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Bi^{3+} -doped $CH_3NH_3PbI_3$: red-shifting absorption edge and longer charge carrier lifetime

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ABSTRACT. Ion doping is an effective approach to improve the properties of hybrid perovskite $CH_3NH_3PbI_3$, such as chemical stability and solar absorption. Here Bi^{3+} -doped $CH_3NH_3PbI_3$ was synthesized *via* cooling crystallization process in aqueous solution. Along with the Bi^{3+} doping, the bandgap of $CH_3NH_3PbI_3$ could be significantly narrowed, by the maximum value of 140 meV at the optimal doping level of 1.6 molar %. Transient photovoltage measurement (TPV) revealed the Bi^{3+} -doped $CH_3NH_3PbI_3$ could achieve a charge carrier lifetime of 280 µs, which was almost twice longer than that of pristine $CH_3NH_3PbI_3$ (157 µs). The prolonged carrier lifetime of Bi^{3+} -doped $CH_3NH_3PbI_3$ was supposed to be attributed to its lower packing factor (PF), which was caused by the $CH_3NH_3^+$ vacancy (V_{MA}) after doping This work provides a new approach to tune the band gap and charge carrier lifetime of the hybrid perovskite $CH_3NH_3PbI_3$, which should be promising to further improve the performance of perovskite-based photovoltaic devices.

Keywords. Hybrid perovskite, Doping, Band gap energy, Charge carrier lifetime.

1. Introduction

The organic-inorganic hybrid perovskite CH₃NH₃PbI₃ has attracted much scientific interests for its extraordinary photovoltaic properties. Since the first report about its photovoltaic performance in 2009,[1] the record of the photoelectric conversion efficiency (PEC) of the perovskite-based solar cells (PSCs) has been broken continuously in the past few years, [2-9], and the highest certified efficiency now comes to 22.1%.[10] Recently a PCE of 19.6 % has been achieved with an aperture area exceeding 1 cm², which paves the way to realize highly efficient large-area PSCs for practical deployment. [11] In addition to the facile deposition techniques, the suitable band gap value (1.52 eV), long carrier diffusion length (over 175 µm in single crystals and over 1 µm in optimized thin film) are the main factors determining the excellent photovoltaic performance of CH₃NH₃PbI₃. [4, 9, 11-18] Recent study revealed that the photon recycling can make the travel distance of charge carriers even longer than the chargecarrier diffusion length in perovskite layer [19] Moreover, the defect-tolerated talent of the perovskite framework makes it possible to optimize its performance by isovalent doping at different sites. For instance, monovalent cations $(CH(NH_2)_2^+, Cs^+, Rb^+)$ doping at the $CH_3NH_3^+$ site can not only increase the thermal stability, but broaden the absorption range of hybrid perovskites. [7, 20-26] Cl⁻ doping at the I⁻ site can significantly improve the crystallization behavior and morphology of the polycrystalline thin film.[27-35] Now the highest-efficiency perovskites are with mixed MA/FA cations and Br/I halides.[3, 11, 36]. Besides, low-toxic bivalent ion Sn^{2+} doping at the Pb²⁺ site can also broaden the absorption range of hybrid perovskites.[37-45] And the PCE of Sn-based planar perovskite solar cell now achieves 15%.[46] In contrast, the heterovalent doping is rare to be investigated. Ahmed et al. first reported the heterovalent doping of Bi^{3+} , In^{3+} or Au^{3+} at the Pb^{2+} site in $CH_3NH_3PbBr_3$ by a rapid crystallization method.[47] It was remarkable that Bi³⁺-doped CH₃NH₃PbBr₃ showed a narrower band gap, a significant increase of carrier concentration and an electronic conduction transformation from p- to ntype semiconductor. Although the rapid crystallization method benefits the incorporation of heterovalent dopant, it would also cause an explosive growth of defects in the crystal structure. Such high defect density can impede the charge carrier diffusion. In order to suppress the formation of defects, doped perovskite should be grown in near-equilibrium state. Al³⁺-doping was also reported to be able to improve the quality of the perovskite film, as well as the PCE of related PSC.[48] However, Al³⁺ dopants are unlikely to be incorporated within the perovskite crystal lattice. Ion doping can always modify the electronic structure of the host compound, along with the charge carrier properties. For example, Cl-doping resulted in longer carrier lifetime of CH₃NH₃PbI₃-based thin film devices, because it can improve the carrier transport characteristics of the interface between the perovskite layer and the charge transport layers.[49] Theoretical calculations also showed that Cl⁻ doping can suppress electronhole recombination in perovskite, because Sn²⁺-doping tended to result in defects which could act as the non-radiative recombination centers.[46, 52]

