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Effect of lead-free (CH₃NH₃)₃Bi₂I₉ perovskite addition on spectrum absorption and enhanced photovoltaic performance of bismuth triiodide solar cells

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Abstract

Active composite layers of bismuth triiodide (BiI₃) and lead-free (CH₃NH₃)₃Bi₂I₉ (MBI) perovskite were prepared using a simple chemical solution method under ambient conditions for thin-film solar cells. Results of X-ray diffraction and scanning electron microscopy indicated that the crystallization and surface morphologies of the composite films varied with perovskite contents. Multi-absorption was observed in the composite films due to the bandgap difference between BiI₃ and MBI perovskite. Moreover, band bending at the BiI₃-perovskite interfaces resulted in the realignment of energy levels in the composite films, and this phenomenon was beneficial to the efficient injection of excited electrons from the active layers into the TiO₂ layers. Accordingly, due to the optimized crystallization and realigned energy level, when 20% of MBI perovskite was introduced into the active layers, the open-circuit voltage obviously increased from 0.44 V to 0.57 V in the $(BiI_3)_{0.8}(MBI)_{0.2}$ composites solar cells, enhancing their power conversion efficiency by 67% compared with that in pure BiI₃ solar cell. This study developed a new route for designing more efficient lead-free solar cells.

Keywords: Bismuth triiodide; Lead-free perovskite; Spectrum absorption; Photovoltaic performance.

1. Introduction

Organo-lead halide perovskites display many excellent optical properties, such as suitable bandgaps and small effective mass, making them excellent absorption materials for solar cells [1–3]. The power conversion efficiency (*PCE*) of organo-lead halide perovskite solar cells certified by the National Renewable Energy Laboratory has sharply increased to 22.1% in the past six years, making them quite comparable to silicon solar cells in the near future [4]. However, these solar cells still face several serious drawbacks, such as degradation of perovskite when exposed to air [5,6], hysteresis [7], and lead pollutions [8], limiting their further commercialization. Recent work indicated that bismuth compounds are potential candidates for perovskite solar cells to address the problem on lead pollution [5,9].

Lead-free bismuth compounds, such as Bi_2CrFeO_6 [10,11], bismuth triiodide (BiI_3) [12], and $A_3Bi_2I_9$ perovskites (A = CH_3NH_3, Cs) [13], have attracted a considerable attention in photovoltaic applications. Among these materials, $A_3Bi_2I_9$ are halide perovskites that are air stable and environment friendly. Unfortunately, their bandgaps reach up to 2.1 eV, which is too high for efficient absorption of visible light. Accordingly, $A_3Bi_2I_9$ solar cells exhibit a *PCE* of not higher than 1.02% [13–17]. BiI_3 is a promising absorber because of its proper bandgaps of 1.43–2.2 eV, high absorption coefficient ($10^5\,cm^{-1}$), high electron mobility ($260 \pm 50\,cm^2/(V \cdot s)$) and low carrier concentration ($1 \times 10^8\,cm^{-3}$) [12,18–20]. However, due to mismatching alignment of energy levels between BiI_3 and TiO_2, BiI_3 solar cells still exhibit a low *PCE* as well as a low open circuit voltage (V_{oc}) of 0.42 V [12]. In this case, neither single BiI_3 nor $A_3Bi_2I_9$ perovskites are currently suitable for highly efficient solar cells. Therefore, spectral absorption tuning and energy level realignment are important topics in development of bismuth compounds for lead-free solar cells.

Co-absorption of two dyes in an active layer is an efficient approach to tune spectral absorption in dye-sensitized solar cells; for instance, mixed organic dyes PcS15 and D131 exhibit a dramatic enhancement of photocurrent response for the entire visible-light region with tuning of the electron-pushing abilities [21]. In addition, integration of ZnS, CdS, $Cu_{2-x}S$ and CdSe inorganic semiconductors can lead to staggered gap alignment, full-spectrum solar energy absorption, and efficient charge separation [22,23]. Moreover, *PCE* of Pb-In binary perovskites solar cells is higher than that of single In-based perovskite solar cells [24]. Therefore, integration of lead-free materials is a potential method to tune their spectral absorption and realign their energy levels. In this work,

composite absorbing layers of BiI_3 and $(CH_3NH_3)_3Bi_2I_9$ perovskite were prepared, and their optical properties were studied for their applications in lead-free solar cells.

