of the absorption and emission processes of Cs_2MoCl_6 is completely different from the prior report,²⁸ where the E_I absorption was attributed to defect states and the NIR emission was assigned as STE emission.

In order to ascertain that these low energy peaks originate from $d-d$ transitions within Mo^{4+} , we have computed the band structure using the Quantum ESPRESSO software, which is a plane wave-based implementation of density functional theory. The computed lattice parameters and Mo-Cl bond lengths with different levels of theory are given in the Table 2.3. We find that the results are in excellent agreement with the experimental values.

Table 2.3: Computed lattice parameter and Mo-Cl bond lengths with different levels of theory.

Level of theory	Lattice parameter (Å)	Mo-Cl bond length (Å)
PBE	10.25	2.40
PBE+SOC	10.26	2.40
PBE+U (U=1.0 eV)	10.24	2.40
PBE+U (U=4.0 eV)	10.25	2.42

In the crystal, the d -states of the Mo ion occupying the zero-dimensional $[\text{MoCl}_6]^{2-}$ octahedra are split into two sets, namely, low-energy triply degenerate t_{2g} (comprising d_{zx} , d_{zy} and d_{xy}) and high-energy doubly degenerate e_g (comprising d_{z^2} and $d_{x^2-y^2}$). Since Mo^{4+} is a d^2 system, the two unpaired electrons give rise to a magnetic moment of $2 \mu_B$. The valence band of the crystal consists of partially filled t_{2g} states in the spin-up channel while the conduction band originates from the empty t_{2g} states in the spin-down channel, as shown in Figure 2.9c. The empty e_g states for both the spin channels are above 2.25 eV. Moreover, from the projected density of states (PDOS) plots (right panel of Figure 2.9c), we see that there is very little contribution from Cl- p states indicating negligible hybridization between Mo- d and Cl- p states, a consequence of which the frontier states

in this system are highly localized on the Mo atoms. This results in very small dispersion of the valence and conduction bands. Hence, these states will behave more like atomic orbitals and the crystal will not have delocalized free electrons, even though the Fermi energy passes through the valence band. We note that our results are in agreement with those reported by Zhang et al.³⁵ On incorporating the spin-orbit interactions into our calculations, we did not observe any significant change in the band positions (left panel of Figure 2.9d). However, we observe that the degeneracies in the electronic states at the Γ -point of the Brillouin zone are lifted. Moreover, it is interesting to note that now both the valence and conduction band edges have contributions from $j = 3/2$ and $j = 5/2$ states (right panel of Figure 2.9d). The SOC relaxes the spin-forbidden nature of the electronic transitions between the valence and conduction bands, which explains the observation of a low intensity long wavelength absorption peak in Figure 2.9a.

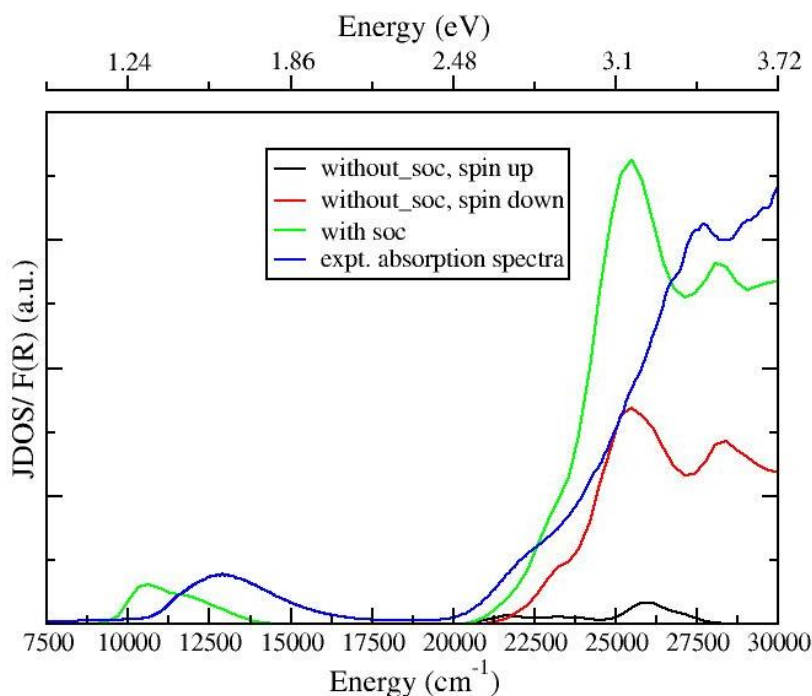


Figure 2.11: The JDOS for Cs_2MoCl_6 , with and without SOC coupling. For the case where spin orbit coupling is not considered, the black and the red plots correspond to JDOS of the electrons occupying the spin-up and spin-down channels. The green plot corresponds to JDOS when SOC is considered while the blue one is the experimental absorption spectrum. The DFT calculations were done by Prof. Prasenjit Ghosh of Physics Department of IISER Pune. The study has been included here for the sake of completion of the work.

To further ascertain this hypothesis and understand the electronic states involved in the excitations corresponding to the E_1 , E_2 and E_3 peaks in the experimental absorption spectrum of Cs_2MoCl_6 , we have computed the joint density of states (JDOS) with and without SOC. The results and their comparison with the experimental absorption spectrum are shown in Figure 2.11. We observe that without SOC, the lowest energy edge of the JDOS starts from about 2.79 eV, which is much higher in energy than the lowest energy peak (1.57 eV) observed in the experimental spectrum. This is because the lowest energy empty states available for the electrons occupying the spin-up states to be excited to correspond to the spin-down channel and such transitions are spin-forbidden. On the contrary, the JDOS computed with SOC is in reasonably good agreement with the experimentally observed absorption spectra. Consistent with the experimental spectrum, we observe that the JDOS has a broad peak at about 1.24 eV that corresponds to transitions from the partially occupied states just below the Fermi energy to the empty states at around 1.24 eV (turquoise vertical arrow in Figure 2.9d). The broad nature of this peak can be attributed to the fact that, unlike in the case of molecules, in Cs_2MoCl_6 crystal, the bands corresponding to the occupied and empty states have a finite width of about 0.5 eV. The shoulder at 2.73 eV of the experimental spectrum can be attributed to transitions corresponding to the empty states at about 2.60 eV above the Fermi energy (red vertical arrow in Figure 2.9d), while the third peak corresponds to transitions to the empty band at about 2.9 eV above the Fermi energy (black vertical line in Figure 2.9d).

2.3.3 Vibronically coupled electronic excitation and emission and structural rigidity of Cs_2MoCl_6

At 300 K, the NIR PL is asymmetric one with appearance of multiple shoulders. To have a better spectral resolution, PL spectra are measured at lower temperatures until 8 K. Figure 2.12a presents the evolution of the PL spectra upon lowering the measurement temperature. The shoulder-like features at 300 K, become more prominent as the temperature is reduced, and below 150 K the broad emission splits into three prominent peaks. This evolution of three sharp PL peaks, measured at many more temperatures, is also clearly observed from the pseudo-colormap shown in Figure 2.12b. The peak positions of all three peaks remain almost unchanged throughout the temperature range. Expectedly, the intensity of PL emission (in Figure 2.12b) increases as the temperature is lowered due to the suppression of thermally activated non-radiative recombination channels at lower temperatures.

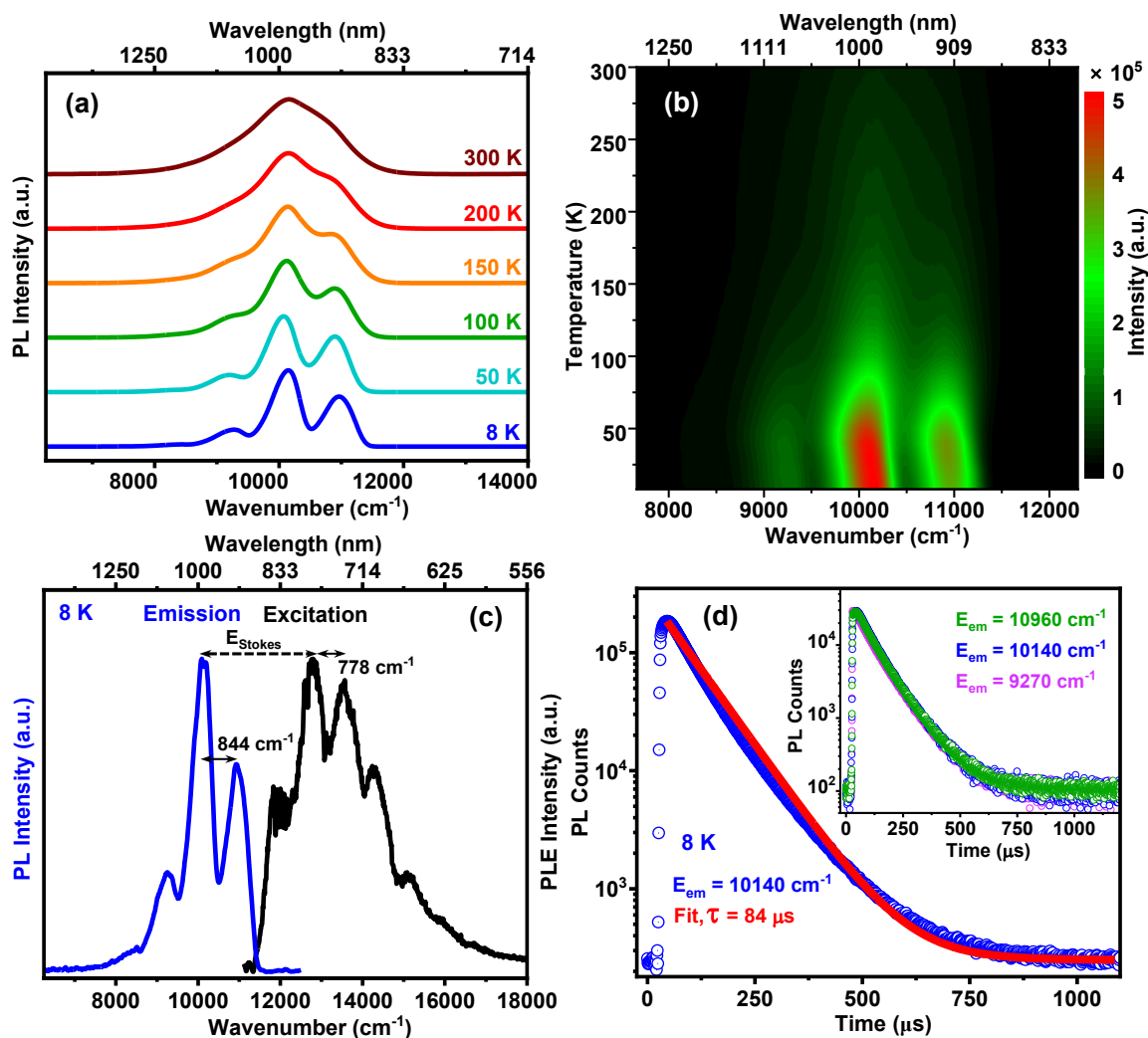


Figure 2.12: Temperature-dependent PL (excited at 25000 cm^{-1} or 400 nm) of Cs_2MoCl_6 crystal. (a) PL spectra recorded at a few representative temperatures with powdered sample in the temperature range of 8-300 K. (b) Pseudo-colormap of temperature-dependent PL throughout the temperature range of 8-300 K. (c) PL emission (blue) and excitation (black) spectra showing vibrational fine lines with splitting energies (844 and 778 cm^{-1} , respectively) recorded at 8 K. PL excitation (PLE) was recorded for emission at 10140 cm^{-1} . (d) PL decay dynamics measured at 8 K for emission at 10140 cm^{-1} with a mono-exponential decay fitting. Inset shows overlapped PL decay profiles of three emission peaks shown in (c).

What are the multiple narrow peaks in the PL spectra at low temperatures? To address this questions, Figure 2.12c represents PL emission (blue) and excitation (black) spectra of Cs_2MoCl_6 recorded at 8 K. Nearly equi-spaced (844 cm^{-1}) progression of split peaks is observed for the emission spectrum, and the case is similar for the excitation spectrum. It is to be noted that the

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

PLE spectrum has minor contributions from the scattered excitation light, particularly around 12000 cm^{-1} , as shown in Figure 2.13. The data appear somewhat similar to the mirror-image electronic excitation and emission spectra coupled with vibrational states.^{36, 37} These results suggest that the excitation and emission originate from the same pair electronic states: excitation is because of $^3T_{1g} \rightarrow ^1T_{2g}/^1E_g$ and emission (de-excitation) is because of $^1T_{2g}/^1E_g \rightarrow ^3T_{1g}$ transitions. And the nearly equi-spaced fine lines in PL excitation (PLE) and PL emission are the vibronic progression coupled with the electronic transitions. This assignment is also supported by the Raman spectrum of Cs_2MoCl_6 (Figure 2.14) that shows vibrational feature at $\sim 860\text{ cm}^{-1}$, similar to the spacing between PL fine structures.

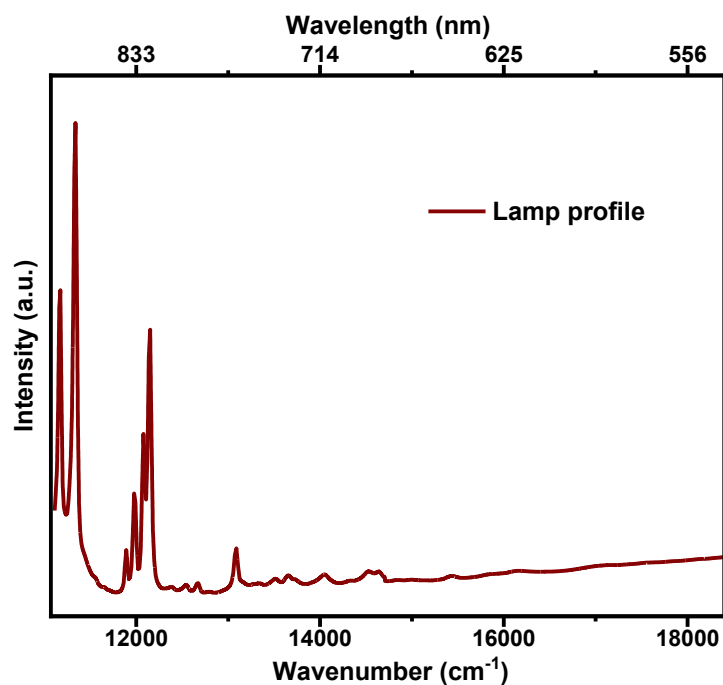


Figure 2.13: The lamp profile of Xe lamp used as excitation source for measuring PL emission and excitation spectra.

To further verify our PL peak assignments, we measured PL decay profiles of Cs_2MoCl_6 at the three major peaks, 10960 , 10140 , and 9270 cm^{-1} . Figure 2.12d shows the experimental decay profile for emission at 10140 cm^{-1} measured at 8 K , along with the mono-exponential decay fitting. Inset represents the overlapped decay profiles for all three peaks. This overlap suggests that all three peaks have almost identical decays with a lifetime of $84\text{ }\mu\text{s}$ at 8 K . This similarity again

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

suggests that all three peaks evolve from the same electronic transition but involve different vibrational levels. The obtained lifetime of $\sim 84 \mu\text{s}$ agrees with partially spin- and Laporte-forbidden $^1T_{2g}/^1E_g \rightarrow ^3T_{1g}$ d-d transition of the Mo^{4+} in Cs_2MoCl_6 . The PL lifetimes decrease with increasing temperature. For example, Figure 2.10 shows that the lifetime of the 10140 cm^{-1} emission decreases monotonously from $84 \mu\text{s}$ at 8 K to $24 \mu\text{s}$ at 300 K. This decrease is because of the faster non-radiative relaxation pathways of the excited state at higher temperatures.

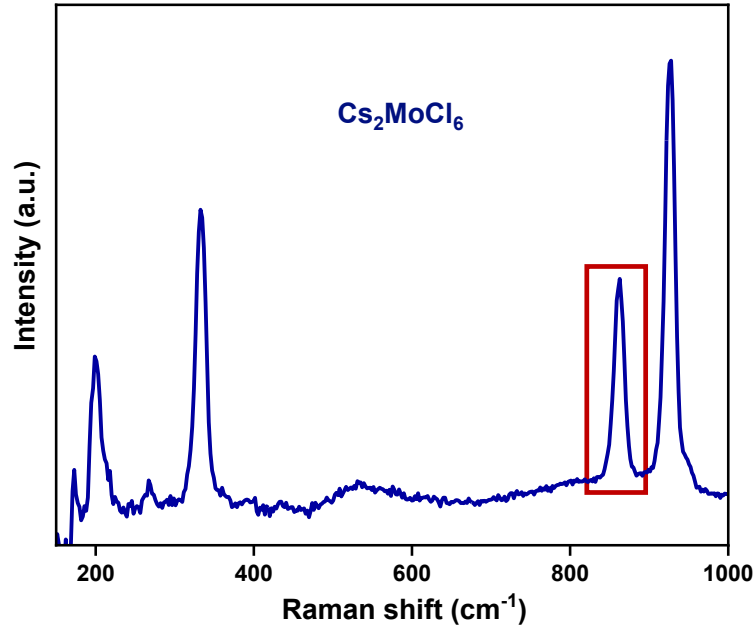


Figure 2.14: Raman spectrum of Cs_2MoCl_6 powder at room temperature after excitation at 633 nm. The experiment has been carried out by Ms. Riteeka Tanwar of IISER Pune.

To obtain further insights into the structural rigidity and electron-phonon coupling for the NIR emission of Cs_2MoCl_6 , we estimated Huang-Rhys parameter (S) by following equation (3):³⁶

$$S = \left(\frac{1}{2} \frac{E_{\text{Stokes}}}{\hbar\omega_{\text{phonon}}} + \frac{1}{4} \right) \pm \frac{1}{4} \quad (3)$$

From the PL emission spectra at 8 K (Figure 2.12c), we find the vibrational energy or phonon energy, $\hbar\omega_{\text{phonon}} = 844 \text{ cm}^{-1}$. We can also estimate the Stokes shift, $E_{\text{Stokes}} = 2650 \text{ cm}^{-1}$, at 8 K. E_{Stokes} is the energy difference between maxima of absorption (excitation) and emission originating from the same electronic transition. Using these values, we estimated $S = 1.82 \pm 0.25$. The obtained value of S is quite small, indicating that the bond length change during the electronic transition is

small. The small S indicates minimal electron-phonon coupling and higher crystal rigidity for 0D Cs₂MoCl₆. This small value of S also supports our finding that the origin of NIR emission is the $d-d$ transition, and not a STE, for which typically S is more than an order of magnitude larger (~ 40).^{38, 39} Also, the small value of E_{Stokes} and observation of vibrational lines in PL are not expected for STE emission.⁴⁰⁻⁴²

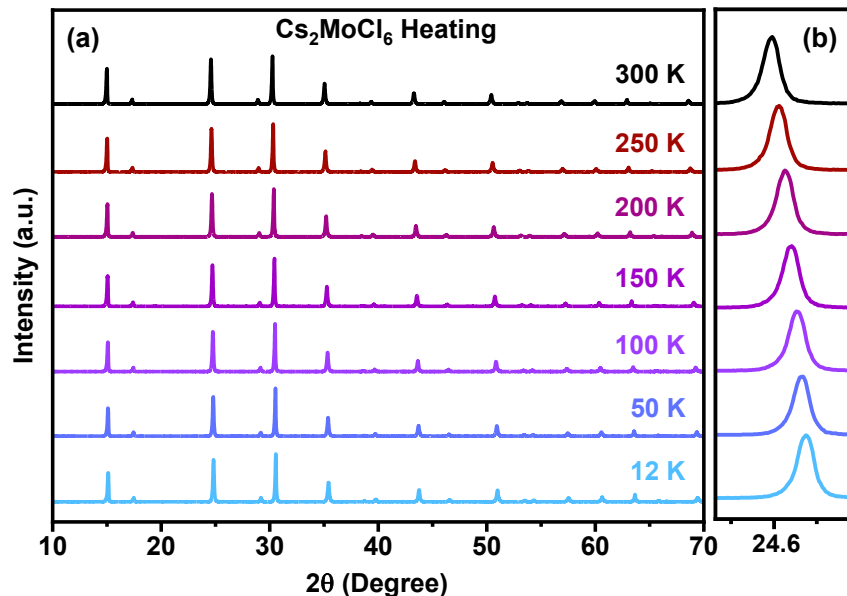


Figure 2.15: (a) PXRD patterns of Cs₂MoCl₆ at variable temperatures in the range of 12-300 K. The patterns show no phase change in this temperature range. (b) Enlarged view of one peak showing the shift towards lower 2θ values with the increase of temperature due to lattice expansion.

To correlate the low-temperature PL data with the stability and rigidity of the crystal structure, we have measured PXRD patterns in the temperature range of 12-573 K. Figure 2.15a and Figure 2.6 show that the structural phase of Cs₂MoCl₆ remains unchanged (cubic, $Fm\bar{3}m$) throughout the temperature range of 12-573 K. Figure 2.15b shows a systematic shift of XRD peaks toward lower 2θ values, with increasing temperature. Lower 2θ indicates higher interplanar distances because of the larger unit cell volume. Figure 2.16 shows a linear expansion of unit cell volume with increasing temperature in the entire range of 12-573 K. The data are fitted, yielding a thermal volume expansion coefficient, $\gamma_{v, 300 K} = 8.6 \times 10^{-5} \text{ K}^{-1}$. This thermal expansion coefficient is smaller than those for typical hybrid perovskites and comparable to those for typical all-inorganic halide perovskites,⁴³ suggesting reasonably good structural rigidity of Cs₂MoCl₆.

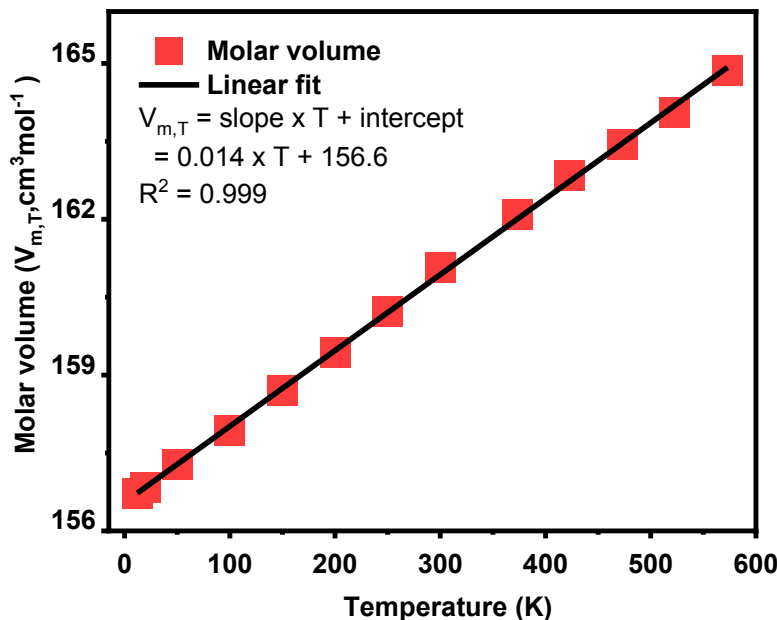


Figure 2.16: (a) Variation of molar volume ($V_{m,T}$) of Cs_2MoCl_6 with increasing temperature, calculated from the corresponding PXRD patterns (Figure 2.6 and Figure 2.15a). $V_{m,T} = V_T \times N_A/Z_F$, where N_A is Avogadro number and Z_F is the number of formula unit per unit cell (for Cs_2MoCl_6 FCC crystal structure, $Z_F = 4$). Now, at temperature T , coefficient of volume thermal expansion, γ_v can be defined as $\gamma_{v,T} = (1/V_{m,T}) \times (dV_{m,T}/dT)$ (at a constant pressure).⁴⁴ In the temperature range 12-573 K, molar volume is increasing linearly with the increase of temperature and therefore fitted with linear equation (in inset). The $\gamma_{v,T}$ at 300 K is calculated by dividing the slope ($0.014 \text{ cm}^3/\text{mol} \cdot \text{K}$) with molar volume at 300 K ($161.082 \text{ cm}^3/\text{mol}$) and becomes as, $\gamma_{v, 300 \text{ K}} = 8.6 \times 10^{-5} \text{ K}^{-1}$.

The structural stability and rigidity, small value of S , and electronically isolated $[\text{MoCl}_6]^{2-}$ units in Cs_2MoCl_6 0D perovskite derivative, lead to the observation of vibrationally coupled $d-d$ electronic transitions in both excitation and emission spectra (Figure 2.12). Also, Tanabe-Sugano (Figure 2.9b) diagram shows that the energy of the excited state ${}^1T_{2g}/E_g$ is largely constant for different crystal field strengths around $Dq/B \approx 2.39$. This aspect might have reduced the spectral broadening, improving the resolution of vibrational fine structure in both PL emission and excitation. Also note that the optical transitions for the centrosymmetric $[\text{MoCl}_6]^{2-}$ octahedral unit are Laporte forbidden. Asymmetric vibrations can remove the centrosymmetry, making the optical transition partially allowed. Consequently, we observe the PL emission maximum (Figure 2.12c) for

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

transitions involving higher vibrational levels. Vibrationally coupled *d-d* transitions have been observed in molecular complexes at lower temperatures, but many times, the magnitude of the emission quenches at room temperature.^{25, 26, 45} Doping of transition metal ions also shows vibrationally coupled *d-d* transitions.⁴⁶ But our observation of vibrationally coupled *d-d* transition from an undoped sample is rather unique, and has become possible because of the attributes discussed above.

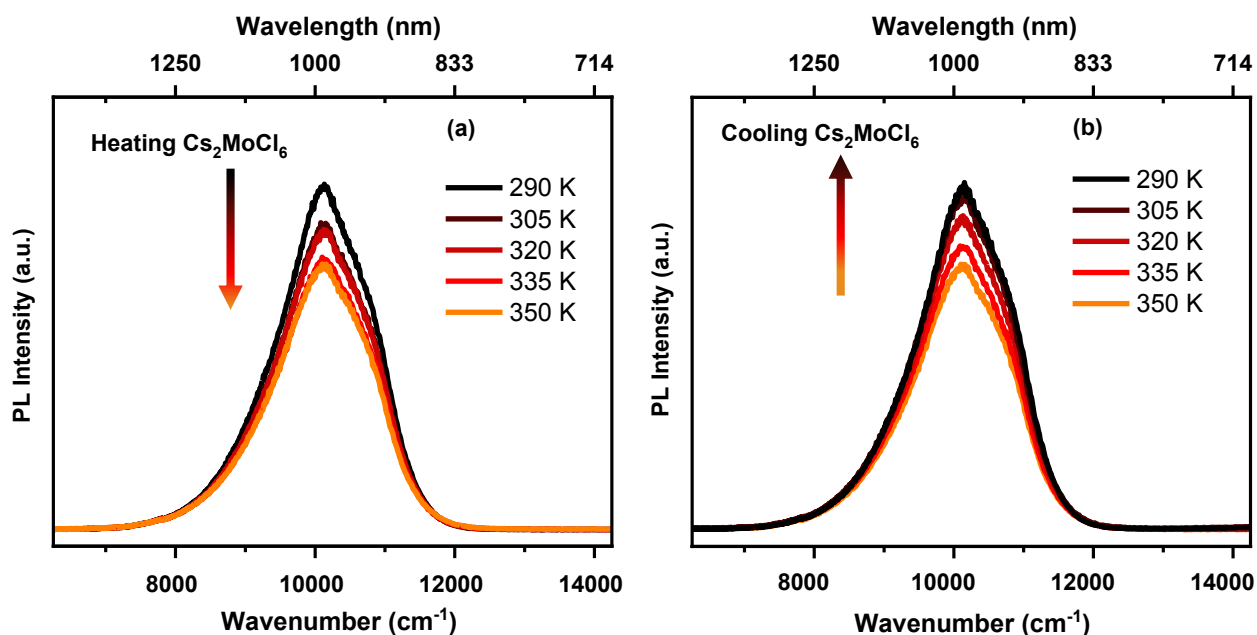


Figure 2.17: Temperature dependent photoluminescence spectra of Cs_2MoCl_6 powder in (a) heating and (b) cooling cycles in the temperature range of 290 – 350 K.

We also looked at the stability of the NIR PL of Cs_2MoCl_6 at higher temperatures in the range of 290 – 350 K (Figure 2.17). About 81% of the PL intensity is retained at 350 K, compared to that at 290 K. Similar results were shown in ref 28 up to around 350 K, along with an interesting observation that the PL intensity increases with further increase in temperature up to around 470 K. Table 2.4 compares the thermal stability of PL intensity of Cs_2MoCl_6 with that of some other NIR phosphor materials emitting in the range of 800 – 1200 nm. The comparison suggests that Cs_2MoCl_6 has reasonably good thermal stability of the NIR PL.

Table 2.4: Comparison of thermal stability of PL intensity among different NIR emitting phosphors in the wavelength range of 800 – 1200 nm.

Sample	Peak position (nm)	Heating temperature (K)	% of PL intensity retained compared to that at room temperature	References
$\text{NaIn}_{0.96}\text{P}_2\text{O}_7: 0.04\text{Cr}^{3+}$	870	373	42	47
		350	60	
$\text{LiGaP}_2\text{O}_7:\text{Cr}^{3+}$	846	373	51	48
		350	70	
$\text{LiInP}_2\text{O}_7:\text{Cr}^{3+}$	860	373	47	49
		350	63	
$\text{LiScP}_2\text{O}_7: 6\% \text{Cr}^{3+}, 3\% \text{Yb}^{3+}$	880, ~1000	373	79	50
		350	93	
$\text{Lu}_{0.2}\text{Sc}_{0.8}\text{BO}_3: 2\% \text{Cr}^{3+}, 5\% \text{Yb}^{3+}$	830, 990	350	92	51
Cs_2MoCl_6	995	373	141	28
		350	125	
Cs_2MoCl_6	986	350	81	This work

2.3.4 Variation of crystal field in Cs_2MoCl_6 , Cs_2MoBr_6 and Cs_2WCl_6

To explore the effect of crystal field on optical excitation and emission processes, we compared Cs_2MoCl_6 , with Cs_2MoBr_6 and Cs_2WCl_6 . Changing the ligand from Cl^- to Br^- , is expected to reduce the crystal field in Cs_2MoBr_6 compared to Cs_2MoCl_6 . Whereas, the extended $5d$ orbitals of W^{4+} in Cs_2WCl_6 is expected to experience more crystal field splitting compared to the $4d$ orbitals of Mo^{4+} in Cs_2MoCl_6 . So, the increasing order of crystal field is expected to be $\text{Cs}_2\text{MoBr}_6 < \text{Cs}_2\text{MoCl}_6 < \text{Cs}_2\text{WCl}_6$.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

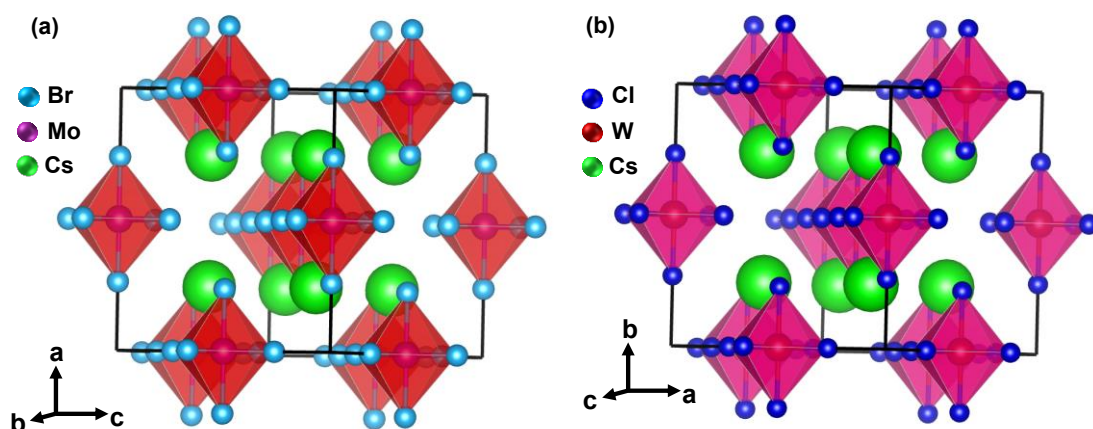


Figure 2.18: Crystal structure of (a) Cs_2MoBr_6 and (b) Cs_2WCl_6 obtained from SCXRD data measured at room temperature. Structural refinement parameters are shown in Table 2.1.

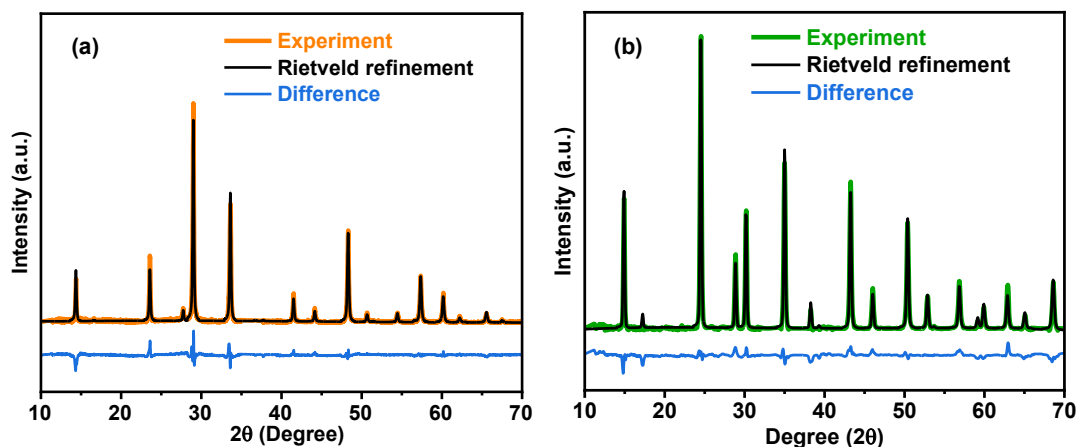


Figure 2.19: Rietveld refinement of PXRD pattern of (a) Cs_2MoBr_6 and (b) Cs_2WCl_6 . Structural refinement parameters are shown in Table 2.2.

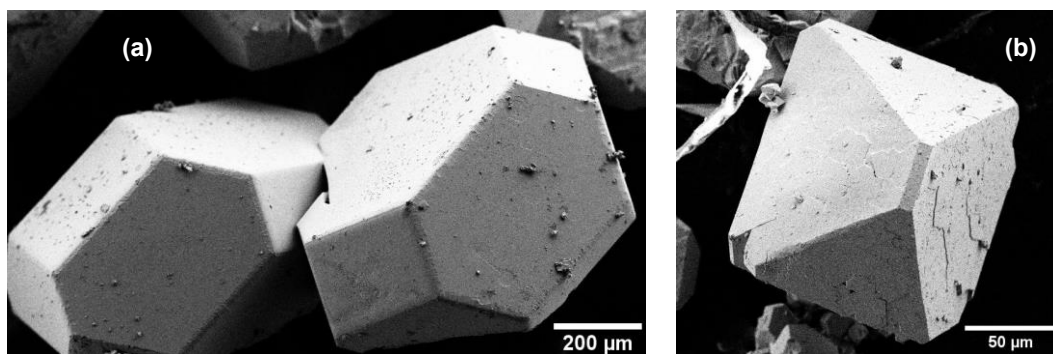


Figure 2.20: FESEM images of (a) Cs_2MoBr_6 and (b) Cs_2WCl_6 show sub-millimeter sized crystals with truncated octahedron and octahedron morphology, respectively.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

We prepared Cs_2MoBr_6 and Cs_2WCl_6 crystals using methods similar to that of Cs_2MoCl_6 . Details of synthesis is provided in SI. The as prepared crystals are characterized by SCXRD data, which are presented in Figure 2.18 and Table 2.1. Phase purity of powdered sample is also confirmed by PXRD and Rietveld refinement (Figure 2.19 and Table 2.2). FESEM images (Figure 2.20) show the sub-millimeter sized crystals. Temperature-dependent phase purity and TGA are presented in Figure 2.21 and Figure 2.5b-c. Stability studies up to 150 days of Cs_2MoBr_6 and Cs_2WCl_6 are provided in Figure 2.22, 2.23 and 2.24. Overall, Cs_2MoBr_6 and Cs_2WCl_6 show structure (0D perovskite derivative), morphology and stability, similar to that of Cs_2MoCl_6 , discussed above.

