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ANALYSIS OF THE PROPERTIES OF VACANCY MEDIATED METHYL AMMONIUM LEAD IODIDE PEROVSKITE: A DFT BASED STUDY

Md. Abdullah Al Asad[a]*, Md. Abdul Alim[b], Mst. Halima Khatun[c], Abinash Chandro Sarker[d], Md. Arifur Rahman[e]
[a]Dept. of Electrical and Electronic Engineering, Bangabandhu Sheikh Mujibor Rahman Science and Technology University, Gopalganj, Bangladesh- 8100
[b]Dept. of Chemistry, Bangabandhu Sheikh Mujibor Rahman Science and Technology University, Gopalganj, Bangladesh- 8100
[c]Dept. of Physics, Bangabandhu Sheikh Mujibur Rahman Science and Technology University, Gopalganj, Bangladesh- 8100
[d]Dept. of Chemistry, Begum Rokeya University, Rangpur 5404, Bangladesh
[e]Dept. of Electrical and Electronic Engineering, First Capital University of Bangladesh, Chuadanga, Bangladesh- 7200
**Corresponding Author e-mail: dr.asad.eee@gmail.com*

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Intrinsic defects have a significant impact on carrier transport properties of Methyl Ammonium Lead Iodide (MAPI) Perovskite $CH_3NH_3PbI_3$. In this paper, we investigated how lead vacancies affect the photovoltaic properties of MAPI using density functional theory (DFT) studies. Lead vacancies in perovskite materials can significantly impact carrier dynamics and device efficiency. Our findings indicate that the lower energy configuration of the Pb vacancy does not create deep trap states that would otherwise reduce carrier lifetime. This suggests that Pb vacancies in MAPI might not be as detrimental to carrier dynamics as previously thought. Pb vacancies could potentially be compensated by other defects or dopants in the material, which might mitigate their negative effects on carrier dynamics. The introduction of a Pb vacancy leads to additional electronic states near the conduction band minimum (CBM) within the fundamental band gap. This indicates that the vacancy introduces localized electronic states that influence carrier behavior. The Highest Occupied Molecular Orbital (HOMO) becomes more localized around the vacant area, while the Least Unoccupied Molecular Orbitals (LUMOs) are only partially localized. This localization around the vacancy does not create strong trapping states that could hinder carrier movement. The presence of vacancies causes atomic movements that result in a more distorted optimized structure. This structural distortion can influence the overall material properties and potentially impact device performance. The HOMO and LUMO levels are primarily derived from the p orbitals of the atoms involved. This highlights the importance of p orbital interactions in determining the electronic properties of the material

Keywords: *$CH_3NH_3PbI_3$; Density functional theory; Pb vacancy; Band gap energy; Structural distortion*
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INTRODUCTION

Hybrid organic/inorganic perovskites (HOIPs) have drawn significant research interests due to the incomparable rapid rise in energy conversion efficiency seen in photovoltaic devices based on CH3NH3PbI3. Current research attempts in this field have concentrated on searching for similar perovskites with better properties, manifested by good carrier mobility and long carrier lifetime with efficient transport properties. Defects play a vital role in carrier transport in semiconductors [1]. The carrier traps and nonradiative recombination center are basically created due to the presence of deep defect centers which are still detrimental for carrier transportation [1]. A great deal of studies has been examined a large number of native point defects under density functional theory (DFT) [2-5] that show the conflicted results regarding the positions of defect level in $CH_3NH_3PbI_3$. Indeed, a list of particular native defect can introduce deep charge transition in the band gap whenever other native defects have been shown a shallow level of transition. Due to the record of discrepancy outcome in the calculated defect level of $CH_3NH_3PbI_3$, it might be expeditious to reexamine the computational calculation of defected structure. Additionally, the point defects undergo a critical role in determining the electron hole diffusion length which are responsible for non-radiative recombination center [6]. A long electron hole diffusion length resumed the unusual defect properties of $CH_3NH_3PbI_3$. On the other hand, the thermodynamic stability under a humid condition and/or irradiation of $CH_3NH_3PbI_3$ and the formation mechanism of the dominant intrinsic defects are crucial for the efficiency improvement of halide perovskite based thin film solar cells [6]. Therefore, understanding defect properties is immensely important for optimizing the performance of halide perovskite solar cells.

