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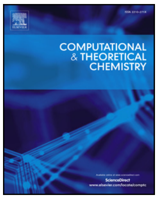

The computational probing of carrier transport in $MAPbI_{3-x}Cl_x$

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ABSTRACT

$MAPbI_{3-x}Cl_x$ (MA) perovskite has attracted much research attention because of its remarkable carrier transport performance. However, the influence of Cl incorporation in $MAPbI_{3-x}Cl_x$ perovskite on the carrier transport performance still remains unclear. With the first-principles calculations, we found that with the incorporation of the small ionic radius of Cl^-, it forces the orientation of MA molecule turning from diagonal direction to axial direction. As a result, this induced lattice polarization enhances the carrier transport along the axial direction. In the light doping direction, we confirmed that the carrier transports for both electrons and holes are suppressed due to a large lattice scattering. However, in the heavy doping direction, we found that the decrease of carrier mobility is mainly caused by the energy states up-shift because of the Pb position deviation for electrons and the strong localization of Cl 3p states for holes.

1. Introduction

Solar cell device performance has a large dependency on the optical absorption and the carrier transport of the involved photovoltaic materials. Organic-inorganic perovskites materials (ABX_3, A = organic molecule, B = metal, X = halide) are one type of promising solar cell materials because of their outstanding optical and electronic properties with the low-cost synthetic methods [1–3]. The tunable band-gaps make the optical absorption spectrum almost over the entire visible range and the long balanced carrier diffusion length larger than 100 nm in solution-processed pure iodide perovskites also shows their great capability of carrier transport [4]. Therefore, high photoelectric conversion efficiencies of 20.1% for perovskites are recently achieved [5], indicating the great potential in thin-film solar cell application for organic-inorganic perovskites materials.

Besides the rapid developments of $MAPbI_3$ perovskites, it is also reported that their optical and electronic properties can be further optimized by introducing other halide ions like Cl^- and Br^- into the perovskite materials. Stranks et al. have first reported that the electron-hole diffusion lengths could have a tenfold increase by introducing Cl^- ions into $MAPbI_3$ perovskites, indicating better carrier transport [6]. Wehrenfenning et al. have also confirmed the improved carrier mobility in mixed halide perovskites by using transient THz spectroscopy [7]. Furthermore, it has been obtained the improved carrier mobility and the reduced carrier recombination rates for $MAPbI_{3-x}Br_x$ and $MABr_{3-x}Cl_x$ [8,9].

However, the research about mixed halide $MAPbI_{3-x}Cl_x$ perovskite is still under debate since the existence and effects of the incorporated chlorine is questionable and unclear. Scientists were confused about the exact role of the doping chloride for the enhanced carrier transport performance. Some researchers believed that the incorporated Cl has a direct influence to the enhanced carrier transport. For example, Wehrenfenning et al. suggested that the incorporated Cl would change the electronic structure of perovskite to reduce the spatial overlap of the electron and holes [7]. Therefore, the bimolecular recombination rates can be decreased for the long carrier diffusion length. Colella et al. also proposed that the Cl in the $MAPbI_3$ perovskite can act as a dopant to improve the transport properties [10]. However, other researchers suggested that the incorporated Cl would make an indirect influence like the suppression of impurities and defects. Du reported that the incorporated Cl can suppress the formation of interstitial I defect which is calculated to be a deep level defect [11]. It implied that the high carrier transport performance is an instinct character of $MAPbI_3$ perovskite, and the incorporated Cl is just helpful to remove the carrier recombination center in the perovskites. Furthermore, some reports pointed out that the Cl has little or even none contribution to the enhanced carrier transport since the Cl is hard to incorporate into $MAPbI_3$ perovskite [10]. Only a very low concentration (below 3–4%) of

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chloride can be incorporated into an iodide-based structure, in accordance with DFT calculations that the formation energy of MAPbI$_{3-x}$Cl$_x$ (MA) is much higher than MAPbI$_3$ perovskite [12].

The mechanism for the enhanced carrier transport in MAPbI$_3$ perovskite still remains challenging. Therefore, we have systematically studied the influence of incorporated Cl on the carrier transport property of MAPbI$_3$ perovskite by using the first-principles calculations. We found that the Cl incorporation was not able to directly improve the carrier transport performance, but cause a large decrease for carrier mobility due to the energy state up-shift and the lattice scattering. We suggest that the observed high carrier transport performance of MAPbI$_{3-x}$Cl$_x$ perovskites in reported experiments could be attributed to the suppression of the disorder orientation of polar molecule MA caused by the Cl incorporation.