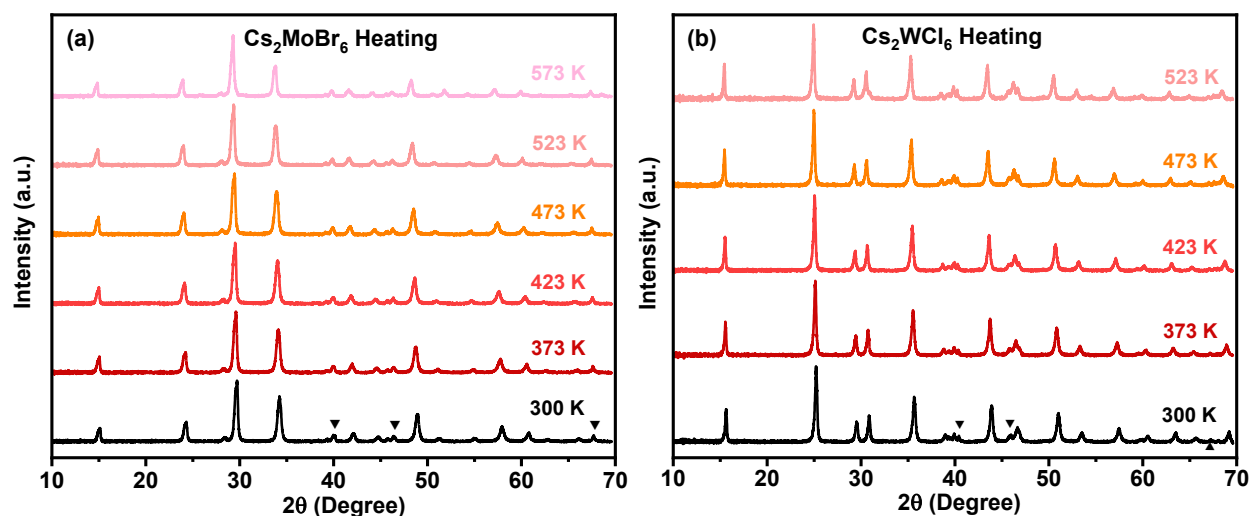


Figure 2.21: PXRD data of (a) Cs_2MoBr_6 and (b) Cs_2WCl_6 while heating the sample. Peaks with triangular mark are due to Pt substrate.

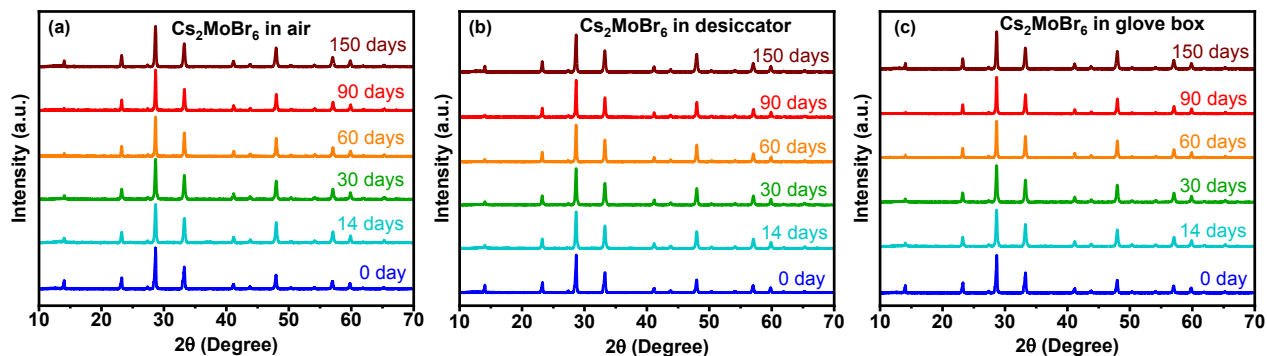


Figure 2.22: PXRD patterns of Cs_2MoBr_6 crystals after storing the sample in (a) air, (b) vacuum desiccator, and (c) nitrogen filled glovebox for different time intervals. The patterns suggest phase purity in all three cases above 150 days.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

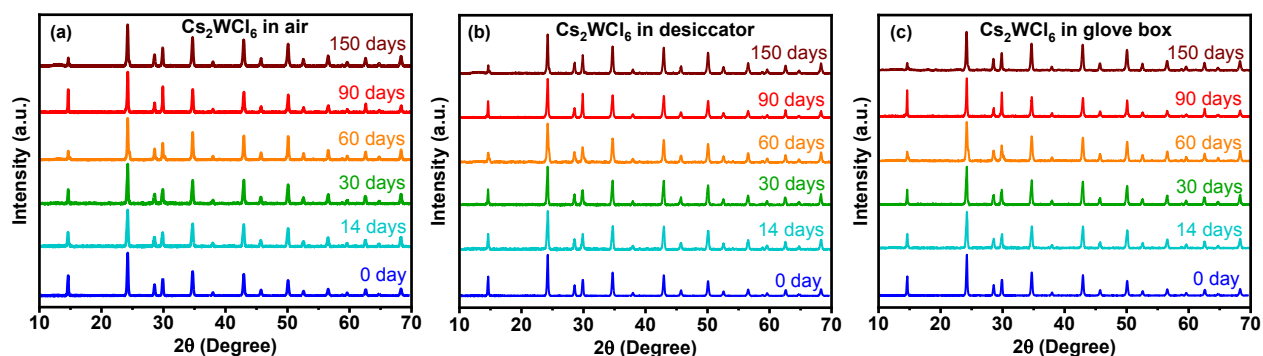


Figure 2.23: PXRD patterns of Cs_2WCl_6 after storing the sample in (a) air, (b) vacuum desiccator, and (c) nitrogen filled glovebox for different time intervals. The patterns suggest phase purity in all three cases above 150 days.

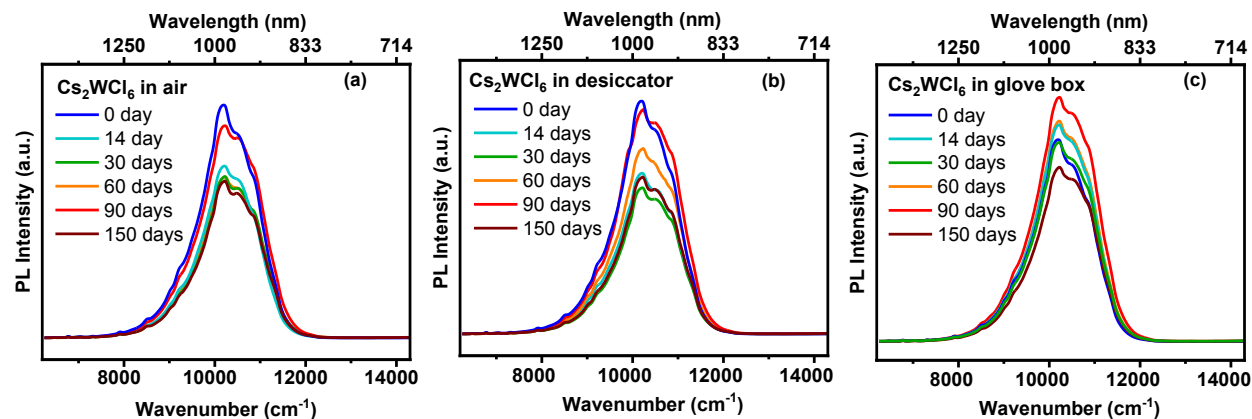


Figure 2.24: PL spectra of Cs_2WCl_6 after storing the sample in (a) air, (b) vacuum desiccator, and (c) nitrogen filled glovebox for different time intervals. In all spectra, excitation wavenumber is 25000 cm^{-1} (400 nm), other instrumental parameters are kept same and same amount of sample is taken. The spectral features do not change with time, but a small decrease in intensity is observed. Overall, the data suggest a reasonable stability of PL over 150 days.

Optical absorption and PL spectra in Figure 2.25a-b show that the optical transitions of Cs_2MoBr_6 and Cs_2WCl_6 are similar to that of Cs_2MoCl_6 , because for all the three samples, the transitions originate from the d^2 electrons. But there are differences in transition energies, owing to the different crystal fields of the three samples. The lowest energy optical absorption E_1 changes slightly showing peaks at wavenumbers 12700, 13000 and 12760 cm^{-1} , for Cs_2MoCl_6 , Cs_2MoBr_6 and Cs_2WCl_6 , respectively. Likewise, the wavenumber or energy of NIR emission originating from

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

de-excitation of E_1 are also similar for the three samples. Figure 2.9b shows that the E/B values of ${}^1T_{2g}/{}^1E_g$ states does not change with the crystal field energy, and it remains parallel with the Dq/B axis. Therefore, the similarity in experimental E_1 values suggest that the B values of all three compounds are also similar, with a slightly higher B value for the bromide sample.

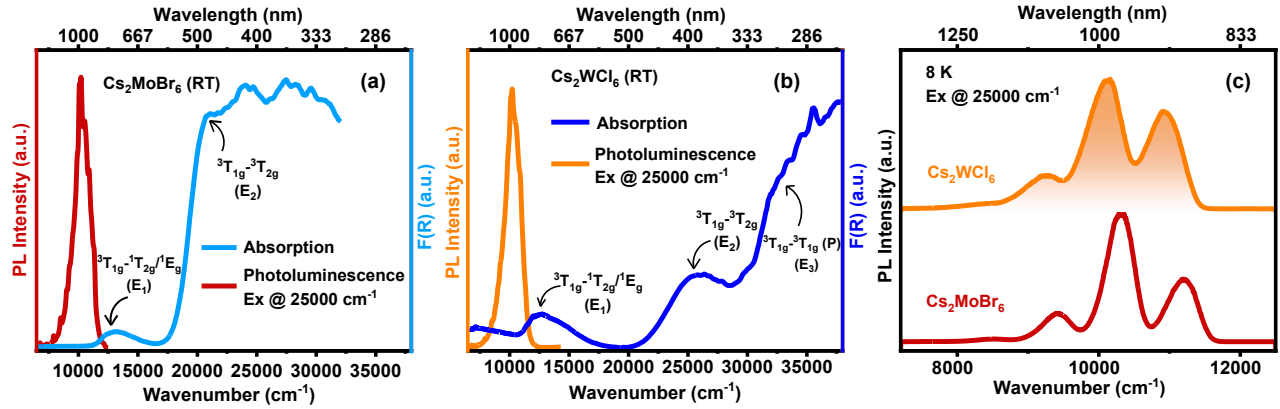


Figure 2.25: (a) Optical absorption in terms of Kubelka-Munk function $F(R)$ (sky) and emission (maroon) spectra of Cs_2MoBr_6 powder recorded at room temperature (RT). (b) Optical absorption in terms of Kubelka-Munk function $F(R)$ (blue) and emission (orange) spectra of Cs_2WCl_6 powder recorded at RT. The transitions E_1 , E_2 and E_3 correspond to $d-d$ transitions assigned in the Tanabe-Sugano diagram (Figure 2.9b). (c) PL emission spectra of Cs_2MoBr_6 (maroon) and Cs_2WCl_6 (orange), recorded at 8 K.

But clear differences are observed in the wavenumbers of E_2 and E_3 transitions for different samples. Tanabe-Sugano diagram (Figure 2.9b) predicts that energy difference (E/B values) between ${}^3T_{2g}$ and ${}^3T_{1g}$ increases with increasing Dq/B . Perhaps, our experimental data also show the same trend, where E_2 increases in the order Cs_2MoBr_6 (20000 cm^{-1}) $<$ Cs_2MoCl_6 (22000 cm^{-1}) $<$ Cs_2WCl_6 (25250 cm^{-1}). Likewise, E_3 also increases with Dq/B . Based on these results, we estimated the Dq/B values for all the three samples, which increases in the following order 2.22 (Cs_2MoBr_6) $<$ 2.39 (Cs_2MoCl_6) $<$ 3.28 (Cs_2WCl_6). The corresponding Tanabe-Sugano diagram assignments for Cs_2MoBr_6 and Cs_2WCl_6 are shown in Figure 2.26.

Figure 2.25c shows PL emission spectra of Cs_2MoBr_6 and Cs_2WCl_6 at 8 K. Both spectra show equi-spaced vibrational splitting, similar to the data of Cs_2MoCl_6 (Figure 2.12). Figure 2.27 compares the emission and excitation spectra for E_1 transition at 8 K, estimating E_{Stokes} as 2820

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br)

and 2970 cm⁻¹, and $\hbar\omega_{\text{phonon}}$ as 890 and 837 cm⁻¹ for Cs₂MoBr₆ and Cs₂WCl₆, respectively. Substituting these values in equation 3, we obtain $S = 1.84 \pm 0.25$ and 2.02 ± 0.25 for Cs₂MoBr₆ and Cs₂WCl₆, respectively. PL spectral evolution and corresponding pseudo color map at different temperatures for both Cs₂MoBr₆ and Cs₂WCl₆ are shown in Figure 2.28. Low temperature PXRD data (Figure 2.29) of Cs₂MoBr₆ and Cs₂WCl₆ confirm phase stability of both samples in the temperature range of 12 K – 300 K, along with expected increase in unit cell volume with increasing temperature.

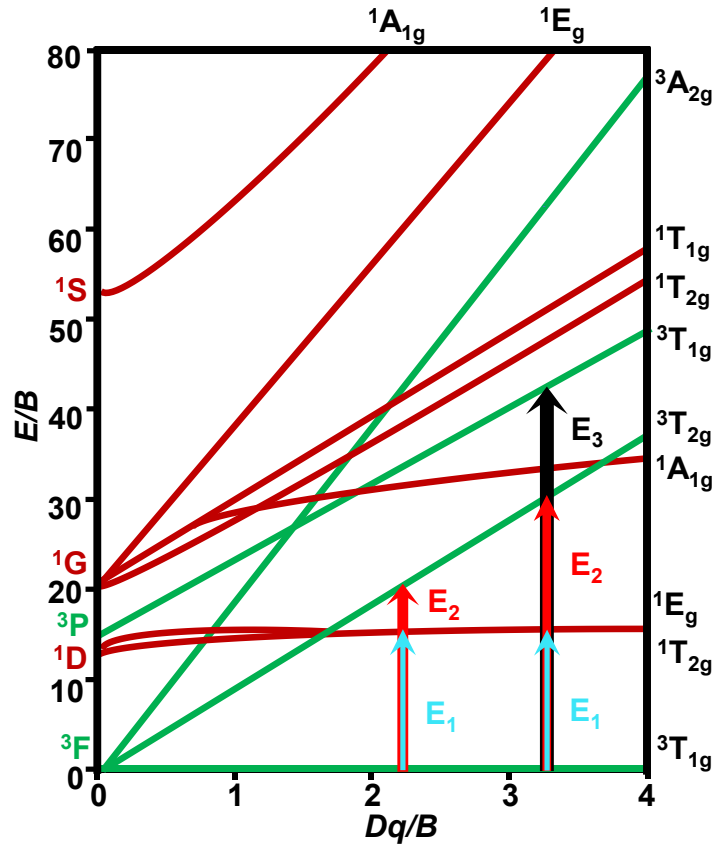


Figure 2.26: Tanabe-Sugano diagram of d^2 configuration ($\text{Mo}^{4+}/\text{W}^{4+}$) in octahedral environment showing the transitions of Cs₂MoBr₆ and Cs₂WCl₆ crystals at their respective Dq/B values. The Dq/B value of 2.22 corresponds to Cs₂MoBr₆, whereas the Dq/B of 3.28 corresponds to Cs₂WCl₆. E_1 (turquoise arrow), E_2 (red arrow) and E_3 (black arrow) correspond to transitions ${}^3T_{1g} \rightarrow {}^1T_{2g}/{}^1E_g$, ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}(P)$, respectively. From different E/B and Dq/B values in the diagram, Racah parameter B and crystal field splitting energy ($10Dq$) have been calculated. For Cs₂MoBr₆, B and $10Dq$ values are about 909 cm⁻¹ and 20100 cm⁻¹, whereas for Cs₂WCl₆, B and $10Dq$ values are about 820 cm⁻¹ and 27000 cm⁻¹, respectively.

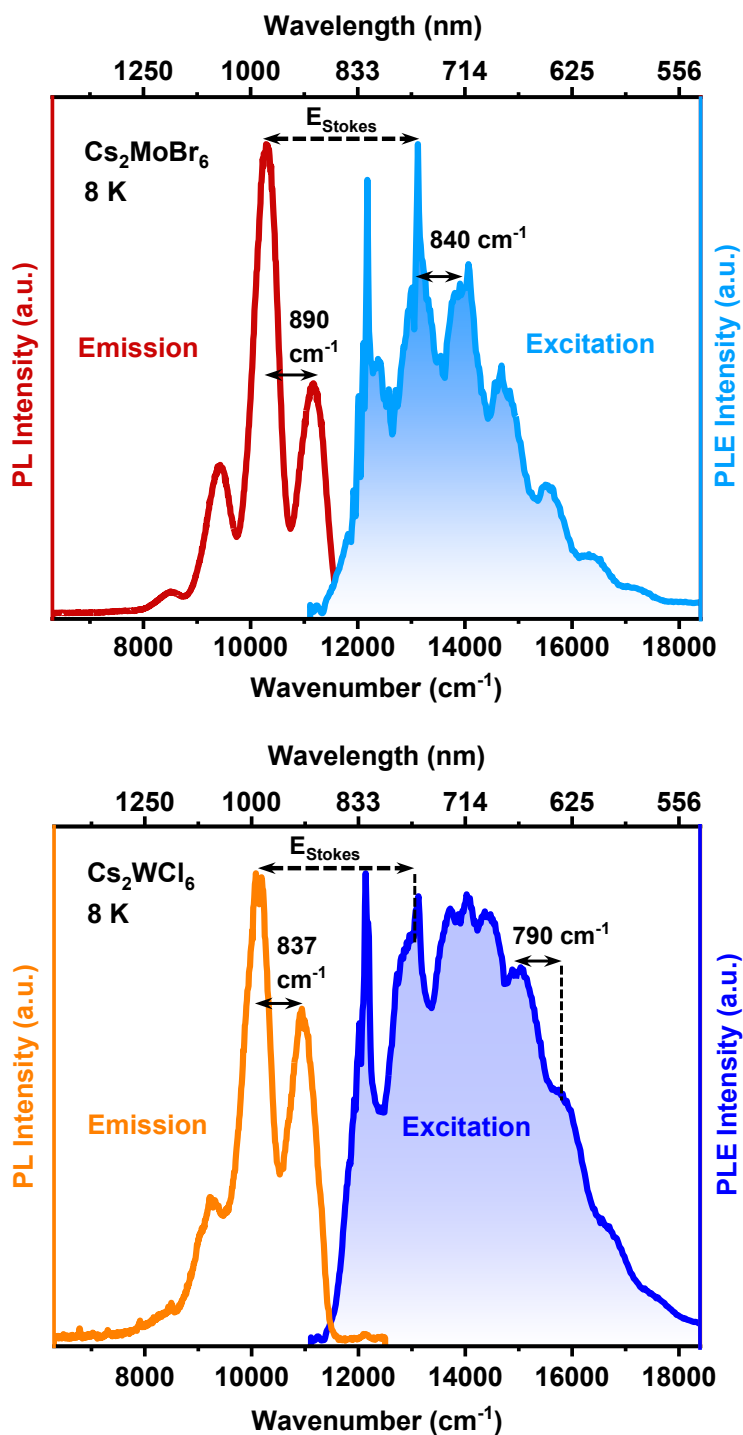


Figure 2.27: (a) PL emission (maroon) and excitation (sky) spectra of Cs_2MoBr_6 at 8 K. (b) PL emission (orange) and excitation (blue) spectra of Cs_2WCl_6 at 8 K. For both the PL spectra, excitation wavenumber was E_I transition, i.e., 13000 cm^{-1} and 12760 cm^{-1} for Cs_2MoBr_6 and Cs_2WCl_6 respectively.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo}/\text{W}$, $X = \text{Cl}/\text{Br}$)

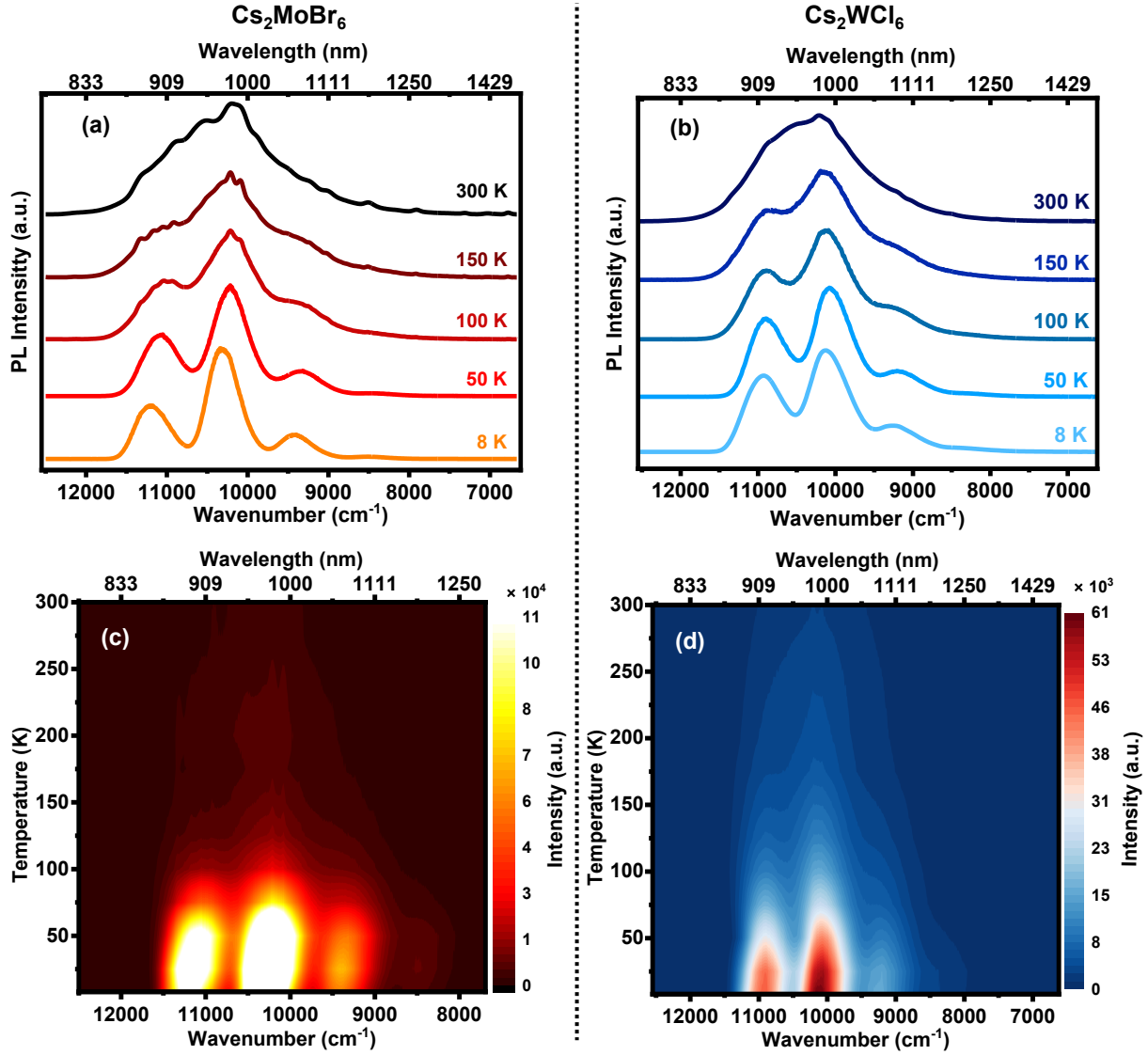


Figure 2.28: Temperature dependent PL at a few representative temperatures of (a) Cs_2MoBr_6 and (b) Cs_2WCl_6 . Pseudo colormap of temperature-dependent PL of (c) Cs_2MoBr_6 and (d) Cs_2WCl_6 in the temperature range of 8-300 K. Excitation at 25000 cm^{-1} .

Figure 2.30 shows that the PL lifetime of Cs_2WCl_6 is 46 μs at 8 K, which is shorter compared to 84 μs lifetime of Cs_2MoCl_6 . This decrease in lifetime might be because of the increased spin-orbit coupling in Cs_2WCl_6 . The spin-orbit coupling increases with atomic number, and therefore, the spin-orbit coupling constant (ξ) increases from Mo ($\xi_{\text{Mo}} = 900 \text{ cm}^{-1}$) to W ($\xi_{\text{W}} = 2700 \text{ cm}^{-1}$).⁵² Consequently, more relaxation of the spin-forbiddenness for E_1 ($^1T_{2g}/^1E_g \rightarrow ^3T_{1g}$) transition in the case of Cs_2WCl_6 compared to Cs_2MoCl_6 . Note that all the three vibronically coupled PL peaks of

E_1 transition of Cs_2WCl_6 have almost identical PL decay profiles. Likewise, all the major PL peaks of Cs_2MoBr_6 at 8 K also have almost identical PL decay profiles, with intermediate lifetime around 77 μs (Figure 2.31).

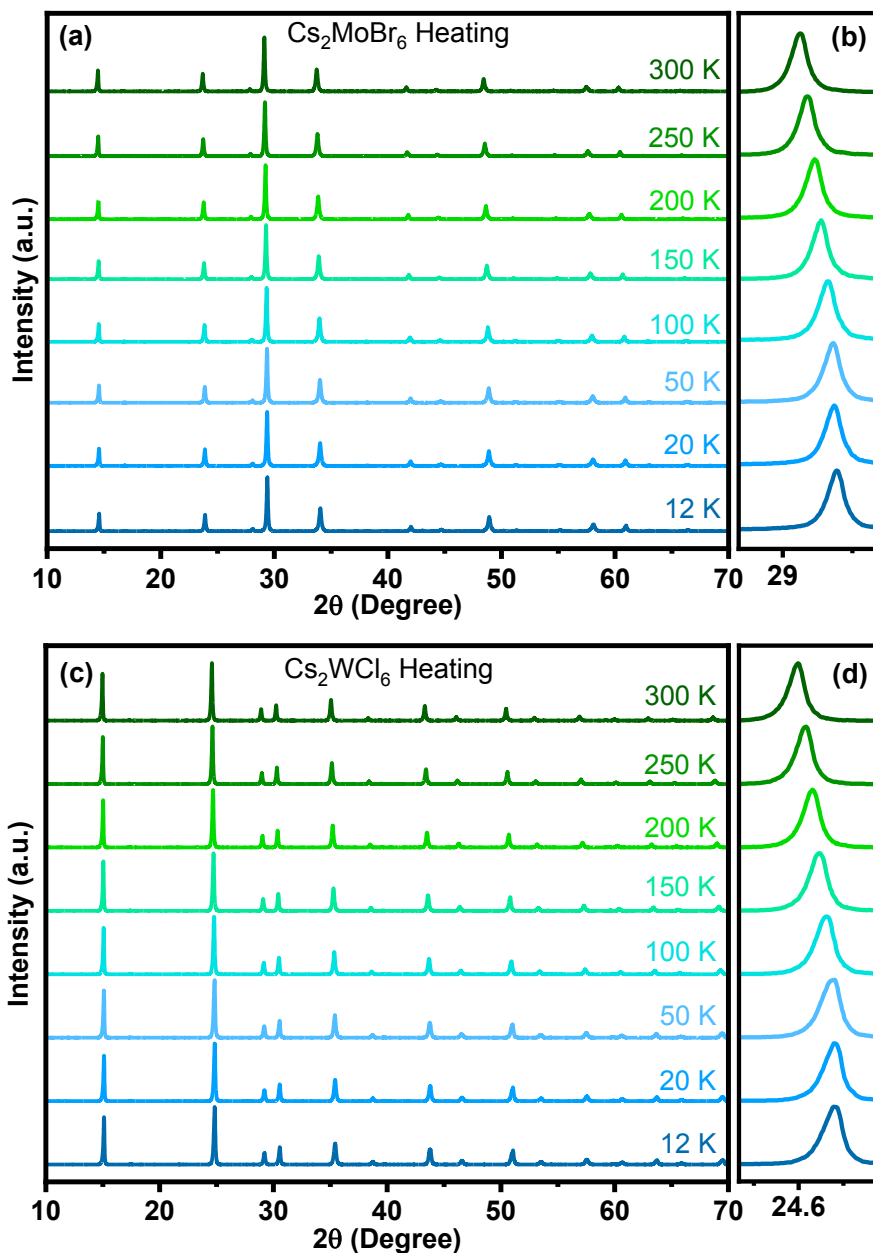


Figure 2.29: PXRD patterns of (a) Cs_2MoBr_6 and (c) Cs_2WCl_6 at variable temperatures in the range of 12-300 K. The patterns show no phase change in this temperature range. Enlarged view of one peak for (b) Cs_2MoBr_6 and (d) Cs_2WCl_6 showing the shift towards lower 2θ value with the increase of temperature imply lattice expansion.

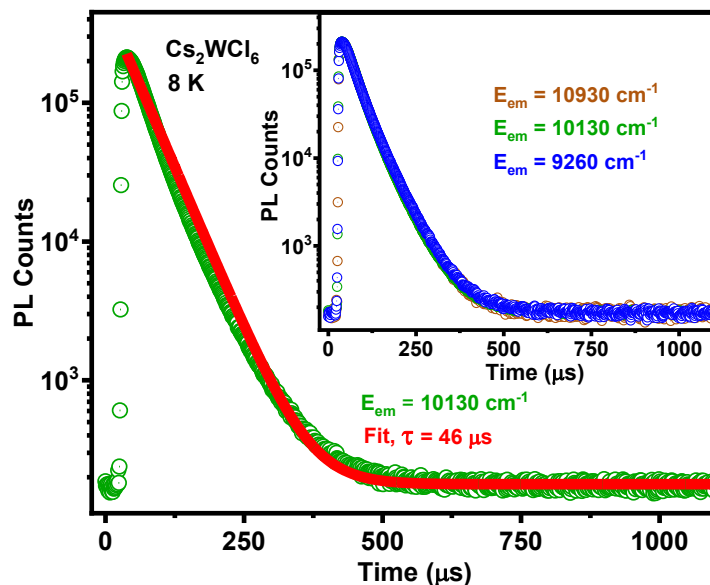


Figure 2.30: PL decay dynamics of Cs_2WCl_6 measured at 8 K for emission at 10130 cm^{-1} . The experimental data is fitted using a mono-exponential decay equation 2. Inset shows overlapped PL decay profiles at 8 K of three emission peaks shown at Figure 2.27 b. All decays are measured after excitation at 25000 cm^{-1} .

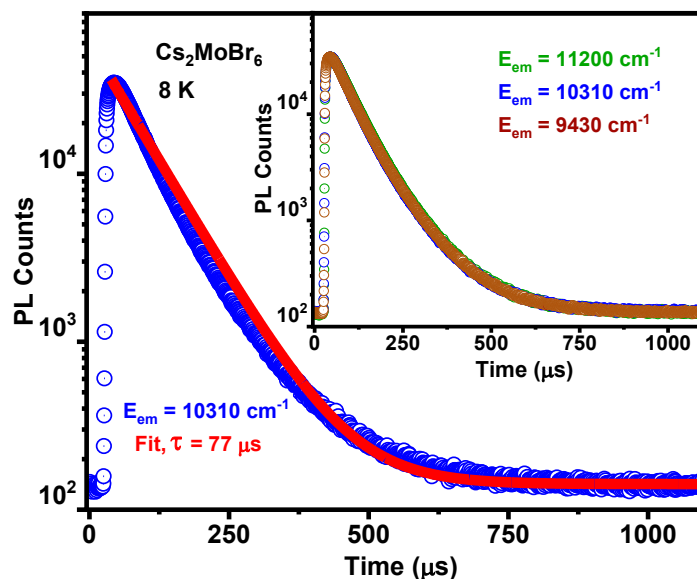


Figure 2.31: PL decay dynamics of Cs_2MoBr_6 measured at 8 K for emission at 10310 cm^{-1} with a mono-exponential decay fitting. Inset shows overlapped PL decay profiles at 8 K of three emission peaks shown at Figure 2.27 a. All decays are measured after excitation at 25000 cm^{-1} .

2.3.5 NIR pc-LEDs

We have prepared pc-LEDs by coating Cs_2MoCl_6 (with 25 weight % of poly (methyl methacrylate) (PMMA) in toluene) on two different kinds of commercial LED chips emitting at 400 nm (blue) and 730 nm (far-red). Insets of Figure 2.32a and b present schematics of the two pc-LEDs, blue and red colors in center correspond to 400 and 730 nm LEDs, respectively. And the phosphor coating is represented by green color layer on top. Figure 2.9a shows that Cs_2MoCl_6 can be excited by both 400 nm and 730 nm light. Consequently, both pc-LEDs emit NIR radiations as shown in Figure 2.32a-b. In addition to the NIR emission of Cs_2MoCl_6 , Figure 2.32a also shows the blue-emission of the commercial LED at 400 nm. The 400 nm commercial LED starts operating at an onset voltage just below 2.8 V, and then higher voltages increase both the blue and NIR emission. In difference, Figure 2.32b shows that the onset voltage reduced below 1.5 V for the pc-LED coated on 730 nm LED.

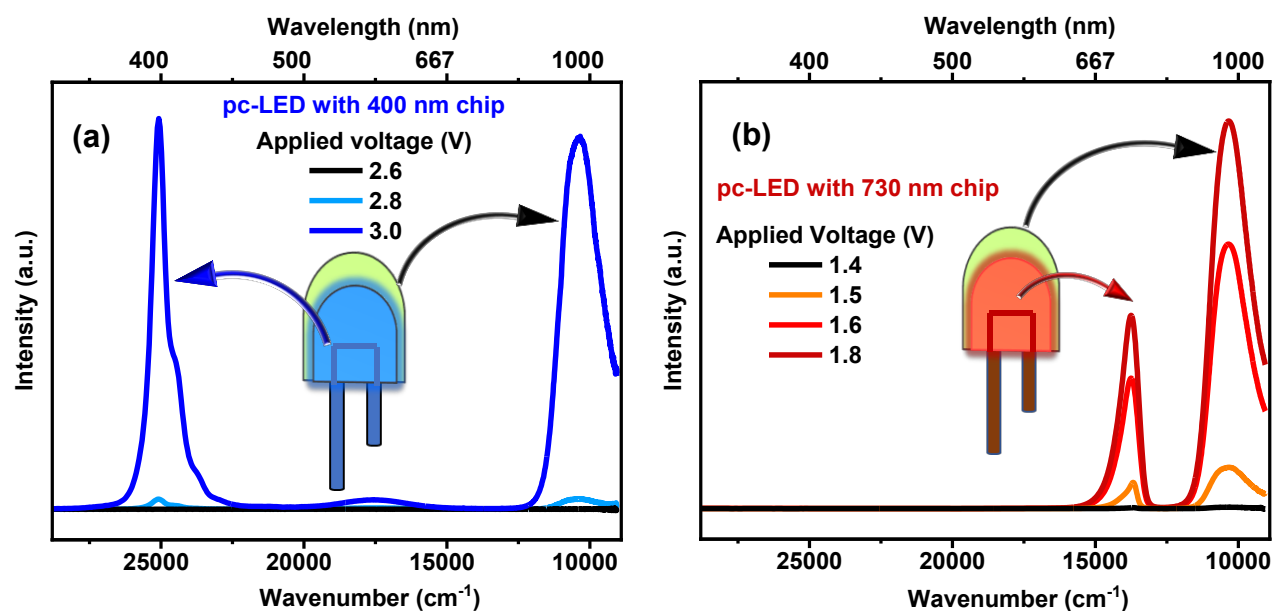


Figure 2.32: NIR pc-LEDs fabricated by coating Cs_2MoCl_6 (green) on 400 nm (blue) and 730 nm (far-red) LED chips, as schematically shown in the insets of (a) and (b), respectively. Luminescence spectra of the pc-LEDs on (a) 400 nm and (b) 730 nm chips at different applied voltages.

