

**MODULATING OPTICAL PROPERTIES OF
LEAD-FREE HALIDE DOUBLE PEROVSKITES
BY CHEMICAL SUBSTITUTION**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

RAMAN

DEPARTMENT OF CHEMISTRY

Submitted

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



INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2023

Dedicated to

My Parents

CERTIFICATE

It is to certify that the thesis entitled, “**Modulating Optical Properties of Lead-Free Halide Double Perovskites by Chemical Substitution**” being submitted by **Mr. RAMAN** 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. RAMAN** 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

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ABSTRACT

The unique properties of halide double perovskite (DP) materials include defect tolerance and tunable bandgap. The double perovskite materials are greener potential alternatives of well-known lead based halide perovskite semiconductors. The most of halide double perovskites have wide bandgap and are weakly luminescent, hence these are not useful for most of the optoelectronic properties. It becomes very important to modulate their optical properties to make them more useful for optoelectronic device applications. Doping and alloying are the chemical substitution approach which are proved to be an effective way to modify the properties of these materials. $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Cl}, \text{Br}$) are the well-known double perovskites having wide indirect bandgap and very weak photoluminescence (PL) intensity. These halide double perovskites are stable and well-studied, but their poor optoelectronic properties limit their application. To tune the bandgap of $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Cl}, \text{Br}$) we did the alloying of these materials with Na and synthesized a series of $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiX}_6$ ($X = \text{Cl}, \text{Br}$) nanocrystals (NCs) by colloidal hot injection method. These alloyed materials have tunable bandgap which increase with increase in Na/Ag ratio in the lattice. Also the PL intensity of alloyed materials is higher than end members of the series. To make the $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiCl}_6$ materials more useful we add the NIR PL in these materials and sensitize the emission of Er^{3+} and Yb^{3+} ions using these host lattices. We doped Er^{3+} and Yb^{3+} in the $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiCl}_6$ NCs which make them luminescent in the NIR region. The NIR PL centred at 1540 nm and 1000 nm is attributed to the f-f transition of Er^{3+} and Yb^{3+} . $\text{Cs}_2\text{AgBiCl}_6$ is a high bandgap double perovskite with narrow absorption window which makes it useless for light harvesting application. To tackle this problem, we doped the transition metal Cu in $\text{Cs}_2\text{AgBiCl}_6$ by using hydrothermal method and solvent free mechanochemical grinding methods. The Cu doping extend the absorption window to NIR region and make this material a potential candidate for light harvesting applications. The work in this thesis emphasizes how to modulate the optical properties of these different

lead free halide double perovskite materials to make them useful for different optoelectronic applications.

Chapter 1 deals with the structure and properties of lead halide perovskites and lead free halide double perovskites. This chapter includes the advantage and limitations of lead halide perovskite materials, and we also discussed about the need of lead free double perovskite materials, and different strategies like doping and alloying to modify their optoelectronic properties. This chapter also comprises the objective of the thesis. **Chapter 2** includes different tools and methods for characterizing synthesized double perovskites. In this chapter we also discussed the working principle of the various characterization techniques in detail. Next two chapters (**Chapter 3 and 4**) are dedicated towards the synthesis and characterization of a series of $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiX}_6$ ($\text{X} = \text{Cl, Br}$) alloyed double perovskite nanocrystals (NCs) with tunable bandgap. The optical properties $\text{Cs}_2\text{AgBiX}_6$ ($\text{X} = \text{Cl, Br}$) NCs is tuned by inseting the Na+ cation and varying the ratio of Na and Ag cations, resulting in the formation of $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiX}_6$ ($\text{X} = \text{Cl, Br}$) NCs (where x varies between 0 to 1). In **Chapter 5**, we synthesized the Ln^{3+} ($\text{Ln}^{3+} = \text{Er}^{3+}$ and Yb^{3+}) doped $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiCl}_6$ NCs using hot injection method. These doped NCs emit a sharp NIR photoluminescence (PL) at 1540 nm and 1000 nm which is attributed to $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of the Er^{3+} and $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of the Yb^{3+} , respectively. The $\text{Cs}_2\text{Na}_{0.75}\text{Ag}_{0.25}\text{BiCl}_6$ is found to be the best host lattice to sensitize the emission of Er^{3+} and Yb^{3+} , out of all the members of the series of $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiCl}_6$. We also explore the co-doping of Er^{3+} and Yb^{3+} in $\text{Cs}_2\text{Na}_{0.75}\text{Ag}_{0.25}\text{BiCl}_6$, photoluminescence (PL) at 1540 nm and 1000 nm which is attributed to $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of the Er^{3+} and $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition of the Yb^{3+} , respectively. We also discuss the energy transfer from host lattice to these Ln^{3+} dopant ions. In **Chapter 6**, we discuss the synthesis and characterization of Cu doped $\text{Cs}_2\text{AgBiCl}_6$ by hydrothermal method, and we also explored the Cu doping with two other methods namely, post synthetic grinding method and solvent free mechanochemical

