N and p-type properties in organo-metal halide perovskites studied by Seebeck effects

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Abstract

Organo-metal halide perovskites can exhibit co-existed electrical polarizations and semiconducting properties respectively from organic and inorganic components. Here, we find that the Seebeck coefficient can be changed between positive and negative values when the concentration of chloride ions is varied between single-halide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and mixed-halide structures ($\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$). This indicates that varying the concentration of chloride ions can tune the semiconducting properties between the n-type and p-type regimes in the organo-metal halide perovskites. Our temperature-dependent capacitance measurement shows that increasing temperature can cause a change on internal electrical polarization. As a result, we can propose that the internal polarization functions as the underlying mechanism responsible for large temperature-dependent Seebeck coefficients in organo-metal halide perovskites operating between n-type and p-type regimes.

Keywords: organo-metal halide perovskite; Seebeck effect; n-type property; p-type property; polarization effect

Introduction

Organo-metal halide perovskites have become interesting multifunctional materials with high-efficiency photovoltaic response [1], [2] and [3], largely tunable electroluminescence [4], [5] and [6], low-threshold lasing actions [7] and [8], and magneto-optic properties [9] and [10]. These fascinating functions can be un-ambiguously attributed to superior bipolar transport [11], easy-controllable charge dissociation and recombination behaviors, and multifold spin states in excited states [9] and [10]. In general, the organic-inorganic perovskites can be prepared with single-halide or mixed-halide structures with co-existed electrical polarizations and semiconducting properties respectively from organic and inorganic components [12], [13] and [14]. The experimental studies have shown that the single-halide and mixed halide perovskites can exhibit largely different properties in charge transport and excited states in photovoltaic [15] and [16], light-emitting [5], [6] and [7], and lasing applications [7] due to their different properties in transport and excited states. In this work we explore p-type and n-type semiconducting properties from single and mixed halide perovskites (called $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ hereafter) by using Seebeck effects. In principle, the n-type and p-type perovskites can exhibit distinctive behaviors in both charge transport and excited states due to different majority carriers [11], [17], [18] and [19]. Here, we vary the composition between organic and inorganic components to change the electrical polarizations and semiconducting properties in the organic-inorganic halide perovskites. In general, varying the electrical polarizations and semiconducting properties can largely change the charge/exciton ratio and consequently influences the photovoltaic, light-emitting, lasing, and magneto-optic responses [20], [21], [22], [23] and [24]. We find that the n-type and p-type properties in organo-metal halide perovskites can be gradually switched when the organic and inorganic compositions are varied between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskites based

on Seebeck measurements. In principle, the Seebeck effects can be measured in two different ways by applying a temperature gradient vertically or laterally to film-plane direction, namely vertical and lateral Seebeck measurements. In our early studies we have found that the Seebeck measurements based on the vertical multi-layer device provide an opportunity to explore an additional driving force to diffuse majority carriers between high and low temperature surfaces, based on temperature-dependent surface polarization, for developing Seebeck effects [25], [26] and [27]. However, the sign of Seebeck coefficient becomes ambiguous to determine the majority carriers in the Seebeck measurements based on vertical thin film devices. In this work, we use the lateral Seebeck measurements as an un-ambiguous method to determine the n-type or p-type semiconducting properties. With this lateral design the Seebeck effects are essentially developed by the diffusion of majority carriers driven by the entropy difference between high and low-temperature contacts. Therefore, measuring the Seebeck coefficients can indicate the n-type and p-type properties in the organic-inorganic halide perovskites while the electrical polarizations and semiconducting properties are changed by varying the organic/inorganic compositions.