In this letter, we discussed the electronic properties of intrinsic vacancy (Lead) defect of $CH_3NH_3PbI_3$ as the representative material for the methylammonium lead halide (MALHs). More importantly, the defect in $CH_3NH_3PbI_3$ with low formation energy creating only shallow levels can be ascribed to the unique electronic properties through DFT. The HOMO and LUMO level electronic charge distributions both of bulk and defected conditions and their corresponding optimized distorted structure are also considered under this discussion.

Computational Details: All calculations were performed with the Vienna ab initio simulation package (VASP, version 5.4.1), [7] based on DFT and the results were visualized by the VESTA (visualization for electronic and structural

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analysis). The projector augmented wave (PAW) method [8] was used to describe the electron-ion interaction with the kinetic energy cutoff set to 600.0 eV. The Brillouin-zone was sampled with a gamma Γ centered k-point grid for structural relaxation. Spin-polarized calculations were performed, using the Perdew-Burke-Ernzerhof (PBE) [9] functional under electronic and ionic self-consistent, with convergence criteria of 10−8 eV and -10−7 eV·Å−1, respectively. In this study, the simple PBE calculation is performed for pristine $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_3$ with Pb vacancy mediated defected structure without incorporating the effect of spin-orbit coupling (SOC). We have considered the following valence electrons for the atomic species involved: Pb (5d106s26p2), I (5s25p5), O (2s22p4), N (2s2 2p3), C (2s2 2p2) and H(1s1).

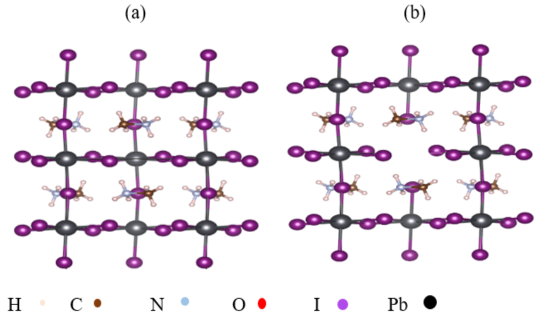

Figure 1. The structures of a) pristine super cell includes 48 atoms and b) defected structure after removing one Pb from the center of the bulk

We reproduced the experimentally verified simple orthorhombic $CH_3NH_3PbI_3$ super cell that consists of lattice parameter units (a = 8.836Å, b = 12.580Å, c = 8.555Å) at low temperature [10]. The supercell of $CH_3NH_3PbI_3$ includes 48 atoms where the reference unit cell was fully relaxed until the atomic configuration converged to within convergence criteria. The orthorhombic phase [10] (space group Pm3m) of CH3NH3PbI3 with the optimized supercell structure consisting the geometry of (a) 48-atoms ideal $CH_3NH_3PbI_3$ and (b) 47-atoms with Pb vacancy mediated defected $CH_3NH_3PbI_3$ structure as depicted in (Figure 1a,1b) respectively. Here, this elementary Pb vacancy leading structure shows the smallest formation energy, in excellent agreement to search the activation energies for diffusion processes that can be computed from the total energy difference between the diffusing species in their ground-state configuration and at the saddle point of the diffusion process. We found the smallest formation energy by the formula:

$$2\Delta E_{GB,n} = E_{GB,n} - E_{bulk}. \tag{1}$$

Where, ΔE_{GB} = energy difference in GB structures, n = consecutive configuration number, E_{bulk} = energy of a bulk system

RESULT AND DISCUSSION

We have examined how Pb vacancies in $CH_3NH_3PbI_3$ perovskites affect their properties through simulations. The low formation energy of these defects means they are likely to occur and can significantly impact the material's electronic characteristics, which is crucial for optimizing the performance of devices like solar cells. In organic –inorganic MALH crystalline structure, we focus on the role of elemental defects in the perovskite structure, specifically in the context of methylammonium lead iodide ($CH_3NH_3PbI_3$). The general formula for a perovskite structure is ABX3, where 'A' and 'B' are cations and 'X' is an anion. In $CH_3NH_3PbI_3$, 'A' is methylammonium (CH_3NH^{3+}), 'B' is lead (Pb^{2+}), and 'X' is iodide (I−). Defects such as vacancies (missing atoms) in the perovskite structure can significantly impact its properties. In our case, we are focusing on lead (Pb) vacancies. The formation energy of defects refers to the energy required to create these defects within the crystal lattice. A low formation energy suggests that defects are more likely to occur under certain conditions. To study defects, simulations are often conducted in a supercell, which is a larger unit cell that can accommodate defects while still representing the material's bulk properties. Perovskite materials like $CH_3NH_3PbI_3$ typically have a low band gap and adjustable Fermi levels, the creation of charged defects is more feasible [4]. These defects can influence the electronic properties of the material, such as conductivity and optical properties.

