TUNING THE OPTICAL AND MAGNETIC PROPERTIES OF HALIDE LAYERED DOUBLE PEROVSKITES VIA DOPING AND ALLOYING

PRIYESH

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

PRIYESH

DEPARTMENT OF CHEMISTRY

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy
to the

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Dedicated to

my parents

CERTIFICATE

This is to certify that the thesis entitled, "**TUNING THE OPTICAL AND MAGNETIC PROPERTIES OF HALIDE LAYERED DOUBLE PEROVSKITES VIA DOPING AND ALLOYING**" being submitted by **Mr. Priyesh** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Priyesh has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Date

Dr. Sameer Sapra
Professor
Department of Chemistry
Indian Institute of Technology Delhi
New Delhi-110016

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Priyesh

ABSTRACT

The process of dimensional reduction leads to substantial modifications in the physical and electronic properties of a material. The dimensional reduction of inorganic sublattice of double perovskites by using organic molecule is an important strategy for achieving layered double perovskites (LDPs). LDPs significantly expand the compositional variety of halide perovskites and broadens their accessible electronic platforms. The distinct photophysical characteristics exhibited by two-dimensional (2D) double perovskites compared to their Pb-based counterparts, serve as a driving force for further exploration of this unexploited category of mixed-metal hybrids. Though LDPs are green alternatives of their Pb-based analogues, they are non-fluorescent at ambient conditions, which hinders their use in optoelectronic applications. Also, LDPs possess wide band gaps and most of them have their absorption in the ultraviolet (UV) region that limits their ability to fully utilize photons within the visible spectrum. The wide band gap of these LDPs hinders their further use in the field of photovoltaics and in other optoelectronic applications. The vast chemical and structural diversity of LDPs provides an unprecedented opportunity to modulate their structural, optical, magnetic and electronic properties. The present thesis focuses on how to utilize the vast chemical and structural diversity of LDPs to add new functionalities like optical emission, band gap reduction can be achieved via alloying or doping with some suitable metal ion in their inorganic sublattice or through intercalating certain molecules in the organic layer.

Chapter 1 and **2** are dedicated to the extensive literature survey of research work and the structure of halide Pb based three dimensional (3D) perovskites, 2D perovskites, and double perovskites and LDPs and a summary of different techniques used to analyse as-synthesized materials. In **Chapter 3**, we have successfully showed the synthesis of Mn^{2+} doped 2D $(BA)_4AgBiBr_8$ using a facile and cost-efficient method, which involves post synthetic cation exchange using mechanochemical grinding followed by thermal annealing. The structural,

optical, and magnetic studies confirm the successful incorporation of Mn^{2+} ions into the perovskite lattice. Interestingly, these Mn^{2+} doped 2D LDPs exhibit dual emission peak at low temperature, corresponding to host emission and the Mn^{2+} emission. In **Chapter 4**, we have shown that emission of $(PEA)_4NaInCl_8$ improved greatly at ambient conditions on doping it with Mn^{2+} cation. The shift in PXRD pattern, and XPS spectra of pure and doped materials confirms the presence of Mn^{2+} doped into both substitutional as well as interstitial sites of $(PEA)_4NaInCl_8$ lattice. The excitation at 420 nm light radiation for higher dopant concentrations, manifests the presence of magnetic interaction between Mn^{2+} pairs at interstitial sites, which is further confirmed by the merging of sextet into single broad peak with increase in dopant amount in EPR spectra. In **Chapter 5**, we have studied the incorporation of terbium into layered double perovskite $(PEA)_4NaInCl_8$ to enhance and control its luminescent characteristics. The doping was done via two ways: direct substitutional doping with Tb^{3+} ions and with Tb^{3+} in the form of tetrakis β-diketonate complex $Tb(hfa)_4.P(Ph)_4$, Tb(L). In case of $(PEA)_4NaInCl_8$:Tb^{3+}, sensitization of Tb^{3+} is achieved through host to dopant energy transfer process. However, the non-ideal arrangement of energy levels of host and dopants, obstruct the complete energy transfer to Tb^{3+}, resulting in the non-radiative transitions which results into the reduction of the PLQY (3%). On the other hand, by protecting Tb^{3+} using hfa (hexafluoroacetylacetone) ligands to form Tb(L), we have optimized the energetic landscape for Tb^{3+} sensitization, resulting in the improvement in luminescence efficiency, with PLQY enhanced to 62% in $(PEA)_4NaInCl_8$:Tb(L). In **Chapter 6**, we report the synthesis of transition metal alloyed Fe^{3+} : $(PEA)_4NaInCl_8$ LDP using different concentrations of Fe^{3+}. From the PXRD analysis, we observed the different trend of d-spacing of (0k0) planes than the other planes. This abnormal observation was obtained due the combined effect of smaller size of Fe^{3+} as compared to In^{3+} and due to the increase in M^{I}-Cl-M'^{III} bond angle on alloying with Fe^{3+}. Again on alloying with Fe^{3+}, their optical band gap reduces from 4.46 eV in pure