Experimental section

Figure 1 shows the device structure to measure Seebeck effects with a lateral Au-perovskite-Au geometry. The perovskite film has the thickness of around 200 nm with the length of ~2 mm between the two Au film contacts. Specifically, according to the publications [2] and [9], the organo-metal halide perovskite precursors were prepared by mixing Methylammonium iodide (MAI) separately with lead chloride (PbCl_2) and lead iodide (PbI_2) in anhydrous dimethylformamide (DMF). The single halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_3$) were prepared by mixing MAI and PbI_2 with the molar ratio of 1:1. The mixed halide perovskites ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$)

were prepared by mixing MAI and PbCl₂ with the molar ratio of 3:1. The single and mixed halide perovskite precursors were then stirred for 12 hours at 60°C and followed by filtration (0.45µm PVDF filters). The CH₃NH₃PbI₃ and CH₃NH₃PbI_{3-x}Cl_x perovskites were both prepared by spin coating on top of substrate followed by a thermal annealing of 100°C for 2 hours. The gold (Au) electrodes were thermally deposited with film thicknesses of 220 nm under the vacuum of 7×10⁻⁷ torr. The Seebeck measurements were performed based on Au/perovskite/Au lateral device structure by using an InstruNet Model 100 Input/Output System. The K-type thermocouples and copper wires were connected to measure the temperature and electrical potential differences, respectively. The Seebeck measurements were performed under dark condition. The Seebeck coefficient is defined as $S = -\frac{\Delta V}{\Delta T}$ (ΔV =voltage difference; ΔT =temperature difference). The thermal power of Au and measurement wires were subtracted from the results. The thermal power of Au and Cu is 1.94 & 1.84 µV/K at room temperature, respectively, and is still extremely small, <20 µV/K, within the experimental temperature range. The reference experiment was done by connecting wires on only Au film and the Seebeck coefficient was measured. The obtained Seebeck coefficients were subtracted from that of the devices.

Figure 1. The device geometry for Seebeck measurements. ΔV : Seebeck voltage; ΔT : Temperature difference.

Results and Discussions

Figure 2(a) shows the Seebeck coefficients generated from the single organo-metal halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and mixed organo-metal halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ with initial mole ratio of $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$) under different temperatures. The Seebeck measurements were performed under dark condition. Here, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ ($\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$) organo-metal halide perovskites exhibit positive and negative Seebeck coefficients with large values of about 3.5 mV/K and -4.8mV/K at 80°C, respectively. This experimental result indicates that $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ organo-metal halide perovskites function as p-type and n-type semiconductors. Generally, the Seebeck effect is developed by charge diffusion driven by entropy difference between high and low temperature surfaces. The hole and electron diffusion can normally lead to positive and negative Seebeck effects under the driving force of entropy difference. Therefore, using the Seebeck coefficients can indicate the intrinsic property of charge transport (p-type or n-type) in organo-metal halide perovskites. **Figure 2(b)** shows power factor estimation of the perovskite materials based on the equation, $P = \sigma S^2$, where P is power factor, σ is electrical conductivity, and S is Seebeck coefficient. Here we use 3.5 E-4 S/m and 2.0 E-4 S/m for electrical conductivity of $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film based devices, respectively, based on our electrical conductivity measurement for the devices. It could be seen that the power factor can respectively reach 0.005 and 0.001 (mV/K)²*S*m⁻¹ at 80 °C for $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite materials here. Meanwhile, $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ thin film device shows higher power factor than the $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film device.

Figure 2. The Seebeck effects for organo-metal halide perovskite films based on lateral Au/perovskite/Au device design (●: $\text{CH}_3\text{NH}_3\text{PbI}_3$, ▲: $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ with initial mole ratio of $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$).

Now we confirm that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ ($\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$) perovskites are p-type and n-type semiconductors by using time-resolved photoluminescence with different types of quenching layer (as shown in **Figure 3**). Here we choose two different quenching layers: the poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and the Phenyl-C61-butyric acid methyl ester (PCBM). The PEDOT:PSS and PCBM are known as p-type and n-type materials. When a perovskite film forms a p-n type contact with PEDOT:PSS or PCBM, the photoluminescence from the perovskite film can be largely quenched [28] and [29]. Therefore, measuring photoluminescence quenching can provide an evidence to confirm the intrinsic n-type or p-type semiconducting properties in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite films. Figure 3(a) shows the results of the photoluminescence lifetime of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite with and without quenching layers. We can see that applying p-type PEDOT:PSS and n-type PCBM quenching layers lead to a longer and shorter lifetimes on the photoluminescence from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. The lifetimes associated with the p-type PEDOT:PSS and n-type PCBM quenching layers are about 18 ns and 14 ns. This confirms that the single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$

perovskite is a p-type semiconductor. On contrast, the $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite exhibits longer (12 ns) and shorter (8 ns) photoluminescence lifetimes when the n-type PCBM and p-type PEDOT quenching layers are separately applied (Figure 3(b)). This shows that the mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite is an n-type semiconductor.