Vibronically coupled near-infrared emission and excitation from d-d transitions of Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$)

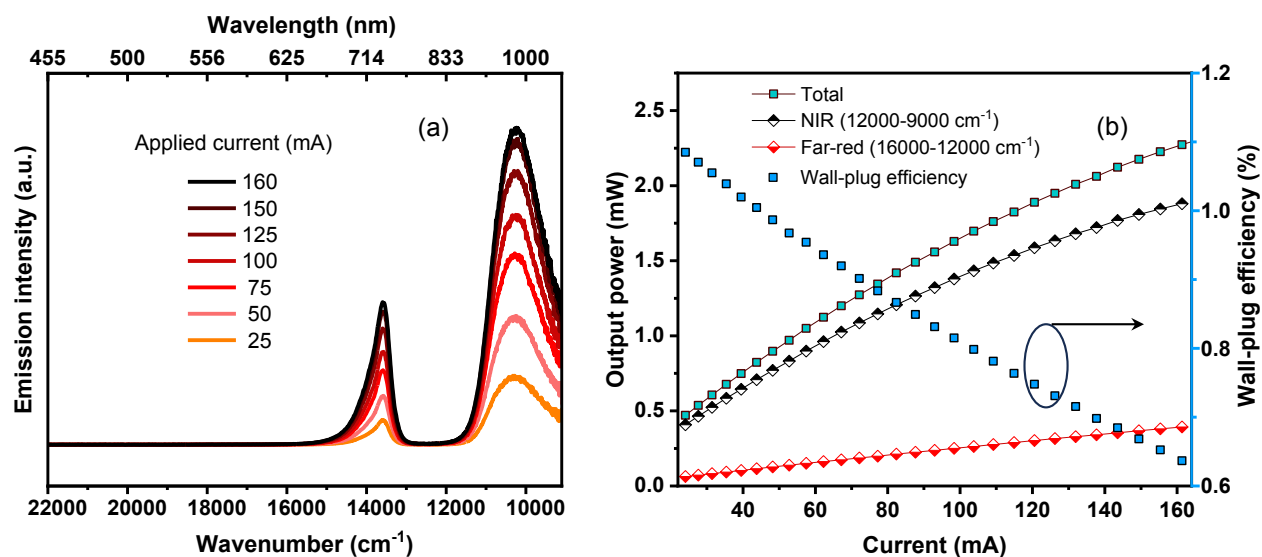


Figure 2.33: (a) Emission spectra of Cs_2MoCl_6 pc-LED with 730 nm chip within the current range of 25-160 mA. (b) Radiant flux (or output power) for total spectral region shown in Figure (a), (teal green cube), NIR region (black rhombus) corresponding to Cs_2MoCl_6 emission and far-red region (red rhombus) corresponding the 730 nm chip emission. Wall-plug efficiency (sky cube) of pc-LED is also presented.

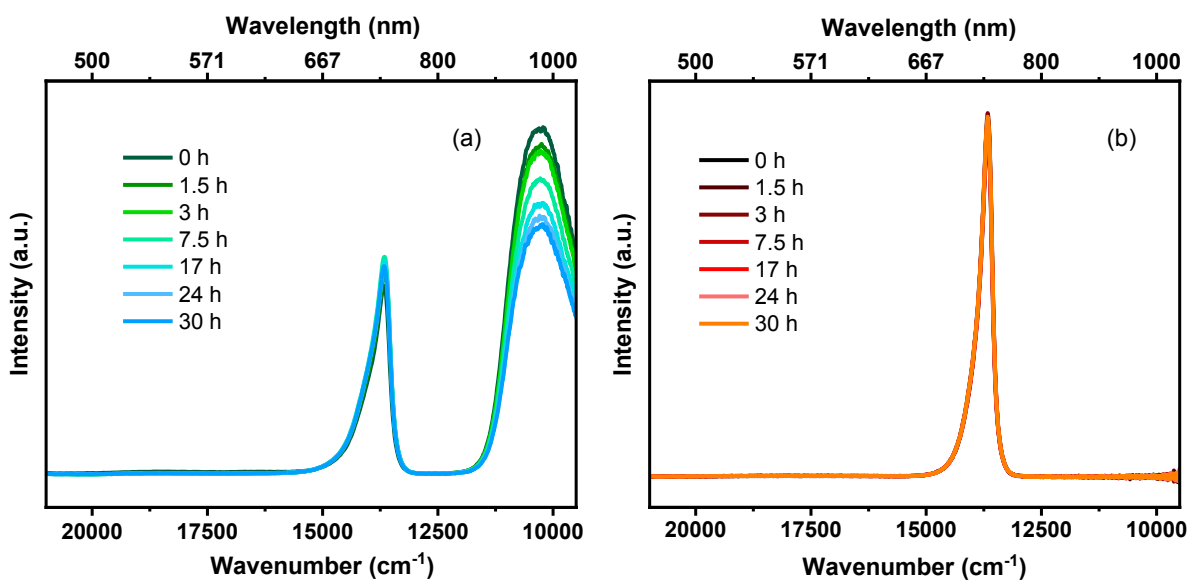


Figure 2.34: Luminescence spectra of (a) Cs_2MoCl_6 pc-LED (Cs_2MoCl_6 coated on 730 nm chips) and (b) 730 nm chips operating at 1.8 V applied voltage, over a period of continuous operation for 30 hours. The pc-LED shows a reasonable stability of the NIR emission, with small decrease in intensity with operation time.

Expectedly, the radiant flux or output power of pc-LEDs increases with drive current (25-160 mA), as shown in Figure 2.33. The pc-LED coated on 730 nm LED show a radiant flux ~ 2 mW at 160 mA, that can be improved further by optimizing the device geometry and excitation LED chip. The wall-plug efficiency is poor. Overall, the observance of reasonable NIR pc-LED output with far-red 730 nm excitation became possible because the excitation and emission (de-excitation) happen through the same pair of electronic states (E_I transition), exhibiting small Stokes shift. Such phosphor design strategy has the potential to increase wall-plug efficiency of future NIR pc-LEDs in comparison with the widely available NIR pc-LEDs with UV-blue chips.^{6, 16, 53, 54}

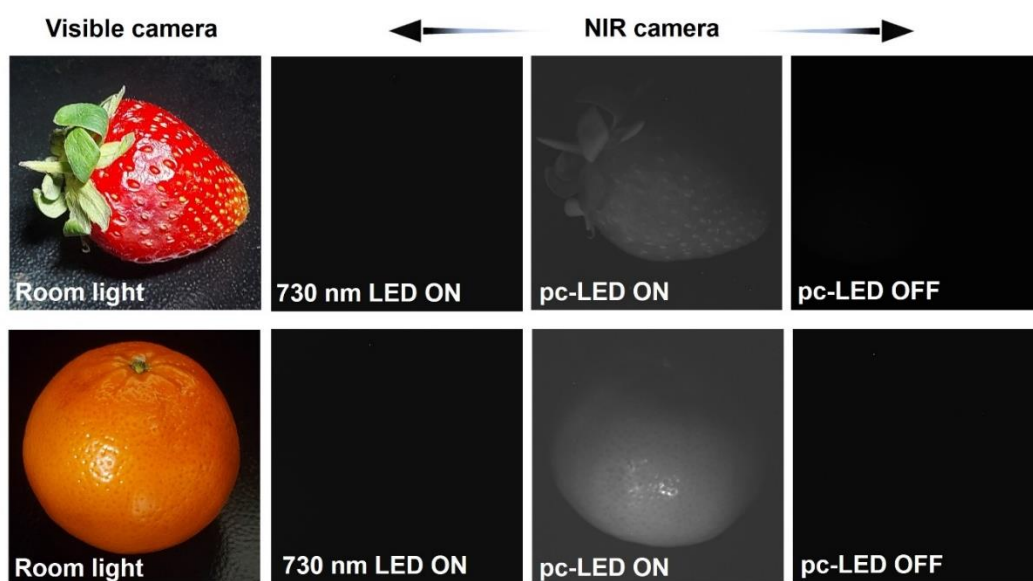


Figure 2.35: Images of objects captured using visible camera under white room light illumination (1st panel). Images of objects captured using NIR camera with different conditions: under 730 nm LED illumination (2nd panel), under our NIR pc-LED (Cs_2MoCl_6 coated on 730 nm chip) illumination (3rd panel), and when the pc-LED is switched off (4th panel).

The Cs_2MoCl_6 pc-LED (coated on 730 nm chip) shows a reasonable stability over continuous operation for 30 hours (Figure 2.34). Figure 2.35 shows that reasonable quality of images of objects can be captured using illumination of our NIR pc-LED. However, it is to be noted that both the absorption cross-section of the phosphor for red-light (excitation) and the quantum yield of corresponding NIR emission need to be increased further for NIR pc-LED applications. For the general purpose of illumination, a broad band IR pc-LEDs is desired, whereas, narrow band IR

light sources also find multiple applications like encryption/decryption, or low-loss optical fiber communication. Here we demonstrate a simple encryption/decryption application by writing patterns with our Cs_2MoCl_6 on paper. Both under visible room light and under UV illumination, the pattern appears as the misleading number “8888” to human eyes and to regular camera operating in the visible range. But when the image is captured using a NIR camera, the actual secret pattern is observed as number “7173”. Figure 2.36 provides the encryption/decryption data along with necessary discussion.

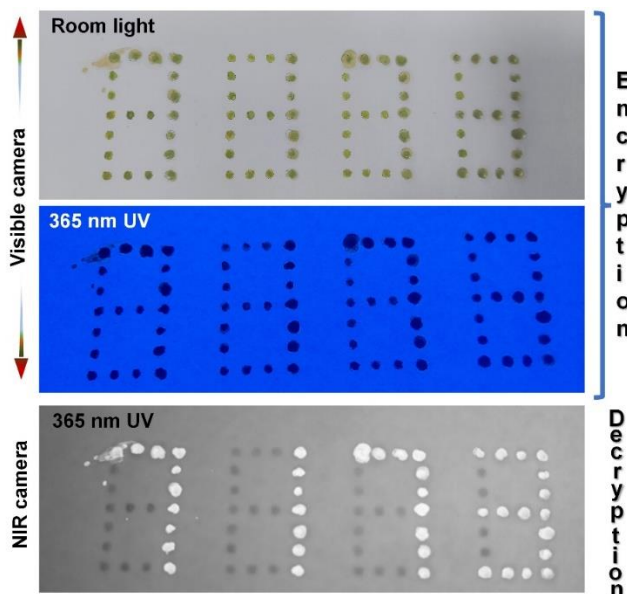


Figure 2.36: Encrypted pattern made with Cs_2MoCl_6 under room light and 365 nm UV light captured with visible camera. Here the dots which can make unique “7173” pattern are made with Cs_2MoCl_6 , rest of the dots are filled with painting color having similar shade with the Cs_2MoCl_6 phosphor. Now this misleading “8888” pattern in room light and 365 nm UV light under visible camera is decrypted as “7173” when we capture the photograph with NIR camera under 365 nm UV light illumination. This decryption is due to the NIR emission of Cs_2MoCl_6 phosphor.

2.4 Conclusions

We show that the $d-d$ transitions in Cs_2MX_6 ($M = \text{Mo/W}$, $X = \text{Cl/Br}$) 0D perovskite derivatives yield NIR excitation and emission (10140 cm^{-1} , 986 nm) with small Stokes shift $= 2650\text{ cm}^{-1}$ and $S = 1.82 \pm 0.25$. Tanabe-Sugano diagram of d^2 electronic configuration of M^{4+} in a $[\text{MX}_6]^{2-}$ octahedron environment explains the excitation and emission processes. Surprisingly, vibrational fine structures are observed in both electronic excitation and emission spectra below 200 K. Such

vibrational fine structures, something like mirror-image kind of excitation and emission are typically not observed in the electronic transitions of undoped inorganic crystals. Cs₂MX₆ shows this unique feature owing to (i) 0D structure with isolated [MX₆]²⁻ octahedra, (ii) structural stability and rigidity, and (iii) crystal-field independent energy of *E_I* transition (Figure 2.9b). The high spin-orbit coupling along with the vibrational coupling makes the *E_I* transition partially allowed. Subsequently, we fabricated pc-LED by coating Cs₂MoCl₆ on a 730 nm far-red commercial LED chip, that can operate at a nominal applied voltage of 1.8 V. The demonstrated phosphor design principles, with both excitation and emission in the NIR region with small Stokes shift, have the potential to improve wall-plug efficiency in future NIR pc-LEDs.

2.5 References

1. Qiao, J.; Zhou, G.; Zhou, Y.; Zhang, Q.; Xia, Z. Divalent Europium-Doped Near-Infrared-Emitting Phosphor for Light-Emitting Diodes. *Nat. Commun.* **2019**, *10* (1), 5267.
2. Chen, J.; Luo, Z.; Fu, Y.; Wang, X.; Czech, K. J.; Shen, S.; Guo, L.; Wright, J. C.; Pan, A.; Jin, S. Tin(IV)-Tolerant Vapor-Phase Growth and Photophysical Properties of Aligned Cesium Tin Halide Perovskite (CsSnX₃; X = Br, I) Nanowires. *ACS Energy Lett.* **2019**, *4* (5), 1045-1052.
3. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Co-doped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, *59* (28), 11307-11311.
4. Gao, L.; Quan, L. N.; Arquer, F. P. G. D.; Zhao, Y.; Munir, R.; Proppe, A.; Bermudez, R. Q.; Zou, C.; Yang, Z.; Saidaminov, M. I.; Voznyy, O.; Kinger, S.; Lu, Z.; Kelley, S. O.; Amassian, A.; Tang, J.; Sargent, E. H. Efficient Near-Infrared Light-Emitting Diodes Based on Quantum Dots in Layered Perovskite. *Nat. Photonics* **2020**, *14* (4), 227-233.
5. Jia, Z.; Yuan, C.; Liu, Y.; Wang, X.-J.; Sun, P.; Wang, L.; Jiang, H.; Jiang, J. Strategies to Approach High Performance in Cr³⁺-doped Phosphors for High-Power NIR-LED Light Sources. *Light Sci. Appl.* **2020**, *9* (1), 86.
6. Yao, L.; Shao, Q.; Shi, M.; Shang, T.; Dong, Y.; Liang, C.; He, J.; Jiang, J. Efficient Ultra-Broadband Ga₄GeO₈:Cr³⁺ Phosphors with Tunable Peak Wavelengths from 835 to 980 nm for NIR pc-LED Application. *Adv. Opt. Mater.* **2022**, *10* (4), 2102229.

7. Wang, S.; Pang, R.; Tan, T.; Wu, H.; Wang, Q.; Li, C.; Zhang, S.; Tan, T.; You, H.; Zhang, H., Achieving High Quantum Efficiency Broadband NIR Mg₄Ta₂O₉:Cr³⁺ Phosphor Through Lithium-Ion Compensation. *Adv. Mater.* **2023**, 35 (22), 2300124.
8. Berger, F. J.; Poli, I.; Aktas, E.; Martani, S.; Meggiolaro, D.; Gregori, L.; Albaqami, M. D.; Abate, A.; Angelis, F. D.; Petrozza, A. How Halide Alloying Influences the Optoelectronic Quality in Tin-Halide Perovskite Solar Absorbers. *ACS Energy Lett.* **2023**, 8 (9), 3876-3882.
9. Supran, G. J.; Song, K. W.; Hwang, G. W.; Correa, R. E.; Scherer, J.; Dauler, E. A.; Shirasaki, Y.; Bawendi, M. G.; Bulović, V. High-Performance Shortwave-Infrared Light-Emitting Devices Using Core–Shell (PbS–CdS) Colloidal Quantum Dots. *Adv. Mater.* **2015**, 27 (8), 1437-1442.
10. Hong, W. L.; Huang, Y. C.; Chang, C. Y.; Zhang, Z. C.; Tsai, H. R.; Chang, N. Y.; Chao, Y. C. Efficient Low-Temperature Solution-Processed Lead-Free Perovskite Infrared Light-Emitting Diodes. *Adv. Mater.* **2016**, 28 (36), 8029-8036.
11. Qu, J.; Rastogi, P.; Gréboval, C.; Lagarde, D.; Chu, A.; Dabard, C.; Khalili, A.; Cruguel, H.; Robert, C.; Xu, X. Z.; Ithurria, S.; Silly, M. G.; Ferré, S.; Marie, X.; Lhuillier, E. Electroluminescence from HgTe Nanocrystals and Its Use for Active Imaging. *Nano Lett.* **2020**, 20 (8), 6185-6190.
12. Vasilopoulou, M.; Kim, H. P.; Kim, B. S.; Papadakis, M.; Gavim, A. E. X.; Macedo, A. G.; Silva, W. J. D.; Schneider, F. K.; Teridi, M. A. M.; Coutsolelos, A. G.; Yusoff, A. R. B. M. Efficient Colloidal Quantum Dot Light-Emitting Diodes Operating in the Second Near-Infrared Biological Window. *Nat. Photon.* **2020**, 14 (1), 50-56.
13. Franco, M. D.; Zhu, D.; Asaithambi, A.; Prato, M.; Charalampous, E.; Christodoulou, S.; Kriegel, I.; Trizio, L. D.; Manna, L.; Jalali, H. B.; Stasio, F. D. Near-Infrared Light-Emitting Diodes Based on RoHS-Compliant InAs/ZnSe Colloidal Quantum Dots. *ACS Energy Lett.* **2022**, 7 (11), 3788-3790.
14. Rajendran, V.; Fang, M.-H.; Guzman, G. N. D.; Lesniewski, T.; Mahlik, S.; Grinberg, M.; Leniec, G.; Kaczmarek, S. M.; Lin, Y.-S.; Lu, K.-M.; Lin, C.-M.; Chang, H.; Hu, S.-F.; Liu, R.-S. Super Broadband Near-Infrared Phosphors with High Radiant Flux as Future Light Sources for Spectroscopy Applications. *ACS Energy Lett.* **2018**, 3 (11), 2679-2684.
15. Saikia, S.; Joshi, A.; Arfin, H.; Badola, S.; Saha, S.; Nag, A. Sb³⁺–Er³⁺-Codoped Cs₂NaInCl₆

for Emitting Blue and Short-Wave Infrared Radiation. *Angew. Chem. Int. Ed.* **2022**, 61 (32), e202201628.

16. Zhong, J.; Li, C.; Zhao, W.; You, S.; Brgoch, J. Accessing High-Power Near-Infrared Spectroscopy Using Cr³⁺-Substituted Metal Phosphate Phosphors. *Chem. Mater.* **2022**, 34 (1), 337-344.

17. Saikia, S.; Ghosh, A.; Nag, A. Broad Dual Emission by Codoping Cr³⁺ (d→d) and Bi³⁺ (s→p) in Cs₂Ag_{0.6}Na_{0.4}InCl₆ Double Perovskite. *Angew. Chem. Int. Ed.* **2023**, 62 (33), e202307689.

18. Arfin, H.; Rathod, R.; Shingote, A. S.; Priolkar, K. R.; Santra, P. K.; Nag, A. Short-Wave Infrared Emissions from Te⁴⁺-Ln³⁺ (Ln: Er, Yb)-Codoped Cs₂NaInCl₆ Double Perovskites. *Chem. Mater.* **2023**, 35 (17), 7133-7143.

19. Gan, W.; Cao, L.; Gu, S.; Lian, H.; Xia, Z.; Wang, J. Broad-Band Sensitization in Cr³⁺-Er³⁺ Co-Doped Cs₂AgInCl₆ Double Perovskites with 1.5 μm Near-Infrared Emission. *Chem. Mater.* **2023**, 35 (14), 5291-5299.

20. Rajendran, V.; Chen, K.-C.; Huang, W.-T.; Majewska, N.; Leśniewski, T.; Grzegorzczak, M.; Mahlik, S.; Leniec, G.; Kaczmarek, S. M.; Pang, W. K.; Peterson, V. K.; Lu, K.-M.; Chang, H.; Liu, R.-S. Pentavalent Manganese Luminescence: Designing Narrow-Band Near-Infrared Light-Emitting Diodes as Next-Generation Compact Light Sources. *ACS Energy Lett.* **2023**, 8 (1), 289-295.

21. Rao, M. J.; Shibata, T.; Chattopadhyay, S.; Nag, A. Origin of Photoluminescence and XAFS Study of (ZnS)_{1-x}(AgInS₂)_x Nanocrystals. *J. Phys. Chem. Lett.* **2014**, 5 (1), 167-173.

22. Hughes, B. K.; Blackburn, J. L.; Kroupa, D.; Shabaev, A.; Erwin, S. C.; Efros, A. L.; Nozik, A. J.; Luther, J. M.; Beard, M. C. Synthesis and Spectroscopy of PbSe Fused Quantum-Dot Dimers. *J. Am. Chem. Soc.* **2014**, 136 (12), 4670-4679.

23. Pradhan, S.; Stavrinadis, A.; Gupta, S.; Christodoulou, S.; Konstantatos, G. Breaking the Open-Circuit Voltage Deficit Floor in PbS Quantum Dot Solar Cells through Synergistic Ligand and Architecture Engineering. *ACS Energy Lett.* **2017**, 2 (6), 1444-1449.

24. Voggu, V. R.; Sham, J.; Pfeffer, S.; Pate, J.; Fillip, L.; Harvey, T. B.; Brown, R. M., J.; Korgel, B. A. Flexible CuInSe₂ Nanocrystal Solar Cells on Paper. *ACS Energy Lett.* **2017**, 2 (3), 574-581.

25. Isovitsch, R. A.; Beadle, A. S.; Fronczek, F. R.; Maverick, A. W. Electronic Absorption Spectra

- and Phosphorescence of Oxygen-Containing Molybdenum(IV) Complexes. *Inorg. Chem.* **1998**, 37 (17), 4258-4264.
26. Savoie, C.; Reber, C., Coupled Electronic States in Trans-Dioxo Complexes of Rhenium(V) and Osmium(VI) Probed by Near-Infrared and Visible Luminescence Spectroscopy. *J. Am. Chem. Soc.* **2000**, 122 (5), 844-852.
27. Grey, J. K.; Butler, I. S.; Reber, C. Effect of Pressure on Coupled Electronic Ground and Excited States Determined from Luminescence Spectra of Trans-Dioxorhenium(V) Complexes. *J. Am. Chem. Soc.* **2002**, 124 (39), 11699-11708.
28. Liu, Z.; Qin, X.; Chen, Q.; Chen, Q.; Jing, Y.; Zhou, Z.; Zhao, Y. S.; Chen, J.; Liu, X., Highly Stable Lead-Free Perovskite Single Crystals with NIR Emission Beyond 1100 nm. *Adv. Opt. Mater.* **2022**, 10 (21), 2201254.
29. Eickhoff, T.; Grosse, P.; Theiss, W. Diffuse Reflectance Spectroscopy of Powders. *Vib. Spectrosc.* **1990**, 1 (2), 229-233.
30. Maughan, A. E.; Ganose, A. M.; Scanlon, D. O.; Neilson, J. R. Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors. *Chem. Mater.* **2019**, 31 (4), 1184-1195.
31. Morgan, E. E.; Kent, G. T.; Zohar, A.; O'Dea, A.; Wu, G.; Cheetham, A. K.; Seshadri, R. Hybrid and Inorganic Vacancy-Ordered Double Perovskites A₂WCl₆. *Chem. Mater.* **2023**, 35 (17), 7032-7038.
32. Panigrahi, K.; Nag, A. Challenges and Strategies to Design Phosphors for Future White Light Emitting Diodes. *J. Phys. Chem. C* **2022**, 126 (20), 8553-8564.
33. Kammoun, S.; Dammak, M.; Maalej, R.; Kamoun, M. Electronic States of Vanadium(III) in Trans-VCl₂(H₂O)⁴⁺ Chromophore. *J. Alloys Compd.* **2008**, 453 (1), 64-68.
34. Sánchez, A. M.; Sangalli, D.; Hummer, K.; Marini, A.; Wirtz, L. Effect of Spin-Orbit Interaction on the Optical Spectra of Single-Layer, Double-Layer, and Bulk MoS₂. *Phys. Rev. B* **2013**, 88 (4), 045412.
35. Zhang, T.; Hara, D.; Murakami, S. Unique Surface-State Connection between Weyl and Nodal Ring Fermions in Ferromagnetic Material Cs₂MoCl₆. *Phys. Rev. Research* **2021**, 3 (4), L042037.
36. Jong, M. D.; Seijo, L.; Meijerink, A.; Rabouw, F. T. Resolving the Ambiguity in the Relation

between Stokes Shift and Huang–Rhys Parameter. *Phys. Chem. Chem. Phys.* **2015**, *17* (26), 16959-16969.

37. Senden, T.; Moes, R. J. A. V. D.; Meijerink, A. Quenching of the Red Mn⁴⁺ Luminescence in Mn⁴⁺-doped fluoride LED phosphors. *Light Sci. Appl.* **2018**, *7* (1), 8.

38. Fonger, W. H.; Struck, C. W. Temperature Dependences of Cr³⁺ Radiative and Nonradiative Transitions in Ruby and Emerald. *Phys. Rev. B* **1975**, *11* (9), 3251-3260.

39. Yang, B.; Yin, L.; Niu, G.; Yuan, J.-H.; Xue, K.-H.; Tan, Z.; Miao, X.-S.; Niu, M.; Du, X.; Song, H.; Lifshitz, E.; Tang, J. Lead-Free Halide Rb₂CuBr₃ as Sensitive X-Ray Scintillator. *Adv. Mater.* **2019**, *31* (44), 1904711.

40. Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X.-G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C.-J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Seró, I. M.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Prieto, J. P.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roelofs, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Buschbaum, P. M.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L., State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775-10981.

41. Zhang, Z.; Zhao, R.; Teng, S.; Huang, K.; Zhang, L.; Wang, D.; Yang, W.; Xie, R.; Pradhan, N. Color Tunable Self-Trapped Emissions from Lead-Free All Inorganic IA-IB Bimetallic Halides Cs-Ag-X (X = Cl, Br, I). *Small* **2020**, *16* (44), 2004272.

42. Kipkorir, A.; Kamat, P. V. Managing Photoinduced Electron Transfer in AgInS₂–CdS Heterostructures. *J. Chem. Phys.* **2022**, *156* (17).

43. Haeger, T.; Heiderhoff, R.; Riedl, T. Thermal Properties of Metal-Halide Perovskites. *J. Mater. Chem. C* **2020**, *8* (41), 14289-14311.

44. Corsepius, N. C.; DeVore, T. C.; Reisner, B. A.; Warnaar, D. L. Using Variable Temperature Powder X-ray Diffraction to Determine the Thermal Expansion Coefficient of Solid MgO. *J. Chem. Educ.* **2007**, *84* (5), 818.

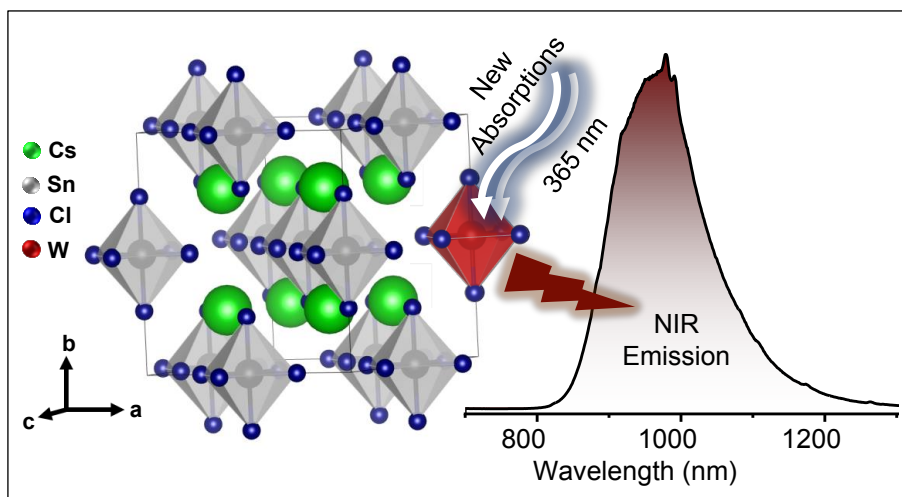
45. Lanthier, E.; Bendix, J.; Reber, C., Pressure-Dependent Luminescence Spectroscopy of Molybdenum(iv) Oxo Complexes. *Dalton Trans.* **2010**, 39 (15), 3695-3705.
46. Hu, T.; Lin, H.; Cheng, Y.; Huang, Q.; Xu, J.; Gao, Y.; Wang, J.; Wang, Y. A Highly-Distorted Octahedron with a C_{2v} Group Symmetry Inducing an Ultra-Intense Zero Phonon Line in Mn⁴⁺-Activated Oxyfluoride Na₂WO₂F₄. *J. Mater. Chem. C* **2017**, 5 (40), 10524-10532.
47. Zeng, L.; Zhong, J.; Li, C.; Zhuang, Z.; Chen, L.; Zhao, W. Broadband Near-Infrared Emission in the NaInP₂O₇:Cr³⁺ Phosphor for Light-Emitting-Diode Applications. *J. Lumin.* **2022**, 247, 118909.
48. Yuan, C.; Li, R.; Liu, Y.; Zhang, L.; Zhang, J.; Leniec, G.; Sun, P.; Liu, Z.; Luo, Z.; Dong, R.; Jiang, J. Efficient and Broadband LiGaP₂O₇:Cr³⁺ Phosphors for Smart Near-Infrared Light-Emitting Diodes. *Laser Photonics Rev.* **2021**, 15 (11), 2100227.
49. Zhang, H.; Zhong, J.; Zhang, X.; Yang, H.; Mu, Z.; Zhao, W. Achieving an Ultra-Broadband Infrared Emission through Efficient Energy Transfer in LiInP₂O₇: Cr³⁺, Yb³⁺ Phosphor. *J. Alloys Compd.* **2022**, 894, 162386.
50. Yao, L.; Shao, Q.; Han, S.; Liang, C.; He, J.; Jiang, J. Enhancing Near-Infrared Photoluminescence Intensity and Spectral Properties in Yb³⁺ Codoped LiScP₂O₇:Cr³⁺. *Chem. Mater.* **2020**, 32 (6), 2430-2439.
51. Zhang, Y.; Miao, S.; Liang, Y.; Liang, C.; Chen, D.; Shan, X.; Sun, K.; Wang, X.-J. Blue LED-Pumped Intense Short-Wave Infrared Luminescence Based on Cr³⁺-Yb³⁺-Co-doped Phosphors. *Light Sci. Appl.* **2022**, 11 (1), 136.
52. Sproules, S.; Banerjee, P.; Weyhermüller, T.; Yan, Y.; Donahue, J. P.; Wieghardt, K. Monoanionic Molybdenum and Tungsten Tris(dithiolene) Complexes: A Multifrequency EPR Study. *Inorg. Chem.* **2011**, 50 (15), 7106-7122.
53. Zhao, F.; Cai, H.; Song, Z.; Liu, Q. Structural Confinement for Cr³⁺ Activators toward Efficient Near-Infrared Phosphors with Suppressed Concentration Quenching. *Chem. Mater.* **2021**, 33 (10), 3621-3630.
54. Fang, L.; Zhang, L.; Wu, H.; Wu, H.; Pan, G.; Hao, Z.; Liu, F.; Zhang, J. Efficient Broadband Near-Infrared CaMgGe₂O₆:Cr³⁺ Phosphor for pc-LED. *Inorg. Chem.* **2022**, 61 (23), 8815-8822.

Chapter 3A

W⁴⁺-doped Cs₂SnCl₆ for near-infrared emission

Abstract

Doped halide double perovskites and vacancy-ordered variants ($A_2M'M''X_6$ and A_2MX_6 ; A and M' = monovalent cation, M'' = trivalent cation, M = tetravalent cation and X = halide anion) are becoming important class of materials due to their intriguing optical property and environmentally benign nature. The octahedral coordination site of metal ions makes them perfect host for accommodating various dopants. Now for efficient near-infrared (NIR) emission out of these wide band-gap stable materials, both *s*-electron (can absorb lower energy light) and *d/f*-electron (emit NIR light) dopants are required. Here we report, a comparatively less explored *d*-electron dopant W⁴⁺ into the lattice of vacancy-ordered perovskite derivative Cs₂SnCl₆. Here W⁴⁺ (*d*²) can absorb sub-band light due to different *d-d* transitions in the octahedral crystal environment and emit effectively in 800 – 1300 nm range with maxima at 965 nm. Optimized emission is obtained for 3.3% W⁴⁺-doped Cs₂SnCl₆, further increment of dopant percentage results concentration quenching. Temperature dependent photoluminescence study (300 – 7 K) elucidate the emission mechanism. Moreover, a phosphor-converted light emitting diode (pc-LED) has been fabricated by coating the optimized sample on top of a 400 nm LED, this produces reasonably good NIR output power of 10.3 mW at 401 mA.

Graphical abstract

3A.1 Introduction

Halide double perovskites¹⁻⁴ ($A_2M'M''X_6$, A and M' = monovalent cation, M'' = trivalent cation and X = halide anion) or vacancy-ordered double perovskites⁵⁻⁷ (A_2MX_6 , M = tetravalent cation) are more stable and environmentally benign in comparison with hybrid lead halide perovskites⁸⁻¹⁰. But optical property of the priors is compromised, either they are weakly emissive¹¹ or non-emissive^{12, 13}. Fortunately, the octahedral coordination and trivalent (M'') or tetravalent (M) metal ion sites provide room to incorporate different dopant ions, starting from large *s*-electron dopants to trivalent *f*-electron dopant lanthanides.¹⁴⁻¹⁹ This is not easy for many traditional semiconductors like Si, InP, GaAs etc. having smaller tetrahedral coordination site. Dopant incorporation in crystal lattice, on one hand, would generate some sub-band gap states resulting better absorption of lower energy light, on the other hand would introduce new emission properties from visible to near-infrared (NIR) optical windows. For instance, different *ns*² ions like Bi³⁺, Sb³⁺ and Te⁴⁺ doped perovskite hosts can emit efficiently in visible region with significantly high photoluminescence quantum yield (PL QY).^{13, 16, 20, 21}

Whereas, NIR emission mostly originates from forbidden *f-f* and *d-d* transitions of lanthanides and transition metals respectively in case of perovskites. Sharp lanthanide emission can be tuned from red to 1540 nm (NIR-II) by varying the lanthanide ion From Eu³⁺ to Er³⁺.²² But the precursor to final dopant amount ratio is quite high for lanthanide doping.^{17, 23, 24} Whereas transition metal like Cr³⁺ can give rise to comparatively broad NIR emission due to *d*-orbitals' involvement. But, in this case, mostly solid-state synthesis method is used.^{19, 25} Apart from these, some recent reports^{26, 27} introduce a set of transition metal (Mo⁴⁺, W⁴⁺) based halide perovskite derivatives emitting in NIR region. Based on those, here, we dope W⁴⁺ in Cs₂SnCl₆ host lattice by employing a facile hydrothermal synthesis method for NIR emission.

We have synthesized undoped Cs₂SnCl₆ and four different percentages of W⁴⁺ doped Cs₂SnCl₆ in a modified hydrothermal method. All the doped compounds show sub-band absorption and NIR emission peaking at 965 nm due to W⁴⁺ dopant with 5*d*² electronic configuration in octahedral environment. Maximum emission was obtained for 3.3% of W⁴⁺ doped sample, further increase in doping percentage resulted in concentration quenching of emission. Due to this small amount of doping (3.3% W⁴⁺), concentration quenching effect has been significantly prevented in comparison with Cs₂WCl₆. The decrease of concentration quenching in the doped sample enhances its PL

intensity and PL lifetime at room temperature (RT) in comparison with Cs₂WCl₆. Temperature dependent (7-300 K) PL study provides insights on excitation and emission processes. Besides, phosphor-converted light emitting diodes (pc-LED) were fabricated emitting NIR radiation with a reasonable output power of 10.3 mW at 400 mA current.

3A.2 Methodology section

3A.2.1 Chemicals

Cesium chloride (CsCl, Sigma Aldrich, Reagent plus, 99.9 %), tin (II) chloride (SnCl₂, anhydrous powder, ≥99.99 %), tungsten (IV) chloride (Sigma Aldrich, WCl₄, 95%), hydrochloric acid (Sigma Aldrich, HCl, 37 wt %, 99.99%) and 2-propanol (Rankem) have been purchased and used without any further purification.

