

**DESIGNING LAYERED HALIDE PEROVSKITES
FOR EFFICIENT OPTOELECTRONICS:
A COMPUTATIONAL APPROACH**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

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DEPARTMENT OF CHEMISTRY

Submitted

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



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JUNE 2026

Dedicated to Swostik, Reyansh, and my parents

Certificate

This is to certify that the thesis entitled “**Designing Layered Halide Perovskites for Efficient Optoelectronics: A Computational Approach**” being submitted by **Pabitra Kumar Nayak**, 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 under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which, to the best of my knowledge, has reached the required standard. The material contained in the thesis has not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

Prof. Dibyajyoti Ghosh

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Pabitra Kumar Nayak

Abstract

The global transition toward renewable energy has positioned solar photovoltaics as a cornerstone technology for sustainable electricity generation. Metal halide perovskites (MHPs) have emerged as transformative optoelectronic materials, with power conversion efficiencies surpassing 27% in merely 14 years of development. However, three-dimensional MHPs face critical challenges, including intrinsic instability under operational conditions, concerns about lead toxicity, and performance limitations due to nonradiative carrier recombination. Layered halide perovskites (LHPs), particularly Dion-Jacobson (DJ) phase materials with dicationic organic spacers, address several of these limitations through enhanced environmental stability, compact interlayer architectures that enable improved charge transport, and extensive compositional tunability. Despite remarkable experimental progress, a fundamental understanding of atomic-scale structural dynamics governed excited-state carrier behavior, recombination pathways, and charge transfer mechanisms, as well as influential structural descriptors for elusive structure-property correlations, remains inadequate, hindering rational materials design for optimized optoelectronic performance. This thesis presents a comprehensive computational investigation of DJ-phase LHPs and related lead-free perovskite architectures, systematically establishing structure-property relationships through integrated application of Density Functional Theory (DFT), *ab initio* molecular dynamics (AIMD), nonadiabatic molecular dynamics (NAMD), time-domain density functional theory (TD-DFT), and interpretable machine learning. The overarching objective is to develop atomistic design principles that enable simultaneous optimization of carrier lifetimes, charge transport characteristics, and stability in environmentally sustainable materials. First, we explore spacer layer engineering strategies to control structural dynamics and the behavior of excited-state carriers. We demonstrate that halogen functionalization of aromatic spacers, particularly strategic bromination patterns, dramatically extends carrier lifetimes by suppressing lattice fluctuations and weakening electron-phonon coupling through enhanced non-covalent interactions. Systematic investigations reveal that regioisomeric substitution, the spatial positioning of functional groups, serves as a decisive control parameter, producing 3-fold variations in hot carrier cooling times despite identical chemical composition. Most transformatively, we establish design principles for electroactive spacers featuring nitrogen-rich aromatic heterocycles that create type-II heterojunctions, enabling ultrafast interfacial charge transfer and potentially resolving the chronic out-of-plane transport bottleneck in layered architectures. Second, we systematically explore inorganic layer compositional engineering. A-cation mixing investigations reveal that cesium incorporation with methylammonium suppresses inter-octahedral angle fluctuations, extending carrier lifetimes in multilayered structures. B-site metal engineering reveals that mixed Pb-Sn compositions exhibit cooperative lattice strain relaxation, resulting in uniquely rigid frameworks with suppressed

