UNRAVELLING ELECTRONIC STRUCTURE IN MODULATING FUNCTIONAL PROPERTIES OF MATERIALS FOR ENERGY APPLICATIONS

PREETI BHUMLA

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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by

PREETI BHUMLA

Department of Physics

Submitted

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

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Dedicated to my beloved parents

Certificate

This is to certify that the thesis entitled "**Unravelling Electronic Structure in Modulating Functional Properties of Materials for Energy Applications**," being submitted by **Preeti Bhumla** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Physics, is a record of bonafide research work carried out by her under my supervision and guidance. She 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. Saswata Bhattacharya
Thesis Supervisor
Department of Physics,
Indian Institute of Technology Delhi,
Hauz Khas, New Delhi 110016, India.
Date:.....
Place: New Delhi

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Abstract

Energy materials encompass a wide range of materials crucial for various energy-related processes, including energy generation, storage, and transformation. With the world facing an ever-increasing need for energy resources, the advancement and utilization of energy materials are paramount for ensuring a sustainable future. Here, we study–catalysts for methane activation and hydrogen production, and perovskites for solar cells and thermoelectric devices.

Methane is a potent greenhouse gas, making its conversion into valuable products essential. However, the efficient activation of methane poses a significant challenge due to its strong C-H bonds (4.5 eV), low polarizability, and negligible electron affinity. To circumvent this challenge, an appropriate catalyst is required. In view of this, we study the transition metal, Ni_4 in a reactive atmosphere of O_2 and CH_4 gas. It adsorbs these gases and form intermediate phases $[Ni_4O_x(CH_4)_y]$. We examine the thermodynamic stability of these phases at finite temperatures and pressures using *ab initio* atomistic thermodynamics (*ai*AT). Additionally, to account for anharmonicity in the vibrational free energy contribution to the configurational entropy, we employ thermodynamic integration method. The inclusion of anharmonic effects proves crucial in detecting the activation of the C-H bond.

After this, we explore the perovskite materials for energy applications. Lead halide perovskites have gained considerable attention due to their unique characteristics in optoelectronics and spintronics. We study inorganic $CsPbF_3$ perovskite in terms of its spintronic applications. The presence of spin-orbit coupling (SOC) arising from lead (Pb) in the non-centrosymmetric phase of $CsPbF_3$ indicates the possibility of Rashba-Dresselhaus (RD) splitting within this material. We investigate this RD splitting and reversible spin textures in $R3c$ phase employing the perturbative ***k.p*** formalism alongside first-principles calculations. Subsequently, we investigate the vacancy-ordered double perovskites (VODPs) and their prospective applications in optoelectronics and thermoelectrics. These VODPs exhibit bandgaps in the visible region, making them promising candidates for optoelectronic devices. Notably, they possess

ultralow thermal conductivity, rendering them appealing for thermoelectric applications. In our work, we thoroughly investigate the thermoelectric properties of these VODPs. Furthermore, we enhance the thermoelectric characteristics of the GeTe semiconductor by manipulating its electronic structure and lattice dynamics through doping.

We employ a robust methodological approach that integrates different levels of theories combined into one multi-scale simulation to address the various properties of materials. In this thesis, the state-of-the-art methodologies utilized to obtain the desired objectives are: (i) density functional theory (DFT) for ground-state properties, (ii) cascade genetic algorithm (cGA) to determine global minimum structures (ii) *ab initio* atomistic thermodynamics to predict the stability, (iii) many-body perturbation theory (GW) for excited-state properties, (iv) climbing image nudged elastic band (CINEB) method to calculate activation energies, and (v) boltzmann transport theory to compute thermoelectric properties.

सार

ऊर्जा सामग्री में ऊर्जा उत्पादन, भंडारण और परिवर्तन सहित विभिन्न ऊर्जा-संबंधित प्रक्रियाओं के लिए महत्वपूर्ण सामग्रियों की एक विस्तृत श्रृंखला शामिल है। दुनिया को ऊर्जा संसाधनों की लगातार बढ़ती आवश्यकता का सामना करने के साथ, एक स्थायी भविष्य सुनिश्चित करने के लिए ऊर्जा सामग्रियों की उन्नति और उपयोग सर्वोपरि है। यहां, हम मीथेन सक्रियण और हाइड्रोजन उत्पादन के लिए उत्प्रेरक, और सौर कोशिकाओं और थर्मोइलेक्ट्रिक उपकरणों के लिए पेरोव्स्काइट्स का अध्ययन करते हैं।