3A.2.2 Synthesis of undoped Cs₂SnCl₆ crystals

Cs₂SnCl₆ crystals have been synthesized according to a reported hydrothermal method¹³. For this, 336.7 mg (2 mmol) CsCl, 189.6 mg (1 mmol) SnCl₂ and 4 mL 12 M HCl have been taken in a 25 mL polytetrafluoroethylene (PTFE) hydrothermal autoclave. This is heated at 180 °C for 12 hours, after that cooled down to room temperature in 24 hours. White colored powdered crystals are obtained. Then it is washed several times with 2-propanol and dried in vacuum desiccator. The crystal is stored and used for further characterization and measurements.

3A.2.3 Synthesis of W⁴⁺ doped Cs₂SnCl₆ crystals

The synthesis method is exactly similar with that of the undoped one. The difference is: along with CsCl, SnCl₂, four different amounts of WCl₄ are taken. These are 5, 10, 15 and 20 precursor percentages of WCl₄ with respect to SnCl₂, i.e., 0.05 mmol (16.3 mg), 0.1 mmol (32.6 mg), 0.15 mmol (48.8 mg) and 0.2 mmol (65.1 mg) respectively for four different percentages of W⁴⁺ doped Cs₂SnCl₆ crystals. These are light cyan colored powders. Rest of the washing and drying methods are same as the undoped one.

3A.2.4 Synthesis of Cs₂WCl₆ crystals

Cs₂WCl₆ crystals have been synthesized by following a reported hydrothermal method²⁶. For the synthesis, 168.4 mg (1 mmol) CsCl, 162.8 mg (0.5 mmol) WCl₄ and 5 mL 10 M HCl (made with

4.2 mL 12 M HCl and 0.8 mL distilled water) have been taken in a 25 mL PTFE hydrothermal autoclave. This mixture is heated at 180 °C for 12 hours, after that cooled down to room temperature in 30 hours. Green colored micrometer sized crystals are obtained as product. Then it is washed with 2-propanol and dried in vacuum desiccator. The crystal is stored for further use.

3A.2.5 Structural and optical characterization

Structural characterization: Powder X-ray diffraction (PXRD) measurements are performed on Bruker D8 Advance X-ray diffractometer using Cu K α radiation (1.54 Å) at room temperature. Low temperature PXRD measurements are carried out on Malvern Panalytical Empyrean Series 3 X-ray diffractometer with Oxford Cryosystems PheniX which can achieve up to 12 K. Chromium-plated copper sample holder has been used with the X-ray source of Cu K α radiation (1.54 Å). For elemental analysis of W⁴⁺ inductively coupled plasma mass spectroscopy (ICP–MS) is performed by using a quadrupole–ICP–MS (Thermo iCAP-Q) spectrometer. The dopant percentages are determined with respect to the metal Sn present in respective sample. Electron paramagnetic resonance (EPR) spectra are measured using JON Bruker BioSpin connected to Bruker EMX plus spectrometer with a radio wave source (9.737205 GHz). Thermogravimetric analysis (TGA) is done using Perkin-Elmer STA 6000, TGA analyzer under N₂ atmosphere and the heating rate was 10 °C/min.

Optical properties: Optical diffused-reflectance measurements have been carried out on Shimadzu UV-3600 plus UV-VIS-NIR spectrophotometer. The reflectance data are transformed to absorbance by utilizing Kubelka-Munk transformation,²⁸ using equation given below:

$$F(R) = \alpha/S = (1-R)^2/2R \dots\dots(1)$$

Here, F(R) is the Kubelka-Munk function, R is reflectance, α is the absorption coefficient and S is scattering factor. Steady state photoluminescence (PL) measurements (PL excitation and emission) have been done using FLS 980 (Edinburgh Instruments) with Xe-lamp as an excitation source. Time-resolved PL decay profiles have been measured with same instrument using a microsecond flash lamp to excite (365 nm). The decay profiles are fitted with mono-exponential decay function:

$$I_t = I_0 + A \exp(-t/\tau) \dots\dots(2)$$

Here, I_t is PL counts at any variable time = t , I_0 is the offset and τ is PL lifetime with the amplitude A . Temperature-dependent PL measurements have also been carried out on the FLS980 (Edinburgh Instruments). Ground sample has been sandwiched between two sapphires and it is mounted on a gold-plated sample holder that is attached to a closed cycle He cryostat (Advanced Research Systems) with a temperature controller (Lake Shore Cryotronics) for achieving the expected temperatures.

3A.2.6 Phosphor converted light emitting diodes (pc-LEDs)

With the optimized sample, i.e., 3.3% W⁴⁺-doped Cs₂SnCl₆, pc-LED has been fabricated. Finely ground powdered sample (50 mg) is mixed with 50 weight % of PMMA (50 mg) in 250 μ L toluene and the mixture is heated at 60 °C for 1 hour to get a dispersion. The paste is now drop casted on top of the commercial LED chip of 400 nm. The pc-LEDs are measured with variable drive current from 11 – 421 mA. The measurements are performed with Hamamatsu photonic multi-channel analyzer C10028 with Keithley 2450 source meter.

3A.3 Results and discussion

3A.3.1 Synthesis and structural characterization

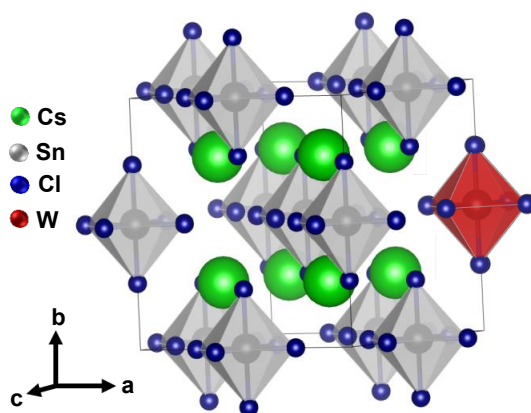


Figure 3A.1: Schematic representation of crystal structure of Cs₂SnCl₆, doped with W⁴⁺, where, the grey octahedra are implying [SnCl₆]²⁻ and the maroon octahedron is implying [WCl₆]²⁻, all octahedra are separated from each other with large Cs⁺ cation forming a 0D perovskite derivative structure.

Undoped and W⁴⁺-doped Cs₂SnCl₆ with different dopant percentages have been synthesized by employing a hydrothermal method. The methodology for synthesizing the undoped sample is

similar to a previous report¹³. Stoichiometric amount of CsCl and SnCl₂ have been taken in a hydrothermal autoclave containing 4 mL of 12 M HCl. The autoclave was then heated at 180 °C for 12 hours, followed by cooling over a period of 24 hours. This reaction results into white colored powdered crystals of Cs₂SnCl₆. For synthesizing doped samples, a similar method has been followed along with addition of different amounts of WCl₄ salt in the reaction mixture. Details of the precursor amount, synthesis and characterizations are described in methodology section. Elemental analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) shows 1.6, 2.4, 3.3 and 3.7% W⁴⁺ doping with respect to Sn⁴⁺ in the product, for 5, 10, 15 and 20 mole % of WCl₄ precursor with respect to SnCl₂ in the reaction mixture, respectively (shown in Table 3A.1).

Table 3A.1: ICP-MS result of undoped Cs₂SnCl₆ and W⁴⁺ doped Cs₂SnCl₆ compounds. Dopant % = $\frac{[W]}{[Sn]} \times 100$, where, [W] and [Sn] are molar concentrations of tungsten and tin respectively.

Sample code	Precursor molar % of W ⁴⁺ , $\frac{[W]}{[Sn]} \times 100$	Actual molar % of W ⁴⁺ from ICP-MS, $\frac{[W]}{[Sn]} \times 100$
Undoped Cs ₂ SnCl ₆	0	0
1.6% W ⁴⁺	5	1.6
2.4% W ⁴⁺	10	2.4
3.3% W ⁴⁺	15	3.3
3.7% W ⁴⁺	20	3.7

The crystal structure of Cs₂SnCl₆ is an antiferro arrangement with secluded [SnCl₆]²⁻ octahedra bridged with Cs⁺ cations.⁷ Such a structure is broadly named as vacancy-ordered double perovskites or 0D perovskite derivatives. If W⁴⁺ dopant ions replace Sn⁴⁺ ions, the structure of W⁴⁺-doped Cs₂SnCl₆ can be schematically represented as Figure 3A.1. To verify the structure, Figure 3A.2a compares the powder X-ray diffraction patterns (XRD) patterns of undoped Cs₂SnCl₆ (grey circles) and 3.3% W⁴⁺-doped Cs₂SnCl₆ (maroon circles) samples. Both experimental patterns look very similar and their Rietveld refinement can be carried out taking the reference pattern²⁹ of Cs₂SnCl₆. The experimental patterns are in good agreement with the simulated Cs₂SnCl₆ with the goodness of fit (GOF) values of 1.1 and 1.5 for the undoped and 3.3% W⁴⁺-doped Cs₂SnCl₆,

respectively. Similar powder XRD patterns and Rietveld refinement of all W⁴⁺-doped Cs₂SnCl₆ with different doping percentages are shown in Figure 3A.2 b-d along with detailed refinement parameters in Table 3A.2.

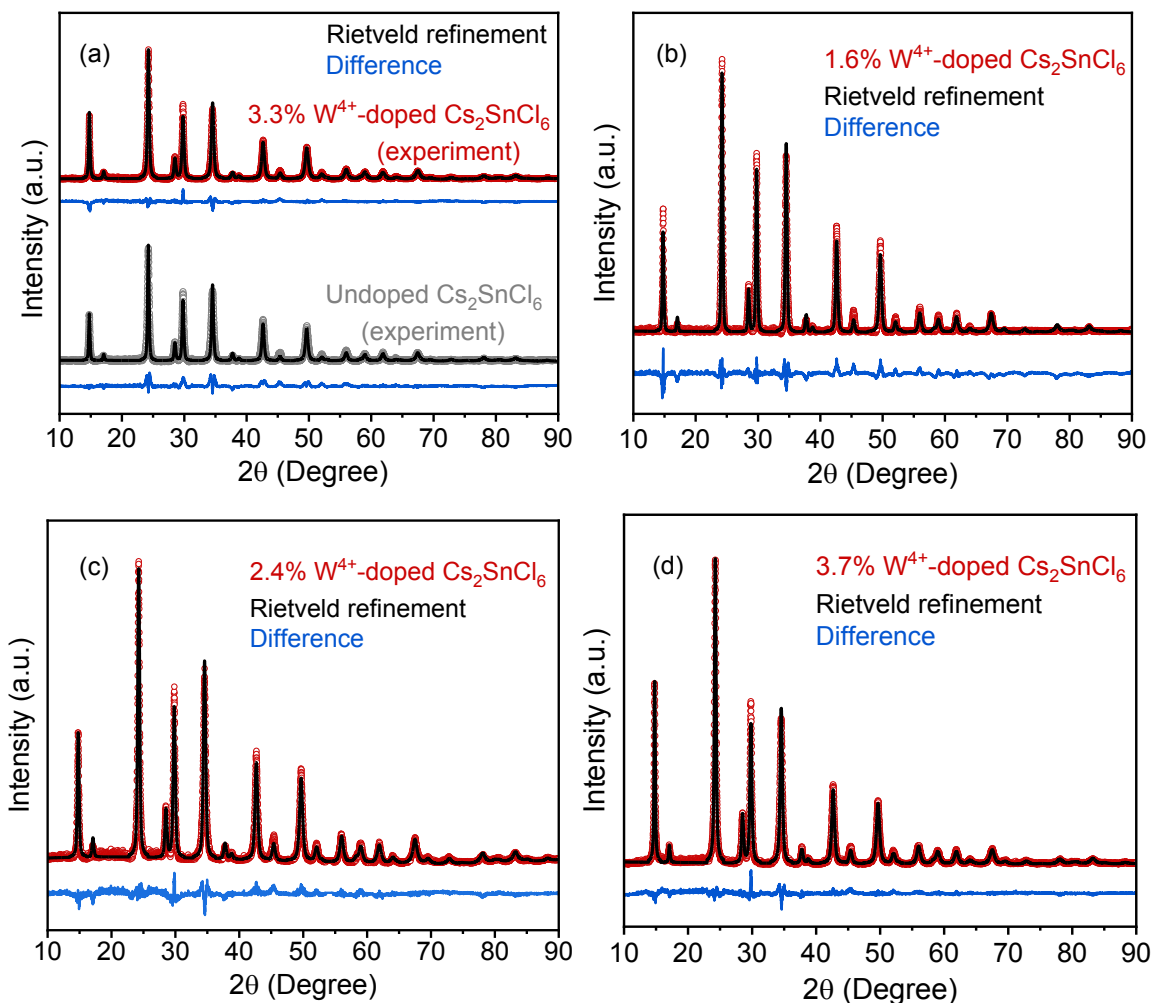


Figure 3A.2: (a) Rietveld refinements (black lines) of powder X-ray diffraction (PXRD) patterns of undoped Cs₂SnCl₆ (grey circles) and 3.3% W⁴⁺ doped Cs₂SnCl₆ (maroon circles). No peak-shift has been observed after W⁴⁺ doping due to the comparable size of Sn⁴⁺ and W⁴⁺ ions. PXRD patterns (maroon circles) and corresponding Rietveld refinement (black line) of other doping percentages, i.e., (b) 1.6% W⁴⁺-doped Cs₂SnCl₆, (c) 2.4% W⁴⁺-doped Cs₂SnCl₆ and (d) 3.7% W⁴⁺-doped Cs₂SnCl₆. Various refinement parameters are provided in Table 3A.2.

Overall, the powder XRD patterns suggest phase purity of all the W⁴⁺-doped samples that crystallizes in cubic Fm $\bar{3}$ m space group, similar to their undoped counterpart. However, one needs to be more careful since both Cs₂SnCl₆ and Cs₂WCl₆ show similar powder XRD patterns, as shown

in Figure 3A.3. Interestingly, at higher 2θ values of 70° to 90° , the XRD patterns of Cs_2SnCl_6 and Cs_2WCl_6 differ significantly. Figure 3A.3 confirms that the powder XRD data W^{4+} -doped Cs_2SnCl_6 resembles with that of Cs_2SnCl_6 , without having any impurity phase corresponding to Cs_2WCl_6 . The ionic radius of Sn^{4+} and W^{4+} in octahedral environment are similar with values of 69 and 66 picometer, respectively.³⁰ Consequently, no peak shift has been observed from undoped to W^{4+} -doped Cs_2SnCl_6 .

Table 3A.2: Different structural parameters obtained from Rietveld refinement of PXRD patterns of Cs_2SnCl_6 , various W^{4+} -doped Cs_2SnCl_6 and Cs_2WCl_6 at room temperature (298 K).

Chemical formula	Cs_2SnCl_6	1.6% W^{4+}	2.4% W^{4+}	3.3% W^{4+}	3.7% W^{4+}	Cs_2WCl_6
Wavelength	1.5406 Å (Cu K α)	1.5406 Å (Cu K α)	1.5406 Å (Cu K α)	1.5406 Å (Cu K α)	1.5406 Å (Cu K α)	1.5406 Å (Cu K α)
Crystal system	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	$\text{Fm}\bar{3}\text{m}$	$\text{Fm}\bar{3}\text{m}$	$\text{Fm}\bar{3}\text{m}$	$\text{Fm}\bar{3}\text{m}$	$\text{Fm}\bar{3}\text{m}$	$\text{Fm}\bar{3}\text{m}$
$a = b = c$ (Å)	10.3797(5)	10.3798(4)	10.3794(7)	10.3795(3)	10.3799(9)	10.2162(4)
$\alpha = \beta = \gamma$ (deg)	90.000(4)	90.000(6)	90.0000(3)	90.000(1)	90.0000(4)	90.0000(2)
Unit cell volume (Å ³)	1118.3(2)	1118.3(1)	1118.2(2)	1118.2(1)	1118.3(3)	1066.26(12)
R_p (%)	1.6	3.1	8.9	7.5	6.7	6.9
R_{wp} (%)	2.3	4.1	9.8	8.8	7.6	8.6
R_{exp} (%)	2.1	3.1	8.5	7.2	7.7	6.7
χ^2	1.21	3.24	1.69	2.25	1	2.89
GoF	1.1	1.8	1.3	1.5	1	1.7

To further rule out the possibility of formation of Cs_2WCl_6 impurity, we have measured electron paramagnetic resonance (EPR) spectroscopy. Cs_2SnCl_6 does not have any unpaired electron, and

therefore, EPR inactive (Figure 3A.4a). In difference, W⁴⁺ has two unpaired *d*-electrons. Figure 3A.4a and b show the EPR data of Cs₂WCl₆ and 3.3% W⁴⁺-doped Cs₂SnCl₆ at 300 K and 100 K respectively. Both the samples show EPR peaks at same position because of the unpaired electrons of W⁴⁺. The spectrum broadens with increasing dipole-dipole interaction between W⁴⁺ ions.³¹ In the 3.3% W⁴⁺-doped Cs₂SnCl₆, the W⁴⁺ ions are located far from each other, and therefore a narrow spectral width with peak-to-peak linewidth (ΔH_{pp}) of 85.8 G is observed at 100 K. The EPR spectrum broadens significantly for Cs₂WCl₆ with ΔH_{pp} = 239.5 G at 100 K, because of the close proximity of W⁴⁺ ions. EPR spectra measured at room temperature also show the similar spectral broadening in Cs₂WCl₆ compared to the doped sample.

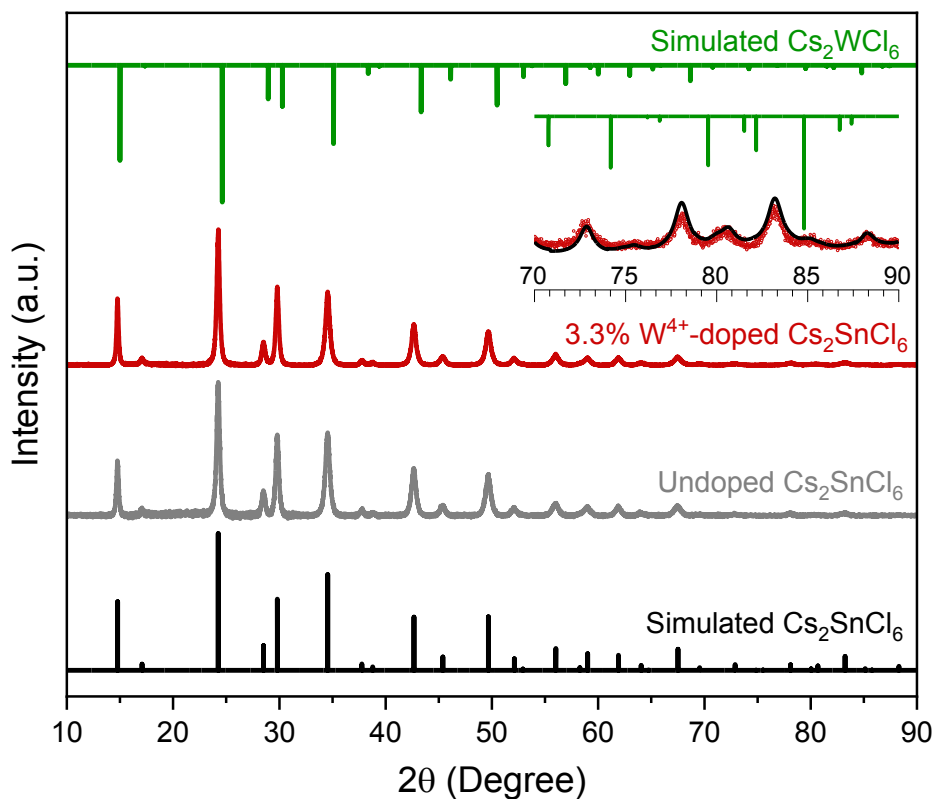


Figure 3A.3: PXRD patterns of undoped Cs₂SnCl₆ (grey line) and 3.3% W⁴⁺-doped Cs₂SnCl₆ (maroon line) along with the simulated patterns of Cs₂SnCl₆ (black line, CDS No 2216627) and Cs₂WCl₆ (olive line) imply that there is no impurity of Cs₂WCl₆ phase in the doped sample. Inset showing the enlarged view of higher 2θ position of 3.3% W⁴⁺-doped Cs₂SnCl₆ (with refinement) and simulated Cs₂WCl₆ represents the difference between the two patterns.

Figure 3A.5 presents the thermogravimetric analysis (TGA) data of Cs₂SnCl₆, 3.3% W⁴⁺-doped Cs₂SnCl₆ and Cs₂WCl₆. Cs₂SnCl₆ and 3.3% W⁴⁺-doped Cs₂SnCl₆ don't have any weight loss till

700 K whereas Cs₂WCl₆ starts to decompose from 500 K. This implies better thermal stability in case of W⁴⁺-doped sample than that of Cs₂WCl₆.

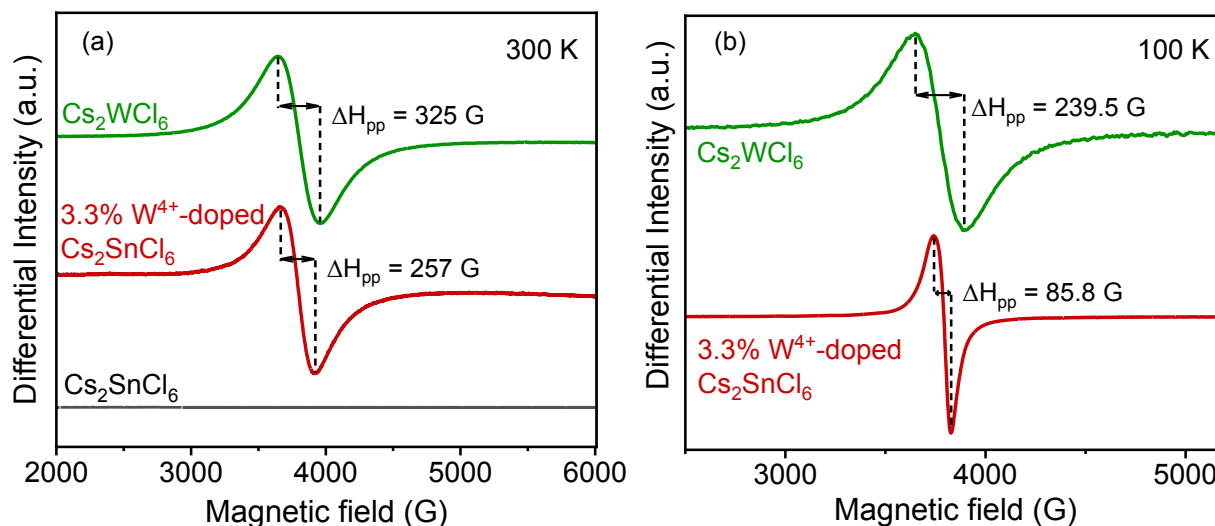


Figure 3A.4: Room temperature (a) and (b) 100 K EPR signals of Cs₂SnCl₆ (black), 3.3% W⁴⁺-doped Cs₂SnCl₆ (maroon) and Cs₂WCl₆ (olive) compounds. ΔH_{pp} presents the peak-to-peak linewidth.

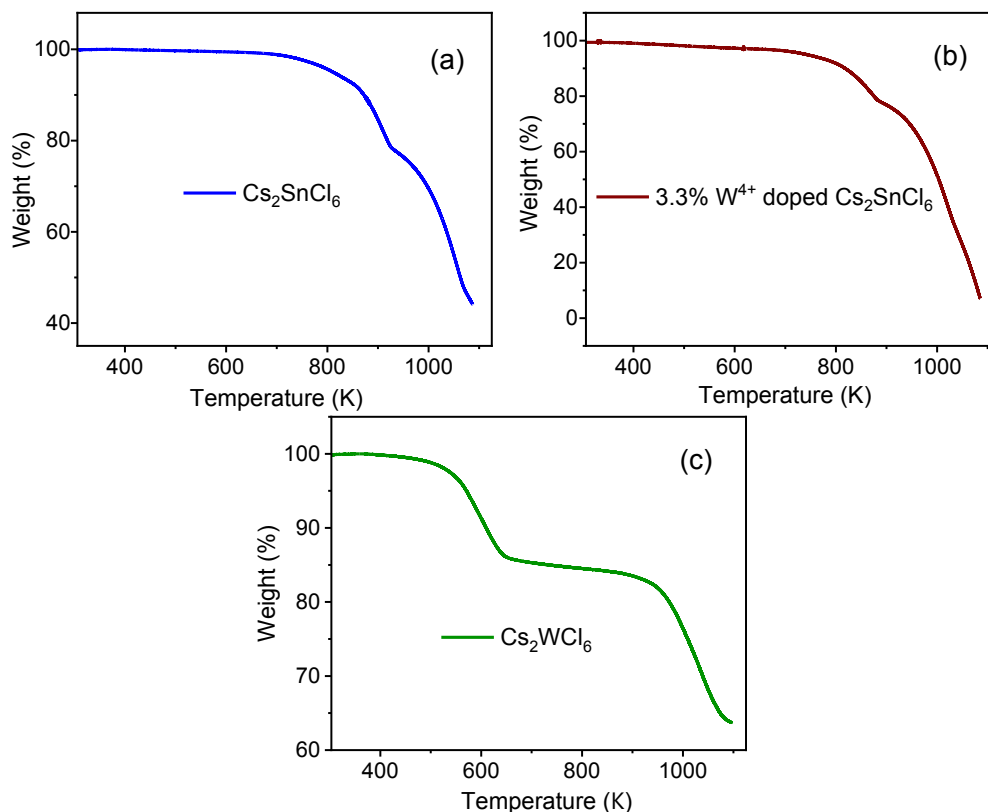


Figure 3A.5: TGA data of (a) Cs₂SnCl₆, (b) 3.3% W⁴⁺-doped Cs₂SnCl₆, and (c) Cs₂WCl₆.

3A.3.2 Room-temperature optical properties

Figure 3A.6a presents UV-visible-NIR absorption spectra of undoped Cs₂SnCl₆ (grey), 3.3% W⁴⁺-doped Cs₂SnCl₆ (blue) and Cs₂WCl₆ (maroon) powders at room temperature. Cs₂SnCl₆ has a wide band gap showing absorption edge at ~313 nm. After doping W⁴⁺, new absorption features start appearing at ~300 nm, ~393 nm and ~775 nm. The absorbance of these features increases with increasing the W⁴⁺ dopant concentrations as shown in Figure 3A.7. Furthermore, the absorption of these features become significantly stronger for Cs₂WCl₆. Therefore, the new absorptions at ~300 nm, ~393 nm and ~775 nm are expected to originate from the *d-d* electronic transition of W⁴⁺. Tanabe–Sugano diagram for *d²* electronic configuration W⁴⁺ in octahedral environment is shown in the inset to Figure 3A.6a. The transitions corresponding to $^3T_{1g} \rightarrow ^3T_{2g}$ and $^3T_{1g} \rightarrow ^3T_{1g}(P)$ and $^3T_{1g} \rightarrow ^1T_{2g}/^1E_g$, can be assigned to the ~300 nm, ~400 nm and ~775 nm absorption features, respectively.²⁷ The $^3T_{1g} \rightarrow ^1T_{2g}/^1E_g$ is spin-forbidden, but can become partially allowed because of the large spin-orbit coupling in W⁴⁺.³²

Cs₂WCl₆ is known to emit NIR radiation because of d-d transition of W⁴⁺.²⁷ Figure 3A.6b presents the PL spectra of Cs₂WCl₆ and 3.3% W⁴⁺-doped Cs₂SnCl₆ powders after normalization at their respective excitation wavelengths. Both samples show similar NIR emission spectra, but the doped sample exhibit a significant enhancement in intensity compared to Cs₂WCl₆. In Cs₂WCl₆, the W⁴⁺ ions are very close to each other causing concentration quenching³³ of PL intensity. We note that the EPR peak broadening because of dipole-dipole interaction between W⁴⁺ ions of Cs₂WCl₆ also corroborates the observed concentration quenching of PL. Whereas for lower level of doping in W⁴⁺-doped Cs₂SnCl₆, the W⁴⁺ ions remain far from each other, that avoids significant concentration quenching. Figure 3A.6c shows that the NIR emission intensity increases with increasing the dopant concentration from 1.6 to 3.3% W⁴⁺, but further increase in the dopant concentration leads to concentration quenching. Figure 3A.6d presents the stability of the optimized 3.3% W⁴⁺-doped Cs₂SnCl₆ in terms of phase purity and NIR emission. PL emission intensity of the optimized W⁴⁺ doped sample is perfectly retained up to 250 days, whereas the inset PXRD patterns of 0 day (red) and 250 days (blue) of this sample indicate that the structural stability is being maintained as well throughout this time period. Therefore, from these stability experiments it can be said that 3.3% W⁴⁺-doped Cs₂SnCl₆ compound is appreciably stable up to long period both in terms of structure as well as NIR emission property.

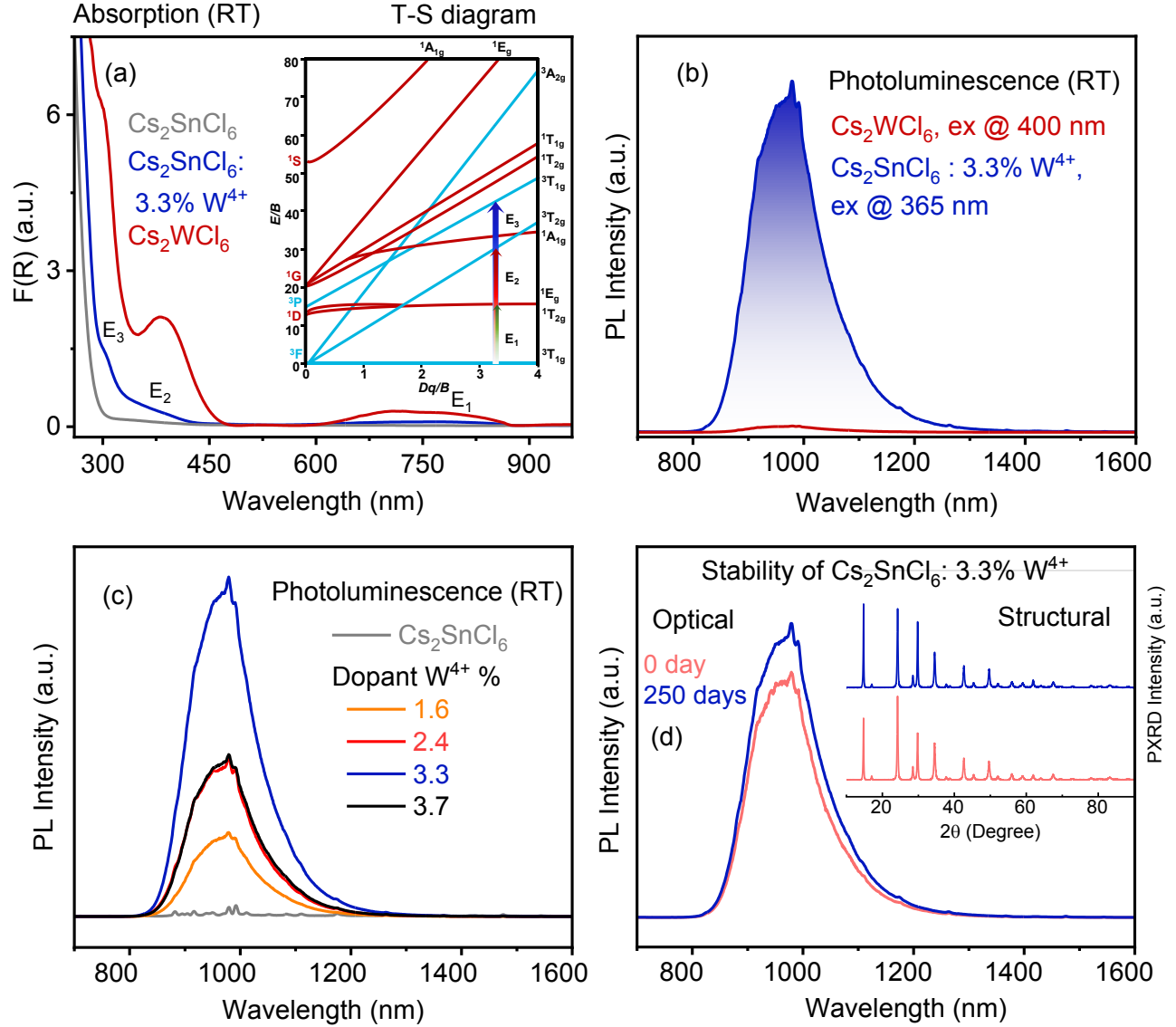


Figure 3A.6: Room temperature (RT) optical property of Cs_2SnCl_6 , various % W^{4+} doped Cs_2SnCl_6 and Cs_2WCl_6 . (a) UV-visible-NIR absorption of Cs_2SnCl_6 (grey), 3.3% W^{4+} doped Cs_2SnCl_6 (blue) and Cs_2WCl_6 (maroon) at room temperature. The reflectance (R) data have been transformed to absorbance by using Kubelka-Munk function $F(R) = (1-R)^2/2R$.²⁸ Inset shows the Tanabe-Sugano diagram of d^2 system in octahedral field showing three transitions E_1 (green), E_2 (red) and E_3 (blue) with arrows at Dq/B value of 3.3 for W^{4+} dopant. (b) Room temperature PL spectra of 3.3% W^{4+} doped Cs_2SnCl_6 (blue, ex @ 365 nm) and Cs_2WCl_6 (maroon, ex @ 400 nm) after normalization with the absorption value (in Figure 3A.6a) at respective excitation wavelength. (c) Photoluminescence of undoped Cs_2SnCl_6 and different percentages of W^{4+} doped Cs_2SnCl_6 samples after the excitation with 365 nm light. Concentration quenching in emission happens after 3.3% W^{4+} . (d) Emission and structural stability of 3.3% W^{4+} doped Cs_2SnCl_6 . Blue (0 day) and red (250 days) data signify that the phase purity and PL are largely maintained for 250 days.

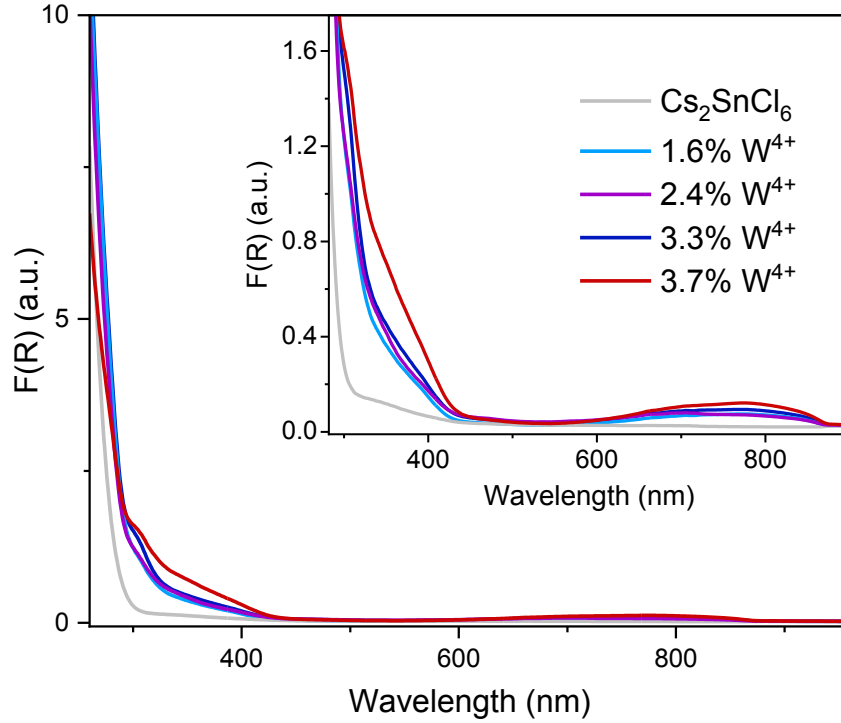


Figure 3A.7: UV-Visible-NIR absorption spectra of undoped and four different percentages of W^{4+} doped Cs_2SnCl_6 . Inset shows the enlarged view of all five absorptions, indicating the increase of dopant absorptions with increasing W^{4+} amount.