2. Experimental procedures

2.1. Preparation of $(BiI_3)_{1-x}(MBI)_x$ composite films

BiI_3 (589 mg, 99.99%, Sigma-Aldrich) was dissolved in *N,N*-dimethyl-formamide (1 mL, super dehydrated, Sigma-Aldrich) at room temperature. The solution was filtered using PTFE syringe filters (0.45 μm) before being processed further. MBI perovskites can be prepared from the solution of BiI_3 and CH_3NH_3I (MAI, 99%, Dyesol) (molar ratio = 1:1.5) [15]. Therefore, the precursors of BiI_3 and MBI mixtures were prepared by adding different contents of MAI into the BiI_3 solution (stoichiometric $(BiI_3)_{1-x}(MBI)_x$, $x = 0$, 0.10, 0.20, 0.50, 0.75 and 1.0). After mixing by using an ultrasonic mixer for 20 min, 0.15 mL of the precursors were dropped onto the regular glass substrates, which were covered with mesoporous TiO_2 layer, and then the substrates were spin coated at 2000 rpm for 20 s by using a spin coater (SC-150, Oshigane). These films were annealed at 100 °C for 30 min under ambient conditions to obtain different $(BiI_3)_{1-x}(MBI)_x$ films with a thickness of approximately 170 μm for X-ray diffraction and for measurement of UV-visible spectrum and surface morphology. For valence band measurement, samples were prepared on fluorine-doped tin oxide (FTO) glass substrates (Yingkou OPV Tech New Energy) by using the same method.

2.2. Fabrication of devices

FTO glass substrates were etched with 2 M HCl and zinc powder, washed with IPA, acetone, and clean water, and dried before use. The TiO_2 precursor was prepared as reported in Ref. [25], wherein it was spin coated on substrates at 3000 rpm for 30 s and then sintered at 450 °C for 1 h to form a compact layer. A mesoporous TiO_2 gel was subsequently spin coated on the compact layer at 5000 rpm for 30 s and then sintered at 500 °C for 30 min. When the substrates were cooled down, 0.15 mL of $(BiI_3)_{1-x}(MBI)_x$ precursors were dropped on them, and they were spin coated at 2000 rpm for 20 s. These films were annealed on hotplate at 100 °C for 30 min. For the preparation of the hole transport material (HTM), 72.3 mg of Spiro-OMeTAD (99.7%, Macklin), 28.8 μL of 4-tert-butylpyridine (AR, Sigma-Aldrich), and 17.5 μL of a stock solution of 520 mg· mL^{-1} lithium bis-(trifluoromethyl sulphonyl) imide (99.99%, Macklin) in acetonitrile (super dehydrated, Wako)

were dissolved in 1 mL of chlorobenzene (99.9%, Sigma-Aldrich). The solution was spin coated on the bismuth composite layers to form a hole transport layer. Finally, 30 nm of silver was evaporated on the samples to form an electrode. In our experiment, each group consisted of four devices. Moreover, all procedures were conducted under ambient conditions with a humidity of approximately 55%.

2.3. Characterization

An X-ray diffractometer (XRD, RINT 2100, Rigaku) with Cu $K\alpha$ radiation (λ = 1.54056 Å) was used to record the X-ray diffraction diagram at 10° to 40° at a scanning step of 0.01°/s. A scanning electron microscope (SEM, JCM-6000, JEOL) was used to characterize the microstructures of the films. Energy dispersive X-ray spectrometry (EDX, Genesis XM2, EDAX) was used to determine the stoichiometric ratio of the composite films by detecting the molar ratios of I:Bi atoms. A UV-VIS-NIR spectrophotometer (V-670, JASSCO) was used to determine the optical properties of the products based on the absorption spectra, and the bandgaps were calculated using Tauc Plot. The valence band was determined by using a photoelectron yield spectroscope (PYS, KV205-HK, Bunkoukeiki). A solar simulator (CEP-2000, Bunkoukeiki) interfaced with a xenon lamp (BSOX150LC, Bunkoukeiki) was used to measure the photovoltaic characteristics of the solar devices at 100 mW/cm^2 under AM 1.5 conditions. The power of the light exposure from the solar simulator was fixed with an amorphous Si photodetector (BS-520 S/N 353, Bunkoukeiki) to avoid discrepancy between the calibrated diode and the measured devices. The cell area was precisely controlled using a 0.12 cm^2 black metal mask to measure the photovoltaic performances. Moreover, *I-V* characteristic was determined through forward and reserve scanning.