To investigate the impacts of vacancy defect on electronic properties of $CH_3NH_3PbI_3$ perovskites, we calculate the density of states (DOS) of pristine crystalline structure as well as defect mediated supercell structure in relaxed conditions. DOS calculations provide valuable information about the electronic structure of both pristine and defected perovskite structures. By comparing the DOS of the ideal (pristine) structure with that of the defected supercell, we observed how the presence of vacancies affects the material's electronic properties. The reduction in the band gap energy for the defected structure indicates that the material's electronic properties are altered by the presence of vacancies. A smaller band gap generally suggests that the material may have increased optical absorption in the visible range, which is beneficial for applications like solar cells. However, this can also lead to increased recombination rates of charge carriers if not properly managed. The absence of new deep trap states within the band gap (as indicated by Figure 2) suggests that the vacancies do not introduce significant mid-gap states that could act as electron or hole traps.

This is a positive aspect, as deep trap states can negatively impact carrier mobility and recombination efficiency. The Valence Band Maximum (VBM) moving slightly downward indicates that the energy of the valence band has been lowered. This could be due to the creation of localized states near the valence band edge, which can affect the material's ability to absorb light and participate in charge transfer. An additional peak near the Conduction Band Minimum (CBM) appears in defected cell due to the effect of surrounding atom near the vacancy and CBM coming closer to the Fermi level suggests that the conduction band is now more accessible to electrons. This can improve the material's electrical conductivity and make it easier for electrons to transition from the valence band to the conduction band. The extended CBM edges implies that the conduction band states are spread over a wider energy range. This can facilitate better electron transport because the smaller potential barriers and wider band edges allow for more efficient movement of charge carriers. This is beneficial for the overall performance of devices like solar cells, where efficient electron transport is crucial for high power conversion efficiencies.

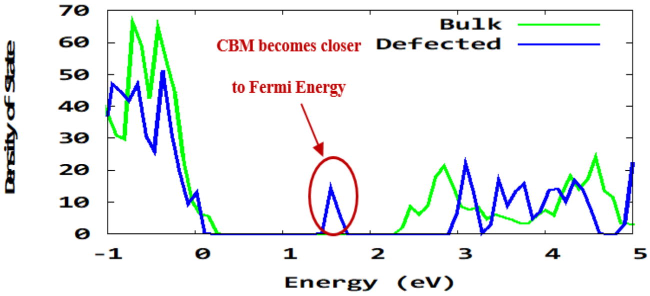

Figure 2. The total density of state (DOS) of bulk and detected structure

To clarify and enhance the accuracy of our findings, we conducted a detailed analysis comparing the Projected Density of States (PDOS) of a representative atom near the defect with that of a non-defective atom in the bulk structure (see Figure 3a and 3b). The addition density of State in Figure 3b is generated due to the charging contribution of surrounding atoms as indicated by red circle. This comparison clearly shows that an additional peak appears in the band gap region of the defected structure, whereas no such peak is present in the pristine material.

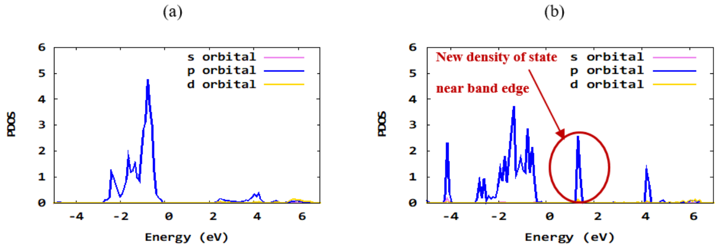
(a) (b)

Figure 3. The partial density of state (PDOS) of one the representative atom (Iodine) nearer the vacant area of a) bulk and b) defected structure

We propose that the observed peak in the PDOS is responsible for generating the additional feature in the fundamental energy gap of the defected structure. This phenomenon is consistent with the behavior of shallow dopants [4], which are known to exhibit extended states within the band gap. Since the conduction and valence band edges are primarily contributed by the p orbitals of iodine (I) atoms, the additional charge introduced by vacancy defects creates a shallow level near the band edge that extends throughout the $CH_3NH_3PbI_3$ material. Consequently, it is important to note that vacancy defects are unlikely to act as non-radiative recombination centers.