3A.3.3 Temperature-dependent photoluminescence and structure

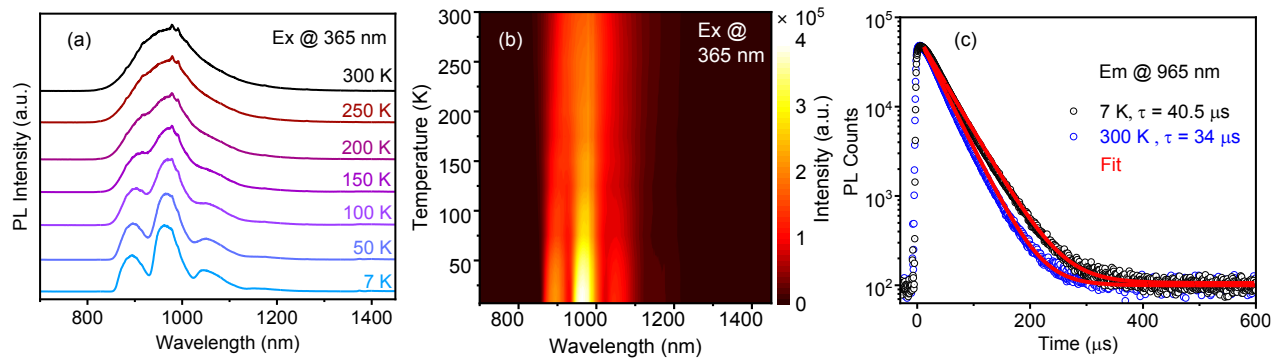


Figure 3A.8: Temperature dependent photoluminescence of 3.3% W^{4+} -doped Cs_2SnCl_6 . Excitation wavelength is 365 nm. (a) Photoluminescence emission spectra, measured with powdered sample at some representative temperatures in the range of 7-300 K. (b) Pseudo-color map of temperature dependent PL emission spectra throughout the temperature range of 7-300 K. (c) PL decay profiles measured at two representative temperatures 7 K (black circle) and 300 K (blue circle) with mono-exponential decay fitting (red line). The equation for fitting these decay profiles has been provided in equation 2 of the methodology section 3A.2.

For more insights, we performed temperature-dependent PL measurements. Figure 3A.8a shows the evolution of PL spectra of 3.3% W⁴⁺-doped Cs₂SnCl₆ at a few temperatures from 300-7 K. With decreasing the temperature, the asymmetric PL spectrum at 300 K splits into multiple peaks and the splitting becomes more prominent below 150 K. Similar peak splitting has been recently observed for Cs₂WCl₆, and was attributed to vibronically coupled *d-d* transition of W⁴⁺ ions.²⁷ Figure 3A.9 shows that the PL decay profiles measured at 895 nm, 965 nm, and 1045 nm corresponding to the split peaks at 7 K are identical with each other. This similarity suggests that the electronic nature of all these peaks is same, and therefore, agrees with the assignment of vibronically coupled *d-d* transition in 3.3% W⁴⁺-doped Cs₂SnCl₆.

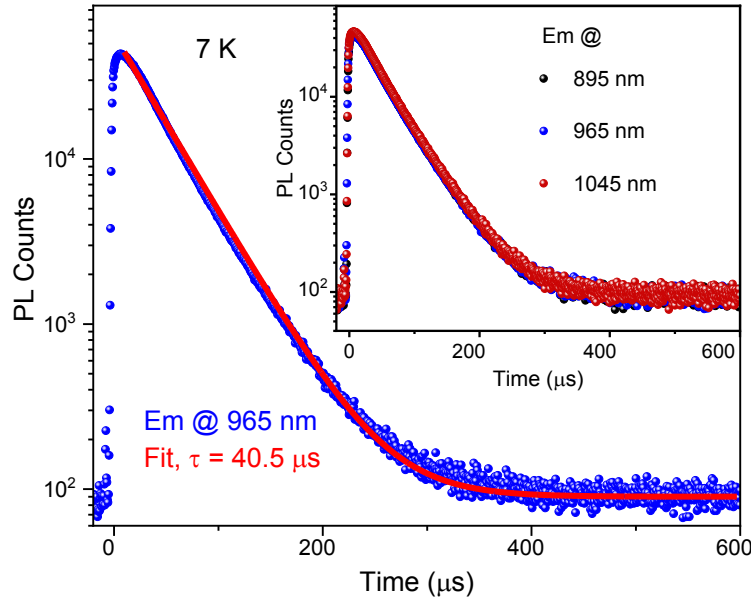


Figure 3A.9: PL decay dynamics of 3.3% W⁴⁺ doped Cs₂SnCl₆ measured at 7 K after setting the emission at 965 nm, the decay profile has been fitted with a mono-exponential decay function shown in equation 2. Inset presents overlapped PL decay profiles at 7 K for all three emission peaks shown in Figure 3A.8a. The excitation wavelength for all the decays is 365 nm.

PL spectra at many other temperatures from 7-300 K have been presented through the pseudo-colormap of Figure 3A.8b. The PL intensity somewhat increases with decreasing temperature, but not much. Figure 3A.10 shows mirror-image like PL excitation and emission originating from same pair of electronic states at 7 K. From this we can calculate the separation between absorption and emission maxima, i.e., $E_{\text{Stokes}} = 2580 \text{ cm}^{-1}$, and phonon energy ($\hbar\omega_{\text{phonon}} = 830 \text{ cm}^{-1}$). Using these we can calculate Huang-Rhys parameter *S*, by using the following equation:

$$S = \left(\frac{1}{2} \frac{E_{\text{Stokes}}}{\hbar \omega_{\text{phonon}}} + \frac{1}{4} \right) \pm \frac{1}{4} \quad \dots\dots (3) \quad \text{Thus, } S = 1.8 \pm 0.25.$$

This small value of Huang-Rhys parameter indicates weak electron phonon-coupling in the system. Therefore, the temperature dependent change in PL intensity is not much. Likewise, Figure 3A.8c and Figure 3A.11 show that the PL decay profiles of 3.3% W⁴⁺-doped Cs₂SnCl₆ also do not change much with decreasing temperature from 300 – 7 K. The decay profiles are fitted with mono-exponential decay equation (equation 2). The obtained lifetimes are 40.5 μ s, 37.1 μ s, 36.9 μ s, and 34 μ s at 7 K, 100 K, 200 K, and 300 K respectively.

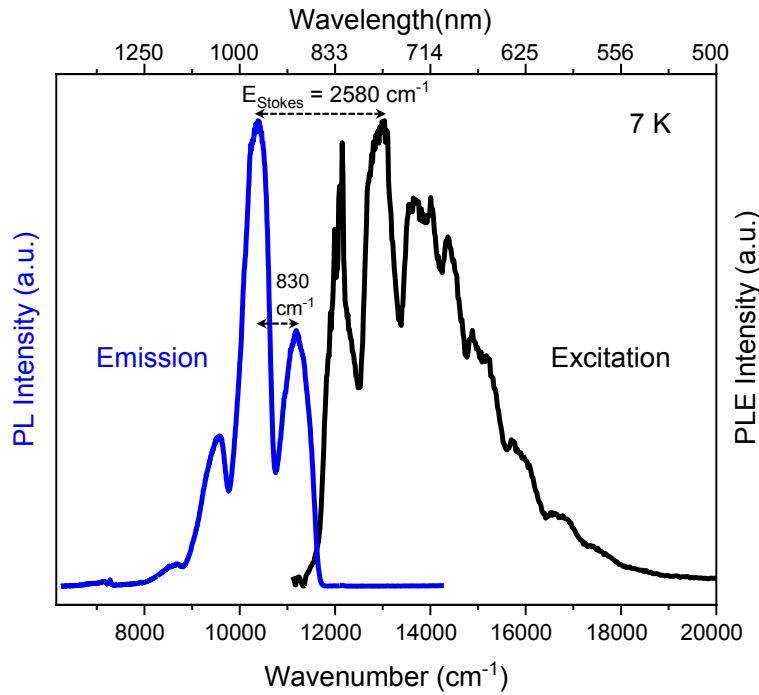


Figure 3A.10: PL emission (blue) and excitation (black) spectra of 3.3% W⁴⁺ doped Cs₂SnCl₆ measured at 7 K. Here, the Stokes shift, $E_{\text{Stokes}} = 2580 \text{ cm}^{-1}$, phonon energy ($\hbar \omega_{\text{phonon}} = 830 \text{ cm}^{-1}$). Therefore, we calculate Huang-Rhys parameter ($S \sim 2$) by following equation 3³⁴

To elucidate the structural stability of W⁴⁺-doped Cs₂SnCl₆ at lower temperature, we measured powder XRD patterns in the temperature range 12-300 K. Figure 3A.12a shows that the same cubic phase (Fm $\bar{3}$ m space group) retained in the temperature range. Expectedly, Figure 3A.12b shows a systematic shift towards lower 2θ value indicating expansion of the unit cell with increasing the temperature. Similar temperature dependent XRD patterns are also observed for Cs₂SnCl₆ and Cs₂WCl₆, as shown in Figure 3A.13 and 3A.14, respectively. Figure 3A.15 presents the calculation of coefficient of volume thermal expansion for all the three samples. Since the molar volume of

them are similar, therefore, coefficient of volume thermal expansion ($\gamma_{v, 300\text{ K}}$) of Cs₂SnCl₆, 3.3% W⁴⁺-doped Cs₂SnCl₆ and Cs₂WCl₆ are also similar, with values 1.04×10^{-4} , 1.06×10^{-4} and $1.08 \times 10^{-4} \text{ K}^{-1}$, respectively.

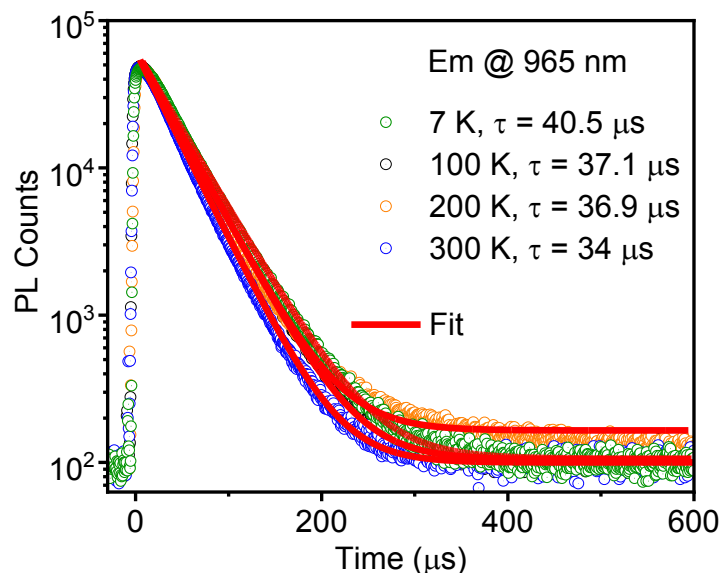


Figure 3A.11: PL decay dynamics of 3.3% W⁴⁺ doped Cs₂SnCl₆ measured at different temperatures in the range of 300 - 7 K for emission at 965 nm. The excitation for all the PL decay profiles is 365 nm.

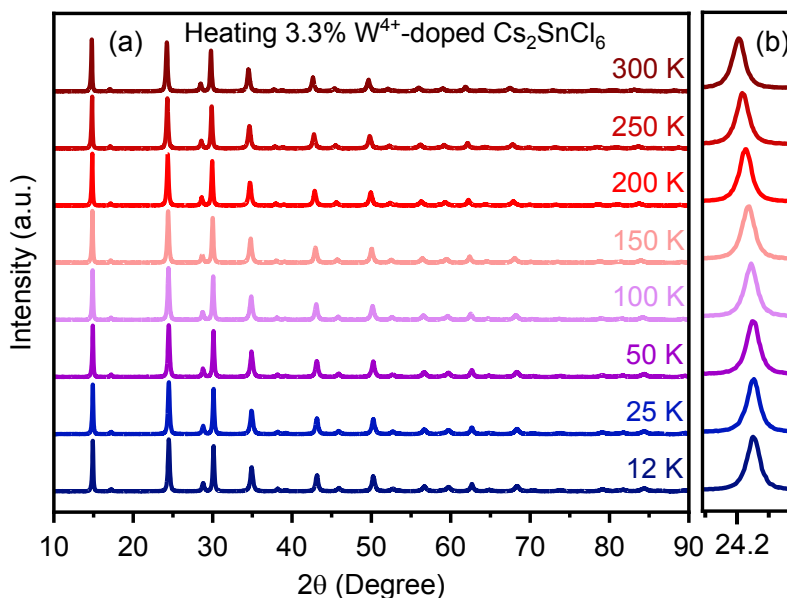


Figure 3A.12: (a) Temperature dependent PXRD patterns of 3.3% W⁴⁺ doped Cs₂SnCl₆ in a range of 12-300 K showing no phase change throughout this temperature range. (b) Enlarged visualization of one peak implies with increasing temperature the peak shifts towards lower 2θ due to lattice expansion.

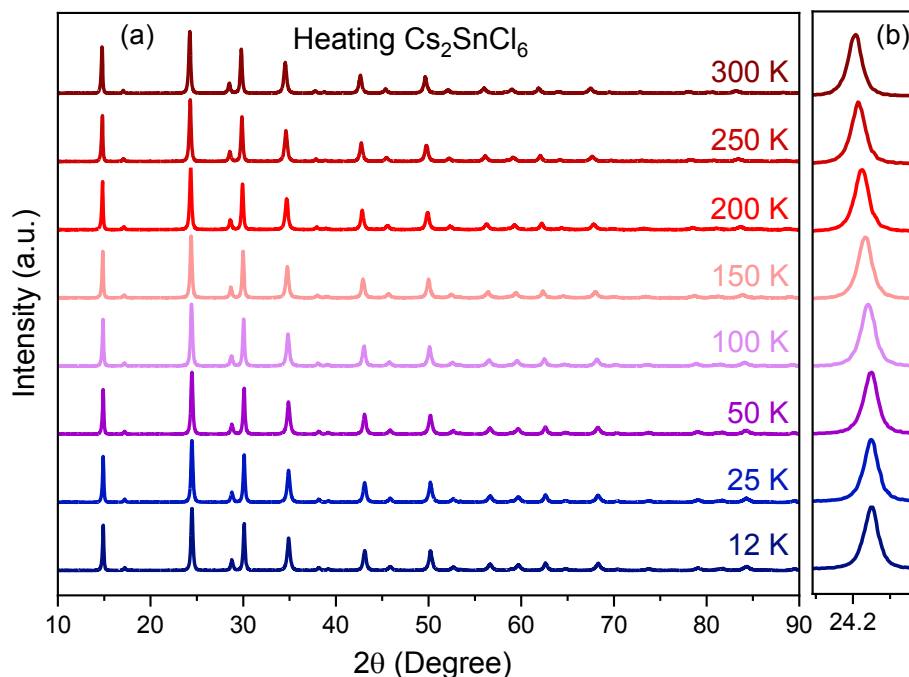


Figure 3A.13: (a) PXRD patterns of Cs₂SnCl₆ throughout the temperature range of 12-300 K. The patterns imply same phase of the material in this temperature range. (b) Zoomed view of one peak shows lower 2θ shift with the increase of temperature implying lattice expansion.

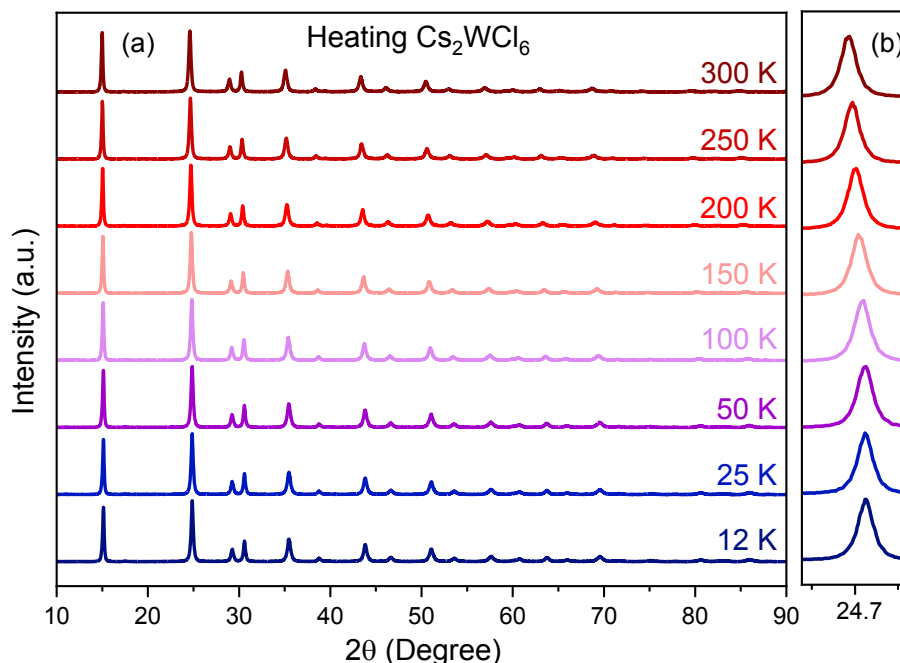


Figure 3A.14: (a) PXRD patterns of Cs₂WCl₆ throughout the temperature range of 12-300 K. The patterns imply same phase of the material in this temperature range. (b) Zoomed view of one peak shows lower 2θ shift with the increase of temperature implying lattice expansion.

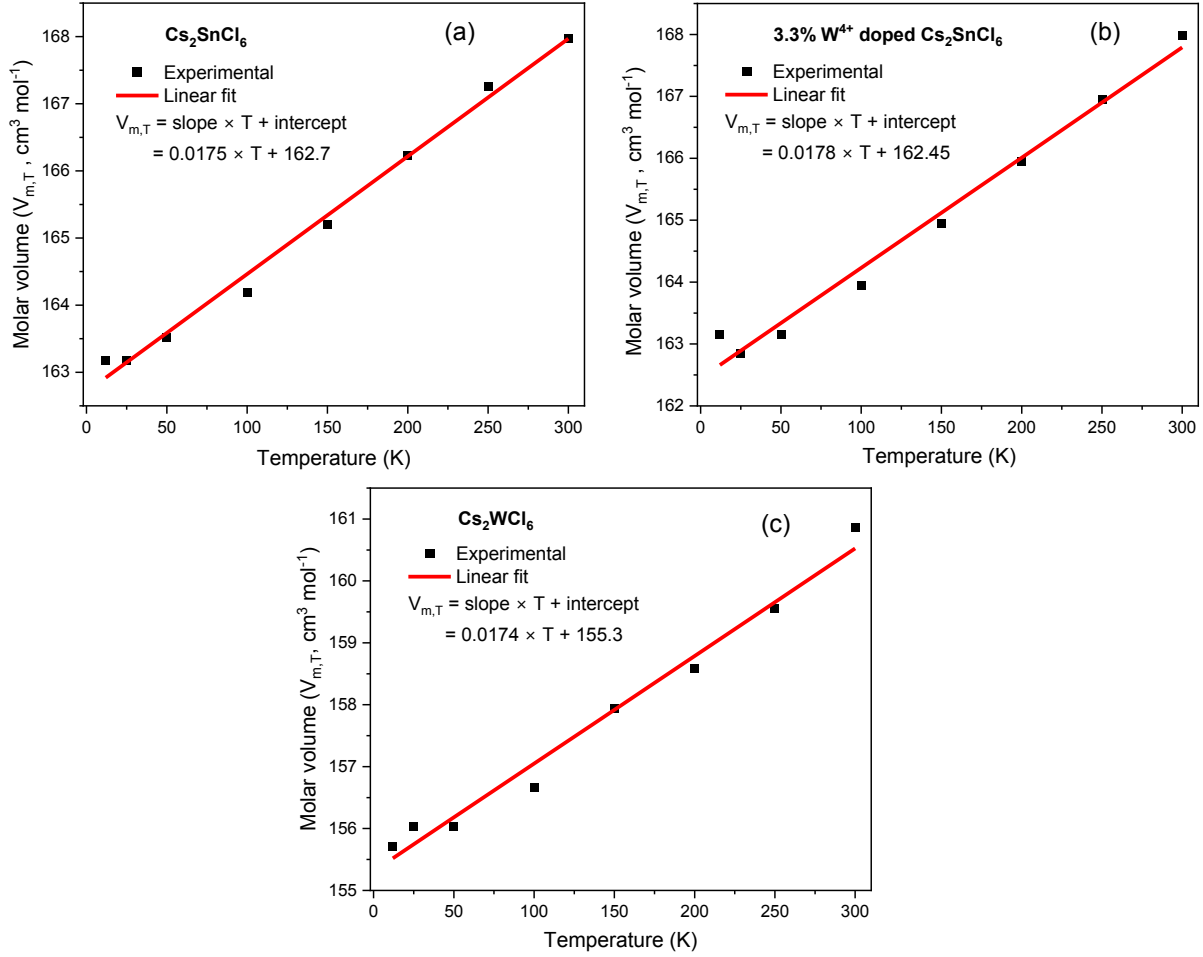


Figure 3A.15: Variation of molar volume ($V_{m,T}$) of (a) Cs_2SnCl_6 , (b) 3.3% W^{4+} doped Cs_2SnCl_6 and (c) Cs_2WCl_6 in the temperature range of 12-300 K. This has been estimated from respective PXRD patterns given in Figure 3A.13-3A.14 and Figure 3A.12 using the formula $V_{m,T} = V_T \times N_A/Z_F$. Here, V_T = unit cell volume, N_A = Avogadro number and Z_F = number of formula unit per unit cell (all three samples have FCC crystal structure, therefore, $Z_F = 4$). Using this, coefficient of volume thermal expansion, $\gamma_{v,T} = (1/V_{m,T}) \times (dV_{m,T}/dT)$ (at temperature T and at a constant pressure).³⁵ For all three samples molar volume is increasing with increasing temperature and the graphs of molar volume vs temperature are fitted with linear equation. The slopes of (a) Cs_2SnCl_6 , (b) 3.3% W^{4+} doped Cs_2SnCl_6 and (c) Cs_2WCl_6 are 0.0175, 0.0178 and 0.0174 $\text{cm}^3/\text{mol} \cdot \text{K}$ respectively and volumes at 300 K are 167.98, 167.98 and 160.86 cm^3/mol . Therefore, $\gamma_{v, 300 \text{ K}} = 1.04 \times 10^{-4}$, 1.06×10^{-4} and $1.08 \times 10^{-4} \text{ K}^{-1}$ respectively.

3A.3.4 NIR pc-LED of 3.3% W^{4+} doped Cs_2SnCl_6

The 3.3% W^{4+} -doped Cs_2SnCl_6 phosphor is mixed with 50 weight% of poly(methyl methacrylate) (PMMA) in toluene forming slurry. Phosphor converted LEDs (pc-LED) were fabricated by coating the slurry on top of a LED chip emitting 400 nm light. Figure 3A.16a shows the emission

spectra of the pc-LED after applying different currents in the range of 11-421 mA. The pc-LED show the NIR emission along with the 400 nm emission of the chip. Expectedly, the intensity of both emissions increases with increasing the device current.

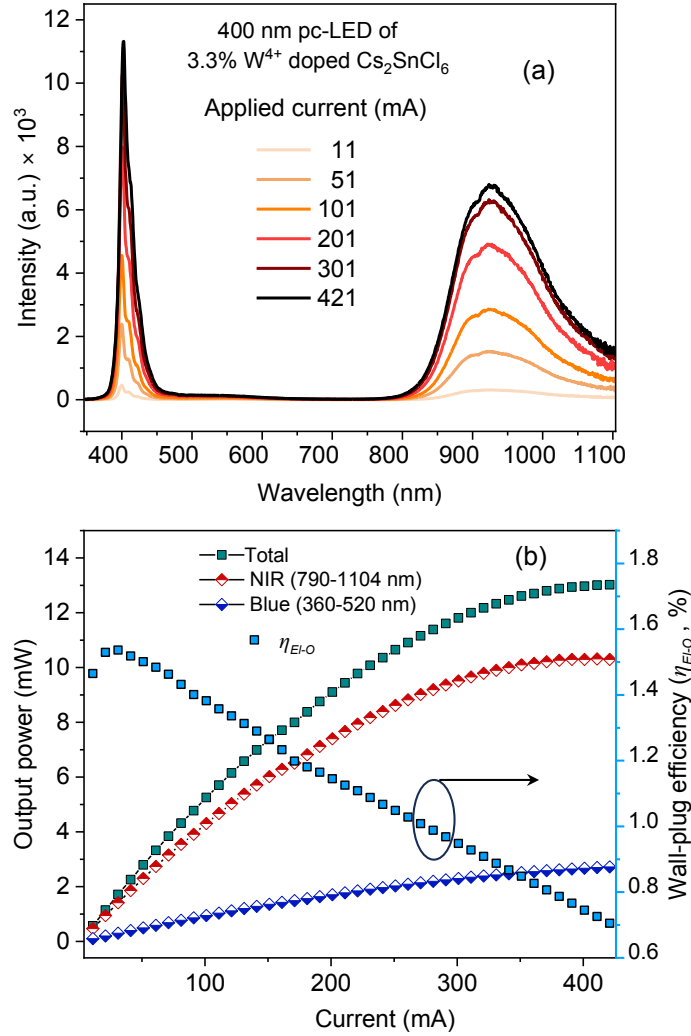


Figure 3A.16: (a) Emission spectra of 3.3% W^{4+} doped Cs_2SnCl_6 pc-LED made with 400 nm commercial LED chip after applying current in the range of 11-421 mA. (b) Output power for total spectral region of Figure (a), (teal green cube); NIR region (maroon rhombus) corresponding to 3.3% W^{4+} doped Cs_2SnCl_6 emission and blue region (blue rhombus) corresponding to the 400 nm chip emission. Wall-plug efficiency (sky cube) of pc-LED is also presented.

Accordingly, the output power of the pc-LED increases with increasing current, as shown in Figure 3A.16b. Teal green cube represents total output power of the spectral region shown in Figure 3A.16a. NIR contribution (790-1104 nm) from the phosphor (3.3% W^{4+} doped Cs_2SnCl_6) has been represented with maroon rhombus and blue contribution (360-520 nm) from commercial LED chip

is shown with blue rhombus. Though, the wall-plug efficiency (sky cube) is poor, but a maximum NIR output power of 10.3 mW is obtained at 401 mA current. This is about an order of magnitude higher output power compared to pc-LED prepared using Cs₂WCl₆, as shown in Figure 3A.17. The enhanced pc-LED power of W⁴⁺-doped Cs₂SnCl₆ agrees with enhanced PL intensity shown in Figure 3A.6b, because of the suppression of concentration quenching in the doped sample compared to Cs₂WCl₆. Also, the fact that the output power starts saturating at a high current around ~400 mA, indirectly suggest a reasonable thermal stability of the phosphor emission. Overall, the pc-LED results are promising, though a further improvement in the output power and wall-plug efficiency is desired for real life applications.

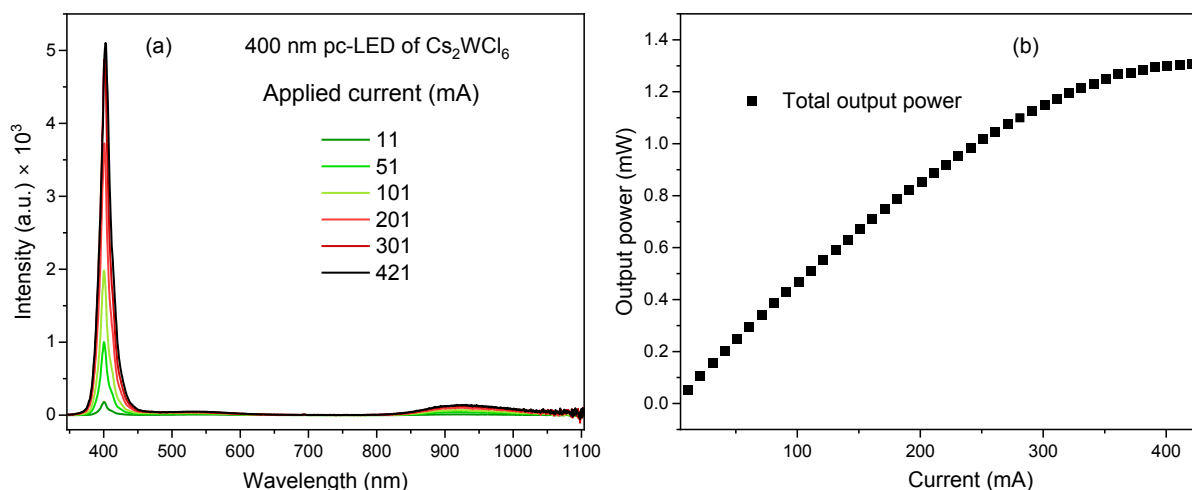


Figure 3A.17: (a) Emission spectra of Cs₂WCl₆ pc-LED made with 400 nm commercial LED chip after applying current in the range of 11-421 mA. (b) Output power for total spectral region of Figure 3A.17(a) is shown with black cubes.

3A.4 Conclusions

To conclude, we have successfully synthesized W⁴⁺ doped Cs₂SnCl₆ crystals which show NIR emission with peak at 965 nm. The PL emission intensity increases with increasing the dopant percentage and is maximum for 3.3% W⁴⁺, after that PL intensity decreases with increasing the W⁴⁺ amount due to concentration quenching. The suppression non-radiative concentration increases both the PL intensity and lifetime of W⁴⁺ doped Cs₂SnCl₆ samples compared to Cs₂WCl₆. This is the reason why doping W⁴⁺ in Cs₂SnCl₆ host is important in spite of the existence of Cs₂WCl₆ as an NIR emitting phosphor. Temperature dependent PL study describes the emission mechanism of 3.3% W⁴⁺ doped Cs₂SnCl₆. Vibronic transition and fine structures are seen in PL

emission at lower temperatures. Due to minimal interaction between [WCl₆]²⁻ and [SnCl₆]²⁻, the temperature does not have much effect on PL intensity and decay lifetime. Finally, NIR pc-LEDs were fabricated by coating a composite 3.3% W⁴⁺ doped Cs₂SnCl₆ and PMMA on a 400 nm LED chip. The pc-LED emits NIR radiation (965 nm) with output power of 10.3 mW at 401 mA current. This kind of NIR emissive doped phosphors would be important for future NIR pc-LED applications.

3A.5 References

1. Morss, L. R.; Siegal, M.; Stenger, L.; Edelstein, N. Preparation of Cubic Chloro Complex Compounds of Trivalent Metals: Cs₂NaMCl₆. *Inorg. Chem.* **1970**, *9* (7), 1771-1775.
2. McClure, E. T.; Ball, M. R.; Windl, W.; Woodward, P. M. Cs₂AgBiX₆ (X = Br, Cl): New Visible Light Absorbing, Lead-Free Halide Perovskite Semiconductors. *Chem. Mater.* **2016**, *28* (5), 1348-1354.
3. Meyer, G.; Gaebell, H. C. Halogen-Elpasolithe, IV [1] Über Brom-Elpasolithe C s₂B^IM^{III}Br₆ (B^I = Li, Na; M^{III} = Sc, Y, La-Lu, In, V, Cr). *Naturforsch.* **1978**, *33*, 1476-1478.
4. Volonakis, G.; Haghighirad, A. A.; Milot, R. L.; Sio, W. H.; Filip, M. R.; Wenger, B.; Johnston, M. B.; Herz, L. M.; Snaith, H. J.; Giustino, F. Cs₂InAgCl₆: A New Lead-Free Halide Double Perovskite with Direct Band Gap. *J. Phys. Chem. Lett.* **2017**, *8* (4), 772-778.
5. Maughan, A. E.; Ganose, A. M.; Bordelon, M. M.; Miller, E. M.; Scanlon, D. O.; Neilson, J. R. Defect Tolerance to Intolerance in the Vacancy-Ordered Double Perovskite Semiconductors Cs₂SnI₆ and Cs₂TeI₆. *J. Am. Chem. Soc.* **2016**, *138* (27), 8453-8464.
6. Cai, Y.; Xie, W.; Ding, H.; Chen, Y.; Thirumal, K.; Wong, L. H.; Mathews, N.; Mhaisalkar, S. G.; Sherburne, M.; Asta, M. Computational Study of Halide Perovskite-Derived A₂BX₆ Inorganic Compounds: Chemical Trends in Electronic Structure and Structural Stability. *Chem. Mater.* **2017**, *29* (18), 7740-7749.
7. Maughan, A. E.; Ganose, A. M.; Scanlon, D. O.; Neilson, J. R. Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors. *Chem. Mater.* **2019**, *31* (4), 1184-1195.
8. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X =

Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692-3696.

9. Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat. Mater.* **2018**, *17* (5), 394-405.

10. Xiao, Z.; Song, Z.; Yan, Y. From Lead Halide Perovskites to Lead-Free Metal Halide Perovskites and Perovskite Derivatives. *Adv. Mater.* **2019**, *31* (47), 1803792.

11. Ahmad, R.; Zdražil, L.; Kalytchuk, S.; Naldoni, A.; Rogach, A. L.; Schmuki, P.; Zboril, R.; Kment, Š. Uncovering the Role of Trioctylphosphine on Colloidal and Emission Stability of Sb-Alloyed Cs₂NaInCl₆ Double Perovskite Nanocrystals. *ACS Appl. Mater. Interfaces* **2021**, *13* (40), 47845-47859.

12. Nocolak, A.; Morad, V.; McCall, K. M.; Yakunin, S.; Shynkarenko, Y.; Würle, M.; Kovalenko, M. V. Bright Blue and Green Luminescence of Sb(III) in Double Perovskite Cs₂MInCl₆ (M = Na, K) Matrices. *Chem. Mater.* **2020**, *32* (12), 5118-5124.

13. Tan, Z.; Li, J.; Zhang, C.; Li, Z.; Hu, Q.; Xiao, Z.; Kamiya, T.; Hosono, H.; Niu, G.; Lifshitz, E.; Cheng, Y.; Tang, J. Highly Efficient Blue-Emitting Bi-Doped Cs₂SnCl₆ Perovskite Variant: Photoluminescence Induced by Impurity Doping. *Adv. Funct. Mater.* **2018**, *28* (29), 1801131.

14. Arfin, H.; Rathod, R.; Shingote, A. S.; Priolkar, K. R.; Santra, P. K.; Nag, A. Short-Wave Infrared Emissions from Te⁴⁺-Ln³⁺ (Ln: Er, Yb)-Codoped Cs₂NaInCl₆ Double Perovskites. *Chem. Mater.* **2023**, *35* (17), 7133-7143.

15. Arfin, H.; Nag, A. Origin of Luminescence in Sb³⁺- and Bi³⁺-Doped Cs₂SnCl₆ Perovskites: Excited State Relaxation and Spin-Orbit Coupling. *J. Phys. Chem. Lett.* **2021**, *12* (41), 10002-10008.

16. Tan, Z.; Chu, Y.; Chen, J.; Li, J.; Ji, G.; Niu, G.; Gao, L.; Xiao, Z.; Tang, J. Lead-Free Perovskite Variant Solid Solutions Cs₂Sn_{1-x}TeXCl₆: Bright Luminescence and High Anti-Water Stability. *Adv. Mater.* **2020**, *32* (32), 2002443.

17. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Codoped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, *59* (28), 11307-11311.

