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# Optical absorption coefficient red shift effect of iodine vacancy in $MAPbI_3$

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ABSTRACT

The Density Function Theory with van der Waals correction are employed to investigate the materials of $CH_3NH_3PbI_3$ ($MAPbI_3$). For the two phases of tetragonal and orthorhombic, the high optical absorption coefficients (OAC) result from electrons jumping from I 5*p* to the Pb 6*p* near the Fermi level. The two different kinds of iodine vacancy result in the doping energy band appearing in the band gap, and the doping energy band is from Pb 6*p* electrons mainly, which is below the Fermi level. The iodine vacancy result in the red shift of OAC, which result in the optical absorption of $MAPbI_3$ with the iodine vacancy locating in the range from 0.5 eV to 1.47 eV, which locate at the infrared ray part occupying 51% of radiant energy of sunlight. And the red shift favors power transfer between sunlight and electric. The red shift of the OAC originate electrons jumping from Pb 6*p* (doping energy bands) to Pb 6*p* (conduction bands).

## 1. Introduction

In recent years, the power conversion efficiencies of the peroveskite solar cells improve rapidly from 3.8% [1] in 2009 to over 22.7% [2], which is near the theoretical maximum value of 30% [3]. Thus the organic-inorganic halide perovskite materials attracted worldwide attention as ideal light absorber for photovoltaic applications. The materials have many excellent properties, such as higher optical absorption coefficient [4], unique defect properties [5–9], and high mobility of carrier [10]. Although this perovskite materials have many outstanding properties, their low stability limit large-scale commercial production. The anomalous current density-voltage (J-V) hysteresis make an impact on the performance stability and difficult to evaluate accurately the power conversion efficiency of perovskite solar cells [11,12]. Analyzing the experiments and theoretical results, it is noted that the J-V hysteresis may be caused by the ion defects or the ions migration.

Based on the defect energy distribution in $CH_3NH_3PbI_3$ ($MAPbI_3$) from the admittance spectroscopy results, it is thought that the iodine interstitials defect state is the main factor causing J-V hysteresis [13]. At same time, it is found in experiments that the surface trap states and grain boundaries of the perovskite result in the J-V hysteresis mainly [14]. Depositing the fullerene layer on the perovskite layer can effectively passivate these trap states and suppress the J-V hysteresis. The isopropanol solvent was also used to treat perovskite solar cells, the efficiency is improved and the J-V retardation is reduced, mainly because the isopropanol solvent removes impurities and defects during film growth [15]. Defects that create deep levels usually act as Shockley-Read-Hall non-radiative recombination centers and are responsible for short minority carrier lifetime and thus low open circuit voltage [16]. In order to understand the mechanism of ions defect causing the J-V hysteresis effecting material properties, some theoretical investigations [5–9] are carried out. The DFT calculated results show that only the shallow levels are created by the dominant intrinsic defects, which partially explain the long electron-hole diffusion length and high open-circuit voltage in the cubic phase of $MAPbI_3$ solar cell [5]. However, among native point defects (including vacancies, interstitials, and antisites) of the tetragonal phase of $MAPbI_3$, only the iodine interstitials is a low energy deep trap and non-radiative recombination center [6], which have been observed by the admittance spectroscopy in experiments [13]. At same time, the DFT calculations [8] show that both the Pb cations and I anions in this material exhibit strong covalency as characterized by the formation of Pb dimers and I trimers with strong covalent bonds at some of the intrinsic defects. The Pb dimers and I trimers are only stabilized in a particular charge state with significantly lowered energy, which leads to deep charge-state transition levels within the band gap. The hybrid density functional calculations including the spin–orbit coupling [9] results show that, among native point defects, only the iodine vacancy and its complexes result in the deep electron and hole trapping levels inside of the band gap, acting as

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non-radiative recombination centers. Based on the above investigations, it is thought that the iodine vacancies create the shallow energy levels, which increase the carrier diffusion length, and enhance the open circuit voltage of solar cells.

Recently, Yuan et al. firstly observed the organic group of MA migrate in $MAPbI_3$, the activation energy ($E_a$) characterizing the ability of ion migrates is estimated about 0.36 eV [17]. Experimentally [18], it is observed that the ionic conductivity ($7.7 \times 10^{-9}$ $Scm^{-1}$) is higher than the electronic conductivity ($1.9 \times 10^{-9}$ $Scm^{-1}$), the ionic conductivity may result from the iodine ions migrate in $MAPbI_3$ with $E_a$ of 0.43 eV. Tress et al. [19] demonstrate that the J-V hysteresis attributed to the build-up of space charge close to the contacts, independent of illumination and most likely due to ionic displacement. Theoretically, Nudged elastic band and constrained energy minimization methods were used to calculate the $E_a$ of $I^-$, $MA^+$ and $Pb^{2+}$ ions through Schottky defects in $MAPbI_3$. It is noted that $I^-$ has the lowest $E_a$ of 0.58 eV [20] or 0.32 eV [21] than other ions, this implies that $I^-$ ions migrate more easily than other ions.

Though many investigations have been carried out on the iodine vacancy ($V_I$) have an influence on J-V hysteresis, there are few studies on the effect of $V_I$ on the optical absorption coefficient (OAC) of $MAPbI_3$, which give insight into understanding the materials properties effect of the $V_I$. In this article, first-principles calculations are used to study the effect of the $V_I$ on the electronic structures, optical absorption coefficient of the $MAPbI_3$. It is found that the red shift of the optical absorption coefficient are caused by the $V_I$, which favors power transfer between sunlight and electric.

