Doping optimization of organic-inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ for high thermoelectric efficiency

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A R T I C L E   I N F O

Article history:
Received 22 September 2016
Received in revised form 7 December 2016
Accepted 9 January 2017
Available online 19 January 2017

Keywords:
Organic-inorganic hybrid perovskite
Thermoelectric transport
First-principles calculations

A B S T R A C T

The newly discovered photovoltaic hybrid perovskite materials have been suggested for thermoelectric applications as they possess very low thermal conductivity and large Seebeck coefficient. However, to achieve a high figure of merit, chemical doping is necessary to increase the electrical conductivity. In the present work, we examined the thermoelectric figure of merit for CH$_3$NH$_3$PbI$_3$ as a function of carrier concentration based on first-principles calculations. For doped semiconductors, the impurity scattering usually plays a dominant role in the charge transport. Both impurity scattering and acoustic phonon scattering have been incorporated in our calculations. We showed that at the impurity concentration of 10$^{10}$ cm$^{-3}$, the room temperature $zT$ value of tetragonal CH$_3$NH$_3$PbI$_3$ could be optimized to reach unity at the carrier concentration on the same order of magnitude as 10$^{18}$ cm$^{-3}$. The hole-doped CH$_3$NH$_3$PbI$_3$ exhibits superior thermoelectric property than the electron-doped one, and we propose to engineer the vacancies of organic cations for the enhanced hole concentration and thermoelectric efficiency.

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1. Introduction

Thermoelectric (TE) materials provide a direct energy conversion scenario between heat and electricity, and have attracted intensive interests for their potential applications in waste heat recycle and space power generation [1–3]. The efficiency of a TE material is characterized by the dimensionless figure of merit $zT$, defined as $zT = \frac{S^2 \sigma T}{k}$, where $S$, $\sigma$, $T$, and $k$ are Seebeck coefficient, electrical conductivity, temperature and thermal conductivity, respectively. The thermal conductivity is constituted by two parts, the electrical thermal conductivity ($\kappa_{e}$) and the lattice thermal conductivity ($\kappa_{l}$). High performance TE materials should possess high Seebeck coefficient and electrical conductivity as well as low thermal conductivity, i.e., the electrical transport properties should be enhanced but the phonon transport should be suppressed.

To compete with other renewable energy solutions, $zT$ is expected to exceed 1.5 for the entire relevant temperature range. Among bulk inorganic TE materials, the commercialized bismuth telluride based alloys possess $zT$ around one [4,5]. The newly reported SnSe single crystal possesses $zT$ ranging from 0.7 to 2.0 in the temperature range of 300–773 K, which is mainly ascribed to the enhanced Seebeck coefficient and high electrical conductivity achieved by hole doping [6]. However, the cost of inorganic TE modules per watt for power generation, cooling, or heating is so high as to have limited their applications [7]. As compared to inorganic materials, organic materials are low-cost, solution processable, and flexible. Organic TE materials have low thermal conductivity, but their electrical properties are poor, often leading to very low energy conversion efficiency. The best known organic TE materials are conducting polymers, particularly PEDOT:ToS and PEDOT:PSS. Lab researches show that the $zT$ value of p-type PEDOT has achieved 0.2–0.5 by doping engineering [8,9], and that of n-type metal coordination polymer poly(nickel-ethylenetetrathio-late) has reached 0.30 at room temperature [10].