bandgap fluctuations and extended carrier lifetimes, while simultaneously reducing lead content while maintaining performance. Interestingly, we discover that site-selective halide positioning within octahedra produces order-of-magnitude variations in carrier lifetimes despite identical stoichiometry. Equatorial bromide placement with axial iodides yields prolonged carrier lifetimes, surpassing even pure bromide systems, while the reverse arrangement reduces lifetimes to values comparable to pure iodide materials. This counterintuitive finding establishes spatial atomic arrangement as equally important as elemental composition in determining optoelectronic properties. Finally, we explore alternative lead-free architectures beyond layered structures. Investigations of vacancy-ordered perovskites reveal that inorganic A-site cations (cesium, rubidium) constrain lattice dynamics more effectively than organic methylammonium, reducing electron-phonon coupling and extending carrier lifetimes. Systematic studies of double perovskites demonstrate that external strain engineering modulates band structures, carrier effective masses, and exciton binding energies, providing pathways to optimize these inherently stable, lead-free materials for specialized applications. Throughout this thesis, interpretable machine learning frameworks, including SHAP analyses and mutual information correlations, identify critical structural descriptors that govern the hetero-interfacial dynamic interplay and spacer packing efficiency. These data-driven insights complement mechanistic understanding from atomistic simulations, establishing robust structure-property relationships. This work makes several novel contributions: (1) quantitative design principles for spacer functionalization and electroactive spacer engineering; (2) compositional engineering of inorganic octahedral frameworks, such as B-cation mixing or site-selective halide positioning as a powerful dimension for optoelectronic property control; (3) systematic evaluation of alternative lead-free architectures expanding the materials palette for sustainable optoelectronics; and (4) demonstration of integrated computational-ML methodologies for predicting complex structure-property relationships in hybrid organic-inorganic semiconductors. Collectively, these investigations provide a comprehensive roadmap for rational design of high-performance, environmentally sustainable perovskite optoelectronics, contributing to the urgent global transition toward renewable energy technologies.

संक्षेप

नवीकरणीय ऊर्जा की दिशा में वैश्विक संक्रमण ने सौर फोटोवोल्टिक प्रौद्योगिकी को सतत विद्युत उत्पादन की एक आधारशिला के रूप में स्थापित किया है। धातु हैलाइड पेरॉव्सकाइट (Metal Halide Perovskites; MHPs) अत्यंत परिवर्तनकारी प्रकाश-विद्युत सामग्रियों के रूप में उभरे हैं, जिनकी शक्ति रूपांतरण दक्षता केवल 14 वर्षों के विकास में 27% से अधिक हो चुकी है। तथापि, त्रि-आयामी MHPs को परिचालन परिस्थितियों में अंतर्निहित अस्थिरता, सीसे की विषाक्तता से संबंधित चिंताओं, तथा गैर-विकिरणीय वाहक पुनर्संयोजन के कारण प्रदर्शन सीमाओं जैसी गंभीर चुनौतियों का सामना करना पड़ता है।

परतदार हैलाइड पेरॉव्सकाइट (Layered Halide Perovskites; LHPs), विशेष रूप से द्विसंयोजक कार्बनिक स्पेसर युक्त डीऑन-जैकबसन (Dion-Jacobson; DJ) चरण की सामग्रियाँ, बेहतर पर्यावरणीय स्थिरता, सघन अंतःपरत संरचनाओं के माध्यम से उन्नत आवेश परिवहन, तथा व्यापक संघटनात्मक अनुकूलन क्षमता प्रदान कर इन सीमाओं को प्रभावी रूप से संबोधित करती हैं। इसके बावजूद, उत्तेजित अवस्था के वाहक व्यवहार, पुनर्संयोजन मार्गों एवं आवेश अंतरण तंत्रों को नियंत्रित करने वाली परमाण्विक स्तर की संरचनात्मक गतिकी, तथा जटिल संरचना-गुणधर्म सहसंबंधों को परिभाषित करने वाले निर्णायक संरचनात्मक वर्णकों की मौलिक समझ अभी भी अपर्याप्त बनी हुई है, जो तर्कसंगत सामग्री अभिकल्पना में बाधा उत्पन्न करती है।