grinding method. The absorption band of $\text{Cs}_2\text{AgBiCl}_6$ double perovskite having high bandgap (2.77 eV) is significantly broadened upto NIR region (~ 1800 nm) by doping with transition metal Cu. Furthermore, the materials synthesized by mechanochemical grinding method have stronger absorption in NIR region as compared to those synthesized hydrothermally. Extended absorption edge upto ~ 850 nm and broad absorption between 850 nm to 1800 nm is attributed to the formation of new sub band gap states and d-d transition of Cu doped in the lattice, respectively. In **Chapter 7**, we have summarized the thesis, emphasizing the use of different chemical substitution approach like doping and alloying to modify the optical properties of halide double perovskites.

सार

हैलाइड डबल पेरोस्काइट (डीपी) सामग्री के अद्वितीय गुणों में दोष सहिष्णुता और ट्यून करने योग्य बैंडगैप शामिल हैं। डबल पेरोस्काइट सामग्रियां सुप्रसिद्ध Pb आधारित हैलाइड पेरोस्काइट अर्धचालकों के हरित संभावित विकल्प हैं। अधिकांश हैलाइड डबल पेरोस्काइट्स में व्यापक बैंडगैप होता है और कमजोर ल्यूमिनसेंट होते हैं, इसलिए ये अधिकांश ऑप्टोइलेक्ट्रॉनिक गुणों के लिए उपयोगी नहीं होते हैं। ऑप्टोइलेक्ट्रॉनिक डिवाइस अनुप्रयोगों के लिए उन्हें अधिक उपयोगी बनाने के लिए उनके ऑप्टिकल गुणों को संशोधित करना बहुत महत्वपूर्ण हो जाता है। डोपिंग और मिश्रधातु रासायनिक प्रतिस्थापन दृष्टिकोण हैं जो इन सामग्रियों के गुणों को संशोधित करने का एक प्रभावी तरीका साबित होते हैं। Cs_2AgBiX_6 ($X = Cl, Br$) व्यापक अप्रत्यक्ष बैंडगैप और बहुत कमजोर फोटोल्यूमिनेसेंस (PL) तीव्रता वाले प्रसिद्ध डबल पेरोस्काइट हैं। ये हैलाइड डबल पेरोस्काइट स्थिर और अच्छी तरह से अध्ययन किए गए हैं, लेकिन उनके खराब ऑप्टोइलेक्ट्रॉनिक गुण उनके अनुप्रयोग को सीमित करते हैं। Cs_2AgBiX_6 ($X = Cl, Br$) के बैंडगैप को ट्यून करने के लिए हमने इन सामग्रियों को Na के साथ मिश्रित किया और कोलाइडल हॉट इंजेक्शन विधि द्वारा $Cs_2Na_xAg_{1-x}BiX_6$ ($X = Cl, Br$) नैनोक्रिस्टल (NCs) की एक श्रृंखला को संश्लेषित किया। इन मिश्रित सामग्रियों में ट्यून करने योग्य बैंडगैप होता है जो जाली में Na/Ag अनुपात में वृद्धि के साथ बढ़ता है। इसके अलावा मिश्रधातु सामग्रियों की पीएल तीव्रता श्रृंखला के अंतिम सदस्यों की तुलना में अधिक है। $Cs_2Na_xAg_{1-x}BiCl_6$ सामग्रियों को अधिक उपयोगी बनाने के लिए हम इन सामग्रियों में NIR PL जोड़ते हैं और इन होस्ट लैटिस का उपयोग करके Er^{3+} और Yb^{3+} आयनों के उत्सर्जन को संवेदनशील बनाते हैं। हमने $Cs_2Na_xAg_{1-x}BiCl_6NCs$ में Er^{3+} और Yb^{3+} को डोप किया जो उन्हें NIR क्षेत्र में चमकदार बनाता है। 1540 एनएम और 1000 एनएम पर केंद्रित एनआईआर पीएल को Er^{3+} और Yb^{3+} के एफ-एफ संक्रमण के लिए जिम्मेदार ठहराया गया है। $Cs_2AgBiCl_6$ संकीर्ण अवशोषण खिड़की वाला एक उच्च बैंडगैप डबल पेरोस्काइट है जो इसे हल्के संचयन अनुप्रयोग के लिए बेकार बनाता है। इस समस्या