Organic-inorganic composite materials have the potential to combine the advantages of their organic and inorganic constituents, i.e., poor thermal transport in the organic component, and excellent charge transport in the inorganic component. However, how to process such composite materials to achieve the best TE
performance is yet to be explored. Recently, organic anions have been intercalated in layered transition metal dichalcogenide TiS₂ to fabricate the hybrid, which possesses a ZT value of 0.28 at 373 K [11]. It was shown that the organic intercalation causes a significant reduction of the thermal conductivity, while the hybrid retains the high electrical power factor of TiS₂. The newly discovered organic-inorganic hybrid perovskite materials are originally used as sensizers in photovoltaics [12]. Afterwards, it has been demonstrated with a planar heterojunction solar cell device structure [13], and the photo conversion efficiency reaches 22.1% [14]. The great success of CH₃NH₃PbI₃ in photovoltaics can be largely ascribed to its excellent optical absorption, high carrier mobility and long diffusion length of charge carriers. Though CH₃NH₃PbI₃ has a low formation energy and suffers from the poor stability in moisture and air, progress has been made to improve the stability of perovskite solar cells against water and oxygen degradation [15–18]. CH₃NH₃PbI₃ has also been reported to have an ultralow thermal conductivity (0.59 W m⁻¹ K⁻¹ at room temperature) [19,20]. These properties have inspired great interests in CH₃NH₃PbI₃ for solar TE applications [21–23]. We noted that the TE figure of merit for CH₃NH₃PbI₃ has been studied from first-principles calculations [22,23]. In Ref. [22], He and Galli only accounted for the acoustic phonon scattering of charge carriers in the calculation of electrical transport properties, while in Ref. [23], the TE properties were calculated by solving the Boltzmann transport equation under the constant relaxation time approximation, and the relaxation time was supplied as an empirical parameter. We have shown in our previous works that when only the acoustic phonon scattering is taken into account, the charge carrier mobility and the ZT value would be overestimated [24,25]. We found that in PEDOT:Tos after the ionized impurity scattering process was included to account for the effect, the calculated TE transport coefficients were in reasonable agreement with the available experimental data [24]. Indeed, for TE applications, doping is an effective way to enhance power factors, so the ionized impurity scattering becomes an important scattering mechanism of charge carriers that needs to be considered to give good evaluations of TE properties. Our earlier study of the charge carrier mobility in CH₃NH₃PbI₃ perovskite showed that the ionized impurity scattering dominates over the acoustic phonon scattering when the density of impurity reaches 10¹⁸ cm⁻³ [26].

Herein we investigate the TE transport properties of CH₃NH₃PbI₃ by using the Boltzmann transport theory in the relaxation time approximation, and incorporating both acoustic phonon scattering and ionized impurity scattering mechanisms. We find that the TE performance of tetragonal CH₃NH₃PbI₃ is better than that of the cubic one due to the higher carrier mobility and the lower thermal conductivity in the tetragonal phase. The p-type CH₃NH₃PbI₃ perovskite has higher figure of merit than the n-type one, and the p-type tetragonal CH₃NH₃PbI₃ can achieve the highest ZT value of 1.26 at the phase transition temperature of 330 K at the carrier density of 6 × 10²⁸ cm⁻³. The hole doping by the accurate control of the vacancy density of organic cations is suggested. Our theoretical predictions may act as a guide in the doping optimization of the TE performance of CH₃NH₃PbI₃ perovskites.

2. Methodological approach

2.1. Electronic structure calculations

The electronic structure calculations were performed within the framework of density functional theory (DFT), using the projector augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) [27,28] for both cubic and tetragonal phases of CH₃NH₃PbI₃ perovskites. The Perdew-Burke-Ernzerhof (PBE) [29] exchange-correlation functional and the generalized gradient approximation (GGA) were adopted. The spin-orbit coupling (SOC) effect was included in all the calculations for the presence of heavy element lead. A k-mesh of 4 × 4 × 4 was used to optimize the lattice parameters and atomic positions until the forces on each atom were less than 0.01 eV Å⁻¹. The energy convergence criterion in the self-consistent field iteration was 10⁻³ eV. The converged charge density was obtained on a k-mesh of 7 × 7 × 7 and 9 × 9 × 9 for tetragonal and cubic CH₃NH₃PbI₃, respectively.

2.2. Boltzmann transport theory

The Boltzmann transport equation describes how a single-particle state population function of charge carries evolves as time in the external fields such as weak electric or magnetic field and thermal gradient. By invoking the relaxation time approximation, TE transport parameters, such as electrical conductivity σ, Seebeck coefficient S and electric thermal conductivity κₜ, can be derived by solving the steady-state Boltzmann transport equation [30]:

\[
\sigma = \frac{e^2}{11} \int \tau(k) \langle \mathbf{v}(k) \rangle \mathbf{v}(k) \frac{\partial f^e(\epsilon_k)}{\partial \epsilon_k} d\epsilon
\]

(1)

\[
\kappa_0 = \frac{1}{11} \int \tau(k) \langle \mathbf{v}(k) \rangle \left( \epsilon_k - \epsilon_0 \right)^2 \frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} d\epsilon
\]

(2)

\[
S = \frac{e}{\sigma T} \int \tau(k) \langle \mathbf{v}(k) \rangle \left( \epsilon_k - \epsilon_0 \right) \left( \frac{\partial f^0(\epsilon_k)}{\partial \epsilon_k} \right) d\epsilon
\]

(3)

\[
\kappa_T = \kappa_0 - S^2 \sigma T
\]

(4)

where \(\tau(k)\) is the relaxation time of charge carriers, \(\mathbf{v}(k)\) is the group velocity, \(\Omega\) is the volume of unit cell, \(f^e\) is the Fermi-Dirac distribution function, \(\epsilon_f\) is the Fermi level, \(\epsilon_k\) is the electronic band eigenvalues, and \(\kappa_0\) is the thermal tensor. The band energies on a fine k-mesh of 41 × 41 × 41 for cubic and 31 × 31 × 31 for tetragonal CH₃NH₃PbI₃, respectively, were calculated based on the converged charge density, and interpolated on a k-mesh of 10 times denser.