मीथेन एक शक्तिशाली ग्रीनहाउस गैस है, जिसका मूल्यवान उत्पादों में रूपांतरण आवश्यक है। हालाँकि, मीथेन का कुशल सक्रियण इसके मजबूत सी-एच बांड (4.5 ईवी), कम ध्रुवीकरण और नगण्य इलेक्ट्रॉन बंधुता के कारण एक महत्वपूर्ण चुनौती पेश करता है। इस चुनौती से निपटने के लिए एक उपयुक्त उत्प्रेरक की आवश्यकता है। इसे देखते हुए, हम O_2 और CH_4 गैस के प्रतिक्रियाशील वातावरण में संक्रमण धातु, Ni_4 का अध्ययन करते हैं। यह इन गैसों को सोख लेता है और मध्यवर्ती चरण $[Ni_4O_x(CH_4)_y]$ बनाता है। हम एब इनिटियो एटमिस्टिक थर्मोडायनामिक्स (एआईएटी) का उपयोग करके सीमित तापमान और दबाव पर इन चरणों की थर्मोडायनामिक स्थिरता की जांच करते हैं। इसके अतिरिक्त, कॉन्फ़िगरेशन एन्ट्रापी में कंपन मुक्त ऊर्जा योगदान में असंगतता को ध्यान में रखते हुए, हम थर्मोडायनामिक एकीकरण विधि को नियोजित करते हैं। सी-एच बांड की सक्रियता का पता लगाने में एनार्मोनिक प्रभावों का समावेश महत्वपूर्ण साबित होता है।
इसके बाद, हम ऊर्जा अनुप्रयोगों के लिए पेरोव्स्काइट सामग्रियों का पता लगाते हैं। ऑप्टोइलेक्ट्रॉनिक्स और स्पिंट्रोनिक्स में अपनी अनूठी विशेषताओं के कारण लेड हैलाइड पेर-ओव्स्काइट्स ने काफी ध्यान आकर्षित किया है। हम इसके स्पिंट्रोनिक अनुप्रयोगों के संदर्भ में अकार्बनिक $CsPbF_3$ पेरोव्स्काइट का अध्ययन करते हैं। $CsPbF_3$ के गैर-सेंट्रोसिमेट्रिक चरण में लेड (Pb) से उत्पन्न होने वाली स्पिन-ऑर्बिट युग्मन (SOC) की उपस्थिति इस सामग्री के भीतर रशबा-ड्रेसलहाउस (RD) के विभाजन की संभावना को इंगित करती है। हम आर3सी चरण में इस आरडी विभाजन और प्रतिवर्ती स्पिन बनावट की जांच करते हैं, जिसमें पहले-सिद्धांतों की गणना के साथ-साथ गड़बड़ी केपी औपचारिकता को नियोजित किया जाता है। इसके बाद, हम रिक्ति-आदेशित डबल पेरोव्स्काइट्स (वीओडीपी) और ऑप्टोइलेक्ट्रॉनिक्स और थर्मोइलेक्ट्रिक्स में उनके संभावित अनुप्रयोगों की जांच करते हैं। ये वीओडीपी दृश्य क्षेत्र में बैंडगैप प्रदर्शित करते हैं, जिससे वे ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए आशाजनक उम्मीदवार बन जाते हैं। विशेष रूप से, उनमें अल्ट्रालो तापीय चालकता होती है, जो उन्हें थर्मोइलेक्ट्रिक अनुप्रयोगों के लिए आकर्षक बनाती है। अपने काम में, हम इन वीओडीपी के थर्मोइलेक्ट्रिक गुणों की गहन जांच करते हैं। इसके अलावा, हम डोपिंग के माध्यम से इसकी इलेक्ट्रॉनिक संरचना और जाली गतिशीलता में हेरफेर करके GeTe सेमीकंडक्टर की थर्मोइलेक्ट्रिक विशेषताओं को बढ़ाते हैं।

हम एक मजबूत पद्धतिगत दृष्टिकोण अपनाते हैं जो सामग्रियों के विभिन्न गुणों को संबोधित करने के लिए विभिन्न स्तरों के सिद्धांतों को एक बहु-स्तरीय सिमुलेशन में एकीकृत करता है। इस थीसिस में, वांछित उद्देश्यों को प्राप्त करने के लिए उपयोग की जाने वाली अत्याधुनिक पद्धतियां हैं: (i) ग्राउंड-स्टेट गुणों के लिए घनत्व कार्यात्मक सिद्धांत (डीएफटी), (ii) वैश्विक न्यूनतम संरचनाओं को निर्धारित करने के लिए कैस्केड जेनेटिक एल्गोरिदम (सीजीए)। (ii) स्थिरता की भविष्यवाणी करने के लिए एबी इनिटियो परमाणु थर्मोडायनामिक्स, (iii) उत्तेजित-अवस्था गुणों के लिए कई-शरीर गड़बड़ी सिद्धांत (जीडब्ल्यू), (iv) सक्रियण ऊर्जा की गणना करने के लिए इमेज नज्ड इलास्टिक बैंड (CINEB) पर चढ़ने की विधि, और (v) थर्मोइलेक्ट्रिक गुणों की गणना करने के लिए बोल्ट्ज़मैन परिवहन सिद्धांत।

List of Publications

1. **Preeti Bhumla**, Manish Kumar, and Saswata Bhattacharya, "Theoretical Insights into C-H Bond Activation of Methane by Transition Metal Clusters: The Role of Anharmonic Effects", Nanoscale Adv. **3**, 575 (2021).

2. **Preeti Bhumla**, Deepika Gill, Sajjan Sheoran, and Saswata Bhattacharya, "Origin of Rashba Spin-splitting and Strain Tunability in Ferroelectric Bulk $CsPbF_3$", J. Phys. Chem. Lett. **12**, 9539 (2021).

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8. Shailesh Pathak, **Preeti Bhumla**, Shashank Bahri, Sreedevi Upadhyayula, Saswata Bhattacharya, "O-vacancy Mediated AB_2O_4 Type Ferrospinels for Enhanced Activity in the Sulfuric Acid Decomposition Step of the Iodine-sulfur Cycle for Hydrogen Production", J. Phys. Chem. Lett. **15**, 97 (2023).

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11. Manjari Jain, Deepika Gill, **Preeti Bhumla**, Pooja Basera, and Saswata Bhattacharya, "Theoretical Insights of Excitonic Effect in Lead Bromide Perovskites", Appl. Phys. Lett. **118**, 192103 (2021).

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18. Hushan Chand, **Preeti Bhumla**, Subhadip Goswami, Nicolo Allasia, Gianvito Vile, Saswata Bhattacharya, and Venkata Krishnan, "Facile Low-Temperature Synthesis of Novel Carbon Nitrides for Efficient Carbon Dioxide Conversion into Value-Added Chemicals" *(under review)*.

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