से निपटने के लिए, हमने हाइड्रोथर्मल विधि और विलायक मुक्त मैकेनोकेमिकल पीसने के तरीकों का उपयोग करके संक्रमण धातु Cu को $\text{Cs}_2\text{AgBiCl}_6$ में मिलाया। Cu डोपिंग अवशोषण विंडो को NIR क्षेत्र तक बढ़ाती है और इस सामग्री को हल्के संचयन अनुप्रयोगों के लिए संभावित उम्मीदवार बनाती है। इस थीसिस में काम इस बात पर जोर देता है कि इन विभिन्न के ऑप्टिकल गुणों को कैसे संशोधित किया जाए विभिन्न ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों के लिए उन्हें उपयोगी बनाने के लिए Pb मुक्त हैलाइड डबल पेरोव्स्काइट सामग्री। अध्याय 1 लेड हैलाइड पेरोव्स्काइट्स और लेड मुक्त हैलाइड डबल पेरोव्स्काइट्स की संरचना और गुणों से संबंधित है। इस अध्याय में Pb हैलाइड पेरोव्स्काइट सामग्रियों के लाभ और सीमाएं शामिल हैं, और हमने Pb मुक्त डबल पेरोव्स्काइट सामग्रियों की आवश्यकता और उनके ऑप्टोइलेक्ट्रॉनिक गुणों को संशोधित करने के लिए डोपिंग और मिश्रधातु जैसी विभिन्न रणनीतियों के बारे में भी चर्चा की है। इस अध्याय में थीसिस का उद्देश्य भी शामिल है। अध्याय 2 में संश्लेषित डबल पेरोव्स्काइट्स को चिह्नित करने के लिए विभिन्न उपकरण और विधियां शामिल हैं। इस अध्याय में हमने विभिन्न लक्षण वर्णन तकनीकों के कार्य सिद्धांत पर भी विस्तार से चर्चा की। अगले दो अध्याय (अध्याय 3 और 4) ट्यून करने योग्य बैंडगैप के साथ $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiX}_6$ ($X=\text{Cl}, \text{Br}$) मिश्रित डबल पेरोव्स्काइट नैनोकristल (NCs) की एक श्रृंखला के संश्लेषण और लक्षण वर्णन के लिए समर्पित हैं। ऑप्टिकल गुण $\text{Cs}_2\text{AgBiX}_6$ ($X = \text{Cl}, \text{Br}$) NCs को Na^+ धनायन को स्थापित करके और Na और Ag धनायनों के अनुपात को अलग-अलग करके ट्यून किया जाता है, जिसके परिणामस्वरूप $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiX}_6$ ($X = \text{Cl}, \text{Br}$) NCs (जहां x 0 से 1 के बीच भिन्न होता है)। अध्याय 5 में, हमने गर्म इंजेक्शन विधि का उपयोग करके Ln^{3+} ($\text{Ln}^{3+} = \text{Er}^{3+}$ और Yb^{3+}) डोपड $\text{Cs}_2(\text{Na}_x\text{Ag}_{1-x})\text{BiCl}_6$ NCs को संश्लेषित किया। ये डोप किए गए एनसी 1540 एनएम और 1000 एनएम पर एक तेज एनआईआर फोटोल्यूमिनेसेंस (पीएल) उत्सर्जित करते हैं, जो क्रमशः Er^{3+} के $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ संक्रमण और Yb^{3+} के $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ संक्रमण के लिए जिम्मेदार है। $\text{Cs}_2\text{Na}_{0.75}\text{Ag}_{0.25}\text{BiCl}_6$ को $\text{Cs}_2\text{Na}_x\text{Ag}_{1-x}\text{BiCl}_6$ की श्रृंखला के सभी सदस्यों में से, Er^{3+} और Yb^{3+} के उत्सर्जन को संवेदनशील बनाने के लिए सबसे अच्छा होस्ट जाली पाया गया है। हम