18. Saikia, S.; Joshi, A.; Arfin, H.; Badola, S.; Saha, S.; Nag, A. Sb³⁺–Er³⁺-Codoped Cs₂NaInCl₆ for Emitting Blue and Short-Wave Infrared Radiation. *Angew. Chem. Int. Ed.* **2022**, *61* (32), e202201628.
19. Saikia, S.; Ghosh, A.; Nag, A. Broad Dual Emission by Codoping Cr³⁺ (*d*→*d*) and Bi³⁺ (*s*→*p*) in Cs₂Ag_{0.6}Na_{0.4}InCl₆ Double Perovskite. *Angew. Chem. Int. Ed.* **2023**, *62* (33), e202307689.
20. Li, J.; Tan, Z.; Hu, M.; Chen, C.; Luo, J.; Li, S.; Gao, L.; Xiao, Z.; Niu, G.; Tang, J. Antimony Doped Cs₂SnCl₆ with Bright and Stable Emission. *Front. Optoelectron.* **2019**, *12* (4), 352-364.
21. Zhang, W.; Zheng, W.; Li, L.; Huang, P.; Gong, Z.; Zhou, Z.; Sun, J.; Yu, Y.; Chen, X. Dual-Band-Tunable White-Light Emission from Bi³⁺/Te⁴⁺ Emitters in Perovskite-Derivative Cs₂SnCl₆ Microcrystals. *Angew. Chem. Int. Ed.* **2022**, *61* (9), e202116085.
22. Pan, G.; Bai, X.; Yang, D.; Chen, X.; Jing, P.; Qu, S.; Zhang, L.; Zhou, D.; Zhu, J.; Xu, W.; Dong, B.; Song, H. Doping Lanthanide into Perovskite Nanocrystals: Highly Improved and Expanded Optical Properties. *Nano Lett.* **2017**, *17* (12), 8005-8011.
23. Dave, K.; Huang, W.-T.; Leśniewski, T.; Lazarowska, A.; Grzegorzczak, M.; Mahlik, S.; Leniec, G.; Kaczmarek, S. M.; Liu, R.-S. Enhancement of Self-Trapped Excitons and Near-Infrared Emission in Bi³⁺/Er³⁺ Codoped Cs₂Ag_{0.4}Na_{0.6}InCl₆ Double Perovskite. *Nanoscale* **2022**, *14* (47), 17735-17742.
24. Ma, J.-P.; Chen, Y.-M.; Zhang, L.-M.; Guo, S.-Q.; Liu, J.-D.; Li, H.; Ye, B.-J.; Li, Z.-Y.; Zhou, Y.; Zhang, B.-B.; Bakr, O. M.; Zhang, J.-Y.; Sun, H.-T. Insights into the Local Structure of Dopants, Doping Efficiency, and Luminescence Properties of Lanthanide-Doped CsPbCl₃ Perovskite Nanocrystals. *J. Mater. Chem. C* **2019**, *7* (10), 3037-3048.
25. Zhao, F.; Song, Z.; Zhao, J.; Liu, Q. Double Perovskite Cs₂AgInCl₆:Cr³⁺: Broadband and Near-Infrared Luminescent Materials. *Inorg. Chem. Front.* **2019**, *6* (12), 3621-3628.
26. Liu, Z.; Qin, X.; Chen, Q.; Chen, Q.; Jing, Y.; Zhou, Z.; Zhao, Y. S.; Chen, J.; Liu, X. Highly Stable Lead-Free Perovskite Single Crystals with NIR Emission Beyond 1100 nm. *Adv. Opt. Mater.* **2022**, *10* (21), 2201254.
27. Mondal, B.; Shinde, A.; Rajput, P. K.; Arfin, H.; Tanwar, R.; Ghosh, P.; Nag, A. Vibronically Coupled Near-Infrared Emission and Excitation from *d*–*d* Transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br). *ACS Energy Lett.* **2024**, *9* (3), 819-828.
28. Eickhoff, T.; Grosse, P.; Theiss, W. Diffuse Reflectance Spectroscopy of Powders. *Vib. Spectrosc.* **1990**, *1* (2), 229-233.

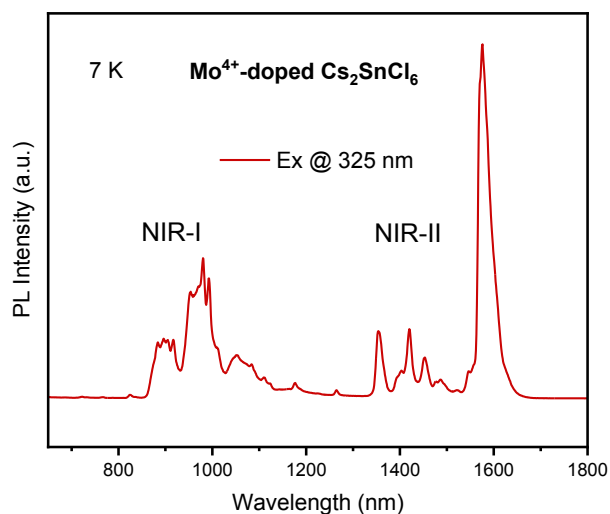
29. Folgueras, M. C.; Jiang, Y.; Jin, J.; Yang, P. High-Entropy Halide Perovskite Single Crystals Stabilized by Mild Chemistry. *Nature* **2023**, 621 (7978), 282-288.
30. Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst. A* **1976**, 32 (5), 751-767.
31. Nag, A.; Sapra, S.; Nagamani, C.; Sharma, A.; Pradhan, N.; Bhat, S. V.; Sarma, D. D. A Study of Mn²⁺ Doping in CdS Nanocrystals. *Chem. Mater.* **2007**, 19 (13), 3252-3259.
32. Sproules, S.; Banerjee, P.; Weyhermüller, T.; Yan, Y.; Donahue, J. P.; Wieghardt, K. Monoanionic Molybdenum and Tungsten Tris(dithiolene) Complexes: A Multifrequency EPR Study. *Inorg. Chem.* **2011**, 50 (15), 7106-7122.
33. Ahmed, H. A. A. S.; Swart, H. C.; Bergman, P.; Kroon, R. E. Concentration Quenching of Eu²⁺ Doped Ca₂BO₃Cl. *Mater. Res. Bull.* **2016**, 75, 47-50.
34. Jong, M. D.; Seijo, L.; Meijerink, A.; Rabouw, F. T. Resolving the Ambiguity in the Relation between Stokes Shift and Huang–Rhys Parameter. *Phys. Chem. Chem. Phys.* **2015**, 17 (26), 16959-16969.
35. Corsepius, N. C.; DeVore, T. C.; Reisner, B. A.; Warnaar, D. L. Using Variable Temperature Powder X-ray Diffraction to Determine the Thermal Expansion Coefficient of Solid MgO. *J. Chem. Educ.* **2007**, 84 (5), 818.

Chapter 3B

Mo⁴⁺-doped Cs₂SnCl₆ for near-infrared emission

Abstract

This study explores the doping of Mo⁴⁺ ions into the lattice site of Cs₂SnCl₆, focusing on its potentiality for near-infrared (NIR) emission. Wide band gap Cs₂SnCl₆ is stable and environmentally benign, it has absorption edge at 313 nm, but non-luminescent. Doping various ions such as ns² ions (for example, Bi³⁺, Sb³⁺, Te⁴⁺) can incorporate significant visible photoluminescence. While NIR-emissive Cs₂SnCl₆ has been explored with lanthanide and Te⁴⁺ cooping; transition metal-based NIR emitters like Mo⁴⁺, W⁴⁺ have not been studied in this context. This chapter discusses that Mo⁴⁺-doped Cs₂SnCl₆ has unusual two peak emission in both the NIR-I and NIR-II regions at room temperature with peaks at 980 nm and 1350 nm respectively. Low-temperature photoluminescence studies (7 K) reveal peak splitting and varying lifetimes, suggesting that emissions might have different origins. The crystal phase remains stable across a wide temperature range of 300 – 12 K. However, the underlying mechanism behind these unusual NIR-emission properties remains unclear, demanding further investigation.

Graphical abstract

3B.1 Introduction

Vacancy-ordered double perovskite^{1,2} Cs₂SnCl₆ has a wide band gap and the absorption edge lies at ~313 nm. The octahedral coordination site of Sn⁴⁺ can accommodate several kinds of dopants. Moreover, Cs₂SnCl₆ microcrystals are non-luminescent, therefore, the optical property of this host does not influence the dopant. There are reports of various types of doping (for example, ns² ions Bi³⁺, Sb³⁺, Te⁴⁺) into the Cs₂SnCl₆ lattice with significant emission and photoluminescence quantum yield (PL QY) in the visible region.³⁻⁶ Apart from visible emission, there are very rare reports of near-infrared (NIR) emissive Cs₂SnCl₆ based on Te⁴⁺ and lanthanide doping.⁷ Excluding the lanthanides, there are some transition metals (Mo⁴⁺ and W⁴⁺) which emit in NIR region due to *d-d* transitions.⁸⁻¹⁰ They have significant absorption in visible and NIR regions as well as broad emission ranging from 800 – 1300 nm.

Based on those, in this chapter, we have explored the transition metal ion Mo⁴⁺ doping in Cs₂SnCl₆ lattice. We have synthesized undoped and Mo⁴⁺-doped Cs₂SnCl₆ with a simple hydrothermal method for near-infrared emission. The compound shows different sub-band absorption in visible region after incorporation of Mo⁴⁺. Interestingly along with the absorptions, the doped compound shows two emission peaks covering both NIR-I and NIR-II regions at room temperature. Cryogenic temperature photoluminescence study (measured at 7 K) reveals even unusual splitting of those peaks with different lifetimes, though the low-temperature powder X-ray diffraction (PXRD) patterns confirm that same crystal phase is being maintained throughout the temperature range of 300 – 12 K. These unusual emission properties from single Mo⁴⁺ dopant in Cs₂SnCl₆ crystals have been obtained with good reproducibility. That is the reason why we were interested in this work. However, an explicit mechanistic understanding behind this rare behavior is yet to be achieved.

3B.2 Methodology section

3B.2.1 Chemicals

Cesium chloride (CsCl, Sigma Aldrich, Reagent plus, 99.9 %), tin (II) chloride (SnCl₂, anhydrous powder, ≥99.99 %), molybdenum (V) chloride (Thermoscientific, MoCl₅, 99.6%, metal basis), hydrochloric acid (Sigma Aldrich, HCl, 37 wt %, 99.99%) and 2-propanol (Rankem) have been procured and utilized without any further refinement.

3B.2.2 Synthesis of undoped Cs₂SnCl₆ crystals

Cs₂SnCl₆ crystals have been synthesized following a prior report using the hydrothermal method¹¹. For this, 336.7 mg (2 mmol) CsCl, 189.6 mg (1 mmol) SnCl₂ and 4 mL 12 M HCl are taken in a 25 mL polytetrafluoroethylene (PTFE) hydrothermal autoclave. This mixture is heated at 180 °C for 12 hours, and then it is cooled down to room temperature in 24 hours. White-colored powder of Cs₂SnCl₆ crystal is obtained. Then it is washed several times with 2-propanol and dried in vacuum desiccator. The product is stored and used for future characterization and experiments.

3B.2.3 Synthesis of Mo⁴⁺ doped Cs₂SnCl₆ crystals

The synthesis method of doped compound is similar with that of the undoped Cs₂SnCl₆. The modification is: along with CsCl, SnCl₂, additional amount of MoCl₅ is taken. The precursor amount of MoCl₅ is 15% with respect to SnCl₂, i.e., 0.15 mmol (41 mg). Mo⁴⁺-doped product is yellow-colored crystal. Rest of the washing and drying procedures are same as the undoped synthesis method.

3B.2.4 Structural and optical characterization

Structural characterization: Powder X-ray diffraction (PXRD) measurements are carried out on Bruker D8 Advance X-ray diffractometer using Cu K α radiation (1.54 Å) at room temperature. Temperature-dependent (300 – 12 K) PXRD measurements are done on Malvern Panalytical Empyrean Series 3 X-ray diffractometer with Oxford Cryosystems PheniX which can achieve up to 12 K. Chromium-plated copper sample holder has been utilized with the X-ray source of Cu K α radiation (1.54 Å). For elemental analysis of Mo⁴⁺ in final product, inductively coupled plasma mass spectroscopy (ICP–MS) experiment is performed by using a quadrupole–ICP–MS (Thermo iCAP-Q) spectrometer. The actual dopant percentage is calculated with respect to the metal Sn.

Optical properties: Optical diffused-reflectance measurements are done on Shimadzu UV-3600 plus UV-VIS-NIR spectrophotometer. The reflectance data are converted to absorbance by utilizing Kubelka-Munk transformation,¹² using the equation given below:

$$F(R) = \alpha/S = (1-R)^2/2R \dots\dots(1)$$

Here, the term F(R) is the Kubelka-Munk function, R is reflectance, α is the absorption coefficient and S is the scattering factor. Steady-state photoluminescence (PL) measurements (PL excitation

and emission) are performed using FLS 980 (Edinburgh Instruments) with Xe-lamp as an excitation source. Time-resolved PL decay profiles have been carried out with the same instrument using a microsecond flash lamp to excite (325 nm). The decay profiles are fitted with mono-exponential decay function:

$$I_t = I_0 + A \exp(-t/\tau) \dots\dots(2)$$

Here, I_t implies PL counts at any variable time = t , I_0 is the offset and τ is the lifetime of PL decay with amplitude A . Temperature-dependent PL experiments are also performed on FLS980 (Edinburgh Instruments). Ground and powdered sample is sandwiched between two sapphires and is mounted on a gold-plated sample holder. This is attached to a closed cycle He cryostat (Advanced Research Systems) with a temperature controller (Lake Shore Cryotronics) to achieve the expected temperature.

3B.3 Results and discussion

3B.3.1 Synthesis and structural characterization

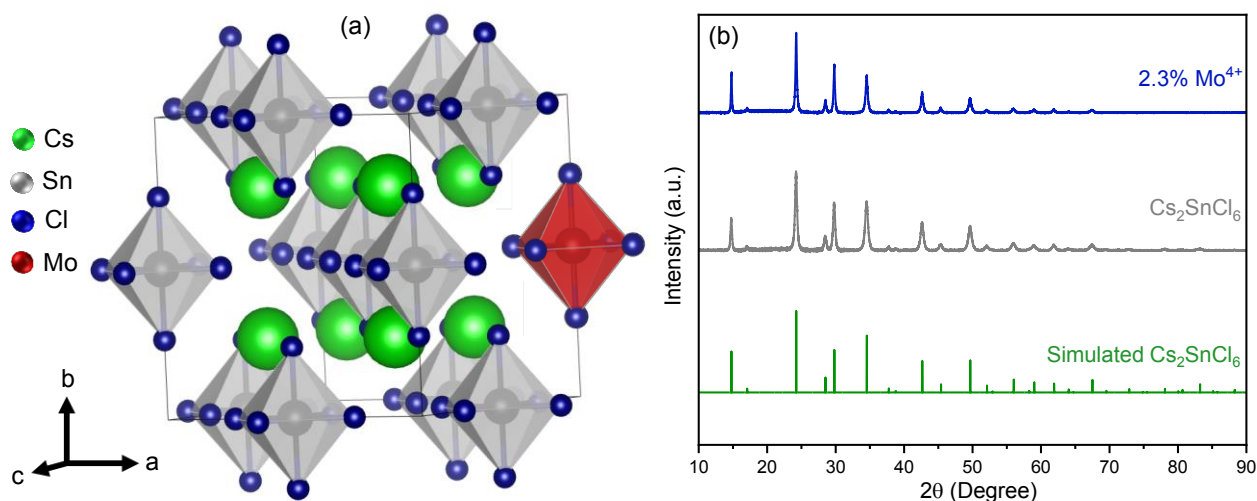


Figure 3B.1: (a) Schematic representation of crystal structure of Mo⁴⁺-doped Cs₂SnCl₆, here, the grey octahedra refer to [SnCl₆]²⁻ and the maroon octahedron implies [WCl₆]²⁻, all octahedra are separated from each other with Cs⁺ cation (green) forming a 0D perovskite derivative structure. (b) Powder X-ray diffraction (PXRD) patterns of undoped Cs₂SnCl₆ (grey) and 2.3% Mo⁴⁺-doped Cs₂SnCl₆ (blue) along with the simulated Cs₂SnCl₆ pattern (green, CDS No. 2216627). No peak-shift has been observed after doping due to the comparable size of Sn⁴⁺ and Mo⁴⁺ ions.

Undoped and Mo⁴⁺-doped Cs₂SnCl₆ have been synthesized by using a modified hydrothermal method.¹¹ Stoichiometric amounts of CsCl and SnCl₂ have been taken in a hydrothermal autoclave with 4 mL of 12 M HCl. The mixture is heated at 180 °C for 12 hours, followed by cooling to room temperature. The product is white-colored powdered crystals of Cs₂SnCl₆. For the synthesis of Mo⁴⁺-doped sample, a similar method has been followed along with the additional amount of MoCl₅ salt in the reaction vessel. Details of synthesis method and characterizations are discussed in methodology section. Elemental analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) confirms 2.3% Mo⁴⁺ dopant with respect to Sn⁴⁺ in the final product, for 15 mole % of MoCl₅ precursor with respect to SnCl₂.

Figure 3B.1a displays the schematic representation of Mo⁴⁺-doped Cs₂SnCl₆, where the grey octahedra are [SnCl₆]²⁻ and the maroon octahedron signifies [MoCl₆]²⁻ doped into the lattice. All these octahedra are separated from each other by Cs⁺ cations (green). These structures are known as vacancy-ordered double perovskites or 0D perovskite derivatives.² The phase purity of undoped and Mo⁴⁺-doped Cs₂SnCl₆ has been confirmed by powder X-ray diffraction (PXRD) measurements at room temperature (Figure 3B.1b). Both undoped (grey) and 2.3% Mo⁴⁺-doped (blue) Cs₂SnCl₆ have similar PXRD patterns which are matching with the standard Cs₂SnCl₆ PXRD (green). Both the crystals crystallize in cubic Fm $\bar{3}$ m space group. Moreover, the ionic radii of Sn⁴⁺ and Mo⁴⁺ in octahedral coordination are 69 and 65 picometers, respectively.¹³ Due to this similar size, the PXRD peaks do not show any shift from undoped to doped compound. These features of similar radii and same charge (+4) of molybdenum and tin create a perfect environment for doping Mo⁴⁺ into the Cs₂SnCl₆ lattice.

3B.3.2 Room-temperature optical properties

Figure 3B.2a shows the absorption spectra of undoped and Mo⁴⁺-doped Cs₂SnCl₆. The undoped compound has a wide band gap with an absorption edge at 313 nm. After Mo⁴⁺ incorporation different sub-band absorption features have appeared. Figure 3B.2b presents the NIR emission spectra of these two samples at room temperature upon excitation with 325 nm UV light. The undoped one is non-luminescent (grey spectrum), interestingly, the Mo⁴⁺ doped compound shows two emission features covering both NIR-I and NIR-II regions (blue spectrum, peaks at 980 nm and 1350 nm respectively). PL decay dynamics of these emission features are presented in Figure 3B.2c. The decay profiles are fitted with mono-exponential decay equation (eq. 2). Both of the

peaks have different PL lifetimes, for instance, 980 nm emission has a longer lifetime of 42.4 μ s than that of 1350 nm emission (5.6 μ s).

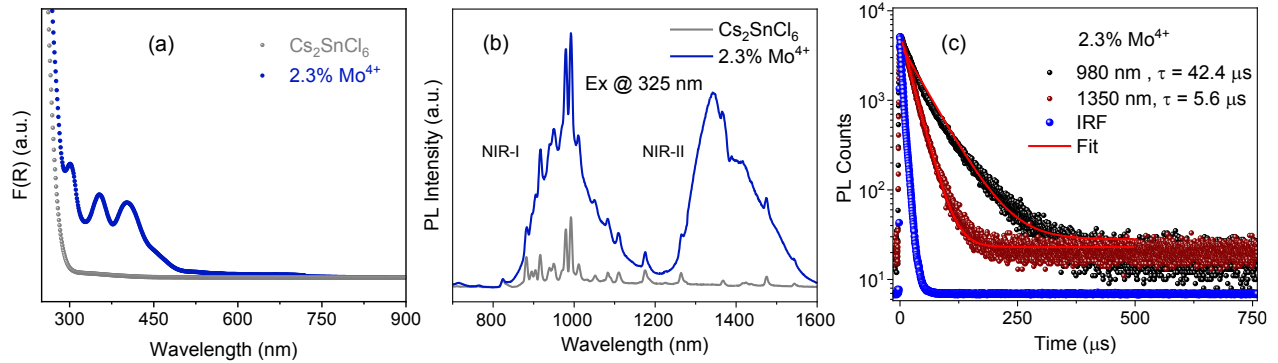


Figure 3B.2: Room temperature (RT) optical property of Cs₂SnCl₆ and Mo⁴⁺-doped Cs₂SnCl₆. (a) UV-visible-NIR absorption of Cs₂SnCl₆ (grey) and 2.3% Mo⁴⁺-doped Cs₂SnCl₆ (blue). Here, the reflectance (R) data have been transformed to absorbance by using Kubelka-Munk function $F(R) = (1-R)^2/2R$.¹² (b) PL spectra of undoped (grey) and 2.3% Mo⁴⁺-doped Cs₂SnCl₆ (blue). (c) PL decay dynamics of the two emission peaks at 980 nm (black) and 1350 nm (maroon) shown in (b) along with mono-exponential decay fitting (red) and instrument response function (blue). Excitation wavelength for PL emission and decay is 325 nm.

3B.3.3 Temperature-dependent photoluminescence and structure

For further insights and understanding, we performed cryogenic temperature PL experiment of Mo⁴⁺-doped Cs₂SnCl₆ at 7 K. Figure 3B.3a shows the PL spectrum upon 325 nm excitation. Interestingly both the broad peaks at room temperature (in Figure 3B.2b) are split into multiple peaks at 7 K. Figure 3B.3b presents the PL decay dynamics of 980 nm emission peak of NIR-I region with a longer lifetime of 67.4 μ s at 7 K. Also inset shows the overlapped decay profiles of all three peaks of this region implying similar lifetime and emission origin of these three peaks. On the other hand, 3B.3c presents the PL decay of 1420 nm emission ($\tau = 58 \mu$ s) along with the overlapped PL decay plots of all four peaks in the NIR-II region. Therefore, this set of four peaks has similar lifetime and emission origin, whereas, the emission at 1576 nm has a much longer lifetime ($\tau = 10.2$ ms, Figure 3B.3d). These findings imply that the first set of three peaks (at NIR-I), the second set of four peaks (at NIR-II) and 1576 nm emission peak, all might have different emission origins. Though, as of now, the exact reason behind this unusual behavior from a single dopant ion is not known.

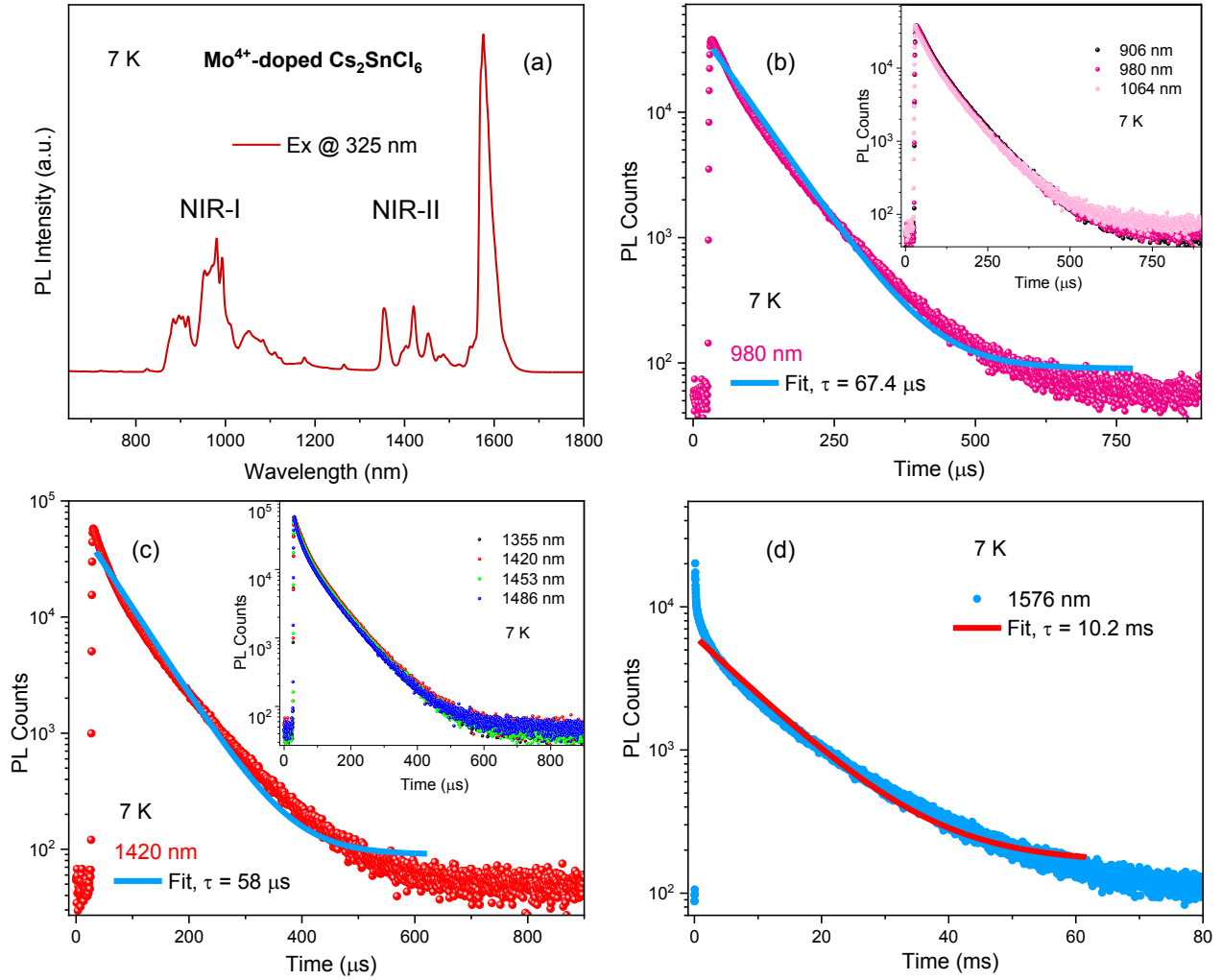


Figure 3B.3: Cryogenic temperature photoluminescence (at 7 K) of Mo⁴⁺ doped Cs₂SnCl₆. Excited at 325 nm. (a) PL emission spectrum (maroon), measured with powdered compound at 7 K. (b) PL decay dynamics of the emission peak at 980 nm. The inset shows the overlapped decay profiles of three emission peaks shown in the NIR-I region of (a). (c) PL decay profile at 1420 nm, inset shows the overlapped PL lifetimes of four emission peaks shown in the NIR-II region of (a). (d) Decay profile of 1576 nm emission. All three decays of (b), (c) and (d) are fitted with mono-exponential decay fitting (red line).

Since these kinds of samples have a tendency to change phase at lower temperatures, therefore, to confirm the structure, we have performed the temperature-dependent PXRD measurements of both undoped and Mo⁴⁺-doped samples in the temperature range of 300 – 12 K (Figure 3B.4). Both the samples retain same cubic phase (Fm $\bar{3}$ m space group) throughout this temperature range with the expected shift of peak towards lower 2 θ upon heating (enlarged view of one peak on the right-hand side of Figure 3B.4) due to lattice expansion.

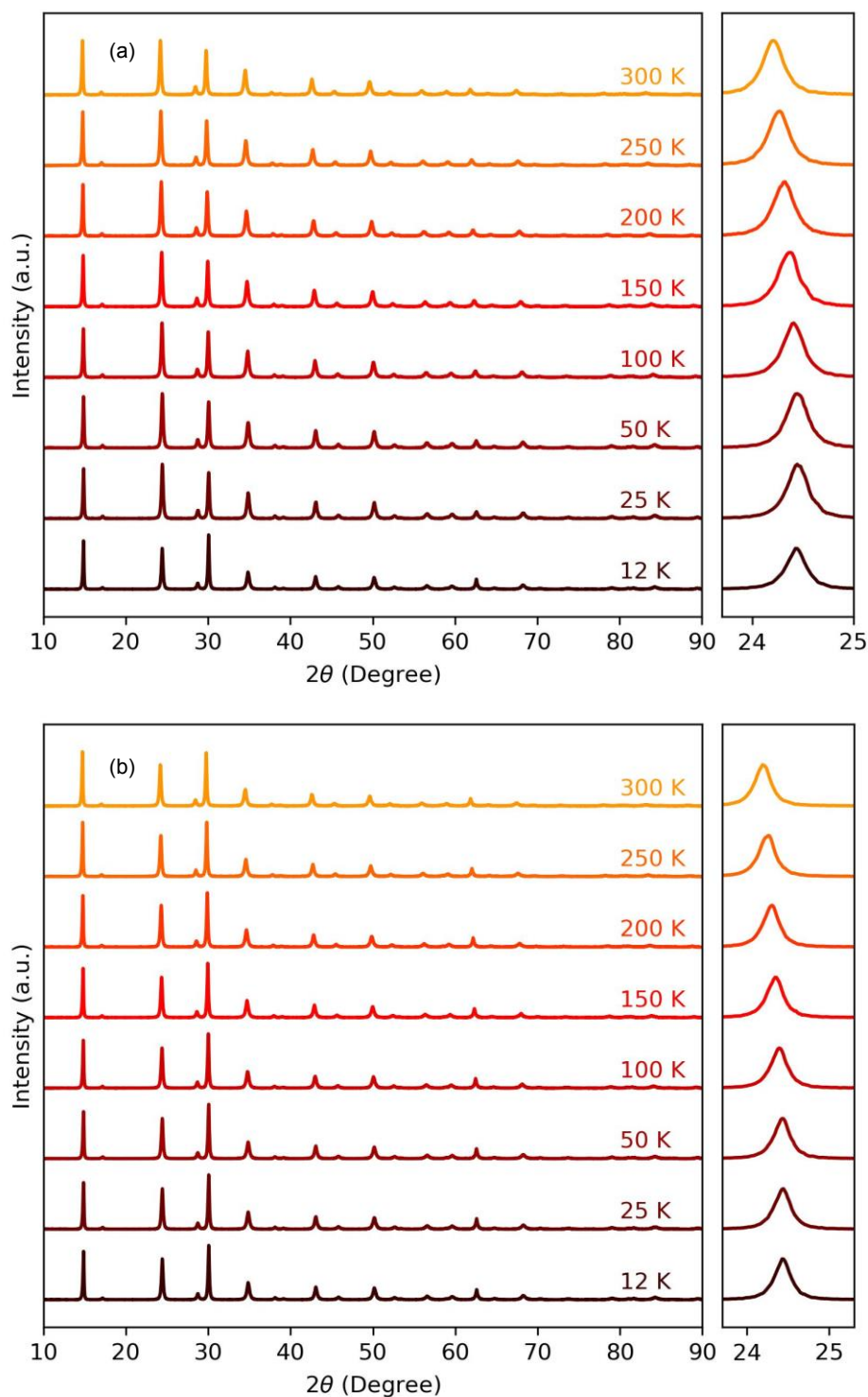


Figure 3B.4: Temperature-dependent PXRD patterns of (a) Cs₂SnCl₆ and (b) Mo⁴⁺-doped Cs₂SnCl₆ in a range of 12-300 K showing no phase change throughout this temperature range. An enlarged view of one peak on the right-hand side of both implies that with increasing temperature the peak shifts towards lower 2θ due to lattice expansion.

3B.4 Conclusions

To summarize, we have successfully synthesized Mo⁴⁺-doped Cs₂SnCl₆ crystals using hydrothermal method. They show sub-band absorptions in the visible region and more surprisingly, exhibit two emission peaks covering both the NIR-I and NIR-II regions. These two emissions have different lifetimes at room temperature implying that they might have different origins. Cryogenic temperature photoluminescence at 7 K shows splitting of both the peaks into multiple sharp peaks whereas the crystal phase remains unchanged from 300 - 12 K. However, we could not achieve the detailed insight of this unusual behavior of Mo⁴⁺ dopant. For a comprehensive understanding, rigorous experimental and theoretical analyses need to be performed.

3B.5 References

1. Maughan, A. E.; Ganose, A. M.; Bordelon, M. M.; Miller, E. M.; Scanlon, D. O.; Neilson, J. R. Defect Tolerance to Intolerance in the Vacancy-Ordered Double Perovskite Semiconductors Cs₂SnI₆ and Cs₂TeI₆. *J. Am. Chem. Soc.* **2016**, *138* (27), 8453-8464.
2. Maughan, A. E.; Ganose, A. M.; Scanlon, D. O.; Neilson, J. R. Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors. *Chem. Mater.* **2019**, *31* (4), 1184-1195.
3. Zhong, Y.; Huang, Y.-E.; Deng, T.; Lin, Y.-T.; Huang, X.-Y.; Deng, Z.-H.; Du, K.-Z. Multi-Dopant Engineering in Perovskite Cs₂SnCl₆: White Light Emitter and Spatially Luminescent Heterostructure. *Inorg. Chem.* **2021**, *60* (22), 17357-17363.
4. Arfin, H.; Nag, A. Origin of Luminescence in Sb³⁺- and Bi³⁺-Doped Cs₂SnCl₆ Perovskites: Excited State Relaxation and Spin–Orbit Coupling. *J. Phys. Chem. Lett.* **2021**, *12* (41), 10002-10008.
5. Tan, Z.; Chu, Y.; Chen, J.; Li, J.; Ji, G.; Niu, G.; Gao, L.; Xiao, Z.; Tang, J. Lead-Free Perovskite Variant Solid Solutions Cs₂Sn_{1-x}Te_xCl₆: Bright Luminescence and High Anti-Water Stability. *Adv. Mater.* **2020**, *32* (32), 2002443.
6. Zhang, W.; Zheng, W.; Li, L.; Huang, P.; Gong, Z.; Zhou, Z.; Sun, J.; Yu, Y.; Chen, X. Dual-Band-Tunable White-Light Emission from Bi³⁺/Te⁴⁺ Emitters in Perovskite-Derivative Cs₂SnCl₆ Microcrystals. *Angew. Chem. Int. Ed.* **2022**, *61* (9), e202116085.
7. Qing, X.; Wu, C.; Han, X. Efficient Near-Infrared Luminescence Based on Double Perovskite Cs₂SnCl₆. *Molecules* **2023**, *28*, 3593.

8. Li, Z.; Xu, M.; Liu, W.; Wang, X.; Li, Y.; Zhou, X.; Fang, Z.; Ning, L. Broadband Near-Infrared Luminescence from Mo⁴⁺ in Zero-Dimensional Perovskite Cs₂Zr(Cl,Br)₆ with an Exceptionally High Quantum Efficiency and Thermal Stability. *Chem. Mater.* **2024**, *36* (2), 901-910.
9. Mondal, B.; Shinde, A.; Rajput, P. K.; Arfin, H.; Tanwar, R.; Ghosh, P.; Nag, A. Vibronically Coupled Near-Infrared Emission and Excitation from *d–d* Transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br). *ACS Energy Lett.* **2024**, *9* (3), 819-828.
10. Kumar, S.; Lamba, R. S.; Monga, S.; Jha, V.; Rachna; Saha, S.; Bhattacharya, S.; Sapra, S. Broad Dual Emission from Cs₂Zr_{1-x}Mo_xCl₆: Enhancing the NIR Emission in Lead-free Vacancy Ordered Double Perovskites. *Chem. Mater.* **2024**, *36* (9), 4561-4570.
11. Tan, Z.; Li, J.; Zhang, C.; Li, Z.; Hu, Q.; Xiao, Z.; Kamiya, T.; Hosono, H.; Niu, G.; Lifshitz, E.; Cheng, Y.; Tang, J. Highly Efficient Blue-Emitting Bi-Doped Cs₂SnCl₆ Perovskite Variant: Photoluminescence Induced by Impurity Doping. *Adv. Funct. Mater.* **2018**, *28* (29), 1801131.
12. Eickhoff, T.; Grosse, P.; Theiss, W. Diffuse Reflectance Spectroscopy of Powders. *Vib. Spectrosc.* **1990**, *1* (2), 229-233.
13. Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst. A* **1976**, *32* (5), 751-767.

Chapter 4

Yb³⁺-doped (Phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

The work of this chapter has been published in the following article:

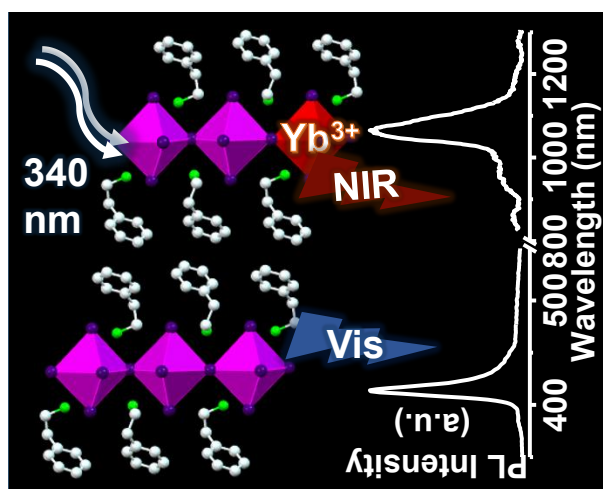
Mondal, B.; Poovathan, A.; Sheikh, T.; Nag, A. Yb³⁺-Doped Phenylethylammonium Lead Bromide 2D Layered Hybrid Perovskite for Near-Infrared Emission. *ChemNanoMat* **2022**, 8, e202200104.

Copyright permission has been taken for the entire article from John Wiley and Sons.