$(PEA)_4NaInCl_8$ to 2.30 eV in $(PEA)_4NaFeCl_8$. This reduction in band gap is due to increase in orbital overlap in M^{I}-Cl-M'^{III} because of increase in bond angle on alloying. Further, our magnetic susceptibility data show that these Fe^{3+} alloyed LDPs have AFM interactions and we found no transition temperature for In/Fe alloyed samples in the measured limit of the temperature. Magnetic parameters like Curie-Weiss temperature, Curie constant, saturation magnetization are readily tuneable with concentration of Fe^{3+} within the LDP lattice. **Chapter 7** provides a comprehensive overview of the thesis, with a particular focus on employing diverse chemical substitution techniques such as doping, intercalation and alloying for adding new functionalities to the halide layered double perovskites and provides a glimpse into the future prospects and potential implications of the work presented in this study.

संक्षेपण

आयामी कमी की प्रक्रिया से किसी सामग्री के भौतिक और इलेक्ट्रॉनिक गुणों में पर्याप्त संशोधन होता है। कार्बनिक अणु का उपयोग करके डबल पेरोव्स्काइट्स के अकार्बनिक सबलैटिस की आयामी कमी स्तरित डबल पेरोव्स्काइट्स (एलडीपी) प्राप्त करने के लिए एक महत्वपूर्ण रणनीति है। एलडीपी हेलाइड पेरोव्स्काइट्स की संरचनागत विविधता का महत्वपूर्ण रूप से विस्तार करते हैं और उनके सुलभ इलेक्ट्रॉनिक प्लेटफार्मों का विस्तार करते हैं। उनके Pb-आधारित समकक्षों की तुलना में द्वि-आयामी (2डी) डबल पेरोव्स्काइट्स द्वारा प्रदर्शित विशिष्ट फोटोफिजिकल विशेषताएं, मिश्रित-धातु संकरों की इस अप्रयुक्त श्रेणी की आगे की खोज के लिए एक प्रेरक शक्ति के रूप में काम करती हैं। यद्यपि एलडीपी उनके Pb-आधारित एनालॉग्स के हरे विकल्प हैं, वे परिवेशी परिस्थितियों में गैर-फ्लोरोसेंट हैं, जो ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों में उनके उपयोग में बाधा डालते हैं। इसके अलावा, एलडीपी में व्यापक बैंड अंतराल होते हैं और उनमें से अधिकांश का अवशोषण पराबैंगनी (यूवी) क्षेत्र में होता है जो दृश्य स्पेक्ट्रम के भीतर फोटॉन का पूरी तरह से उपयोग करने की उनकी क्षमता को सीमित करता है। इन एलडीपी का विस्तृत बैंड गैप फोटोवोल्टिक्स और अन्य ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों के क्षेत्र में उनके आगे के उपयोग में बाधा डालता है। एलडीपी की विशाल रासायनिक और संरचनात्मक विविधता उनके संरचनात्मक, ऑप्टिकल, चुंबकीय और इलेक्ट्रॉनिक गुणों को संशोधित करने का एक अभूतपूर्व अवसर प्रदान करती है। वर्तमान थीसिस इस बात पर केंद्रित है कि ऑप्टिकल उत्सर्जन जैसी नई कार्यक्षमताओं को जोड़ने के लिए एलडीपी की विशाल रासायनिक और संरचनात्मक विविधता का उपयोग कैसे किया जाए, बैंड गैप में कमी को उनके अकार्बनिक सबलैटिस में कुछ उपयुक्त धातु आयन के साथ मिश्रधातु या डोपिंग के माध्यम से या कुछ अणुओं को आपस में जोड़कर प्राप्त किया जा सकता है। अध्याय 1 और 2 शोध कार्य के व्यापक साहित्य सर्वेक्षण और हैलाइड Pb आधारित तीन आयामी (3डी) पेरोव्स्काइट्स, 2डी पेरोव्स्काइट्स और डबल पेरोव्स्काइट्स और एलडीपी की संरचना और संश्लेषित सामग्रियों का