The relaxation time is the inverse of the scattering probability of charge carriers by phonons, impurities and/or defects. The scattering of charge carriers helps to balance the effect of external fields, namely, the deviation of the distribution function from its equilibrium. According to the Mathiessen’s rule, if different scattering events are assumed to be independent of each other, the total relaxation time takes the form:

\[
\frac{1}{\tau} = \frac{1}{\tau_{\infty}} + \frac{1}{\tau_{\text{imp}}}
\]

(5)

where \(\tau_{\infty}\) and \(\tau_{\text{imp}}\) represent relaxation times due to acoustic phonon scattering and impurity scattering, respectively. According to the Fermi’s golden rule, the relaxation time can be expressed as:

\[
\frac{1}{\tau(k)} = \sum_{k'} \frac{2\pi e^2}{h} \delta(\epsilon(k) - \epsilon(k')) |M(k, k')|^2 \cdot (1 - \cos \theta)
\]

(6)

where \(|M(k, k')|\) is the scattering matrix element describing the scattering process of charge carriers from Bloch state \(k\) to \(k'\) and \(\theta\) is the corresponding scattering angle.
2.3. Deformation potential theory for acoustic phonon scattering

The deformation potential (DP) theory [31] has been successfully applied to predicting the carrier mobility in graphene, graphdiyne, and organic molecular crystals [32]. The DP theory describes the acoustic phonon scattering in the long-wave limit. The scattering matrix element can be expressed as

$$|M(k, k')|^2 = \frac{k_B T e^2}{C_0}$$  \hspace{1cm} (7)

where $E_1$ and $C_0$ are deformation potential constant and elastic constant, respectively. Both of them can be easily derived from first-principles calculations. We applied uniaxial strains to the unit cell of CH$_3$NH$_3$PbI$_3$ along the three crystal directions, respectively. The elastic constants were obtained by the parabolic fitting of the total energy to the strain, while the deformation potential constants for electrons and holes were obtained by the linear fitting of the conduction and valence band energy shift, respectively, against the strain.

2.4. Brooks-Herring method for ionized impurity scattering

The Brooks-Herring approach [33] was applied to calculate the scattering matrix element of charge carriers by ionized impurity or defects. The interaction takes the form of a screened Coulomb potential

$$V(r) = \frac{Z_{ion} e^2}{4\pi \varepsilon_0 \varepsilon_r r}$$  \hspace{1cm} (8)

where $Z_{ion}$ is the charge of the ionized impurity, $\varepsilon_r$ and $\varepsilon_0$ are the relative and vacuum dielectric constant, respectively. The experimental value of $\varepsilon_r = 6.5$ [34] was taken in our calculations. $L_D$ is the Debye screening length, $L_D = \sqrt{\varepsilon_0 \varepsilon_r k_BT/e^2 n}$, where $n$ is the free charge carrier density. The scattering matrix element is

$$|M(k, k')|^2 = \frac{n_{imp} Z_{ion}^2 e^4}{\Omega^2 (\varepsilon_r e^2)^2 (L_D^2 + |k - k'|^2)^2}$$  \hspace{1cm} (9)

where $n_{imp}$ is the density of ionized impurity, $\Omega$ is the volume of the unit cell. We take $Z_{ion}$ to be one. The ionized impurities are assumed to affect the scattering of charge carriers independently, and the scattering rate is directly proportional to the density of ionized impurities.