Figure 4. represents the HOMO and LUMO level charge density distributions of ideal $CH_3NH_3PbI_3$ as well as defected structure, calculated at 0 K using the optimized structure.

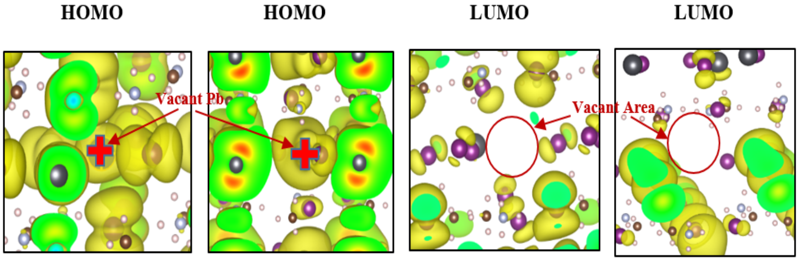

Figure 4. Iso-surface electronic charge distributions of crystalline (left two figures) and defect mediated condition (right two figures)

The charge distributions of both systems reveal the wave function of individuals has no overlapping each with others that mostly composed by orbitals of inorganic atoms. Consequently, the organic group do not show the favor of contribution on electron hole recombination and shows the disabilities to bring the electron and vibrational quanta closer to resonance. In ideal structure, the HOMO is mostly localized on the iodine atoms with a slight contribution from the lead atoms, while the LUMO is primarily derived from the lead atoms, with some contribution from iodine atoms. This indicates a clear separation of the HOMO and LUMO contributions based on their respective atomic origins. In the presence of a Pb vacancy, both HOMO and LUMO become significantly influenced by the iodine atoms. This suggests that the absence of lead atoms alters the charge distribution, with the electronic charge becoming more concentrated around the vacancy. The HOMO is now more localized around the vacancy area, and while this could indicate a localized trapping site, it actually does not trap carriers dynamically, which is a favorable outcome for electronic and optical properties. The HOMO becomes more localized around the Pb vacancy. However, this localization does not negatively impact carrier dynamics as one might expect in other semiconductor materials with trap states. In fact, this is advantageous because it prevents the formation of detrimental trap states that could reduce solar conversion efficiency. The LUMO remains partially localized, but without the formation of bonding between adjacent atoms as observed in the bulk phase. This implies that the Pb vacancy does not introduce new bonding interactions that could disrupt carrier dynamics. Unlike $CH_3NH_3PbI_3$, conventional semiconductors such as silicon (Si) [11] and cadmium telluride (CdTe) [12] suffer from trap states due to structural defects, which decrease their solar conversion efficiency. The presence of the Pb vacancy in $CH_3NH_3PbI_3$ does not exhibit such detrimental effects, suggesting a superior performance in solar optoelectronic applications. [13]. The Pb vacancy in $CH_3NH_3PbI_3$ leads to significant changes in the charge density distribution of HOMO and LUMO, but these changes are beneficial for the material's performance in solar optoelectronic applications. Unlike traditional semiconductors, the Pb vacancy does not create harmful trap states, making $CH_3NH_3PbI_3$ an efficient material for these applications.

Figure 5. The structural distortions due to the Pb vacancy are compared with the bulk structure to show the changes in geometry. This helps visualize how the defect influences the overall structure and its implications for charge distribution and carrier dynamics. The optimized vacant area shrinks as surrounding atoms move toward the vacancy. This atomic movement is primarily demonstrated by lead atoms, although there are also some organic atoms, though they are relatively far from the inorganic ones. As a result of the vacancy-induced motion, the overall atomic positions are altered, leading to the formation of dangling bonds between unsaturated atoms. Consequently, the organized structure is distorted due to the presence of the vacancy. In this distorted structure, the representative atom indicated by the green arrow contributes to a new density of states near the edge of the Conduction Band Minimum (CBM), as shown in Figure 3(b). This new density of states is consistent with experimental evidence suggesting that intrinsic defects may be prevalent in the MALHs layer [4]. Our theoretical results align with the findings of Edri et al. [14], indicating that MALHs could achieve high-performance photovoltaic operation at a low fabrication cost. Further research on organic-inorganic hybrid materials is needed to identify additional potential candidates for photovoltaic applications.