यह शोध प्रबंध DJ-चरण LHPs तथा संबंधित सीसा-मुक्त पेरॉव्सकाइट संरचनाओं का एक व्यापक संगणनात्मक अध्ययन प्रस्तुत करता है, जिसमें Density Functional Theory (DFT), ab initio Molecular Dynamics (AIMD), Nonadiabatic Molecular Dynamics (NAMD), Time-Domain Density Functional Theory (TD-DFT) तथा व्याख्येय मशीन लर्निंग का एकीकृत अनुप्रयोग किया गया है। इस अध्ययन का प्रमुख उद्देश्य ऐसे परमाण्विक अभिकल्प सिद्धांत विकसित करना है, जो पर्यावरणीय रूप से सतत सामग्रियों में वाहक आयु, आवेश परिवहन गुणधर्मों तथा संरचनात्मक स्थिरता का समकालिक अनुकूलन संभव बना सकें।

प्रथम चरण में, संरचनात्मक गतिकी एवं उत्तेजित अवस्था के वाहक व्यवहार को नियंत्रित करने हेतु स्पेसर परत अभियांत्रिकी रणनीतियों का अध्ययन किया गया है। यह प्रदर्शित किया गया है कि एरोमैटिक स्पेसरों का हैलोजन कार्यात्मककरण, विशेष रूप से रणनीतिक ब्रोमिनेशन पैटर्न, गैर-सहसंयोजक अंतःक्रियाओं को सुदृढ़ कर जालकीय उतार-चढ़ाव को दबाता है तथा इलेक्ट्रॉन-फोनॉन युग्मन को कमजोर बनाते हुए वाहक आयु में नाटकीय वृद्धि करता है। प्रणालीबद्ध अध्ययनों से यह स्पष्ट होता है कि समान रासायनिक संघटन के बावजूद कार्यात्मक समूहों की स्थानिक व्यवस्था (regioisomeric substitution) एक निर्णायक नियंत्रण पैरामीटर के रूप में कार्य करती है, जिसके परिणामस्वरूप हॉट कैरियर शीतलन समय में 25-गुना तक का परिवर्तन देखा जाता है। विशेष रूप से, नाइट्रोजन-समृद्ध एरोमैटिक हेटरोसाइक्लिक युक्त विद्युत-सक्रिय स्पेसरों के लिए अभिकल्प सिद्धांत स्थापित किए गए हैं, जो टाइप-II हेटरोजंक्शन का निर्माण कर अतितीव्र अंतःफलक आवेश अंतरण को सक्षम बनाते हैं तथा परतदार संरचनाओं में विद्यमान आउट-ऑफ-प्लेन परिवहन बाधा को संभावित रूप से दूर करते हैं।

द्वितीय चरण में, अकार्बनिक परत संरचनाओं की संघटनात्मक अभियांत्रिकी का व्यवस्थित अध्ययन किया गया है। A-साइट कैटायन मिश्रण अध्ययनों से यह ज्ञात होता है कि मिथाइलअमोनियम के साथ सीज़ियम का सम्मिलन अंतर-अष्टफलीय कोणीय उतार-चढ़ाव को दबाकर बहु-परत संरचनाओं में वाहक आयु को बढ़ाता है। B-साइट धातु अभियांत्रिकी से यह उजागर होता है कि मिश्रित Pb-Sn संरचनाएँ सहकारी जालकीय तनाव शमन

प्रदर्शित करती हैं, जिसके परिणामस्वरूप कठोर ढाँचे, कम बैंडगैप उतार-चढ़ाव तथा दीर्घ वाहक आयु प्राप्त होती है, साथ ही सीसे की मात्रा में भी प्रभावी कमी आती है। विशेष रूप से, यह पाया गया कि अष्टफलक के भीतर हैलाइड आयनों की साइट-विशिष्ट स्थिति समान स्टॉइकियोमेट्री के बावजूद वाहक आयु में परिमाणात्मक परिवर्तन उत्पन्न कर सकती है। भूमध्यस्थ ब्रोमाइड एवं अक्षीय आयोडाइड की व्यवस्था अत्यधिक विस्तारित वाहक आयु प्रदान करती है, जो शुद्ध ब्रोमाइड प्रणालियों से भी अधिक है, जबकि विपरीत व्यवस्था वाहक आयु को शुद्ध आयोडाइड प्रणालियों के तुल्य स्तर तक घटा देती है। यह प्रतिकूल प्रतीत होने वाला निष्कर्ष दर्शाता है कि परमाण्विक स्थानिक व्यवस्था तत्वीय संघटन जितनी ही महत्वपूर्ण है।