Abstract

Two-dimensional (2D) layered hybrid perovskites like phenylethylammonium (C₈H₁₂N) lead bromide [(PEA)₂PbBr₄] show interesting optoelectronic properties and improved moisture stability owing to the repeating quantum-well structure and hydrophobic organic cations, respectively. Doping metal ions in such perovskites leads to exciton-dopant interactions, imparting new optical properties. Here we report synthesis and optical properties of Yb³⁺-doped (PEA)₂PbBr₄. Crystals show plate-like morphology with lateral size of few micro-meters. Also, ~3.5 nm thin nanoplatelets are obtained after sonicating the samples. The host absorbs light via excitonic (and band-band) transition at 340 nm. A part of the generated excitons recombines by emitting light at 414 nm along with host-related non-radiative recombination. Another significant part of the excitons recombines by non-radiatively transferring the energy to the *f*-electrons of Yb³⁺ dopant ions. The Yb³⁺ ions then de-excite via *f-f* (²F_{5/2} → ²F_{7/2}) transition emitting near-infrared (NIR) radiation with a peak at 997 nm. Such NIR-emitting semiconductors with improved performances are desired for NIR light-emitting diode applications.

Graphical abstract



4.1 Introduction

Doping metal ions into the lattice of a semiconductor nanocrystal is a well-known strategy to tailor electronic, optical and optoelectronic properties.¹⁻⁴ In the recent years, metal ion doping in lead halide based perovskite nanocrystals has been explored to obtain new optical properties,⁵⁻¹⁰ and also to improve the structural stability.¹¹⁻¹³ An interesting aspect of Pb-halide based perovskites is the octahedral coordination of Pb²⁺ with six halide ions. Such octahedral coordination is suitable for doping lanthanide ions.¹⁴ Therefore, lanthanide ion doping in Pb-halide perovskites are being explored particularly aiming for dopant related photoluminescence (PL) in the visible and near-infrared (NIR) region of the electromagnetic spectrum.¹⁴⁻¹⁹ For instance, Yb³⁺-doped CsPbCl₃ nanocrystals have been reported with more than 100% NIR PL quantum yield due to a phenomenon called quantum cutting.¹⁵ But the charge difference between the Yb³⁺ and Pb²⁺ often limits the extent of doping. Note that the traditional semiconductors like Si, GaAs, and CdTe have tetrahedral coordination around the metal ions, which is not suitable for doping larger lanthanide ions.

In difference to three-dimensional (3D) perovskite structures, two-dimensional (2D) layered hybrid perovskites like phenylethylammonium lead bromide [(PEA)₂PbBr₄] have a repeating quantum well structure.²⁰⁻²³ As shown in Figure 4.1a, the corner-shared lead-halide octahedra (PbBr₆⁴⁻) are connected in two dimensions. But in the third dimension, they are separated by the insulating organic cations phenylethylammonium (PEA). Consequently, the layered structure with semiconducting Pb-Br inorganic well and insulating organic barrier leads to the quantum-well structure. The charge carriers remain confined in the atomically thin Pb-Br well, giving rise to the strong quantum confinement effect irrespective of the size of the crystal. Besides, the organic spacer has a significantly smaller high-frequency dielectric constant than that of the inorganic Pb-halide layer. This dielectric contrast at the organic/ inorganic interface results into dielectric confinement effect.^{20, 22, 23} Due to these two confinement effects, 2D perovskites possess high exciton binding energy and fast radiative recombination rate. Therefore, the nature of interactions between the host excitons and dopant ions in 2D layered perovskites might be different from 3D perovskites. Besides, 2D layered perovskites with hydrophobic organic cations have improved moisture stability compared to their 3D counterparts.²⁴

There are few reports of doping Eu³⁺ in 2D layered perovskite systems,^{25, 26} yielding red emission. Also, Mn²⁺ ions have been doped in 2D layered perovskites emitting orange- red light.²⁷⁻³⁰ But, to the best of our knowledge, NIR emission has not been achieved by doping lanthanide ions into a 2D layered hybrid perovskite.

Here we report the synthesis and NIR emission of Yb³⁺-doped (PEA)₂PbBr₄, 2D layered hybrid perovskite. The as-synthesized product is micrometer sized crystals having plate-like structure. Some nanoplatelets with thickness ~ 3.5 nm are also found after sonicating the microcrystals. The host (PEA)₂PbBr₄ shows sharp excitonic absorption (407 nm) and emission (414 nm) due to the quantum well structure. Doping Yb³⁺ introduces a new NIR emission at ~ 997 nm because of the *f-f* electronic transitions along with the excitonic emission of the host. The *f-f* transitions are Laporte forbidden, exhibiting a long PL lifetime of 14 μs. The same forbidden transition leads to poor light absorption by the *f*-electrons. Instead, the host absorbs the light, and non-radiatively transfers excitation energy to Yb³⁺ *f*-electrons, which then de-excite by emitting the NIR radiation.

4.2 Methodology section

4.2.1 Chemicals

Lead acetate trihydrate (99.999% trace metals basis), ytterbium (III) acetate tetrahydrate (99.9% trace metals basis), 1-octadecene (technical grade 90%), oleic acid (technical grade 90%), bromotrimethylsilane (≥ 97.0%), phenylethylamine (≥ 97.0%) and toluene (anhydrous, 99.8%) were procured from Sigma-Aldrich and were used without any purification.

4.2.2 Synthesis of undoped (PEA)₂PbBr₄

For the synthesis of undoped (PEA)₂PbBr₄, 0.2 mmol lead acetate trihydrate, 10 mL 1-octadecene and 1 mL oleic acid are taken in a three-necked round bottom flask. The mixture is stirred and degassed under the vacuum (at ~ 120 × 10⁻³ mbar pressure) of a rotary pump for 10 minutes. Then the reaction mixture is heated to 100 °C under a continuous flow of N₂ gas. At this temperature, the reaction mixture is again kept under the same vacuum for 20 minutes. Then 0.2 mL phenylethylamine is injected into the flask under inert N₂, atmosphere followed by repetition of vacuum and N₂ cycle for next 2 minutes. The temperature was then raised to 140 °C under N₂, gas flow and 0.2 mL bromotrimethylsilane is injected. The reaction is quenched immediately by

decreasing the reaction temperature, by partially dipping the flask into an ice-water bath. After the reaction mixture attained a temperature close to room temperature, it was centrifuged at 7000 rpm for 7 minutes using F-35-6-30 rotor of Eppendorf 5430 centrifugation instrument. The supernatant is discarded and the precipitate is re-dispersed in 5 mL toluene and centrifuged again at 7000 rpm for 5 minutes. The precipitate from this second centrifugation is used for further characterization.

4.2.3 Synthesis of Yb³⁺-doped (PEA)₂PbBr₄

For synthesizing Yb³⁺-doped (PEA)₂PbBr₄, ytterbium (III) acetate tetrahydrate is added along with 0.2 mmol lead acetate trihydrate, 10 mL 1-octadecene and 1 mL oleic acid. 0.025, 0.05, 0.1 and 0.2 mmol of ytterbium (III) acetate tetrahydrate resulted into 0.1, 0.4, 0.6 and 1.0% Yb³⁺-doped (PEA)₂PbBr₄, respectively. Rest of the synthesis method of all doped and undoped samples are same.

4.2.4 Structural characterization and optical properties

Powder X-ray diffraction (PXRD) measurements are carried out using a Bruker D8 Advance X-ray diffractometer equipped with Cu Ka radiation (1.54 Å). Field emission scanning electron microscopy (FESEM) measurements are done using the Zeiss Ultra Plus FESEM instrument. Inductively coupled plasma mass spectroscopy (ICP-MS) measurements are performed using an instrument of Thermo Fisher Scientific (Germany). Transmission electron microscopy (TEM) images are taken by using a UHR FEG- TEM, JEOL JEM 2100F field emission transmission electron microscope operated at 200 kV. A Keysight atomic force microscope (model: AFM 5500) is used to record AFM (Atomic force microscopy) images in tapping mode. Optical extinction spectra are recorded using a Cary series UV-vis spectrophotometer. FLS 980 spectrometer (Edinburgh Instruments) is used for measuring steady-state (using Xe-lamp as excitation source) and time-resolved PL. PL decays for excitonic emission with peak around 414 nm are recorded after excitation with a pulsed LED (pulse width 743 ps) at 340 nm. The experimental PL decay profiles for 414 nm emission are fitted using a bi-exponential decay function of the form

$$I_t = I_{t=0} + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \dots\dots (1)$$

where I_t and $I_{t=0}$ are PL counts at any variable time t and time $= 0$ s, τ_1 and τ_2 are PL lifetimes with contributions A_1 and A_2 . The average lifetimes (τ_{avg}) are calculated using the equation.

$$\tau_{avg} = \frac{\sum_{i=1,2} A_i \tau_i^2}{\sum_{i=1,2} A_i \tau_i} \dots\dots (2)$$

The PL decay for Yb³⁺-emission with peak around 997 nm are excited using a microsecond flash lamp at 340 nm. The experimental decay profile is fitted with mono-exponential decay function,

$$I_t = I_{t=0} + A_1 \exp(-t/\tau_1) \dots\dots (3)$$

4.3 Results and discussion

4.3.1 Synthesis, structure, morphology

We have synthesized undoped and Yb³⁺-doped 2D layered (PEA)₂PbBr₄ perovskite after modifying the method reported in ref. [29]. The reaction is carried out in inert N₂ atmosphere after taking lead acetate trihydrate, ytterbium acetate tetrahydrate, and phenylethylamine in a mixture of 1-octadecene and oleic acid. At a temperature of 140 °C, bromotrimethylsilane is injected, and we get the product after subsequent quenching and washing. A more detailed synthesis methodology is provided in the experimental section.

The elemental concentration of Yb³⁺ dopants in the product samples are measured by inductively coupled plasma mass spectroscopy (ICP-MS). Yb³⁺ is expected to substitute Pb²⁺ in the (PEA)₂PbBr₄. So, the Yb³⁺ concentration has been presented with respect to that of Pb²⁺. A big difference is observed between Yb³⁺ concentration present in the precursors with that in the products. For 10, 20, 33 and 50% of Yb³⁺ precursor with respect to Pb²⁺, only 0.1, 0.4, 0.6 and 1.0% Yb³⁺ are obtained in the product, respectively. Similar poor doping of Yb³⁺ has previously also been observed in 3D perovskites like Cs₂AgInCl₆ and CsPbX₃.^{16, 31, 32} Difference in oxidation state between Yb³⁺ and Pb²⁺, along with possible lattice strain might be the cause of poor Yb³⁺ doping resulting in loss of excess Yb³⁺ precursor. It is to be noted that for the optical property discussed here, 1% Yb³⁺ doping is sufficiently large.

The product is first characterized by measuring powder X-ray diffraction (PXRD) patterns. Figure 4.1b shows that the undoped sample has a series of periodic peaks along with other peaks. The periodic peaks at a difference of $2\theta = 5.3^\circ$ agree with the layered structure of (PEA)₂PbBr₄, (reported space group P-1)³³ with interlayer spacing of 1.7 nm. These periodic peaks agree with characteristics (001) peaks for 2D (PEA)₂PbBr₄, layered hybrid perovskite crystals, as shown by

Yb³⁺-doped (phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

the schematics in Figure 4.1a.²⁹ Since the powder is not very fine, the PXRD patterns are dominated by the (00l) planes, but other (hkl) planes are also observed with smaller intensities. The PXRD patterns of all the four Yb³⁺-doped (PEA)₂PbBr₄ samples resemble closely with the undoped samples. This similarity confirms that the introduction of Yb³⁺ precursors in the reaction precursor does not introduce any crystalline impurity. But the amount of Yb³⁺ dopants is too small to notice a measurable shift in PXRD peak positions with doping.

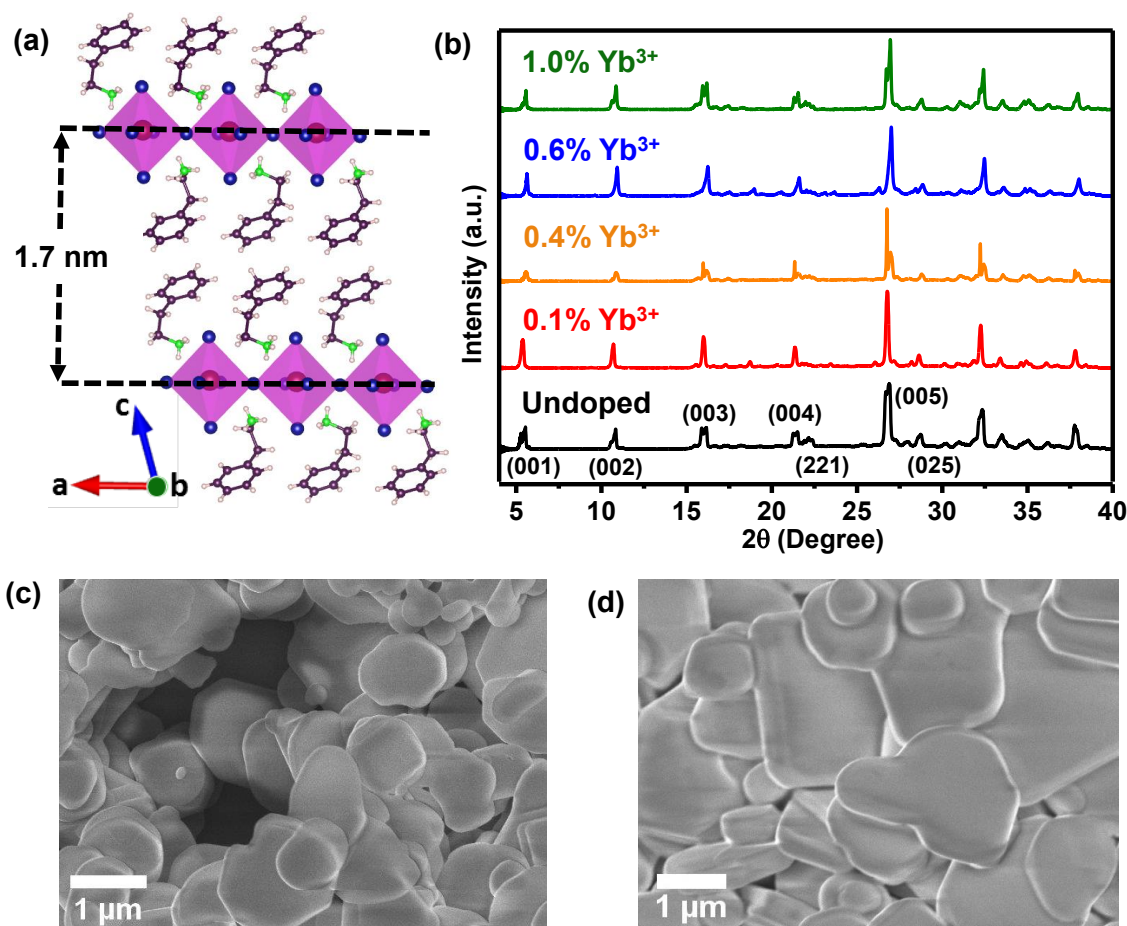


Figure 4.1: (a) Schematic of crystal structure of (PEA)₂PbBr₄ perovskite showing corner-shared lead halide octahedral connected in two dimensions and separated by organic cation PEA⁺. The interlayer distance between two inorganic layers is 1.7 nm. (b) PXRD patterns of Yb³⁺-doped (PEA)₂PbBr₄ with different dopant percentages. FESEM images of (c) undoped and (d) 0.6% Yb³⁺-doped samples showing micrometer-sized crystals with plate-like morphology.

Field emission scanning electron microscopy (FESEM) image of the undoped sample is shown in Figure 4.1c. Plate-like morphology is observed with a lateral dimension of around 1-2 μm. The

Yb³⁺-doped (phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

plate-like morphology agrees with the observed 2D layered crystals crystal structure of (PEA)₂PbBr₄. Similar crystallite size and morphology are obtained for 0.6% Yb³⁺ doped sample as well, as shown in Figure 4.1d.

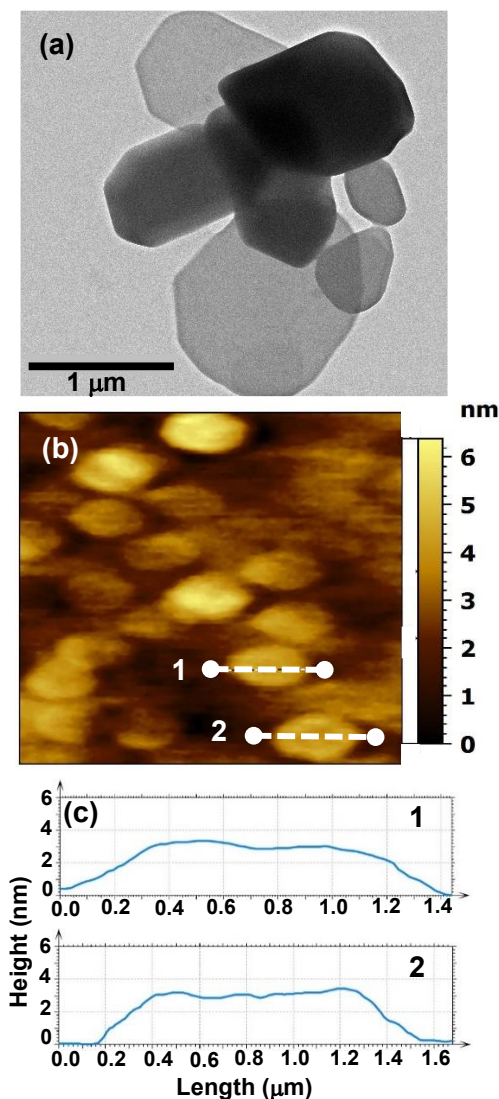


Figure 4.2: After sonicating the (PEA)₂PbBr₄ microcrystals, shown in Figure 4.1, a very small fraction of the sample remains suspended on the supernatant for about an hour. Microscopic characterization of that supernatant part is shown here. (a) TEM and (b) AFM images show formation of nanoplatelets. (c) Height profiles of two crystals labeled as 1 and 2, along the white dashed lines indicated in the AFM image, suggest a thickness of ~3.5 nm for both the crystals.

The plate-like morphology motivated us to explore the possibility of the presence of nanoplatelets in the sample. For that, about 5 mg of the powder sample was mixed with 5 mL hexane, and

sonicated for 10 minutes. A majority of the sample settled down within 15 minutes after the completion of sonication. But a very small fraction of the sample remains suspended in the supernatant liquid. That suspension/dispersion is stable for about an hour. The sample taken from that dispersion is then characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The TEM image of undoped sample in Figure 4.2a shows some platelets with a lateral dimension of $\sim 1 \mu\text{m}$. The poor contrast of the platelets with background indicates that the platelets are probably only a few nm thick. The nanoplatelets are then confirmed by the AFM image (Figure 4.2b) and the corresponding height profile (Figure 4.2c). The two crystals, denoted as 1 and 2 in Figure 4.2b-c have thickness of $\sim 3.5 \text{ nm}$. Figure 4.1a shows that the thickness of one monolayer of $(\text{PEA})_2\text{PbBr}_4$ is 1.7 nm . So, the observed AFM thickness of $\sim 3.5 \text{ nm}$ indicates presence of two monolayer thick $(\text{PEA})_2\text{PbBr}_4$. The lateral dimension of the nanoplatelets is $\sim 1 \mu\text{m}$, which remains similar to the FESEM image of the powder sample. Similar TEM and AFM images (not shown here) are also observed for $0.6\% \text{ Yb}^{3+}$ -doped $(\text{PEA})_2\text{PbBr}_4$.

4.3.2 Optical properties

As discussed above, the samples have plate-like morphology (including few nanoplatelets) with micro- meter size lateral dimension. Consequently, the samples are colloiddally unstable. For measuring optical spectra, we tried to make the dispersion of the sample in toluene, and did the spectral measurements quickly before the samples precipitate out. Figure 4.3 compares optical absorption and emission properties of undoped and $0.6\% \text{ Yb}^{3+}$ -doped $(\text{PEA})_2\text{PbBr}_4$. Both samples (Figure 4.3a) show an excitonic absorption feature at 407 nm (3.05 eV). This observation agrees with the reported excitonic absorption energy (optical band gap) of $(\text{PEA})_2\text{PbBr}_4$.³⁴ Note that in the previous section we mentioned about the existence of both few-nm thick nanoplatelets and significantly thicker platelets. This inhomogeneity in platelet thickness will not change the band gap of the material since the electron and hole are confined in one atomically thin inorganic layer (Figure 4.1a) with excitonic Bohr radius of $\sim 0.7 \text{ nm}$.³⁵ So thinner ($\sim 3.5 \text{ nm}$) nanoplatelets do not impose any additional quantum confinement effect compared to the already existing quantum well structure of bulk $(\text{PEA})_2\text{PbBr}_4$. However, the platelets, particularly thicker ones, scatter enough light even below the band gap. Consequently, a significant light extinction is observed even below the band gap.

Yb³⁺-doped (phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

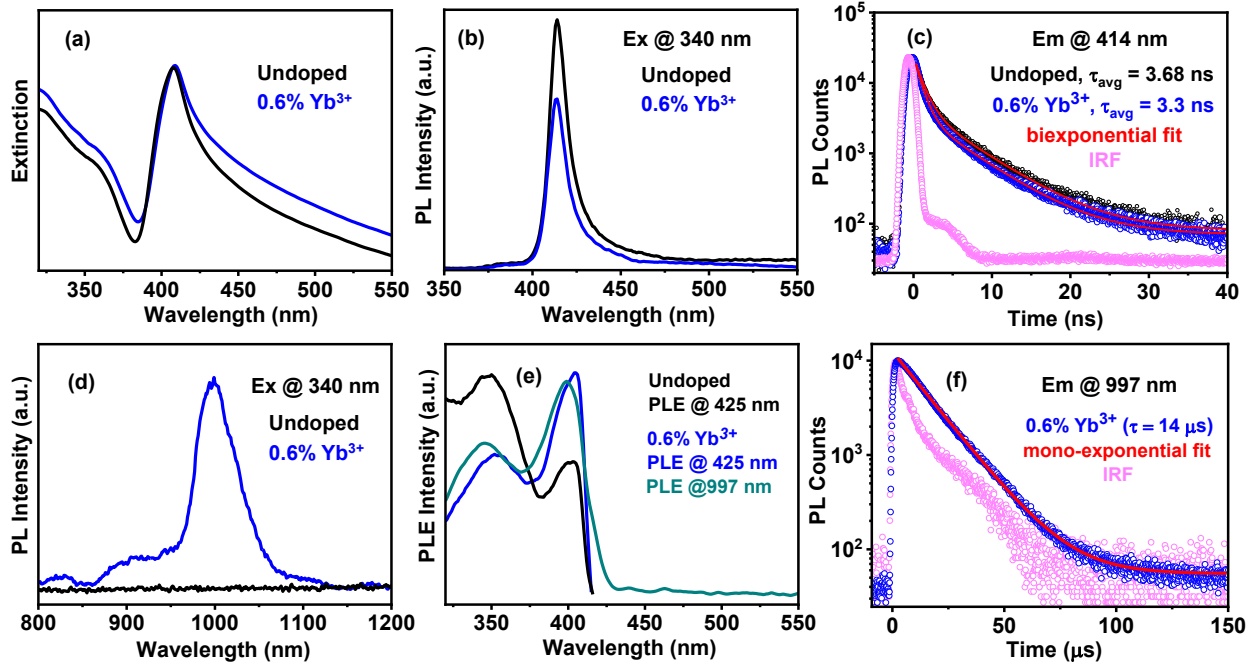


Figure 4.3: Optical properties of undoped and 0.6% Yb³⁺-doped (PEA)₂PbBr₄. (a) UV-visible absorption spectra showing an excitonic absorption at ~407 nm. (b) PL spectra normalized by the absorbance at excitation wavelength 340 nm. (c) PL decay profiles of excitonic emission at 414 nm with bi-exponential decay fitting and the instrument response factor (IRF). Both samples have similar average lifetime (τ_{avg}) values. (d) NIR PL spectra after exciting at 340 nm. (e) PLE spectra of undoped (emission at 425 nm) and of 0.6% Yb³⁺-doped samples (emissions at 425 and 997 nm). (f) PL decay profile with emission at 997 nm for 0.6% Yb-doped sample, along with a mono-exponential decay fit.

The PL spectra shown in Figure 4.3b confirm that both samples exhibit sharp excitonic emission with peak at 414 nm with full width half maxima (FWHM) of ~ 13 nm (90 meV). So, doping does not change the excitonic absorption and emission nature. But typically, 0.6% Yb³⁺-doped sample shows a small decrease in excitonic emission intensity, suggesting a possible non-radiative energy transfer from excitons to Yb³⁺ dopants. PL decay dynamics of both the samples are similar but with a slightly faster decay for the doped sample, as shown in Figure 4.3c. The experimental data are fitted with a bi-exponential decay function. For the undoped sample, the best fit parameters show two lifetimes at 1.1 ns and 5.8 ns with 81% and 19% contributions, respectively, yielding an average PL lifetime of 3.7 ns. A slightly shorter average lifetime of 3.3 ns is observed for 0.6% Yb³⁺-doped (PEA)₂PbBr₄ showing lifetimes of 0.9 ns and 5.6 ns with 85% and 15% contributions, respectively.

Figure 4.3d shows the PL spectra in the NIR region. The undoped sample does not show any NIR emission. Interestingly, 0.6% Yb³⁺-doped (PEA)₂PbBr₄ shows NIR emission with peak at 997 nm. The NIR emission is supposed to originate from ²F_{5/2} → ²F_{7/2} transition of *f*-electrons in Yb³⁺. To find the excitation mechanism, PL excitation (PLE) spectrum for emission at 997 nm is compared with that of the excitonic emission, as shown in Figure 4.3e. Both the PLE spectra of the doped sample are similar, along with the PLE spectrum of excitonic emission of the undoped sample. The peak in PLE spectra matches well with the excitonic absorption features shown in Figure 4.3a. Therefore, both the excitonic emission of host at ~ 414 nm and Yb³⁺ *f*-electron at ~ 997 nm originate via excitation through band gap of the host. The excited host then transfers part of its energy non-radiatively to the Yb³⁺ dopants.

The PL decay profile for 997 nm emission is fitted with a single exponential decay showing a lifetime of about 14 μs, as shown in Figure 4.3f. Similar lifetimes have been observed previously,³⁶ and had been attributed to parity forbidden ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ *f*-electrons. There are some prior literatures showing further longer lifetime for Yb³⁺ emission, close to a millisecond.^{15, 31} It has been suggested that a more rigid crystalline environment surrounding the dopant ions suppresses the faster non-radiative decay channels increasing the average lifetime of Yb³⁺ emission to millisecond scale.

Figure 4.4 shows the effect of dopant concentration on both excitonic and Yb³⁺ emission. The colloidal instability of the samples brings in some uncertainty in the compared PL intensity values. But still, a systematic decrease in excitonic emission intensity at ~ 414 nm is observed with increasing dopant concentration, as shown in Figure 4.4a. For the highest dopant concentration, i.e., 1% Yb³⁺-doped sample, the PL decay profile shown in the inset of Figure 4.4a suggests an average lifetime of 2.3 ns. This average lifetime of the 1% doped sample is lower compared to the average PL lifetime of undoped sample (3.7 ns). So, both the intensity and lifetime of excitonic PL decreases with increasing dopant concentration. This decrease suggests the non-radiative transfer of exciton energy from the host to the dopants. Such observations are also indirect evidences of doping Yb³⁺ into the host lattice.

On the other hand, Yb³⁺ NIR emission increases with increasing the dopant concentration till 0.6%, as shown in Figure 4.4b. Further increase in dopant concentration till 1.0%, starts to decrease the

Yb³⁺-doped (phenylethylammonium)₂PbBr₄ 2D layered hybrid perovskite for NIR emission

NIR emission intensity. Such a decrease in dopant emission with increasing concentration has been usual in prior literature,²⁸ and often referred as concentration quenching. Isolated dopant ions are typically the most emissive ones.

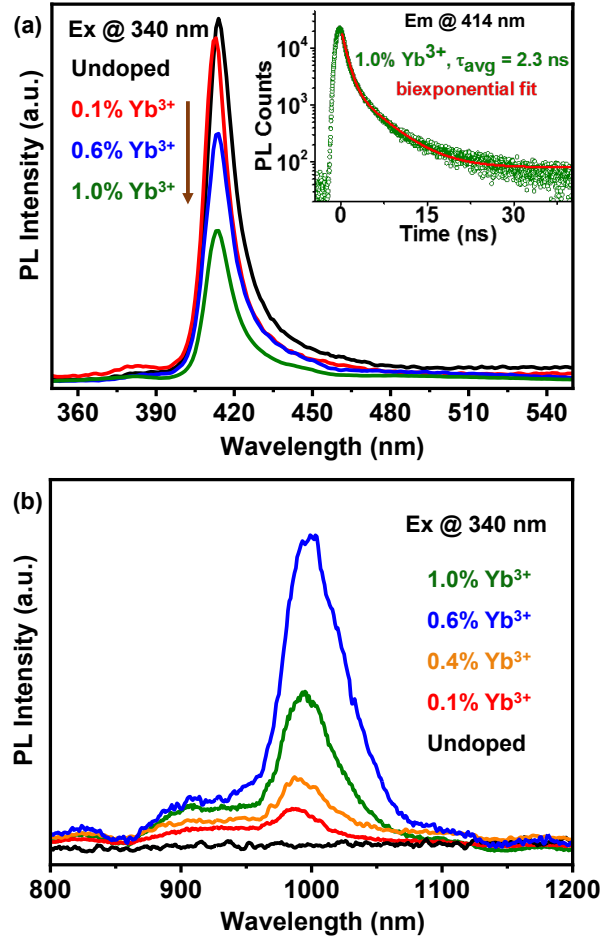


Figure 4.4: PL spectra of Yb³⁺-doped (PEA)₂PbBr₄ with different dopant concentrations in (a) UV-visible and (b) NIR region. The PL intensities are plotted after normalizing with the absorbance at excitation wavelength 340 nm, for the respective samples. Inset in (a) shows the excitonic PL decay of 1% Yb³⁺-doped sample with a noticeable decrease of average lifetime (τ_{avg}).

We summarize the optical excitation and emission processes in Yb³⁺-doped (PEA)₂PbBr₄. The excitation happens through the host at any wavelength lower than (or energy higher than) the band gap. Consequently, a broad excitation spectrum is observed (Figure 4.3e). In the undoped sample, the excitation energy gets released via emitting light through the excitonic (or band edge) emission of the host, along with the unavoidable non-radiative decay channels of the host. When Yb³⁺

dopant is added, a part of excitation energy of host is non-radiatively transferred to the dopants. This energy transfer populates the excited state $^2F_{5/2}$ of the dopant. Note that, optical excitation from $^2F_{7/2} \rightarrow ^2F_{5/2}$ is forbidden. Therefore, non-radiative energy transfer from host is the major way to populate the $^2F_{5/2}$ excited state. The $^2F_{5/2}$ state then de-excites to $^2F_{7/2}$ via emitting 997 nm NIR radiation with a lifetime of $\sim 14 \mu\text{s}$. The instrument response function (IRF) has some overlap with the NIR PL decay profile (see Figure 4.3f), making it difficult to analyze the minor changes in lifetime with dopant concentrations. Also note that the NIR emission in Figure 4.4b shows some asymmetry. Such asymmetry in lanthanide emission is rather common, and it originates from the fine-splitting of the Yb^{3+} f -electron states.³⁷⁻³⁹

4.4 Conclusions

Yb^{3+} -doped $(\text{PEA})_2\text{PbBr}_4$ 2D layered hybrid perovskites have been prepared. The samples are mainly microcrystals with plate-like morphology. If the samples are sonicated enough, then some nanoplatelets with thickness $\sim 3.5 \text{ nm}$ are also formed, along with the thicker platelets. The inhomogeneity in thickness does not impact the optical band gap or excitonic absorption and emission because of the quantum well structure of the layered hybrid perovskites. The undoped sample shows excitonic absorption (407 nm, 3.05 eV) and emission (414 nm, 2.99 eV) with narrow FWHM. After Yb^{3+} doping, a new emission peak appears at 997 nm (1.24 eV), because of f - f electronic transition of Yb^{3+} . This NIR emission has a lifetime of 14 μs , owing to the Laporte forbidden f - f transition. The excitation of f -electrons of Yb^{3+} happens via the excitonic absorption of the host. The host then non-radiatively transfers the excitation energy to Yb^{3+} dopants. Consequently, both intensity and lifetime of excitonic PL systematically decrease with increasing dopant concentrations from 0% (undoped) to 1%. On the other hand, the NIR (997 nm) Yb^{3+} emission intensity reaches a maximum for 0.6% doping, and then decreases with further increase in dopant concentration, which is often termed as concentration quenching. The hydrophobic organic cations make the samples reasonably stable in ambient conditions. Films of such samples with high NIR emission efficiency will be desired for fabricating NIR light-emitting diodes in the future.

4.5 References

1. Santra, P. K.; Kamat, P. V. Mn-Doped Quantum Dot Sensitized Solar Cells: A Strategy to Boost Efficiency over 5%. *J. Am. Chem. Soc.* **2012**, *134* (5), 2508-2511.
2. Buonsanti, R.; Milliron, D. J. Chemistry of Doped Colloidal Nanocrystals. *Chem. Mater.* **2013**, *25* (8), 1305-1317.
3. Pradhan, N.; Adhikari, S. D.; Nag, A.; Sarma, D. D. Luminescence, Plasmonic, and Magnetic Properties of Doped Semiconductor Nanocrystals. *Angew. Chem. Int. Ed.* **2017**, *56* (25), 7038-7054.
4. Dufour, M.; Izquierdo, E.; Livache, C.; Martinez, B.; Silly, M. G.; Pons, T.; Lhuillier, E.; Delerue, C.; Ithurria, S. Doping as a Strategy to Tune Color of 2D Colloidal Nanoplatelets. *ACS Appl. Mater. Interfaces* **2019**, *11* (10), 10128-10134.
5. Liu, W.; Lin, Q.; Li, H.; Wu, K.; Robel, I.; Pietryga, J. M.; Klimov, V. I. Mn²⁺-Doped Lead Halide Perovskite Nanocrystals with Dual-Color Emission Controlled by Halide Content. *J. Am. Chem. Soc.* **2016**, *138* (45), 14954-14961.
6. Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* **2016**, *16* (12), 7376-7380.
7. Mir, W. J.; Jagadeeswararao, M.; Das, S.; Nag, A. Colloidal Mn-Doped Cesium Lead Halide Perovskite Nanoplatelets. *ACS Energy Lett.* **2017**, *2* (3), 537-543.
8. Adhikari, S. D.; Guria, A. K.; Pradhan, N. Insights of Doping and the Photoluminescence Properties of Mn-Doped Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2019**, *10* (9), 2250-2257.
9. Paul, S.; Bladt, E.; Richter, A. F.; Döblinger, M.; Tong, Y.; Huang, H.; Dey, A.; Bals, S.; Debnath, T.; Polavarapu, L.; Feldmann, J. Manganese-Doping-Induced Quantum Confinement within Host Perovskite Nanocrystals through Ruddlesden–Popper Defects. *Angew. Chem. Int. Ed.* **2020**, *59* (17), 6794-6799.
10. Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X.-G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C.-J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Seró, I. M.;

Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Prieto, J. P.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roefsaers, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Buschbaum, P. M.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775-10981.

11. Zou, S.; Liu, Y.; Li, J.; Liu, C.; Feng, R.; Jiang, F.; Li, Y.; Song, J.; Zeng, H.; Hong, M.; Chen, X. Stabilizing Cesium Lead Halide Perovskite Lattice through Mn(II) Substitution for Air-Stable Light-Emitting Diodes. *J. Am. Chem. Soc.* **2017**, *139* (33), 11443-11450.

12. Akkerman, Q. A.; Meggiolaro, D.; Dang, Z.; De Angelis, F.; Manna, L. Fluorescent Alloy CsPb_xMn_{1-x}I₃ Perovskite Nanocrystals with High Structural and Optical Stability. *ACS Energy Lett.* **2017**, *2* (9), 2183-2186.

13. Swarnkar, A.; Mir, W. J.; Nag, A. Can B-Site Doping or Alloying Improve Thermal- and Phase-Stability of All-Inorganic CsPbX₃ (X = Cl, Br, I) Perovskites? *ACS Energy Lett.* **2018**, *3* (2), 286-289.