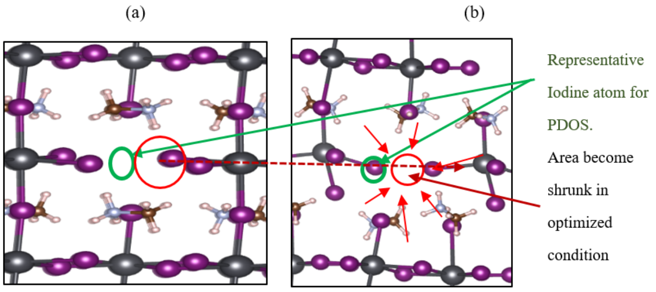

Figure 5. Structural distortion (Fig. 5a); vacancy-oriented movement of surrounding atoms in the optimized structure (Fig. 5b)

CONCLUSION

The Pb vacancy in $CH_3NH_3PbI_3$ does not create deep trap states that could severely impact carrier dynamics but instead introduces shallow states that could potentially influence doping characteristics. The localized nature of the HOMO and LUMO suggests that while there is some localization of electronic states around the vacancy, it does not lead to significant bonding or trapping issues. The structure's adaptation to the vacancy suggests that the material maintains some level of disorder while accommodating the defect.

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Declaration of competing interest:
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ORCID

Mohammad Abdullah Al Asad, https://orcid.org/0000-0002-9660-2860

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АНАЛІЗ ВЛАСТИВОСТЕЙ ПЕРОВСКИТУ МЕТИЛАММОНІЮ ЙОДИДУ СВИНЦЯ, ОПОСЕРЕДКОВАНОГО ВАКАНСІЯМИ: ДОСЛІДЖЕННЯ НА ОСНОВІ DFT

М. Абдулла Аль Асад[a], М. Абдул Алім[b], Мс. Халіма Хатун[c], Абінаш Чандро Саркер[d], М. Аріфур Рахман[e]
[a]Департамент електротехніки та електронної інженерії, Науково-технічний університет імені шейха Муджибора Рахмана Бангабандху, Гопалгандж, Бангладеш
[b]Департамент хімії, Науково-технологічний університет імені шейха Муджибора Рахмана Бангабандху, Гопалгандж, Бангладеш
[c]Департамент фізики, Науково-технічний університет імені шейха Муджібура Рахмана Бангабандху, Гопалгандж, Бангладеш
[d]Департамент хімії, Університет Бегум Рокея, Рангпур, Бангладеш
[e]Департамент електротехніки та електронної інженерії, Перший столичний університет Бангладеш, Чуаданга, Бангладеш

Внутрішні дефекти мають значний вплив на транспортні властивості перовскіту $CH_3NH_3PbI_3$ метиламонію йодиду свинцю (MAPI). У цій статті ми досліджували, як вакансії свинцю впливають на фотоелектричні властивості MAPI, використовуючи дослідження теорії функціоналу густини (DFT). Вакансії свинцю в перовскітних матеріалах можуть суттєво впливати на динаміку носія та ефективність пристрою. Наші висновки показують, що нижча енергетична конфігурація вакансії Pb не створює станів глибокої пастки, які в іншому випадку зменшили б час життя носія. Це свідчить про те, що вакансії свинцю в MAPI можуть бути не такими шкідливими для динаміки носія, як вважалося раніше. Вакансії Pb потенційно можуть бути компенсовані іншими дефектами або легуючими речовинами в матеріалі, що може пом'якшити їхній негативний вплив на динаміку носія. Введення вакансії Pb призводить до додаткових електронних станів поблизу мінімуму зони провідності (CBM) у фундаментальній забороненій зоні. Це вказує на те, що вакансія вводить локалізовані електронні стани, які впливають на поведінку носія. Найвища зайнята молекулярна орбіталь (HOMO) стає більш локалізованою навколо вакантної області, тоді як найменш незайняті молекулярні орбіталі (LUMO) локалізовані лише частково. Ця локалізація навколо вакансії не створює сильних станів захоплення, які могли б перешкоджати руху носія. Наявність вакансій викликає переміщення атомів, що призводить до більш спотвореної оптимізованої структури. Це структурне спотворення може вплинути на загальні властивості матеріалу та потенційно вплинути на продуктивність пристрою. Рівні HOMO і LUMO в основному походять від p-орбіталей залучених атомів. Це підкреслює важливість p-орбітальних взаємодій у визначенні електронних властивостей матеріалу.

Ключові слова: *$CH_3NH_3PbI_3$; теорія функціоналу густини; вакансія Pb; енергія забороненої зони; структурне спотворення*