UNRAVELLING OPTICAL, EXCITONIC AND POLARONIC EFFECTS IN PEROVSKITES USING MANY BODY PERTURBATION THEORY

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by

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Submitted

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Dedicated to my beloved parents

Certificate

This is to certify that the thesis entitled "**Unravelling Optical, Excitonic and Polaronic Effects in Perovskites using Many Body Perturbation Theory**" being submitted by **Manjari Jain**, 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 full to any other University or Institute for the award of any degree or diploma.

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Abstract

Lead halide perovskites have attracted considerable interest as an efficient compound semiconductor alternative to conventional materials to cater to the current energy demand of the world. High charge carrier mobility, low recombination rate, strong absorption of light, long carrier diffusion length along with low manufacturing cost have made these materials very fascinating for applications in optoelectronic devices. However, the concern regarding the toxicity of lead and phase instability restricts their usage on large scale. In one of the lead halide perovskite $FAPbBr_3$, we aim to reduce lead toxicity by performing Sn substitution and Pb-□ and regulating the solar cell efficiency of $FAPb_{1-X-Y}Sn_X\square_Y Br_3$. However, the complete removal of Pb from the perovskite cage hugely hampers its solar cell performance and stability. It's, therefore, of profound interest to introduce suitable dopants that will not only replace the hazardous Pb but also make the material an ideal light harvester.

Lead bromide perovskites ($MAPbBr_3$, $FAPbBr_3$, and $CsPbBr_3$) have been studied widely in the past years for their application in photovoltaic devices. However, several properties such as optical properties, effective mass, exciton binding energy, and the radiative exciton lifetime are largely unknown. Therefore, in order to address these properties, we have carried out an exhaustive study of these perovskites using several state-of-the-art methodologies viz., hybrid density functional theory combined with spin-orbit coupling (SOC), many-body perturbation theory (GW, BSE), model-BSE (mBSE), Wannier-Mott and density functional perturbation theory (DFPT).

Moreover, a few techniques have been developed to create solar cells that are more durable and effective by combining 2D carbon materials with perovskite. By forming heterostructures of $CsPbBr_3$ with the π-conjugated 2D materials to facilitate charge transportations, the photophysical characteristics may be improved. Also, stability of $CsPbBr_3$ perovskite is a significant issue that can also be addressed by creating $CsPbBr_3$ heterostructures using 2D materials and hot carrier (HCs) dynamics. Herein, we have performed the theoretical calculation to under-

stand the charge transfer and slow recombination in the $CsPbBr_3$ PQDs/g-CN NSs heterostructure systems.

In an attempt to deal with toxicity and instability, lead-free halide double perovskites such as $Cs_2AgInCl_6$ have also emerged. In this work, we aim to design lead-free halide double perovskites with improved optoelectronic properties since they have not shown the efficiency as that lead halide perovskites. Furthermore, to calculate the charge carrier mobility of these lead-free double perovskites, we have employed the deformation potential model. In addition, Wannier-Mott approach and Fröhlich model are used to capture the excitonic and polaronic effects in these double perovskites to understand the discrepancy between theoretical and experimental mobility.

Semiconductor-based photocatalysts are acquiring great attention due to their ability to capture and store solar energy. Oxide perovskites are found to be prominent photocatalysts. However, because of their large band gap, they do not serve the purpose. Therefore, from our extensive computational study of structural, electronic, optical, and photocatalytic properties of quaternary oxynitride, oxyfluoride, and nitrofluoride perovskites, we propose them as utmost prospective candidates for the efficient absorption and conversion of solar energy into storable fuel.

सार

दुनिया की वर्तमान ऊर्जा मांग को पूरा करने के लिए पारंपरिक पदार्थ एक कुशल यौगिक अर्धचालक विकल्प के रूप में लेड हलाइड पेरोवस्काइट्स ने काफी रुचि दिखाई है। उच्च आवेश वाहक गतिशीलता, कम पुनर्संयोजन दर, प्रकाश का मजबूत अवशोषण, लंबी वाहक प्रसार के साथ-साथ कम निर्माण लागत ने ऑप्टोइलेक्ट्रॉनिक उपकरणों में अनुप्रयोगों के लिए इन पदार्थों को बहुत आकर्षक बना दिया है। हालांकि, लेड की विषाक्तता और चरण अस्थिरता बड़े पैमाने पर उनके उपयोग को प्रतिबंधित करती है। एक लेड हलाइड पेरोवस्काइट्स $FAPbBr_3$ में, हमारा उद्देश्य Sn प्रतिस्थापन और Pb-▢ प्रदर्शन करके और $FAPb_{1-X-Y}Sn_X\square_YBr_3$ की सोलर सेल दक्षता को विनियमित करके लेड की विषाक्तता को कम करना है। हालाँकि, पेरोवस्काइट्स पिंजरे से Pb को पूरी तरह से हटाने से इसके सोलर सेल के प्रदर्शन और स्थिरता में बाधा उत्पन्न होती है। इसलिए, यह उपयुक्त डोपेंट पेश करने के लिए गहन रुचि है जो न केवल खतरनाक Pb को प्रतिस्थापित करेगा बल्कि पदार्थ को एक आदर्श प्रकाश हारवेस्टर भी बना देगा।