3. Results and discussion

3.1. Tuning carrier concentration for high TE figure of merit

The band structure and charge carrier mobilities of cubic and tetragonal CH$_3$NH$_3$PbI$_3$ have been calculated in our previous work [26]. Both cubic and tetragonal phases of CH$_3$NH$_3$PbI$_3$ are direct band gap semiconductors, but their band gaps are severely underestimated by the SOC-DFT method. In the calculation of charge transport properties, we applied the so-called scissor operator to the conduction band energies to reproduce the experimental band gap of 1.6 eV. The scissor operator does not change the band dispersion and group velocities. When the Fermi level is in the gap and the carrier concentration is low, both conduction and valence bands may contribute to the Seebeck coefficients with opposite signs, resulting in a drop of the Seebeck coefficients at low carrier concentrations. This is known as the bipolar effect. With the underestimated band gap, the bipolar effect would be more pronounced. For this reason, the scissor operator has been widely applied to the conduction band energies to produce the correct carrier concentration dependence of Seebeck coefficients [35,36].

The electrical conductivity, Seebeck coefficient and electronic thermal conductivity all vary with the charge carrier concentration. To tune the carrier type and concentration, we simply shifted the Fermi level towards the conduction or valence band to mimic the n-type or p-type doping, respectively. If the carrier concentration is low, it is safe to assume that the band structures are not influenced by doping. This is known as the rigid band approximation. The electrical conductivity, Seebeck coefficient, electronic thermal conductivity, and power factor as a function of the carrier concentration have been shown in Fig. 1 for tetragonal phase and Fig. 2 for cubic phase at the temperature of 330 K. The hybrid perovskite CH$_3$NH$_3$PbI$_3$ undergoes the phase transition at the temperature of 330 K. At the temperature above 330 K it is cubic and below 330 K it is tetragonal. In tetragonal CH$_3$NH$_3$PbI$_3$, [100] and [010] are degenerate directions. In cubic phase of CH$_3$NH$_3$PbI$_3$, [100] and [001] are degenerate directions. The organic cation CH$_3$NH$_3$ lies parallel to the [100] direction, so it becomes pseudocubic after optimization. We only present the data in [100] and [001] directions.

As shown in Figs. 1 and 2, the electrical conductivity increases with the carrier concentration, and the Seebeck coefficient decreases linearly with the logarithm of the carrier concentration.

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![Fig. 1](image1.jpg)

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![Fig. 2](image2.jpg)

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For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
As a result, the power factor exhibits a maximum at a certain carrier concentration of c.a. $10^{19}$ cm$^{-3}$. In the calculation of charge transport properties, we included two scattering mechanisms of charge carriers, i.e., acoustic phonon scattering and charged impurity scattering. Our previous investigation on intrinsic and extrinsic charge transport in CH$_3$NH$_3$PbI$_3$ perovskites showed that at the impurity density of $10^{18}$ cm$^{-3}$, the charge carrier mobilities derived at low carrier concentrations were in reasonable agreement with the experimental data reported for CH$_3$NH$_3$PbI$_3$ single crystals [26]. In the current study, we therefore set the impurity density to $10^{18}$ cm$^{-3}$. The charged impurity scattering is dependent on the carrier concentration through the Debye screening length $L_D$. For TE applications, the optimal carrier concentration to achieve the largest power factor is on the order of $10^{18}$ cm$^{-3}$. The ionized impurity is so screened by free charge carriers at such carrier concentrations that the impurity scattering is substantially weakened and its contribution to charge transport becomes comparable to the acoustic phonon scattering.

According to our previous work [25], when the carrier concentration is not very high the Seebeck coefficient shows a linear relationship with the logarithm of carrier concentration:

$$S = \frac{k_b}{e} \ln(n) + \frac{k_b}{e} \ln N_{\text{eff}}$$

(10)

where $N_{\text{eff}}$ is the effective density of states (DOS) near the band edge of valence or conduction bands for holes or electrons. The slope is determined by two physical constants, the Boltzmann constant $k_b$ and the elementary charge $e$. The intercept is determined by the effective density of states $N_{\text{eff}}$. This linear relationship is well obeyed by our calculation data as clearly seen from Figs. 1 and 2, and the slope is almost the same irrespective of carrier type and crystal phase. Since the effective density of states near the valence band edge is larger than that near the conduction band edge, the Seebeck coefficient of holes is larger than that of electrons for either cubic or tetragonal phase of CH$_3$NH$_3$PbI$_3$. As the magnitude of Seebeck coefficient is related to the DOS, the Seebeck coefficient is isotropic in different transport directions.