Figure 3. Time-resolved photoluminescence measurements from single-halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ and mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ (mole ratio $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$) with and without interfacial layers (PEDOT:PSS and PCBM). (a) Photoluminescence delay characteristics for $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PCBM}$, and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PEDOT:PSS}$. (b) Photoluminescence delay characteristics for $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$, $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}/\text{PCBM}$, and $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}/\text{PEDOT:PSS}$.

Now, we explore the possibilities of tuning semiconducting properties between n-type and p-type by using Seebeck measurements. **Figure 4** shows the Seebeck coefficient gradually tunable between positive and negative values by changing the molar ratio between PbI_2 and PbCl_2 components. Changing the molar ratio between PbCl_2 and PbI_2 components allows the modification on the content volume of chloride ions in organo-metal halide perovskite crystals. Interestingly, we can see that the Seebeck coefficient changes from positive value to negative value when the concentration of chloride ions are increased. This means that increasing the chloride ions concentration can change the semiconducting properties from p-type to n-type by switching the majority carriers from holes to electrons. It is known that the presence of CH_3NH_3^+ vacancy can

lead to p-type semiconducting properties [30] and [31] by downward shifting the Fermi level. When the chloride ions are introduced in the organo-metal halide perovskites, on one hand, the CH_3NH_3^+ vacancies can be eliminated by removing the by-product of $\text{CH}_3\text{NH}_3\text{Cl}$ during the formation of organo-metal halide perovskite polycrystals [32]. Obviously, as the CH_3NH_3^+ vacancies are eliminated, the chloride doped organo-metal halide perovskites can demonstrate n-type characteristics by upward-shifting the Fermi level. On the other hand, it has been found that positively charged vacancies, the iodine vacancies in the perovskite polycrystals can act as electron traps [24], [31] and [33]. The vacancies originate from the distorted polycrystalline structures caused by impurities during the formation process of polycrystalline domains. It is also noted that the chloride ions can prevent the distortion of polycrystalline structures and increase the crystallinity by reducing the impurities in perovskite precursors and thus reduce the density of positively charged vacancies [34], [35] and [36]. As a result, when the density of electron trapping vacancies is gradually reduced by the introduction of chloride ions, the n-type characteristics will become more predominant in organo-metal halide perovskites. Clearly, the chloride ions serve as the dopants to reduce the density of both CH_3NH_3^+ vacancies and electron trap sites from positively charged vacancies (+), which can increase the n-type characteristics in the chloride doped organo-metal halide perovskites. Therefore, the chloride doped organo-metal halide perovskites can have an n-type semiconducting properties.

Figure 4. Seebeck effects from lateral perovskite devices with different component mole ratios. a: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0:1$; b: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.2:0.8$; c: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.2:0.2$; d: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$.

We further note in Figure 4 that the magnitude of Seebeck coefficient is large and increases with increasing temperature within the given temperature range. This phenomenon suggests that the electrical polarization effect in the film can be accountable for the relatively large temperature-dependent Seebeck coefficients. Now, we use the capacitance-frequency (C-f) measurements to explore the temperature effects on local polarizations in bulk perovskite films. The capacitance-frequency (C-f) measurement were performed under dark condition by using dielectric spectrometer (Agilent E4980A LCR). In general, the capacitance-frequency characteristics can be divided into low and high-frequency regimes. The former and latter are associated with the electrode interface and bulk behaviors. **Figure 5** shows the frequency-dependent capacitance signals at different temperatures. At high frequency the capacitance signals can essentially reflect the bulk polarization in organo-metal halide perovskite films[28]. Here, we can see that at high frequency ($> 100 \times 10^3$ Hz) the capacitance increases with increasing temperature in the ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Au device. This behavior indicates that increasing temperature can essentially lead to an increase in the bulk polarization in the single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, functioning as p-type semiconductor. The increase in the bulk polarization with increasing temperature can be