2. Methods

The geometry optimization and electronic calculations for MAPbI$_3$, MAPbI$_2$Cl, MAPbI$_{2.5}$Cl$_{0.5}$ and MAPbI$_{2.667}$C$_{0.333}$ perovskites are performed using the VASP code in the framework of DFT [13,14]. The PAW pseudo-potential is used with a cut-off energy of 500 eV for the plane-wave basis functions [15]. This computational approach has been carefully tested to guarantee its validity (detailed results are listed in Table S1.). For Cl doping concentration calculations, a cubic MAPbI$_3$ unit cell, 2 × 1 × 1 and 3 × 1 × 1 supercells are built with one Cl replacing with one I atom in the x axis, corresponding to a doping concentration of 33.3%, 16.7 and 11.1%, respectively. The 8 × 8 × 8 Monkhorst-pack k-meshes is employed for structure optimization of MAPbI$_3$, MAPbI$_2$Cl and 4 × 8 × 8, 3 × 8 × 8 Monkhorst-pack k-meshes for MAPbI$_{2.5}$Cl$_{0.5}$ and MAPbI$_{2.667}$C$_{0.333}$ perovskites, respectively. The lattice vectors and atomic positions are relaxed until the total energy changed by less than 1×10^{-5} eV. The carrier mobility is calculated based on the deformation potential theory as shown below [16]:

$$\mu = \frac{8\pi^{1/2}\hbar^4 e c_{ii}}{3(m^*)^{5/2}(k_B T)^{3/2}E_1^2},$$

where $\hbar$ is the reduced Planck constant, e is the element charge, c_{ii} is the elastic constant, m^* is the effective mass of charge, k_B is the Boltzmann constant, T is the absolute temperature, and E_1 is the deformation potential defined as the energy shift of the band energy position (ΔE) with respect to a small lattice dilation (Δl) along a lattice (l_0) direction, i.e., $E_1 = \Delta E/(\Delta l/l_0)$ [17,18]. Room temperature (T = 300 K) is used in our calculation.

3. Results and Discussion

We firstly considered the situation that one Cl atom is incorporated into one cubic phase MAPbI$_3$ perovskite unit cell, which corresponds to a high doping concentration of 33.3%. The optimized lattice structure of MAPbI$_3$ and MAPbI$_2$Cl were shown in Fig. 1. The calculated lattice parameters were $a = b = c = 6.47$ Å for MAPbI$_3$, consistent with previous report [19]; $a = 5.78$ Å, $b = c = 6.53$ Å for the MAPbI$_2$Cl perovskite. Due to the small ionic radius of Cl$^-$, the lattice parameter along x axis is largely shortened, and the orientation of MA molecule has turned from ⟨1 1 1⟩ to nearly ⟨0 1 1⟩ direction because of this spatial compression. Meantime, it can also be found that the deviation of the Pb atom from the lattice central become larger in MAPbI$_2$Cl perovskites with a Cl—Pb—Cl bond angle of 168.0°, much smaller than the average I—Pb—I bond angle of 176.2° along each axis in MAPbI$_3$ perovskites (Fig. 1).

The carrier transport performance for MAPbI$_3$ and MAPbI$_2$Cl perovskites were evaluated based on the deformation potential theory with effective mass approximation as shown in Table 1. The calculated carrier mobility of MAPbI$_3$ perovskite is up to ~16,889 cm^{2}V^{-1}s^{-1} for electrons and 966 cm^{2}V^{-1}s^{-1} for holes, respectively, consistent with other theoretical work [20,21]. Such high carrier mobility can be attributed to the small effective mass for electrons and holes. However, after the Cl is incorporated into the perovskite structure, there is a huge decrease in the carrier mobility for both electrons and holes along the ⟨1 0 0⟩ direction (the Cl doping direction) because of the large carrier effective mass for electrons of 0.86 m$_0$ and holes of 0.47 m$_0$. Especially, the holes have a better carrier transport performance than electrons, opposite to that in the original MAPbI$_3$ perovskite. Meanwhile, along the ⟨0 1 0⟩ direction which is less influenced by the Cl doping, it is surprised to see that both the electrons and holes experience an increase in carrier mobility, even larger than that in the original MAPbI$_3$ perovskite. It is attributed to the smaller effective mass of 0.07 m$_0$ for electrons and 0.17 m$_0$ for holes. It implies that the carriers transport in the MAPbI$_2$Cl perovskite is largely suppressed in the doping direction, but can also be enhanced in other two directions.