Efficient charge separation and transportation can be expected in compounds with more open structures due to their stronger internal electric field caused by larger lattice distortion. Packing factor (PF) can be used to describe the structural opening degree, and lower PF always results in better photoelectric related properties [54-57] In order to decrease the PF of CH₃NH₃PbI₃, one strategy could be the introduction of specific structural defects. Perovskite framework constructed by $[PbI_6]^{4-}$ octahedra is responsible for the charge carrier diffusion. Defects such as Pb vacancy (V_{Pb}) or I vacancy (V₁) can impede the charge carrier diffusion and thus should be avoided. Cations CH₃NH₃⁺ make no contribution to the electron transition between valence band and conduction band, thus the generation of CH₃NH₃⁺ vacancy (V_{MA}) can lower the PF of CH₃NH₃PbI₃ without disturbing the charge carrier diffusion. According to electroneutrality, lattice V_{MA} can be generated if Pb²⁺ sites are partially substituted by

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trivalent or even more highly charged ions. Among the different heterovalent ions, Bi^{3+} has the same electron configuration and similar ion radii with Pb^{2+} . Thus Bi^{3+} doping could be promising to lower the PF of CH₃NH₃PbI₃ and to improve its charge carrier properties.

Here we report the synthesis of Bi³⁺-doped hybrid perovskite CH₃NH₃PbI₃ by slowly cooling crystallization method. All the doped products well maintained the perovskite structure of CH₃NH₃PbI₃, and the highest doping content of 1.6 molar % can be achieved in our experiment. The band gap values decreased significantly along with the increasing of Bi³⁺ content, and the products with the highest Bi³⁺ content showed a band gap of 1.38 eV which is 140 meV narrower than that of the pristine CH₃NH₃PbI₃. Transient photovoltage (TPV) results showed that the incorporation of Bi³⁺ ions could nearly twice increase the charge carrier lifetime of CH₃NH₃PbI₃, which implied that Bi³⁺ doping could be an effective strategy to promote the performance of PSCs.

2. Experimental

2.1 Reagent

Unless stated otherwise, all the starting materials were obtained from Sinpharm Chemical Reagent Beijing Co. Ltd without further purifications. (i) Meghylamine (CH₃NH₂) (40 wt.% in ethanol); (ii) hydroiodic acid (HI) (57 wt.% in water); (iii) PbI₂ (99%); (iv) Bismuth powder (99.99%); (iv) I₂ (99.99%); (v) H₃PO₃ (99.9%). CH₃NH₃I was synthesized in the following procedure. HI was dropped into the equimolar aqueous CH₃NH₂ in a flask placed in an iced bath for 2 h under stirring. Then the mixture was evaporated at 60 °C in a rotary evaporator to remove the solvent. The product was washed with anhydrous diethyl ether for three times, then dried in a vacuum oven at 60 °C for 12 h. Bismuth iodide (BiI₃) was synthesized by heating element Bi powder and I₂ in the radio 2:3 under 300 °C in an evacuated quartz tubes for 10 h.

2.2 Synthesis of Bi³⁺-doped CH₃NH₃PbI₃.

The PbI₂ powder and H_3PO_3 were dissolved in aqueous HI to form a bright yellow solution at 100 °C, then a certain amount of BiI₃ was added and the color of the solution turned to red immediately. Stoichiometric amount of CH₃NH₃I was added into the red solution. Slow cooling of the solution to 40 °C afforded highly crystalline product. The product was filtered from the mother liquor, then washed with diethyl ether for three times. The final product was dried in a vacuum oven at 80 °C overnight.

2.3 Materials characterization

The phase purities of the samples were determined by powder X-ray diffraction (XRD). performed on a Bruker D2 phaser diffractometer equipped with a monochromatized source of Cu K α radiation (λ = 0.15406 nm) at 4 kW (40 kW, 100 mA). The crystalline samples were ground into fine powder for the measurement. The optical diffuse-reflectance spectra of different samples were measured on a UV-4100 spectrophotometer operating form 1500 nm to 400 nm at room temperature. BaSO₄ was used as a non-absorbing reflectance reference. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to quantify the Bi³⁺ doped into the products.