due to the thermally activated detrapping process of electrons, which can lead to more positively charged trap sites in the p-type $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film with increasing temperature. This is because the trap states in perovskites have been demonstrated as shallow traps [33]. With increasing bulk polarization, we can expect that the charge transport experiences less Coulomb scattering due to electrical screening effect, leading to an increase on carrier transport upon increasing temperature. On contrast, we can see in Figure 5 that increasing temperature causes a decrease in the capacitance at high frequency ($>100 \times 10^3$ Hz) in the mixed halide perovskite based ITO/ $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ (mole ratio $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$)/Au device. This result implies that the bulk polarization decreases with increasing temperature in the mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite, functioning as n-type semiconductor. The decrease of bulk polarization upon increasing temperature can be due to Coulombic scattering with increasing temperature in the n-type $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite film since the n-type $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite film exhibits stronger polarization effect than single halide perovskite. In this situation, the decrease of bulk polarization with increasing temperature consequently enhances the electron transport upon increasing temperature due to less Coulomb scattering. Therefore, the bulk polarization provides the underlying mechanism to influence carrier transport in both n-type and p-type organo-metal halide perovskites for development of Seebeck effect.

Figure 5. Capacitance-frequency (C-f) characteristics measured at different temperatures for ITO/Perovskite/Au devices. (a): Single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, (b): Mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite (mole ratio $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$). The C-f measurements were performed at 30, 60, 70, and 80°C.

Figure 6(a) shows the XRD spectra of perovskite films. It can be seen that the peaks at $2\theta=14^\circ$, 28° , 32° reported in Figure 6(a), allowed us to identify the four thin films as the tetragonal perovskite structure [37], [38], [39] and [40]. In addition, for b, the peak at $2\theta=12.5^\circ$ indicates extra PbI_2 in the sample b film, which acts as defects in the perovskite film that can decrease the hole transport by scattering for the Seebeck development. **Figure 6(b)** shows absorption spectra of perovskite films, which also identify the thin films as perovskites [4], [18], [41], [42] and [43].

Figure 6. (a) XRD pattern (measured using Cu $K\alpha$ radiation) and (b) absorption spectra of perovskite films with different initial mole ratio. a: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0:1$; b: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.2:0.8$; c: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.2:0.2$; d: $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$.

Conclusions

In summary, the Seebeck measurements were performed to study the n-type and p-type semiconducting properties in both single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ and mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskites. We observed that the intrinsic semiconducting properties can be switched between n-type and p-type by changing the concentration of chloride ions during the formation of perovskite polycrystals. Here, we suggest that CH_3NH_3^+ vacancies and positively charged trap sites formed during crystallization process are the primary factors to determine the p-type semiconducting characteristic in the single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$. On the other hand, introducing the chloride ions can decrease the density of CH_3NH_3^+ vacancies and positively charged trap sites during the formation process of organo-metal halide perovskites, leading to a n-type semiconducting properties in the mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskites (mole ratio $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$). Moreover, the large temperature-dependent Seebeck effects indicate that electrical polarization effect in the film can lead to an increase on carrier transport in the Seebeck development. Our capacitance-frequency measurements reveal that increasing temperature causes an increase and a decrease on bulk polarization in single and mixed halide perovskites, respectively. In the p-type single halide $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite, increasing bulk polarization with temperature can decrease the Coulomb scattering to the majority carriers (holes) due to electrical screening, leading to an increase on hole transport for Seebeck development. In the mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$ perovskite (mole ratio $\text{CH}_3\text{NH}_3\text{I}:\text{PbCl}_2:\text{PbI}_2=1:0.3:0$) with stronger polarization effect than single halide perovskite, decreasing bulk polarization with temperature can decrease the Coulomb scattering to the majority carriers (electrons), increasing electron transport for Seebeck development. Nevertheless, changing bulk polarization can present a convenient mechanism to influence carrier transport for Seebeck development. Clearly, our studies provide

an insight on tuning intrinsic bulk polarization and semiconducting properties in organo-metal halide perovskites.

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