In order to understand the underlying mechanisms for these carrier mobility changes, we carried out the band structure and density of states calculations for MAPbI$_3$ and MAPbI$_2$Cl perovskites as shown in Fig. 2. Both of these two perovskites are direct band-gap semiconductors with the band-gap of 1.57 and 1.78 eV at the R-point, respectively. In MAPbI$_3$ and MAPbI$_2$Cl perovskites, the conduction band minimum (CBM) is mainly occupied by Pb 6p states and the valence band maximum (VBM) is mainly occupied by I 5p states. No impurity energy bands were found in the band-gap for the Cl incorporation since the energy of Cl 3p states are smaller than the energy of I 5p states, and these energy bands merge into the middle of the VBM.

The decrease in hole mobility along the ⟨1 0 0⟩ direction in MAPbI$_2$Cl can be easily understood since the Cl 3p states have a smaller energy than I 5p. Therefore, the localization for the carriers can be much strong around the Cl, resulting in a large hole effective mass of 0.47 m$_0$ along ⟨1 0 0⟩ direction. For the electron mobility, the CBM is nearly three-fold degenerated in the MAPbI$_3$ perovskite, corresponding to the energy states in Pb 6p$_x$, 6p$_y$ and 6p$_z$ orbits. As a result, we can find that the electrons along the ⟨1 0 0⟩ direction of MAPbI$_3$ perovskite have a light effective mass of 0.09 m$_0$ and two heavy effective masses of 0.42 m$_0$ and 0.74 m$_0$, respectively. In the MAPbI$_2$Cl perovskite, the CBM is only two-fold degenerated, while the third energy state moves up with an energy split of 0.47 eV. Due to this energy state up-shift, only two heavy effective masses for electrons (0.86 m$_0$ and 1.09 m$_0$) were left behind along the R – Q path, leading to a small electron mobility in the ⟨1 0 0⟩ direction. Based on the electron density distribution calculations shown in Fig. 3, we found that the energy state split can be attributed to the strong Pb 6p$_x$ – Cl 3p$_y$ anti-bonding orbital interaction (Fig. 3b). It was caused by the large deviation of Pb position in the ⟨0 1 0⟩ direction, leading to the energy level raising of the CBM state of Pb 6p$_x$ character; while the CBM states of Pb 6p$_y$ and 6p$_z$ character almost remain the same since they only have a little anti-bonding interaction with I 5p$_x$ and 5p$_z$ orbits (Fig. 3a).

Although there is a large decrease in carrier mobility along the ⟨1 0 0⟩ direction due to the Cl incorporation, the MAPbI$_2$Cl perovskite exhibits an enhanced carrier transport performance in the ⟨0 1 0⟩ direction with a carrier mobility of 24,474 cm^{2}V^{-1}s^{-1} for electrons and 1467 cm^{2}V^{-1}s^{-1} for holes, respectively. As there is no Cl involved in the ⟨0 1 0⟩ direction, we believe this enhanced carrier mobility can be attributed to the re-orientated polar molecule MA. Since the MA is orientated from ⟨1 1 1⟩ to nearly ⟨0 1 1⟩ direction, the lattice polarization of MAPbI$_2$Cl perovskite along ⟨0 1 0⟩ direction increases, leading to a smaller carrier effective mass of 0.07 m$_0$ for electrons and 0.18 m$_0$ for holes. Therefore, it enhances the carrier mobility.

To further confirm the MA molecule orientation contribution in the carrier transport performance, we also calculated the electronic properties of the MAPbI$_3$ perovskite with the MA orientation fixed in ⟨1 0 0⟩ direction as shown in Fig. 4. The calculated band gap is 1.67 eV, larger than the band gap of 1.57 eV in the MAPbI$_3$ with the MA orientated in ⟨1 1 1⟩ direction. It originates from the up-shift of the CBM once the polarization direction of MA is changed. The calculated carrier effective mass is 0.70 m$_0$ and 0.20 m$_0$ in ⟨1 0 0⟩ direction for