विश्लेषण करने के लिए उपयोग की जाने वाली विभिन्न तकनीकों के सारांश के लिए समर्पित हैं। अध्याय 3 में, हमने एक सुविधाजनक और लागत-कुशल विधि का उपयोग करके Mn^{2+} डोप्ड 2D $(BA)_4AgBiBr_8$ के संश्लेषण को सफलतापूर्वक दिखाया है, जिसमें मैकेनोकेमिकल पीसने के बाद थर्मल एनीलिंग का उपयोग करके सिंथेटिक कटियन एक्सचेंज शामिल है। संरचनात्मक, ऑप्टिकल और चुंबकीय अध्ययन पेरोव्स्काइट जाली में Mn^{2+} आयनों के सफल समावेश की पुष्टि करते हैं। दिलचस्प बात यह है कि ये Mn^{2+}डोप्ड 2डी एलडीपी कम तापमान पर दोहरे उत्सर्जन शिखर को प्रदर्शित करते हैं, जो मेजबान उत्सर्जन और Mn^{2+}उत्सर्जन के अनुरूप है। अध्याय 4 में, हमने दिखाया है कि $(PEA)_4NaInCl_8$ को Mn^{2+} धनायन के साथ मिलाने पर परिवेशीय स्थितियों में इसके उत्सर्जन में काफी सुधार हुआ है। PXRD पैटर्न में बदलाव, और शुद्ध और डोप्ड सामग्रियों के एक्सपीएस स्पेक्ट्रा, $(PEA)_4NaInCl_8$ जाली के संस्थागत और अंतरालीय दोनों साइटों में डोप किए गए Mn^{2+} की उपस्थिति की पुष्टि करते हैं। उच्च डोपेंट सांद्रता के लिए 420 nm प्रकाश विकिरण पर उत्तेजना, अंतरालीय स्थलों पर Mn^{2+} जोड़े के बीच चुंबकीय संपर्क की उपस्थिति को प्रकट करती है, जिसे EPR स्पेक्ट्रा में डोपेंट मात्रा में वृद्धि के साथ एकल व्यापक शिखर में सेक्सेट के विलय से पुष्टि की जाती है। अध्याय 5 में हमने इसकी ल्यूमिनसेंट विशेषताओं को बढ़ाने और नियंत्रित करने के लिए लेयर्ड डबल पेरोव्स्काइट $(PEA)_4NaInCl_8$ में टेरबियम (Tb) के समावेश का अध्ययन किया है। डोपिंग दो तरीकों से की गई थी: Tb^{3+} आयनों के साथ प्रत्यक्ष संस्थागत डोपिंग और Tb^{3+} के साथ टेट्राकिस β-डाइकेटोनेट कॉम्प्लेक्स $Tb(hfa)_4.P(Ph)_4$, Tb(L) के रूप में। $(PEA)_4NaInCl_8$:Tb^{3+} के मामले में, Tb^{3+} का संवेदीकरण मेजबान से डोपेंट ऊर्जा हस्तांतरण प्रक्रिया के माध्यम से प्राप्त किया जाता है। हालाँकि, मेजबान और डोपेंट के ऊर्जा स्तरों की गैर-आदर्श व्यवस्था, Tb^{3+} में पूर्ण ऊर्जा हस्तांतरण को बाधित करती है, जिसके परिणामस्वरूप गैर-विकिरणीय संक्रमण होता है जिसके परिणामस्वरूप PLQY (3%) में कमी आती है। दूसरी ओर, Tb(L) बनाने के लिए एचएफए (हेक्साफ्लोरोएसिटाइलसिटोन) लिगैंड का उपयोग करके Tb^{3+} की रक्षा करके, हमने Tb^{3+} संवेदीकरण के लिए ऊर्जावान परिदृश्य को अनुकूलित किया है,