2.4 Transient Photovoltaic (TPV) measurement

TPV measurements were carried out in devices described by previous reports.[58, 59] The crystal products were ground into fine powder then pressed into thin pellets. Each device like a parallel-plate capacitor was composed of sample pellet placed on a ITO substance, a piece of mica and a platinum wire electrode. The devices were illuminated by laser pulses (532 nm, 7 ns width from an Opolette 355(HE) LD laser). The energy of each laser pulse is 1.5 μ J and the calculated density of photon is 3×10^{11} /mm⁻² each pulse. A large resistance of 1 M Ω was connected in parallel with the devices to

simulate the open circuit condition. The transient photovoltage was recorded by a 300 MHz Tektronix digital phosphor oscilloscope. The transient photovoltage curves were fitted with single exponential decay functions.

3. Results and discussion

Ion doping has been proved to be an effective way to improve the performance of hybrid perovskite. Compared with isovalent dopants such as Cs^+ for A site, Sn^{2+} for B site and Cl^- for X site, heterovalent dopants are more difficult to be introduced into the host crystal lattice and thus are rarely reported. Cooling crystallization process has been developed into a mature method for either the growth of single crystals or the synthesis of doped perovskites.[37, 40, 60] In this work we used this method to synthesize Bi^{3+} -doped $CH_3NH_3PbI_3$. SEM images of the pure and doped $CH_3NH_3PbI_3$ crystals are presented in Fig.1. Obvious variations of the crystal morphology after doping imply the incorporation of Bi^{3+} into the perovskite structure.



Fig.1. SEM images of (a) pure and (b)~(f) doped CH₃NH₃PbI₃, (b) ~ (f) for Bi % _{solution}= 1%, 2%, 4%, 6%, 10% respectively.

In order to check the phase purities of the products, their powder XRD patterns (Fig.2a) were collected. All the Bi³⁺-doped samples show same XRD pattern with that of pristine CH₃NH₃PbI₃, indicating the perovskite structure is well maintained. The maintaining of the perovskite symmetry after doping is the precondition for further improving the electronic properties of CH₃NH₃PbI₃.[16] Lattice parameters calculated by powder XRD show no significant difference between the pristine and doped samples with a around 8.86 Å and c around 12.63 Å. This is mainly resulted from the similar radii of Bi^{3+} and Pb^{2+} and small amount of the dopant in the crystal. The accurate Bi^{3+} contents of the doped samples are studied by ICP-OES. Fig.2b shows the positive correlation between the Bi molar % in the samples and those in the solution. Detailed Bi % values in solution and crystals are shown in Table S1 in Supporting Information, and the Bi³⁺ content of the optimal doped sample is 1.6 % with a nominal composition 10% in solution. These results indicate that while the cooling crystallization is nearly an equilibrium process, Bi³⁺ ions can be incorporated into the crystal lattice of hybrid perovskite due to the same electron configuration and similar ion radii with Pb^{2+} ions. The perovskite framework can tolerate this doping and keep the host structure unchanged. Along with the decreasing temperature, Pb²⁺ and Bi³⁺ ions show the same tendency to precipitate from the solution which acts as a strong force to incorporate the Bi³⁺ ions into the crystal lattice.



Fig.2. (a) Powder XRD patterns of Bi³⁺-doped CH₃NH₃PbI₃, (b) Bi molar % in crystals as a function of those in solution.

The optical absorption properties of Bi^{3+} -doped $CH_3NH_3PbI_3$ samples were investigated by solid-state diffuse-reflectance spectroscopy. Compared to the pristine $CH_3NH_3PbI_3$, a significant broadness of absorption range can be observed in Bi^{3+} -doped samples, as shown in Fig.3. The absorption edges show red shift along with the increasing amounts of Bi^{3+} . The optimal doping (Bi % =1.6 %) has a band gap of 1.38 eV, which is 140 meV narrower than that of pure $CH_3NH_3PbI_3$ (1.52 eV) (Table S1 in Supporting Information). This bandgap narrowing can be attributed to the generation of impurity bands within the band gap. In Bi^{3+} -doped $CH_3NH_3PbI_3$, parts of Pb^{2+} could be substituted by Bi^{3+} , considering their physical similarities. That substitution results in Bi_{Pb} defects in the lattice. Yan *et al.* predicted that the defects of Bi_{Pb} tend to be shallow donors which could generate energy levels below the conduction band minimum.[61] These energy levels in Bi^{3+} -doped $CH_3NH_3PbI_3$ could account for its enhanced optical response property.



Fig.3. Electronic absorption spectra of Bi³⁺-doped CH₃NH₃PbI₃, inset: the variation of band gap energies as a function of Bi molar % in crystals.