The largest power factor at the optimal doping level and the corresponding transport coefficients, including the Seebeck coefficient, the electrical conductivity, the electronic thermal conductivity have been summarized in Table 1. For tetragonal phase, the largest power factor is 53.0 and 30.0 $\mu$W cm$^{-1}$ K$^{-2}$ at the hole concentration of $1.4 \times 10^{19}$ and $1.2 \times 10^{19}$ cm$^{-3}$ in the [100] and [001] directions, respectively, and it is 32.7 and 23.3 $\mu$W cm$^{-1}$ K$^{-2}$ at the electron concentration of $1.0 \times 10^{19}$ and $8 \times 10^{18}$ cm$^{-3}$ in the [100] and [001] directions, respectively. The power factor of holes is larger than electrons in both directions, indicating that tetragonal CH$_3$NH$_3$PbI$_3$ is a p-type TE material. The power factor of tetragonal CH$_3$NH$_3$PbI$_3$ after doping optimization at 330 K is even comparable to that reported for Na doped SnSe single crystal, which is $\sim 40 \mu$W cm$^{-1}$ K$^{-2}$ at 300 K and $\sim 14 \mu$W cm$^{-1}$ K$^{-2}$ at 773 K [6], suggesting tetragonal CH$_3$NH$_3$PbI$_3$ is an excellent TE cooling material working in the low-temperature regime. We also find that the power factor in the [100] direction is larger than the [001] direction, which comes from the anisotropy of electrical conductivity. The electrical conductivity of both electrons and holes in cubic phase is smaller than that in tetragonal phase, while the Seebeck coefficient in cubic CH$_3$NH$_3$PbI$_3$ is similar to that in tetragonal CH$_3$NH$_3$PbI$_3$. As a result, tetragonal phase CH$_3$NH$_3$PbI$_3$ shows TE properties superior to cubic phase, with larger power factors for both electrons and holes.

According to the Wiedemann-Franz law $\kappa_e = L_0 T$, the electronic thermal conductivity exhibits the same trend as the electrical conductivity. $L$ is called the Lorenz constant, which takes the

Table 1: TE transport properties of CH$_3$NH$_3$PbI$_3$ perovskite at the optimal doping level and the phase transition temperature.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Carrier density (10$^{19}$ cm$^{-3}$)</th>
<th>$S$ (10$^2$ V cm K$^{-1}$)</th>
<th>$\sigma$ (10$^3$ S cm$^{-1}$)</th>
<th>$\kappa_e$ (W m$^{-1}$ K$^{-2}$)</th>
<th>$\rho$ (ohm cm)</th>
<th>$L_0$ T</th>
<th>$e$ (10$^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal</td>
<td>h [100]</td>
<td>1.4</td>
<td>135</td>
<td>2.89</td>
<td>53.0</td>
<td>1.53</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>[001]</td>
<td>1.2</td>
<td>142</td>
<td>1.48</td>
<td>30.0</td>
<td>0.71</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>e [100]</td>
<td>1.0</td>
<td>−130</td>
<td>1.92</td>
<td>32.7</td>
<td>1.04</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>[001]</td>
<td>0.8</td>
<td>−143</td>
<td>1.15</td>
<td>23.3</td>
<td>0.62</td>
<td>0.66</td>
</tr>
<tr>
<td>Cubic</td>
<td>h [100]</td>
<td>1.2</td>
<td>150</td>
<td>0.78</td>
<td>17.5</td>
<td>0.36</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>[001]</td>
<td>1.4</td>
<td>147</td>
<td>1.53</td>
<td>32.8</td>
<td>0.71</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>e [100]</td>
<td>0.8</td>
<td>−153</td>
<td>0.65</td>
<td>35.2</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>[001]</td>
<td>1.8</td>
<td>−126</td>
<td>1.66</td>
<td>26.2</td>
<td>0.96</td>
<td>0.71</td>
</tr>
</tbody>
</table>
approaching such systems doped materials, between derive electrons. using fi Lorenz Sommerfeld comparison 1 K 4.

Theoretical calculations confirmed this. The maximum zT value for p-type CH3NH3PbI3 at 295 K is calculated to be 1.08 when the electrical conductivity is enhanced to ~900 S cm−1, and the corresponding carrier concentration is 6 × 1018 cm−3, four orders of magnitude higher than the photo-generated carrier concentration.