14. Mir, W. J.; Sheikh, T.; Arfin, H.; Xia, Z.; Nag, A. Lanthanide Doping in Metal Halide Perovskite Nanocrystals: Spectral Shifting, Quantum Cutting and Optoelectronic Applications. *NPG Asia Mater.* **2020**, *12* (1), 9.

15. Milstein, T. J.; Kroupa, D. M.; Gamelin, D. R. Picosecond Quantum Cutting Generates Photoluminescence Quantum Yields Over 100% in Ytterbium-Doped CsPbCl₃ Nanocrystals. *Nano Lett.* **2018**, *18* (6), 3792-3799.

16. Mir, W. J.; Mahor, Y.; Lohar, A.; Jagadeeswararao, M.; Das, S.; Mahamuni, S.; Nag, A. Postsynthesis Doping of Mn and Yb into CsPbX₃ (X = Cl, Br, or I) Perovskite Nanocrystals for Downconversion Emission. *Chem. Mater.* **2018**, *30* (22), 8170-8178.

17. Milstein, T. J.; Kluherz, K. T.; Kroupa, D. M.; Erickson, C. S.; Yoreo, J. J. D.; Gamelin, D. R. Anion Exchange and the Quantum-Cutting Energy Threshold in Ytterbium-Doped CsPb(Cl_{1-x}Br_x)₃ Perovskite Nanocrystals. *Nano Lett.* **2019**, *19* (3), 1931-1937.

18. Zhou, D.; Liu, D.; Pan, G.; Chen, X.; Li, D.; Xu, W.; Bai, X.; Song, H. Cerium and Ytterbium Codoped Halide Perovskite Quantum Dots: A Novel and Efficient Downconverter for Improving the Performance of Silicon Solar Cells. *Adv. Mater.* **2017**, *29* (42), 1704149.

19. Pan, G.; Bai, X.; Yang, D.; Chen, X.; Jing, P.; Qu, S.; Zhang, L.; Zhou, D.; Zhu, J.; Xu, W.; Dong, B.; Song, H. Doping Lanthanide into Perovskite Nanocrystals: Highly Improved and Expanded Optical Properties. *Nano Lett.* **2017**, *17* (12), 8005-8011.
20. Pedesseau, L.; Saponi, D.; Traore, B.; Robles, R.; Fang, H.-H.; Loi, M. A.; Tsai, H.; Nie, W.; Blancon, J.-C.; Neukirch, A.; Tretiak, S.; Mohite, A. D.; Katan, C.; Even, J.; Kepenekian, M. Advances and Promises of Layered Halide Hybrid Perovskite Semiconductors. *ACS Nano* **2016**, *10* (11), 9776-9786.
21. Acharyya, P.; Kundu, K.; Biswas, K. 2D Layered All-Inorganic Halide Perovskites: Recent Trends in Their Structure, Synthesis and Properties. *Nanoscale* **2020**, *12* (41), 21094-21117.
22. Chakraborty, R.; Nag, A. Dielectric Confinement for Designing Compositions and Optoelectronic Properties of 2D Layered Hybrid Perovskites. *Phys. Chem. Chem. Phys.* **2021**, *23* (1), 82-93.
23. Nag, A. “Plenty of Room” at the Interface of Hybrid Metal Halide Perovskite Single Crystals. *Nano Lett.* **2021**, *21* (20), 8529-8531.
24. Smith, I. C.; Hoke, E. T.; Ibarra, D. S.; McGehee, M. D.; Karunadasa, H. I. A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem. Int. Ed.* **2014**, *53* (42), 11232-11235.
25. Cortecchia, D.; Mróz, W.; Folpini, G.; Borzda, T.; Leoncino, L.; Leaños, A. L. A.; Speller, E. M.; Petrozza, A. Layered Perovskite Doping with Eu³⁺ and β -diketonate Eu³⁺ Complex. *Chem. Mater.* **2021**, *33* (7), 2289-2297.
26. Xu, D.; Sun, C.; Han, J.; Zhang, H.; Tao, J.; Wei, T.; Fan, C.; Zhang, Z.; Bi, W. Highly Efficient and Stable Eu³⁺-Doped Two-Dimensional Perovskites. *J. Alloys Compd.* **2022**, *902*, 163841.
27. Biswas, A.; Bakthavatsalam, R.; Kundu, J. Efficient Exciton to Dopant Energy Transfer in Mn²⁺-Doped (C₄H₉NH₃)₂PbBr₄ Two-Dimensional (2D) Layered Perovskites. *Chem. Mater.* **2017**, *29* (18), 7816-7825.
28. Sheikh, T.; Nag, A. Mn Doping in Centimeter-Sized Layered 2D Butylammonium Lead Bromide (BA₂PbBr₄) Single Crystals and Their Optical Properties. *J. Phys. Chem. C* **2019**, *123* (14), 9420-9427.

29. Sun, C.; Gao, Z.; Deng, Y.; Liu, H.; Wang, L.; Su, S.; Li, P.; Li, H.; Zhang, Z.; Bi, W. Orange to Red, Emission-Tunable Mn-Doped Two-Dimensional Perovskites with High Luminescence and Stability. *ACS Appl. Mater. Interfaces* **2019**, *11* (37), 34109-34116.
30. Su, B.; Molokeev, M. S.; Xia, Z. Unveiling Mn²⁺ Dopant States in Two-Dimensional Halide Perovskite toward Highly Efficient Photoluminescence. *J. Phys. Chem. Lett.* **2020**, *11* (7), 2510-2517.
31. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. Bi³⁺-Er³⁺ and Bi³⁺-Yb³⁺ Codoped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, *59* (28), 11307-11311.
32. Ma, J.-P.; Chen, Y.-M.; Zhang, L.-M.; Guo, S.-Q.; Liu, J.-D.; Li, H.; Ye, B.-J.; Li, Z.-Y.; Zhou, Y.; Zhang, B.-B.; Bakr, O. M.; Zhang, J.-Y.; Sun, H.-T. Insights into the Local Structure of Dopants, Doping Efficiency, and Luminescence Properties of Lanthanide-Doped CsPbCl₃ Perovskite Nanocrystals. *J. Mater. Chem. C* **2019**, *7* (10), 3037-3048.
33. Kawano, N.; Koshimizu, M.; Sun, Y.; Yahaba, N.; Fujimoto, Y.; Yanagida, T.; Asai, K. Effects of Organic Moieties on Luminescence Properties of Organic-Inorganic Layered Perovskite-Type Compounds. *J. Phys. Chem. C* **2014**, *118* (17), 9101-9106.
34. Liang, D.; Peng, Y.; Fu, Y.; Shearer, M. J.; Zhang, J.; Zhai, J.; Zhang, Y.; Hamers, R. J.; Andrew, T. L.; Jin, S. Color-Pure Violet-Light-Emitting Diodes Based on Layered Lead Halide Perovskite Nanoplates. *ACS Nano* **2016**, *10* (7), 6897-6904.
35. Seitz, M.; Meléndez, M.; York, P.; Kurtz, D. A.; Magdaleno, A. J.; Cano, N. A.; Kshirsagar, A. S.; Gangishetty, M. K.; Buscalioni, R. D.; Congreve, D. N.; Prins, F. Halide Mixing Inhibits Exciton Transport in Two-dimensional Perovskites Despite Phase Purity. *ACS Energy Lett.* **2022**, *7* (1), 358-365.
36. Mahor, Y.; Mir, W. J.; Nag, A. Synthesis and Near-Infrared Emission of Yb-Doped Cs₂AgInCl₆ Double Perovskite Microcrystals and Nanocrystals. *J. Phys. Chem. C* **2019**, *123* (25), 15787-15793.
37. Fang, Z.; Cao, R.; Zhang, F.; Ma, Z.; Dong, G.; Qiu, J. Efficient Spectral Conversion from Visible to Near-Infrared in Transparent Glass Ceramics Containing Ce³⁺-Yb³⁺ Codoped Y₃Al₅O₁₂ nanocrystals. *J. Mater. Chem. C* **2014**, *2* (12), 2204-2211.

38. Liu, Y.; Rong, X.; Li, M.; Molokeev, M. S.; Zhao, J.; Xia, Z. Incorporating Rare-Earth Terbium(III) Ions into Cs₂AgInCl₆:Bi Nanocrystals toward Tunable Photoluminescence. *Angew. Chem. Int. Ed.* **2020**, *59* (28), 11634-11640.
39. Saikia, S.; Joshi, A.; Arfin, H.; Badola, S.; Saha, S.; Nag, A. Sb³⁺-Er³⁺-Codoped Cs₂NaInCl₆ for Emitting Blue and Short-Wave Infrared Radiation. *Angew. Chem. Int. Ed.* **2022**, *61* (32), e202201628.

Chapter 5

Thesis summary and future outlook

5.1 Thesis summary

Three-dimensional lead halide perovskites (APbX_3 , A: monovalent cation, X: Cl, Br, I) are being explored for their extraordinary properties like solution processibility, near unity photoluminescence quantum yield, high carrier mobility and the subsequent optoelectronic applications.¹⁻³ If the three-dimensional connectivity between metal-halide octahedra is lifted, they transform into lower-dimensional perovskite derivatives (2D, 1D and 0D).⁴ This thesis focuses on such low-dimensional (0D and 2D) perovskite derivatives which emit in the near-infrared (NIR) region (900 – 1300 nm) through *d-d* and *f-f* electronic transitions.

NIR emitting materials are widely used in various fields, such as non-invasive bio-imaging, food processing, and therapy.^{5, 6} The emission is usually generated by epitaxially grown III-V semiconductors which are commercially available, but due to their expensive synthesis, these are costly. Apart from these, there are colloidal II-VI, III-V, IV-VI nanocrystals, for example HgTe, InAs, PbS etc.⁷, or filament-based incandescent lamps, but many a time they suffer from emission quenching and efficiency issues. An alternative approach involves the development of NIR-emitting phosphors using Cr^{3+} or lanthanide dopants in halide or oxide-based hosts. However, this typically requires high-energy UV or blue light excitation leading to thermalization loss.

To overcome these, in Chapter 2, we have shown that all-inorganic 0D perovskite derivatives, Cs_2MX_6 (M: Mo/W; X: Cl/Br) can absorb and emission in the far-red (787 nm) and NIR (986 nm) regions, respectively. We assign them as *d-d* transitions of M^{4+} (d^2) in octahedral crystal field based on Tanabe-Sugano diagram. Photoluminescence at 8 K shows mirror-image like excitation and emission spectra with vibrational progression which are rare for an undoped crystal. The less Stokes shift reduces excitation energy significantly which leads to the fabrication of NIR phosphor-converted light-emitting diodes (pc-LEDs) by coating Cs_2MoCl_6 on 730 nm LED chip.

In Chapter 3, we address the issue of concentration quenching^{8, 9} of Cs_2MX_6 which arises due to the close proximity of emission centers $[\text{MX}_6]^{2-}$ throughout the crystal. For that, we dope W^{4+} and Mo^{4+} ions into another 0D host, Cs_2SnCl_6 , which is non-luminescent with a high band gap (4.89 eV)¹⁰. In Chapter 3A, we discuss different percentages of W^{4+} -doped Cs_2SnCl_6 , where we achieve reasonably good NIR emission ranging from 800 – 1300 nm (peak at 965 nm). After reaching maximum emission for 3.3% W^{4+} , further increment of dopant results in concentration quenching.

Moreover, as a proof of concept we fabricate NIR pc-LED by coating the optimized sample on top of 400 nm chip, this results NIR output power of 10.3 mW at 401 mA. In Chapter 3B, we explored Mo^{4+} doping. Here, surprisingly unlike tungsten we obtain dual emission covering NIR-I and NIR-II regions with peaks at 980 nm and 1350 nm respectively from a single dopant. Both the emissions have different lifetimes which suggest that they might have different origins. However, the actual reason and mechanistic understanding behind the unusual photoluminescence is yet to be achieved.

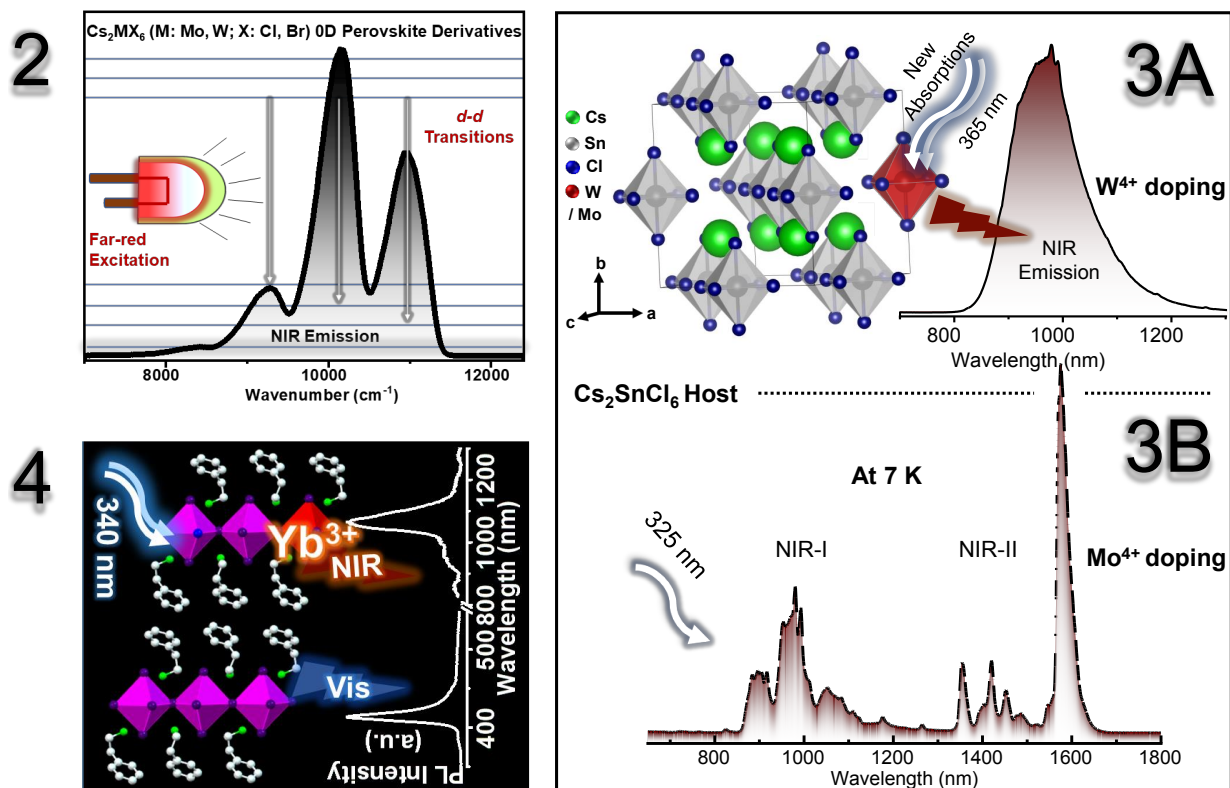


Figure 5.1: Schematic representation of summary of this thesis. Chapter 2 (top left) elucidates the NIR emission mechanism of Cs_2MX_6 ($\text{M} = \text{Mo}/\text{W}$; $\text{X} = \text{Cl}/\text{Br}$) through vibronic $d-d$ transition, additionally, a far-red (730 nm) pc-LED with significantly low input power has been fabricated based on Cs_2MoCl_6 phosphor. To decrease the concentration quenching effect of Cs_2MX_6 , Chapter 3 explores the doping of W^{4+} or Mo^{4+} in Cs_2SnCl_6 . 3A (top right) discusses about W^{4+} doping and subsequent NIR emission in 800 – 1300 nm with a peak at 965 nm. 3B (bottom right) describes about Mo^{4+} doping and its unique emission covering the whole NIR-I and NIR-II region. Chapter 4 (bottom left) explores possible colloidal synthesis and NIR emission in 2D $(\text{PEA})_2\text{PbBr}_4$ through Yb^{3+} doping.

Finally, in Chapter 4, we attempted possible colloidal synthesis of Yb^{3+} -doped phenylethylammonium lead bromide $[(\text{PEA})_2\text{PbBr}_4]$ 2D perovskites. Though doping Yb^{3+} into

(PEA)₂PbBr₄ lattice was not successful. We achieve weak NIR emission at 997 nm due to the f - f transitions of Yb³⁺ and the lifetime of that (14 μ s) was less than usual Yb³⁺ lifetime.¹¹ It is highly possible that, Yb³⁺ was attached on the surface, not inside the crystal lattice. The colloidal stability of the synthesized compound was also poor.

5.2 Future outlook

In a substantial part of the thesis, we discuss about chloride-based NIR emissive vacancy-ordered perovskites (presented on left side of Figure 5.2), where the octahedra are not connected to each other. Therefore, the charge transportation is inhibited throughout the crystal. Moreover, the electronegative chloride ligand further hinders the charge transport. As a result, though the systems are reasonably good NIR emitters due to molybdenum and tungsten, but they are not promising at all for electroluminescence-based applications.

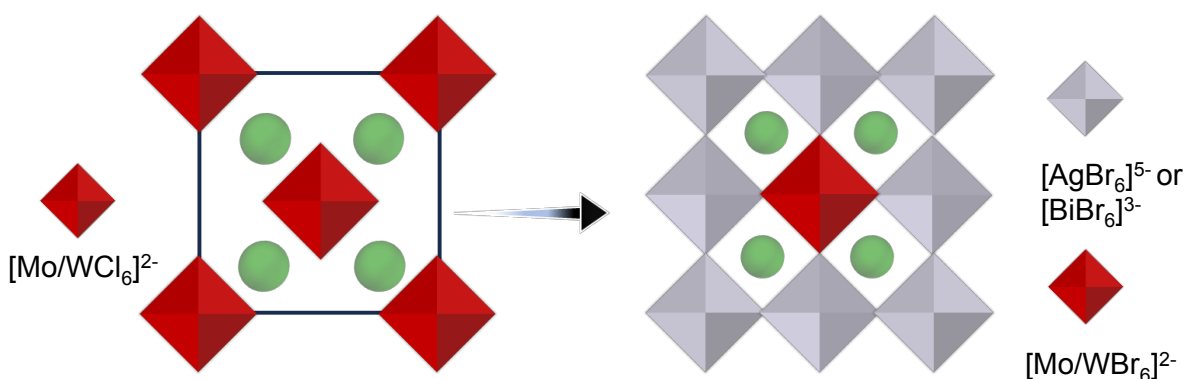


Figure 5.2: Schematic representation of a future direction that might be carried out. The left side diagram presents the crystal structure of vacancy-ordered perovskites Cs₂MCl₆ (M = Mo/W), where the maroon octahedra stand for [Mo/WCl₆]²⁻ octahedra which are separated from each other with green Cs⁺ cation. Now if we convert this to connected octahedra, it results a typical double perovskite structure, shown in the right side diagram. Here, we consider bromine counterpart and the double perovskite Cs₂AgBiBr₆, therefore, the grey octahedra are [AgBr₆]⁵⁻ or [BiBr₆]³⁻ and the maroon octahedron is [Mo/WBr₆]²⁻, doped into Cs₂AgBiBr₆.

Now if we think of three-dimensional connectivity instead of that ordered vacancy, we end up with a typical double perovskite structure (schematically shown on the right side of Figure 5.2) Here, for better charge-transport property, we consider bromide-based double perovskite Cs₂AgBiBr₆ and the grey octahedra are [AgBr₆]⁵⁻ or [BiBr₆]³⁻. Moreover, to achieve NIR emission, we consider doping Mo⁴⁺ / W⁴⁺ into Cs₂AgBiBr₆ lattice. Thus, the maroon octahedron (on the right side of

Figure 5.2) is $[\text{Mo}/\text{WBr}_6]^{2-}$. Therefore, now we have $\text{Mo}^{4+} / \text{W}^{4+}$ -doped $\text{Cs}_2\text{AgBiBr}_6$, which are three-dimensionally connected. Also, more polarizable bromide ligand with larger size is expected to have a better orbital overlap with metal ions than that of chloride. All these characteristics are favorable to increase the charge transport property of these crystals, along with NIR emission from the Mo/W dopant. Therefore, they might be promising for broad electroluminescent LEDs which are rare in the present literatures.

5.3 References

1. Shohl, W. A. D.; Zhou, Y.; Padture, N. P.; Mitzi, D. B. Synthetic Approaches for Halide Perovskite Thin Films. *Chem. Rev.* **2019**, *119* (5), 3193-3295.
2. Dey, A.; Ye, J.; De, A.; Debroye, E.; Ha, S. K.; Bladt, E.; Kshirsagar, A. S.; Wang, Z.; Yin, J.; Wang, Y.; Quan, L. N.; Yan, F.; Gao, M.; Li, X.; Shamsi, J.; Debnath, T.; Cao, M.; Scheel, M. A.; Kumar, S.; Steele, J. A.; Gerhard, M.; Chouhan, L.; Xu, K.; Wu, X.-G.; Li, Y.; Zhang, Y.; Dutta, A.; Han, C.; Vincon, I.; Rogach, A. L.; Nag, A.; Samanta, A.; Korgel, B. A.; Shih, C.-J.; Gamelin, D. R.; Son, D. H.; Zeng, H.; Zhong, H.; Sun, H.; Demir, H. V.; Scheblykin, I. G.; Seró, I. M.; Stolarczyk, J. K.; Zhang, J. Z.; Feldmann, J.; Hofkens, J.; Luther, J. M.; Prieto, J. P.; Li, L.; Manna, L.; Bodnarchuk, M. I.; Kovalenko, M. V.; Roelofs, M. B. J.; Pradhan, N.; Mohammed, O. F.; Bakr, O. M.; Yang, P.; Buschbaum, P. M.; Kamat, P. V.; Bao, Q.; Zhang, Q.; Krahne, R.; Galian, R. E.; Stranks, S. D.; Bals, S.; Biju, V.; Tisdale, W. A.; Yan, Y.; Hoye, R. L. Z.; Polavarapu, L. State of the Art and Prospects for Halide Perovskite Nanocrystals. *ACS Nano* **2021**, *15* (7), 10775-10981.
3. Shamsi, J.; Urban, A. S.; Imran, M.; Trizio, L. D.; Manna, L. Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties. *Chem. Rev.* **2019**, *119* (5), 3296-3348.
4. Lin, H.; Zhou, C.; Tian, Y.; Siegrist, T.; Ma, B. Low-Dimensional Organometal Halide Perovskites. *ACS Energy Lett.* **2018**, *3* (1), 54-62.
5. Qu, J.; Rastogi, P.; Gréboval, C.; Lagarde, D.; Chu, A.; Dabard, C.; Khalili, A.; Cruguel, H.; Robert, C.; Xu, X. Z.; Ithurria, S.; Silly, M. G.; Ferré, S.; Marie, X.; Lhuillier, E. Electroluminescence from HgTe Nanocrystals and Its Use for Active Imaging. *Nano Lett.* **2020**, *20* (8), 6185-6190.

6. Wang, S.; Pang, R.; Tan, T.; Wu, H.; Wang, Q.; Li, C.; Zhang, S.; Tan, T.; You, H.; Zhang, H. Achieving High Quantum Efficiency Broadband NIR $\text{Mg}_4\text{Ta}_2\text{O}_9\text{:Cr}^{3+}$ Phosphor Through Lithium-Ion Compensation. *Adv. Mater.* **2023**, 35 (22), 2300124.
7. Rogach, A. L.; Eychmüller, A.; Hickey, S. G.; Kershaw, S. V. Infrared-Emitting Colloidal Nanocrystals: Synthesis, Assembly, Spectroscopy, and Applications. *Small* **2007**, 3 (4), 536-557.
8. Dexter, D. L.; Schulman, J. H. Theory of Concentration Quenching in Inorganic Phosphors. *J. Chem. Phys.* **1954**, 22 (6), 1063-1070.
9. Ahmed, H. A. A. S.; Swart, H. C.; Bergman, P.; Kroon, R. E. Concentration Quenching of Eu^{2+} Doped $\text{Ca}_2\text{BO}_3\text{Cl}$. *Mater. Res. Bull.* **2016**, 75, 47-50.
10. Karim, M. M. S.; Ganose, A. M.; Pieters, L.; Leung, W. W. W.; Wade, J.; Zhang, L.; Scanlon, D. O.; Palgrave, R. G. Anion Distribution, Structural Distortion, and Symmetry-Driven Optical Band Gap Bowing in Mixed Halide Cs_2SnX_6 Vacancy Ordered Double Perovskites. *Chem. Mater.* **2019**, 31 (22), 9430-9444.
11. Arfin, H.; Kaur, J.; Sheikh, T.; Chakraborty, S.; Nag, A. $\text{Bi}^{3+}\text{-Er}^{3+}$ and $\text{Bi}^{3+}\text{-Yb}^{3+}$ Codoped $\text{Cs}_2\text{AgInCl}_6$ Double Perovskite Near-Infrared Emitters. *Angew. Chem. Int. Ed.* **2020**, 59 (28), 11307-11311.

List of publications

Included in the thesis

1. **Mondal, B.**; Shinde, A.; Rajput, P. K.; Arfin, H.; Tanwar, R.; Ghosh, P.; Nag, A. Vibronically Coupled Near-Infrared Emission and Excitation from $d-d$ Transitions of Cs_2MX_6 ($\text{M} = \text{Mo}/\text{W}$, $\text{X} = \text{Cl}/\text{Br}$). *ACS Energy Lett.* **2024**, 9, 819-828.
2. **Mondal, B.**; Poovathan, A.; Sheikh, T.; Nag, A. Yb^{3+} -Doped Phenylethylammonium Lead Bromide 2D Layered Hybrid Perovskite for Near-Infrared Emission. *ChemNanoMat* **2022**, 8, e202200104.
3. **Mondal, B.**; Nag, A. W^{4+} -Doped Cs_2SnCl_6 for Near-Infrared Emission. (*manuscript under preparation*)

Not included in the thesis

4. Poonia, A. K.; **Mondal, B.**; Beard, M. C.; Nag, A.; Adarsh, K. V. Superfluorescence from Electron-Hole Plasma at Moderate Temperatures of 175 K. *Phys. Rev. Lett.* **2024**, 132 (6), No. 063803.
5. Poonia, A. K.; Yadav, P.; **Mondal, B.**; Mandal, D.; Taank, P.; Shrivastava, M.; Nag, A.; Agarwal, A.; Adarsh, K. V. Room-Temperature Electron-Hole Condensation in Direct-Band-Gap Semiconductor Nanocrystals. *Phys. Rev. Appl.* **2023**, 20, L021002.
6. Kshirsagar, A. S.; Arfin, H.; Banerjee, S.; **Mondal, B.**; Nag, A. Colloidal Sb^{3+} -Doped $\text{Cs}_2\text{InCl}_5 \cdot \text{H}_2\text{O}$ Perovskite Nanocrystals with Temperature-Dependent Luminescence. *J. Phys. Chem. C* **2021**, 125, 27671–27677.
7. Ravi, V. K.; **Mondal, B.**; Nawale, V. V.; Nag, A. Don't Let the Lead Out: New Material Chemistry Approaches for Sustainable Lead Halide Perovskite Solar Cells. *ACS Omega* **2020**, 5 (46), 29631-29641. (mini review)
8. Arfin, H.; Kshirsagar, A. S.; Kaur, J.; **Mondal, B.**; Xia, Z.; Chakraborty, S.; Nag, A. ns^2 Electron (Bi^{3+} and Sb^{3+}) Doping in Lead-Free Metal Halide Perovskite Derivatives. *Chem. Mater.* **2020**, 32, 10255-10267. (perspective)

Copyrights and permissions

One-dimensional organic lead halide perovskites with efficient bluish white-light emission

Author: Zhao Yuan et al

Publication: Nature Communications

Publisher: Springer Nature

Date: Jan 4, 2017

Copyright © 2017, The Author(s)

SPRINGER NATURE

Creative Commons

This is an open access article distributed under the terms of the [Creative Commons CC BY](#) license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

You are not required to obtain permission to reuse this article.

To request permission for a type of use not listed, please contact [Springer Nature](#)

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5911140728643

License date Nov 17, 2024

Licensed Content Publisher John Wiley and Sons

Licensed Content Publication Advanced Materials

Licensed Content Title Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution

Licensed Content Author M.A. Hines, G.D. Scholes

Licensed Content Date Nov 6, 2003

Licensed Content Volume 15

Licensed Content Issue 21

Licensed Content Pages 6

Type of use Dissertation/Thesis

Requestor type University/Academic

Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
Portions	Figure 1.5 on page 9
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE Pune, Maharashtra 411008 India
Publisher Tax ID	EU826007151
Total	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular

work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade

name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com.

**Short-Wave Infrared Light-Emitting Diodes Using Colloidal CuInS₂ Quantum Dots with ZnI₂ Dual-Passivation****Author:** Zhenyang Liu, Chaoqi Hao, Yejing Liu, et al**Publication:** ACS Nano**Publisher:** American Chemical Society**Date:** Aug 1, 2024*Copyright © 2024, American Chemical Society***PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE**

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)[CLOSE WINDOW](#)

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5911150652316

License date Nov 17, 2024

Licensed Content Publisher John Wiley and Sons

Licensed Content Publication Angewandte Chemie International Edition

Licensed Content Title Bi³ -Er³ and Bi³ -Yb³ Codoped Cs₂AgInCl₆ Double Perovskite Near-Infrared Emitters

Licensed Content Author Habibul Arfin, Jagjit Kaur, Tariq Sheikh, et al

Licensed Content Date Mar 31, 2020

Licensed Content Volume 59

Licensed Content Issue 28

Licensed Content Pages 5

Type of use Dissertation/Thesis

Requestor type University/Academic

Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
Portions	Figure 1.7 a on page 11
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE Pune, Maharashtra 411008 India
Publisher Tax ID	EU826007151
Total	0.00 USD

Terms and Conditions

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular

work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade

name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com.



Structural Confinement for Cr³ Activators toward Efficient Near-Infrared Phosphors with Suppressed Concentration Quenching

Author: Fangyi Zhao, Hao Cai, Zhen Song, et al

Publication: Chemistry of Materials

Publisher: American Chemical Society

Date: May 1, 2021

Copyright © 2021, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5911150838032

License date Nov 17, 2024

Licensed Content Publisher John Wiley and Sons

Licensed Content Publication Angewandte Chemie International Edition

Licensed Content Title Broad Dual Emission by Codoping Cr³ (d→d) and Bi³ (s→p) in Cs₂Ag_{0.6}Na_{0.4}InCl₆ Double Perovskite

Licensed Content Author Sajid Saikia, Animesh Ghosh, Angshuman Nag

Licensed Content Date Jul 11, 2023

Licensed Content Volume 62

Licensed Content Issue 33

Licensed Content Pages 10

Type of use Dissertation/Thesis

Requestor type University/Academic

Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
Portions	Figure 1.7 c on page 11
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE Pune, Maharashtra 411008 India
Publisher Tax ID	EU826007151
Total	0.00 USD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular

work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade

name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com.

ELSEVIER LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	5911151173978
License date	Nov 17, 2024
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Alloys and Compounds
Licensed Content Title	Efficient ultra-broadband NIR-II emission achieved by multi-site occupancy in Mg ₃ Ga ₂ GeO ₈ : Ni ²⁺ phosphor
Licensed Content Author	Chengqian Wang, Jian Lin, Xin Zhang, Huafeng Dong, Minru Wen, Shuang Zhao, Shuwen Yuan, Daoyun Zhu, Fugen Wu, Zhongfei Mu
Licensed Content Date	5 May 2023
Licensed Content Volume	942
Licensed Content Issue	n/a
Licensed Content Pages	1
Start Page	168893

End Page	0
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
Portions	Figure 1.8 a on page 12
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE
Publisher Tax ID	Pune, Maharashtra 411008 India
	GB 494 6272 12

Total 0.00 USD

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your RightsLink account and that are available at any time at <https://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given. The material may not be reproduced or used in any other way, including use in combination with an artificial intelligence tool (including to train an algorithm, test, process, analyse, generate output and/or develop any form of artificial intelligence tool), or to create any derivative work and/or service (including resulting from the use of artificial intelligence tools).

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier's permissions helpdesk [here](#)). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional

translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. For journal authors: the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use

- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. For book authors the following clauses are applicable in addition to the above:

Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please

reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access

articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.10

Questions? customercare@copyright.com.

ELSEVIER LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	5911160045856
License date	Nov 17, 2024
Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Alloys and Compounds
Licensed Content Title	Near-infrared emitting microspheres of LaAlO ₃ :Mn ⁴⁺ : Defects engineering via Ge ⁴⁺ doping for greatly enhanced luminescence and improved afterglow
Licensed Content Author	Siyuan Li, Qi Zhu, Xiaodong Li, Xudong Sun, Ji-Guang Li
Licensed Content Date	Jun 25, 2020
Licensed Content Volume	827
Licensed Content Issue	n/a
Licensed Content Pages	1
Start Page	154365

End Page	0
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
Portions	Figure 1.8 b on page 12
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE
Publisher Tax ID	Pune, Maharashtra 411008 India
	GB 494 6272 12

Total 0.00 USD

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your RightsLink account and that are available at any time at <https://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given. The material may not be reproduced or used in any other way, including use in combination with an artificial intelligence tool (including to train an algorithm, test, process, analyse, generate output and/or develop any form of artificial intelligence tool), or to create any derivative work and/or service (including resulting from the use of artificial intelligence tools).

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier's permissions helpdesk [here](#)). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional

translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. For journal authors: the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use

- for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. For book authors the following clauses are applicable in addition to the above:

Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please

reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access

articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.10

Questions? customercare@copyright.com.

Electronic Spectra and Structures of d2 Molybdenum–Oxo Complexes. Effects of Structural Distortions on Orbital Energies, Two-Electron Terms, and the Mixing of Singlet and Triplet States



Author: Ryan E. Da Re, Michael D. Hopkins

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Dec 1, 2002

Copyright © 2002, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

BACK

CLOSE WINDOW

Electronic Absorption Spectra and Phosphorescence of Oxygen-Containing Molybdenum(IV) Complexes

Author: Ralph A. Isovitsch, A. Scott Beadle, Frank R. Fronczek, et al



Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Aug 1, 1998

Copyright © 1998, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)
[CLOSE WINDOW](#)

Coupled Electronic States in trans-Dioxo Complexes of Rhenium(V) and Osmium(VI) Probed by Near-Infrared and Visible Luminescence Spectroscopy



Author: Carole Savoie, Christian Reber

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Feb 1, 2000

Copyright © 2000, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)
[CLOSE WINDOW](#)

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 17, 2024

This Agreement between BARNALI MONDAL ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5911160273031

License date Nov 17, 2024

Licensed Content Publisher John Wiley and Sons

Licensed Content Publication ChemNanoMat

Licensed Content Title Yb3 -Doped Phenylethylammonium Lead Bromide 2D Layered Hybrid Perovskite for Near-Infrared Emission

Licensed Content Author Barnali Mondal, Athunya Poovathan, Tariq Sheikh, et al

Licensed Content Date May 12, 2022

Licensed Content Volume 8

Licensed Content Issue 8

Licensed Content Pages 7

Type of use Dissertation/Thesis

Requestor type Author of this Wiley article

Format	Print and electronic
Portion	Full article
Will you be translating?	No
Title of new work	Near-infrared Emission in Low-Dimensional Halide Perovskite Derivatives: Cs ₂ MX ₆ (M: Mo/W/Sn; X: Cl/Br) and (C ₈ H ₁₂ N) ₂ PbBr ₄ with Doping
Institution name	IISER Pune
Expected presentation date	Jan 2025
The Requesting Person / Organization to Appear on the License	BARNALI MONDAL
Requestor Location	Ms. BARNALI MONDAL MAIN ACADEMIC BUILDING, IISER PUNE Pune, Maharashtra 411008 India
Publisher Tax ID	EU826007151
Total	0.00 USD

Terms and Conditions

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner.**For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts,** You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto
- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS

OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.
- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud)

supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library

<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com.

Vibronically Coupled Near-Infrared Emission and Excitation from d-d Transitions of Cs₂MX₆ (M = Mo/W, X = Cl/Br)



Author: Barnali Mondal, Aparna Shinde, Parikshit Kumar Rajput, et al

Publication: ACS Energy Letters

Publisher: American Chemical Society

Date: Mar 1, 2024

Copyright © 2024, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)

[CLOSE WINDOW](#)