By regulating the growth condition, either *n*- or *p*-type CH₃NH₃PbI₃ can be obtained, depending on the different dominated defects.³⁷ It is worth noting that different growth conditions of Bi³⁺-doped CH₃NH₃PbI₃ can also result in different absorption properties of the final products. The reported Bi³⁺doped CH₃NH₃PbI₃ synthesized *via* a rapid crystallization process showed a 300 meV bandgap narrowing with Bi³⁺ content of 0.3%,[47] while the doped sample we synthesized with 1.6% Bi³⁺ content only showed a 140 meV narrowing. We attribute this deviation to different concentrations and varieties of defects in crystals grown under different conditions. Generally, faster crystallization leads to higher concentration of defects in the crystals. Besides the Bi_{Pb} defects, there are some other defects such as Pb²⁺ vacancy (V_{Pb}) existing in the crystal synthesized by fast crystallization method. V_{Pb} can result in mid-gap states which are responsible for the large extent of bandgap narrowing.[16, 53] However, the existence of V_{Pb} is always detrimental to charge transport because it breaks down the perovskite framework. In contrast, slowly cooling crystallization can suppress the formation of defects and produce more perfect crystals. Although the resulted sample has larger band gap, some undesired defects such as V_{Pb} can be avoid. That is critical to maintain the completeness of the perovskite framework and ensure the charge carrier diffusion.

Charge carrier lifetime τ , mobility μ and diffusion length $L_{\rm D}$ are three key parameters of photovoltaic materials, and the formula $L_{\rm D} = (k_{\rm B} T/e \cdot \mu \cdot \tau)$ (k_B: Boltzmann's constant) shows the relationship of these parameters. Longer τ always leads to longer $L_{\rm D}$ thus better photovoltaic performance. In some cases, ion doping can obviously influence the charge carrier behaviors of hybrid perovskite. For instance, by adding Cl⁻ during the film fabricating, the final polycrystalline film would have longer carrier diffusion length and thus exhibit better photovoltaic performance. In contrast with isovalent doping, hetervalent doping cannot avoid inducing more defects into the crystal lattice. These defects could have different effects on the charge carrier behavior. In order to clarify the impacts of dopant Bi³⁺ toward the charge carrier lifetime, transient photovoltages (TPV) of samples with different Bi³⁺ contents were measured. All samples were assembled into devices with the same structure. The transient photovoltage curves were fitted with single exponential decay functions. As shown in Fig.4a, the pristine CH₃NH₃PbI₃ possesses a photo-induced charge carrier lifetime of 157 µs. Along with the increasing amounts of dopant Bi³⁺, the carrier lifetime increases significantly until the Bi³⁺ content reaches 0.8%. After that, the curve comes to a plateau with a carrier lifetime around 280 µs which is almost twice longer than that of the pristine CH₃NH₃PbI₃, as shown in Fig.4b. The non-normalized TPV values are shown in Fig.S1 in Supporting Information. Theoretical calculations revealed that Bi_{Pb} defect levels are just 173 meV lower than the conduction band minimum which are too shallow to act as Shockley-Read-Hall non-radiative recombination centers.⁴¹ Our samples were grown by slowly cooling method which could avoid the

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formation of V_{Pb} , and ensure the completeness of the carrier-transporting framework. A site vacancy V_{MA} can lead to a more open structure and thus decrease the PF of the compound which results in more efficient charge separation and transportation. So both Bi³⁺ doping and the slowly cooling method are critical to achieving longer charge carrier lifetime.



Fig.4. (a) Transient photovoltaic curves of the devices made with Bi³⁺-doped CH₃NH₃PbI₃. (b) the variation of carrier lifetimes as a function of Bi % in crystals.

4. Conclusions

In summary, Bi^{3+} -doped $CH_3NH_3PbI_3$ was successfully synthesized through a cooling crystallization method. It was demonstrated that Bi^{3+} -doping can not only extend the optical absorption range of the hybrid perovskite, but also facilitate the process of charge separation and transportation. The prolonged carrier lifetime of Bi^{3+} -doped $CH_3NH_3PbI_3$ could be ascribed to the reduced structural PF caused by V_{MA} . Longer carrier lifetime always means longer carrier diffusion length, which is critical for a superior absorber of solar cells. Our results provide a new approach to tune the bad gap and carrier properties of perovskites, which is promising for further improving the performance of perovskite-based photovoltaic devices.

ASSOCIATED CONTENT

Supporting Information.

Bi³⁺ molar % in solution and in crystals and band gap energies of related samples.

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Notes

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Highlights

 Bi^{3+} -doped $CH_3NH_3PbI_3$ crystals were synthesized *via* a cooling crystallization process in aqueous solution.

This doping lead to obvious bandgap narrowing.

The doping of Bi³⁺ lead to an almost twice longer charge carrier lifetime.

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