First Principles Computation on the Photovoltaic and Thermoelectric Properties of MAPbI\(_{3-x}\)Cl\(_x\) Perovskites

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Abstract: This research employs the first principles computation to simulate the chlorine (Cl) doping effect with different proportion (x value) on the photovoltaic and thermoelectric properties of bulk mixed halide methyl-ammonium lead perovskites (MAPbI\(_3\),Cl\(_x\)). In the study, the density functional theory (DFT) and Boltzmann transport equation (BTE) are applied to calculate the optical band gaps, electrical conductivity \(\sigma\), carrier thermal conductivity \(\kappa_c\), and Seebeck coefficient \(S\). The density functional perturbation theory (DFPT) and Debye model are used to calculate the phonon thermal conductivity \(\kappa_{ph}\). Tuning the greatest thermoelectric figure of merit (ZT) with suitable solar absorbance range is the major target for our solar thermoelectric chip design. The simulation results reveal that doping Cl will increase the electronic conductivity, phonon thermal conductivity, and causes a blue shift in the light absorption. The main contribution to the total thermal conductivity is mainly from optical phonons, and the main absorbance wavelength locates in the ultraviolet and visible light region (40nm < \(\lambda\) < 700nm). When x=0.25, MAPbI\(_{2.75}\)Cl\(_{0.25}\) achieves the optimized tuning for both light absorption coefficient \(\alpha\) and figure of merit ZT in our simulation cases.

Keywords: Perovskites, solar thermoelectricity, light absorption

1 Introduction
In recent years, the methyl-ammonium lead iodide perovskite (MAPbI\(_3\)) plays an important role in photovoltaic solar cells. As the light absorber in solar cells, it has a wide range of light absorption, long carrier diffusion length and high carrier mobility [1-3]. Also, MAPbI\(_3\) has an ultra-low thermal conductivity, \(\kappa < 0.5\) W/mK, so it can be considered a potential thermoelectric material, provided with a good electrical property [4]. The latter has been found that doping chlorine (Cl) can improve the electrical performance [5-6]. Thus in this study, we tried to find the optimized Cl concentration x, corresponding to the best light absorption coefficient (\(\alpha\)) and the thermoelectric figure of merit (ZT) of MAPbI\(_{3-x}\)Cl\(_x\). The simulation molecular model of the MAPbI\(_{3-x}\)Cl\(_x\) with tetragonal lattice structure is shown in Figure 1. The Cl substitution position is still unknown, however the recent experiment reported that it occurs at the equatorial position rather than the apical position [7]. Through this study, we intend to understand the effect of Cl doping on MAPbI\(_{3-x}\)Cl\(_x\) photovoltaic and thermoelectric properties and thus will develop a better solar thermoelectric device in the future.

2 Computational Algorithm
A thermoelectric figure of merit is generally defined as \(ZT = \sigma S^2 T / (\kappa_c + \kappa_{ph})\) to evaluate the performance of thermoelectric materials, where \(\sigma\) is the electric conductivity, \(S\) is the Seebeck
coefficient, $T$ is the operating temperature, $\kappa_e$ is the thermal conductivity due to electron transportation, and $\kappa_{ph}$ is the thermal conductivity due to phonon conduction.

Figure 1. The side view of a MAPbI$_{3-x}$Cl$_x$ model with tetragonal lattice structure, the Cl doping concentration varies from $x=0$ to $x=2$, and the equatorial positions are labelled in green. All the simulation models were built up using the CASTEP platform [8].

The first principles density functional theory (DFT) with the Perdew-Burke-Ernzerhof exchange-correlation energy (PBE) and Boltzmann transport equation (BTE) are employed in the detailed simulation of electron transportation. Using the Kohn-Sham equation [9], the total energy, $E$, of a multi-electron system can be represented as the functional of the density function $\rho$:

$$E[\rho] = T_S[\rho] + E_H[\rho] + E_{ext}[\rho] + E_{xc}[\rho]$$  \hspace{1cm} (1)

where $T_S$ is the total kinetic energy from the individual electron movement in system, $E_H$ is the Hartree energy, $E_{ext}$ is the external potential energy due to the external force, and $E_{xc}$ is the exchange-correlation energy, which includes all the remaining unknown energy. Note that all these energies are functional of the density function, which is the fundamental assumption of the density functional theory (DFT).