जिसके परिणामस्वरूप ल्यूमिनेसेंस दक्षता में सुधार हुआ है, PLQY को $(PEA)_4NaInCl_8$:Tb(L) में 62% तक बढ़ाया गया है। अध्याय 6 में, हम Fe^{3+} की विभिन्न सांद्रता का उपयोग करके संक्रमण धातु मिश्रित Fe^{3+}: $(PEA)_4NaInCl_8$ LDP के संश्लेषण की रिपोर्ट करते हैं। PXRD विश्लेषण से, हमने अन्य विमानों की तुलना में (0k0) विमानों के d-स्पेसिंग की अलग प्रवृत्ति देखी। यह असामान्य अवलोकन In^{3+} की तुलना में Fe^{3+} के छोटे आकार के संयुक्त प्रभाव और Fe^{3+} के साथ मिश्रधातु पर M^{I}-Cl-M'^{III} बंधन कोण में वृद्धि के कारण प्राप्त हुआ था। फिर से Fe^{3+} के साथ मिश्रधातु बनाने पर, उनका ऑप्टिकल बैंड गैप शुद्ध $(PEA)_4NaInCl_8$ में 4.46 eV से घटकर $(PEA)_4NaFeCl_8$ में 2.30 eV हो जाता है। बैंड गैप में यह कमी मिश्र धातु पर बॉन्ड कोण में वृद्धि के कारण M^{I}-Cl-M'^{III} में कक्षीय ओवरलैप में वृद्धि के कारण है। इसके अलावा, हमारे चुंबकीय संवेदनशीलता डेटा से पता चलता है कि इन Fe^{3+} मिश्र धातु एलडीपी में AFM इंटरैक्शन हैं और हमें तापमान की मापी गई सीमा में In/Fe मिश्र धातु नमूनों के लिए कोई संक्रमण तापमान नहीं मिला। क्यूरी-वीस तापमान, क्यूरी स्थिरांक, संतृप्ति चुंबकत्व जैसे चुंबकीय पैरामीटर एलडीपी जाली के भीतर Fe^{3+} की सांद्रता के साथ आसानी से ट्यून किए जा सकते हैं। अध्याय 7 थीसिस का व्यापक अवलोकन प्रदान करता है, जिसमें हैलाइड स्तरित डबल पेरोव्स्काइट्स में नई कार्यक्षमताओं को जोड़ने के लिए डोपिंग, इंटरकलेशन और मिश्र धातु जैसी विविध रासायनिक प्रतिस्थापन तकनीकों को नियोजित करने पर विशेष ध्यान दिया गया है और भविष्य की संभावनाओं और संभावित निहितार्थों की एक झलक प्रदान की गई है।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

MHPs	metal-halide perovskites
LHPs	lead halide perovskites
PV	photovoltaic
PLQY	photoluminescence quantum yield
LEDs	light-emitting diodes
MA	methyl amine
FA	formamidium
3D	three dimensional
t	Goldschmidt tolerance factor
τ	new tolerance factor
μ	octahedral factor
r	ionic radii
2D	two-dimensional
RP	Ruddlesden-popper
DJ	Dion-Jacobson
BA	n-butyl amine
PA	n-propyl amine
HA	n-hexyl amine
PEA	Phenylethyl amine
LDPs	layered double perovskites
Pb	Lead
E_g	band gap
E_b	binding energy

EQE	external quantum efficiency
PCE	power conversion efficiency
MQW	multiple-quantum-well
VBM	valence-band maxima
CBM	conduction-band minima
MMCT	metal to metal charge transfer
PXRD	powder X-ray diffraction
CCD	configuration coordination diagram
GS	ground state
ES	excited state
UV	ultraviolet
PL	photoluminescence
θ_{CW}	Curie-Weiss temperature
C	Curie constant
M_s	saturation magnetization
FESEM	field emission scanning electron microscopy
TRPL	time resolved photoluminescence
FTIR	Fourier transform infrared
XPS	X-ray photoelectron spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
EPR	electron paramagnetic resonance
FWHM	full width at half maximum
EDX	Energy dispersive X-ray
ps	picosecond
ns	nanoseconds

μs	microseconds
ms	millisecond
IC	internal conversion
ISC	intersystem crossing
VSM	Vibrating sample magnetometer
χ	magnetic susceptibility
FC	Field cooled
ZFC	Zero field cooled
PPMS	Physical property measurement system
DRS	diffuse reflectance spectra
PLE	photoluminescence excitation
DFT	density functional theory
STEs	self-trapped excitons
PAW	projected augmented wave
VASP	Vienna ab initio Simulation Package
GGA	generalized gradient approximation
PBE	Perdew–Burke–Ernzerhof
CG	conjugate gradient
hfa	hexafluoroacetylacetonate
SSL	solid state lighting
AFM	antiferromagnetic
pm	picometer
Å	angstrom
T_N	Neel temperature