The theoretical calculations by Qian et al. [20] have provided the lattice thermal conductivity of CH3NH3PbI3 spanning a temperature range from 150 K to 400 K. Fig. 4a shows their results on the temperature dependence of lattice thermal conductivity. There is an abrupt increase of the thermal conductivity when CH3NH3PbI3 transits from tetragonal to cubic phase, which has been explained by the higher phonon group velocity and lower anharmonicity in cubic CH3NH3PbI3 [20]. In either phase, the lattice thermal conductivity decreases as the temperature increases. Low thermal conductivity favors high TE efficiency. Fig. 4b shows our predictions of the largest value of zT and the corresponding carrier concentration as a function of temperature, based on the lattice thermal conductivity derived by Qian et al. [20]. As shown above the power factor of tetragonal phase is larger than that of cubic phase, and the lattice thermal conductivity increases abruptly when going from tetragonal to cubic phase, the zT value exhibits an abrupt drop at the phase transition temperature. Moreover, the zT value in both tetragonal and cubic CH3NH3PbI3 increases with the increasing temperature. So the best TE performance is observed in tetragonal CH3NH3PbI3 at the phase transition point, with the zT value of 1.26. This value is very high for bulk TE materials, even comparable to the high-performing nanostructured bismuth antimony telluride bulk alloys, which have a zT value about 1.2 at room temperature [38].

### 3.2. Hole-doping site for efficient TE conversion

In the above, we have demonstrated the importance of tuning carrier concentration for the best TE performance. In our calculations, we assumed that doping has little influence on the band structure of host materials if the dopant concentration is low. Since tetragonal CH3NH3PbI3 has exhibited excellent p-type TE properties when optimally doped, we hope to find a way to tune the hole concentration while minimally alter its band structure. To shed light on the potential hole-doping sites in tetragonal

![Image](image_url)
CH$_3$NH$_3$PbI$_3$, we analyzed its band structure and partial DOS (Fig. 5a). The valence band of CH$_3$NH$_3$PbI$_3$ is composed of I-5p atomic orbital and Pb-6s atomic orbital. The orbitals of methyl-ammonium cations do not contribute to the frontier orbitals. We then expect that vacancies of organic cations will give rise to holes in such organic-inorganic hybrid perovskites, without altering the band structure. As a demonstration, we calculated the band structure of tetragonal CH$_3$NH$_3$PbI$_3$ with one organic cation missing in the unit cell (Fig. 5b). As compared to the perfect crystal, the valence band structure of defect crystal is barely changed, only the Fermi level has shifted into the valence band. There exist four organic cations in one unit cell, with one organic cation missing, the vacancy concentration will be on the order of 10$^{10}$–10$^{11}$cm$^{-3}$, so the hole concentration is on the same order of magnitude. This hole concentration is one order of magnitude higher than the optimal doping level, to achieve the optimal carrier concentration we need one organic cation vacancy in ten unit cells of tetragonal CH$_3$NH$_3$PbI$_3$. In other words, by engineering the vacancy of organic anions in tetragonal CH$_3$NH$_3$PbI$_3$, we can significantly improve its TE efficiency. The silver doping have been shown to enhance the electronic conductivity of the CdI$_2$-type PbI$_2$ polymer sheet β-[EDT-TTF-I$_2$]$\text{[PbI_2(3-x)AgI_3-x(3-x)L$_2$]}$, $x = 0.05$ [39]. By substitution at the Pb-site with Ag, we can also realize p-doping in CH$_3$NH$_3$PbI$_3$. However, in this case the band structure will be modified since the Pb-6s contributed to the valence band. Based on these calculations, we propose to dope optimization of CH$_3$NH$_3$PbI$_3$ by engineering vacancies of organic cations for high TE efficiency.

4. Conclusions

It should be noted that there has been tremendous progresses made in the past decades in the advances in electronic structure theory [40]. Computational evaluation of optoelectronic property for materials becomes realistic [41]. We have studied the TE transport properties of both tetragonal and cubic phases of CH$_3$NH$_3$PbI$_3$ perovskite by combining the first-principles electronic structure calculations and the Boltzmann transport equation. We find that tetragonal CH$_3$NH$_3$PbI$_3$ has superior TE properties than cubic one, and its $zT$ value is the highest at the phase transition temperature of 330K, exceeding one when the accurate hole-doping can be achieved. The optimal doping level is on the order of 10$^{18}$–10$^{19}$cm$^{-3}$. Our results suggest that tetragonal CH$_3$NH$_3$PbI$_3$ is a promising p-type TE cooling material in the low-temperature regime. We also propose that CH$_3$NH$_3$PbI$_3$ can be hole-doped by engineering vacancies of organic cations, without modifying the electronic structure near the valence band edge.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant nos. 21273124, 21673123, 21290190, and 91333202) and the Ministry of Science and Technology of China (Grant nos. 2013CB933503 and 2015CB655002). Computational resources are provided by the Tsinghua Supercomputing Center.

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