लेड ब्रोमाइड पेरोवस्काइट्स ($MAPbBr_3$, $FAPbBr_3$, और $CsPbBr_3$) का फोटोवोल्टिक उपकरणों में अनुप्रयोग के लिए पिछले वर्षों में व्यापक रूप से अध्ययन किया गया है। हालाँकि, कई गुण जैसे कि ऑप्टिकल गुण, प्रभावी द्रव्यमान, एक्साइटन बाइंडिंग एनर्जी और रेडिएटिव एक्साइटन लाइफटाइम काफी हद तक अज्ञात हैं। इसलिए, हमने कई अत्याधुनिक कार्यप्रणालियों अर्थात प्रचक्रण कक्षा युग्मन (एसओसी) के साथ संयुक्त संकर घनत्व कार्यात्मक सिद्धांत, बहुपिण्ड क्षोभ सिद्धान्त (जीडब्ल्यू, बीएसई), मॉडल-बीएसई (एमबीएसई), वानियर-मॉट और घनत्व कार्यात्मक क्षोभ सिद्धांत (डीएफपीटी) का उपयोग करके इन पेरोवस्काइट्स का एक विस्तृत अध्ययन किया है ।

इसके अलावा, सौर कोशिकाओं को बनाने के लिए कुछ तकनीकों का विकास किया गया है जो पेरोवस्काइट्स के साथ कार्बन के 2D पदार्थ के संयोजन से अधिक टिकाऊ और प्रभावी हैं। चार्ज ट्रांसपोर्टेशन को सुविधाजनक बनाने के लिए π –संयुग्मित 2D पदार्थ के साथ $CsPbBr_3$ के हेटरोस्ट्रक्चर बनाकर, फोटोफिजिकल विशेषताओं में सुधार किया जा सकता है। इसके अलावा, $CsPbBr_3$ पेरोवस्काइट्स की स्थिरता एक महत्वपूर्ण मुद्दा है जिसे 2D पदार्थ और गर्म वाहक (एचसी) गतिकी का उपयोग करके $CsPbBr_3$ हेटरोस्ट्रक्चर बनाकर भी संबोधित किया जा सकता है। इसमें, हमने $CsPbBr_3$ PQDs/g-CN NSs हेटरोस्ट्रक्चर सिस्टम में आवेश स्थानांतरण संक्रमण और धीमे पुनर्संयोजन को समझने के लिए सैद्धांतिक गणना की है।

विषाक्तता और अस्थिरता से निपटने के प्रयास में, $Cs_2AgInCl_6$ जैसे लेड-फ्री हैलाइड डबल पेरोवस्काइट्स भी सामने आए हैं। इस कार्य में, हमारा उद्देश्य बेहतर ऑप्टोइलेक्ट्रॉनिक गुणों वाला लेड-फ्री हैलाइड डबल पेरोवस्काइट्स डिजाइन करना है क्योंकि उन्होंने उस लेड हैलाइड पेरोवस्काइट्स के रूप में दक्षता नहीं दिखाई है। इसके अलावा, इन लीड-फ्री डबल पेरोवस्काइट्स की आवेश वाहक गतिशीलता की गणना करने के लिए, हमने विरूपण संभावित मॉडल को नियोजित किया है। इसके अलावा, सैद्धांतिक और प्रयोगात्मक गतिशीलता के बीच विसंगति को समझने के लिए इन डबल पेरोवस्काइट्स में उत्तेजक और पोलरोनिक प्रभावों को पकड़ने के लिए वानियर-मॉट दृष्टिकोण और फ्रोहलिच मॉडल का उपयोग किया जाता है।

सेमीकंडक्टर-आधारित फोटोकैटलिस्ट सौर ऊर्जा को पकड़ने और संग्रहीत करने की उनकी क्षमता के कारण बहुत अधिक ध्यान आकर्षित कर रहे हैं। ऑक्साइड पेरोवस्काइट्स प्रमुख फोटोकैटेलिस्ट पाए जाते हैं। हालाँकि, उनके बड़े बैंड गैप के कारण, वे उद्देश्य की पूर्ति नहीं करते हैं। इसलिए, चतुर्धातुक ऑक्सिनिट्राइड, ऑक्सीफ्लोराइड, और नाइट्रोफ्लोराइड पेरोवस्काइट्स के संरचनात्मक, इलेक्ट्रॉनिक, ऑप्टिकल और फोटोकैटलिटिक गुणों का हम व्यापक कम्प्यूटेशनल अध्ययन से, हम उन्हें कुशल ईंधन में सौर ऊर्जा के कुशल अवशोषण और रूपांतरण के लिए अत्यधिक संभावित उम्मीदवारों के रूप में प्रस्तावित करते हैं।

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1. **Manjari Jain**, Arunima Singh, Pooja Basera, Manish Kumar, and Saswata Bhattacharya, "Understanding the role of Sn-substitution and Pb-$\Box$ in enhancing the stability of $CH(NH_2)_2Pb_{1-X-Y}Sn_X\Box_YBr_3$: A hybrid density functional approach", Journal of Materials Chemistry C **8**, 10362 (2020).

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