To transfer the electron transport phenomenon from nano-scope to macro-scope, we employ the Boltzmann transport equation [10] to represent the movement of electrons as a differential equation of velocity distribution function, $f$, versus time, $t$, space, $r$, and momentum, $p$, i.e.:

$$\frac{\partial f}{\partial t} + v_e \cdot \nabla_r f + e_0 \varepsilon \cdot \nabla_p f = \frac{\partial f}{\partial t}/c \approx \frac{f_0 - f}{\tau_e}$$  \hspace{1cm} (2)

where $\partial f/\partial t$ is the partial derivative of the instant electron distribution function with respect to time, and the subscript $c$ denotes the collision term due to the collisions between the electrons, where $v_e$ is the electron velocity; $\varepsilon$ is the applied external electric field; $\nabla_r$ and $\nabla_p$ are the partial derivative with respect to the electron position vector and the momentum vector respectively; $e_0$ is the elementary charge; $\tau_e$ is the relaxation time of the electron; and $f_0$ is the electron distribution function at the equilibrium state, i.e., the Fermi-Dirac distribution.
2.1 Electron Transport Properties

The summarized electrical conductivity $\sigma$, carrier thermal conductivity $\kappa$, and Seebeck coefficient $S$ are calculated by

$$\sigma_{e, h} = \pm \frac{2 e^2}{3 m^*} K_1$$

$$S_{e, h} = \pm \frac{1}{e_0 T} \left[ \mu - \frac{K_2}{K_1} \right]$$

$$\kappa_{e, h} = \pm \frac{2}{3 m^* T} \left[ K_3 - \frac{(K_2)^2}{K_1} \right]$$

$$K_n = \int_{E_0}^{\infty} D(E) \tau E^n \frac{\partial f_0}{\partial E} dE$$

where $m^*$ is the effective carrier mass, $T$ is the operation temperature, and $\mu$ is the chemical potential. To make the formulas more concise, we define $K_n$, related to the carrier energy $E$. The subscripts $e$ and $h$ denote electrons and holes. The notation $D(E)$ is the density of states, $\tau$ is the carrier relaxation time, $E_0$ denotes the referential energy, which is the conduction band edge (CBE) for electrons and the valence band edge (VBE) for holes.

2.2 Phonon Transport Properties

In the phonon transport simulation, we used the density functional perturbation theory (DFPT) to evaluate the phonon dispersion relation and phonon density of states. Then we applied the Debye model to calculate the phonon thermal conductivity $\kappa_{ph}$, which is expressed by

$$\kappa_{ph} = \int_0^{\omega_D} C_v(\omega) \nu_g^2(\omega) \tau_{ph}(\omega) d\omega$$

where $C_v$, $\nu_g$, $\tau_{ph}$ are phonon specific heat capacity, group velocity, and phonon relaxation time, respectively, which are all functions of frequency $\omega$. The integration limit $\omega_D$ denotes the Debye frequency.

3 Results and Discussion

In our simulations, we pre-set the cut-off energy at 310 eV, maximum force equal to 0.01 eV/Å, and the calculation tolerance at $2.0 \times 10^{-10}$ eV/atom, with a $3\times3\times2$ k-point mesh. The lattice parameters of MAPbI$_3$ are set as $a = b = 8.81$ Å, $c = 12.99$ Å, which are very close to $a = b = 8.83$ Å, and $c = 12.76$ Å from an XRD measurement at 180K [11]. Besides, the predicted band gap $E_g = 1.519$ eV, is in good agreement with the experimental results, which are 1.51 eV (Kubelka–Munk spectrum) and 1.61 eV (UV-Vis spectrum) [12].

3.1 Photovoltaic Property

Figure 2 shows the light absorption spectrum of the MAPbI$_{1-x}$Cl$_x$ versus different Cl concentrations. The results indicate that the main absorbance wavelength locates in the ultraviolet and visible light region ($40nm < \lambda < 700nm$). Also they reveal that the Cl doping will cause a blue shift, which is due to the increase of band gap. Thus, the absorption range and the absorption strength have been reduced simultaneously due to the doping effect. The phenomenon is especially apparent when $x \geq 0.5$. When $x = 0.25$, the absorption coefficient $\alpha$ is nearly same as at the condition $x = 0$, which has the best light absorption.
Figure 2. (a) Band gaps of MAPbI$_{3-x}$Cl$_x$, which increase along with the Cl concentration. (b) Light absorption spectra of MAPbI$_{3-x}$Cl$_x$, in which more Cl causes a blue shift due to increase of the band gap.