अंततः, परतदार संरचनाओं से परे वैकल्पिक सीसा-मुक्त पेरोव्स्काइट वास्तुकलाओं का अध्ययन किया गया है। रिक्ति-आदेशित पेरोव्स्काइटों के विश्लेषण से यह स्पष्ट होता है कि अकार्बनिक A-साइट कैटायन (सीज़ियम, रुबिडियम) कार्बनिक मिथाइलमोनियम की तुलना में जालकीय गतिकी को अधिक प्रभावी रूप से नियंत्रित करते हैं, जिससे इलेक्ट्रॉन-फोनॉन युग्मन में कमी तथा वाहक आयु में वृद्धि होती है। डबल पेरोव्स्काइटों पर किए गए व्यवस्थित तनाव अभियांत्रिकी अध्ययनों से बैंड संरचना, वाहक प्रभावी द्रव्यमान तथा एक्साइटॉन बाइंडिंग ऊर्जा में नियंत्रित परिवर्तन संभव होते हैं, जो इन अंतर्निहित रूप से स्थिर, सीसा-मुक्त सामग्रियों को विशिष्ट अनुप्रयोगों हेतु अनुकूल बनाने के मार्ग प्रशस्त करते हैं।

पूरे शोध प्रबंध में व्याख्येय मशीन लर्निंग ढाँचे, जिनमें SHAP विश्लेषण तथा पारस्परिक सूचना सहसंबंध शामिल हैं, हेटरो-अंतरफलक गतिक अंतःक्रिया एवं स्पेसर पैकिंग दक्षता को नियंत्रित करने वाले महत्वपूर्ण संरचनात्मक वर्णकों की पहचान करते हैं। ये डेटा-आधारित अंतर्दृष्टियाँ परमाण्विक सिमुलेशन से प्राप्त यांत्रिक समझ को पूरक करती हैं तथा सुदृढ़ संरचना-गुणधर्म सहसंबंध स्थापित करती हैं।

यह कार्य निम्नलिखित नवीन योगदान प्रस्तुत करता है:

- (1) स्पेसर कार्यात्मककरण एवं विद्युत-सक्रिय स्पेसर अभियांत्रिकी हेतु मात्रात्मक अभिकल्प सिद्धांत;
- (2) अकार्बनिक अष्टफलकीय ढाँचों की संघटनात्मक अभियांत्रिकी, जैसे B-कैटायन मिश्रण तथा साइट-विशिष्ट हैलाइड व्यवस्था, को प्रकाश-विद्युत गुणधर्म नियंत्रण के एक प्रभावी आयाम के रूप में स्थापित करना;
- (3) वैकल्पिक सीसा-मुक्त वास्तुकलाओं का व्यवस्थित मूल्यांकन, जो सतत प्रकाश-विद्युत अनुप्रयोगों हेतु सामग्री परिदृश्य का विस्तार करता है; तथा
- (4) जटिल संरचना-गुणधर्म संबंधों की भविष्यवाणी हेतु एकीकृत संगणनात्मक-मशीन लर्निंग पद्धतियों का प्रदर्शन।

समग्र रूप से, यह शोध उच्च-प्रदर्शन, पर्यावरणीय रूप से सतत पेरोव्स्काइट प्रकाश-विद्युत सामग्रियों के तर्कसंगत अभिकल्प हेतु एक व्यापक रोडमैप प्रस्तुत करता है, जो नवीकरणीय ऊर्जा की दिशा में वैश्विक संक्रमण में महत्वपूर्ण योगदान देता है।

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