## 2. Computational methods

The Density Function Theory calculation with van der Waals (vdW) correction by using the DFT-D2 method are performed by using the Vienna Ab initio Simulation Package (VASP) [22–24]. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) are used to depict the exchange-correlation function [25]. The electron-core interactions are described by using projector-augmented wave potentials (PAW) [26]. As the error elimination between the GGA and spin-obit coupling (SOC), the SOC of Pb wasn't considered. These cut off energy of plan waves are 400 eV for tetragonal phase and 520 eV for orthorhombic phase. The k-point grid employ Monkhorst–Packscheme [27] with $3 \times 3 \times 2$ and $5 \times 3 \times 5$, respectively. All the structures considered in this study are relaxed with a conjugate-gradient algorithm until the energy on the atoms is less than $1.0 \times 10^{-5}$ eV. The ion relaxation convergence criterion is that the force between the atoms is less than 0.01 eV/Å.

The structures of tetragonal (*I4/mcm*) and orthorhombic (*Pnma)* are shown in Fig. 1. The crystal structures are established according to experimental data ($a = b = 8.800$ Å, $c = 12.685$ Å for tetragonal, $a = 8.836$ Å, $b = 12.580$ Å and $c = 8.555$ Å for orthorhombic) [28]. There are two kinds of iodine atoms in both phases. One is along the equatorial direction and the other is along apical. Therefore, the $V_I$ should have two positions for each structure as marked A and B in Fig. 1.

**Table 1**
Optimized lattice parameters and total energy of the tetragonal (Tet) and orthorhombic (Ort) phases with and without the $V_I$.

| | $V_I$ | Total energy (eV) | $a$ (Å) | $b$ (Å) | $c$ (Å) |
|---|---|---|---|---|---|
| Tet | Intrinsic | | 8.611 | 8.611 | 12.689 |
| | | | 8.800 | 8.800 | 12.658 Ref. [28] |
| | A | −205.498 | 8.486 | 8.423 | 12.564 |
| | B | −205.274 | 8.583 | 8.512 | 12.168 |
| Ort | Intrinsic | | 8.727 | 12.591 | 8.539 |
| | | | 8.836 | 12.580 | 8.555 Ref. [28] |
| | A | −205.851 | 8.686 | 12.403 | 8.193 |
| | B | −205.665 | 8.665 | 12.166 | 8.660 |

## 3. Results and discussions

Considering the main interaction between the organic group MA and framework of Pb-I is the vdW interaction, the method of GGA with vdW correction is employed to optimize the structure of both phases without and with $V_I$ at A and B positions. In order to determinate the iodine vacancies, the total energy of the two phases with different iodine vacancy are calculated, and listed in Table 1, along with the optimized lattice parameters. It is found the total energy of the two kinds of iodine vacancies is similar for each phase. The total energy of the tetragonal phase with iodine vacancy at A and B positions are −205.498 eV and −205.274 eV, respectively. The total energy of the orthogonal phase with iodine vacancy at A and B positions are −205.851 eV and −205.665 eV, respectively. This indicates that their stability of two kinds of iodine vacancy is almost same. From the table, it is noted that the lattice parameters of two intrinsic structures are agree well with experiments value [28]. For the both phases, the lattice constants of the materials with $V_I$ at different positions is less than that of intrinsic materials. This imply that the effect of the $V_I$ is to reduce the lattice constants.

Based on the geometrical structure optimization calculations, the band structures of the tetragonal and orthorhombic phases with and without $V_I$ are calculated and shown in Figs. 2(a) and 3(a). It is noted that our calculated direct energy gaps are 1.45 eV and 1.73 eV for the tetragonal and orthorhombic phases, respectively. Our calculations are in good agreement with experiments of 1.55 eV and 1.68–1.72 eV for the two phases and the previous calculations [29–32]. In general, the band gap energies of solid-state semiconductors are underestimated by using DFT calculations. However, as the organic-inorganic halide perovskite materials usually contain lead element and the interactions

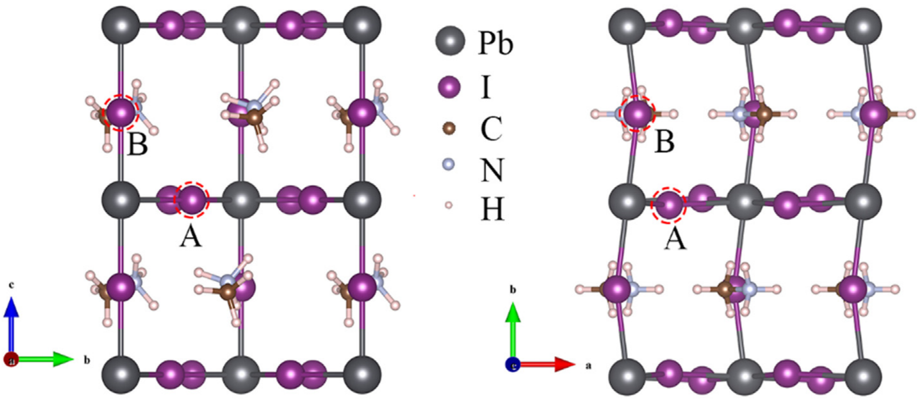

**Fig. 1.** Crystal structures of (a) tetragonal phase, (b) orthorhombic phase.