$\text{Cs}_2\text{Na}_{0.75}\text{Ag}_{0.25}\text{BiCl}_6$ में Er^{3+} और Yb^{3+} के सह-डोपिंग का भी पता लगाते हैं। 1540 एनएम और 1000 एनएम पर फोटोल्यूमिनेसेंस (पीएल) जो क्रमशः Er^{3+} के $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ संक्रमण और Yb^{3+} के $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ संक्रमण के लिए जिम्मेदार है। हम मेजबान जाली से इन Ln^{3+} डोपेंट आयनों में ऊर्जा हस्तांतरण पर भी चर्चा करते हैं। अध्याय 6 में, हम हाइड्रोथर्मल विधि द्वारा Cu डोपड $\text{Cs}_2\text{AgBiCl}_6$ के संश्लेषण और लक्षण वर्णन पर चर्चा करते हैं, और हमने दो अन्य तरीकों, अर्थात् पोस्ट सिंथेटिक पीसने की विधि और विलायक मुक्त मैकेनोकेमिकल पीसने की विधि के साथ Cu डोपिंग का भी पता लगाया है। उच्च बैंडगैप (2.77 eV) वाले $\text{Cs}_2\text{AgBiCl}_6$ डबल पेरोव्स्काइट के अवशोषण बैंड को संक्रमण धातु Cu के साथ डोपिंग द्वारा NIR क्षेत्र (~ 1800 एनएम) तक काफी बढ़ाया गया है। इसके अलावा, मैकेनोकेमिकल पीसने की विधि द्वारा संश्लेषित सामग्रियों का एनआईआर क्षेत्र में हाइड्रोथर्मल रूप से संश्लेषित पदार्थों की तुलना में अधिक मजबूत अवशोषण होता है। ~ 850 एनएम तक विस्तारित अवशोषण बढ़त और 850 एनएम से 1800 एनएम के बीच व्यापक अवशोषण को क्रमशः नए सब बैंड गैप राज्यों के गठन और जाली में डाले गए Cu के डी-डी संक्रमण के लिए जिम्मेदार ठहराया जाता है। अध्याय 7 में, हमने हैलाइड डबल पेरोव्स्काइट्स के ऑप्टिकल गुणों को संशोधित करने के लिए डोपिंग और मिश्रधातु जैसे विभिन्न रासायनिक प्रतिस्थापन दृष्टिकोण के उपयोग पर जोर देते हुए थीसिस का सारांश दिया है।

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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	Formamidinium
EA	ethyl amine
3D	three dimensional
t	Goldschmidt tolerance factor
τ	new tolerance factor
μ	octahedral factor
r	ionic radii
2D	two-dimensional
Pb	Lead
E_g	band gap
B.E	binding energy
EQE	external quantum efficiency
PCE	power conversion efficiency
DPs	double perovskites
VBM	valence-band maxima

PXRD	powder X-ray diffraction
GS	ground state
ES	excited state
UV	ultraviolet
PL	photoluminescence
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
μ s	microseconds
ms	millisecond
IC	internal conversion
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
pm	picometer
Å	angstrom
OA	Oleic acid
OLAm	Oleylamine
TMSCl	trimethylsilylchloride
TMSBr	trimethylsilylbromide
ODE	1-Octadecene
NIR	Near Infra-red
TCSPC	time-correlated single photon counting
TEM	transmission electron microscopy
HRTEM	High resolution transmission electron microscopy
HSE06	Heyd-Scuseria-Ernzerhof
eV	Electron volt
EDS	Energy-dispersive X-ray
IEC	International Electrotechnical Commission
JCPDS	Joint Committee on Powder Diffraction Standards
CCD	Charge-coupled device
NA_{obj}	objective numerical aperture
NA_{cond}	condenser numerical aperture
SAED	Selected area electron diffraction
A	Absorbance
T	Transmittance
ϵ	molar extinction coefficient

λ_{max}	Excitonic peak maxima
ISC	Intersystem crossing
K.E	Kinetic energy
HT	Hydrothermal
PSG	Post synthetic grinding
MCS	Mechanochemical synthesis
TGA	Thermogravimetric analysis
ICP-MS	Inductively Coupled Plasmon Mass Spectrometry