3.2 Thermoelectric Property

In our electrical property evaluation, two carrier types, electrons (e) and electron holes (h) are considered; and in the thermal property calculation, we consider the acoustic phonons as well as those optical ones for the intrinsic MAPbI$_3$ only. The computational results are very close to the experiments from Mettan et al [13] at 300K. The calculation results show that the electrical conductivity is $1.53 \times 10^{-3}$ S/m (while $1.58 \times 10^{-3}$ S/m in the experiment), the Seebeck coefficient is $0.29 \times 10^{-3}$ V/K (0.4 $\times 10^{-3}$ V/K in the experiment), and the thermal conductivity is 0.274 (0.5 in experiment) W/mK. The evaluated ZT is $1.4 \times 10^{-7}$, which is extreme low compared with the commercial ones. To enhance the ZT, we have to improve the electrical performance through doping Cl into the MAPbI$_3$. Figure 3 shows that doping Cl will also increase the phonon thermal conductivity, which is due to the increase of the phonon group velocity. The main reason is that the molecular weight becomes lighter through Cl doping. Comparing to the acoustic phonons, the optical phonons have more contribution to the thermal conductivity. It indicates that the optical phonons dominate the thermal properties of MAPbI$_{3-x}$Cl$_x$.

Figure 3. (a) Thermal conductivities of acoustic and optical phonons of MAPbI$_{3-x}$Cl$_x$. Doping more Cl tends to increase the phonon thermal conductivity. (b) Averaged group velocity of phonons of MAPbI$_{3-x}$Cl$_x$. Doping more Cl increases the phonon group velocity generally, leading to the increase of thermal conductivity.
Next, we move to study the carrier doping effect on the thermoelectric properties. Figure 4 and Figure 5 show that the electrical conductivity and ZT vary with carrier concentrations. Figure 4 shows that both the p-type and n-type doping will proportionally increase the electrical conductivity, which reaches the maximum value at $10^{20}$ cm$^{-3}$. For the p-type condition, the doped ones ($\sigma=9.02$ S/m) can be 27 times greater than the undoped ones ($\sigma=0.33$ S/m). For the n-type condition, the doped ones ($\sigma=0.53$ S/m) are 18 times greater than the undoped ones ($\sigma=0.03$ S/m). It concludes that the Cl doping will significantly enhance the electrical conductivity.

**Figure 4.** Electrical conductivity of MAPbI$_3$$_x$Cl$_x$. When doping Cl, the electric conductivity can be improved from $\sigma=0.33$ S/m to $\sigma=9.02$ S/m for p-type MAPbI$_3$$_x$Cl$_x$. For n-type, $\sigma=0.03$ S/m is improved to 0.53 S/m.

**Figure 5.** Figure of merit, ZT, of p-type and n-type MAPbI$_3$$_x$Cl$_x$, in which $x=0.25$ has the greatest ZT in both intrinsic and extrinsic conditions. For p-type doping, the maximum ZT of MAPbI$_3$ and MAPbI$_{2.75}$Cl$_{0.25}$ are $2.21\times10^{-4}$ and $2.09\times10^{-3}$ respectively. For n-types, the maximum ZT are $2.00\times10^{-5}$ and $2.09\times10^{-4}$ respectively.

**Figure 5** shows that the figure of merit, ZT, of the MAPbI$_3$$_x$Cl$_x$ without and with carrier doping effects. At the room temperature $T=300K$, ZT proportionally increases with the carrier concentration. The minimum and the maximum ZT occur at $x=0$ and $x=0.25$ respectively. In low doping condition, e.g., $x=0.25$, electrical conductivity increases while the thermal conductivity almost remains the same value as MAPbI$_3$. When electron (or hole) doping concentration reaches $10^{20}$ cm$^{-3}$, the ZT value of MAPbI$_3$ will achieve $2.00\times10^{-5}$ (or $2.21\times10^{-4}$), which is 1000 times the value of the intrinsic condition.

**4 Conclusion**

The computation of the photovoltaic properties in this study reveals that MAPbI$_3$ has the best absorbance, either strength or range. However, considering both the photo and electrical properties, MAPbI$_{2.75}$Cl$_{0.25}$ may become the better light absorber than MAPbI$_3$. This is due to the fact that the MAPbI$_{2.75}$Cl$_{0.25}$ has almost the same absorption ability and about 20 times greater of the electrical conductivity than the MAPbI$_3$.

In conclusion, MAPbI$_{2.75}$Cl$_{0.25}$ is the best tuning for the light absorption layer in the solar cell application, and it has the greatest ZT value for the thermoelectric chip device. Hence it may be used to improve the performance of future solar thermoelectric chips.
References