3. Results and discussion

Fig. 1 shows that the color of the as-prepared films was significantly affected by the addition of MAI. The color changed from black to red, implying that certain reaction occurred after addition of MAI. Fig. 2 shows the XRD patterns of the films. For the film without MAI additive, the XRD pattern showed a pure hexagonal BiI$_3$ phase, consistent with the reported diffraction data for BiI$_3$ film [26]. With addition of MAI into the precursors, the intensity of BiI$_3$ peaks changed, and hexagonal MBI formed as the second phase. For x = 0.10 and x = 0.20, the (003) peaks of BiI$_3$ dramatically increased, implying enhanced crystallization. As x increased to 0.50 and 0.75, the

MBI phase replaced BiI_3 as the main phase in the samples. Finally, it formed a pure hexagonal MBI phase when x = 1.0, consistent with the MBI diffraction data reported in Ref. [15]. For the films where BiI_3 was dominant, the (003) orientation of BiI_3 was evaluated by the lotgering factor (LF) [26,27]. As shown in Table S1, the LFs for the films at x = 0, 0.10, 0.20 were 0.686, 0.973, and 0.979, respectively, indicating the higher (003) orientation of BiI_3 in the films containing greater amount of MBI. However, the MAI phase was not observed in any of the films, suggesting that a chemical reaction occurred between MAI and BiI_3 as follows:

$$2 \; BiI_3 + 3 \; CH_3NH_3I \rightarrow (CH_3NH_3)_3Bi_2I_9 \qquad\qquad (1)$$

The SEM images in Fig. 3 show the surface morphologies of the films. The introduction of MBI significantly affected the crystallization and the morphologies of the composite films. Fig. 3(a) shows that the BiI_3 film consists of small grains and displays some micro-cracks. Fig. 3(b) shows that in the composite film with x = 0.10, the BiI_3 grains on which some MBI crystal seeds formed became larger. Fig. 3(c) shows that the dense composite film (x = 0.20) with larger BiI_3 grains formed, and the MBI grains still existed in the BiI_3 grains as nanosheets. However, as shown by the XRD results, when x $\geq$ 0.5, MBI dominated in the composite films. Correspondingly, the surface morphologies were totally changed. As shown in Figs. 3(d) and 3(e), the layer-structured MBI grains were grown mainly as (001)-oriented grains that are larger than 5 μm. Moreover, some gel-like substances and disconnection existed in these films. Fig. 3(f) shows that the MBI film displayed a non-oriented growth of network structure. The composite dramatically affected the surface morphologies of the films. Although BiI_3 and MBI were both hexagonal, they did not form homogenous alloys due to lattice mismatching. By contrast, they created numerous BiI_3-MBI interfaces [15,26]. Regarding the enlarged grains in the composite films, the mechanism involved in this phenomenon remains unclear. One explanation was that the MBI nanosheets served as nucleation centers for the major BiI_3 phase [28]. The other explanation was that lower concentration promoted grain growth, resulting in larger BiI_3 grains [29].

Fig. S1 and Table S2 show the EDX data. The molar ratios of I:Bi atoms calculated from the EDX results were 3.06, 3.19, 3.40, 3.98, 4.20, and 4.68. Correspondingly, the stoichiometric ratios of $(CH_3NH_3)_3Bi_2I_9$: BiI_3 in the films were consistent with that of their precursors. Hence, these films were denoted below as $(BiI_3)_{1-x}(MBI)_x$ (x = 0, 0.10, 0.20, 0.50, 0.75, 1.0). In addition, the

crystallization of the films is not very comparable compared with that of the films processed through a physical method [12], which can influence the performance of solar cells.

Spectral absorption of the films is one of the key factors affecting the performance of thin film solar cells. The UV-visible spectral absorption of the $(BiI_3)_{1-x}(MBI)_x$ films was investigated at 300–1200 nm (Fig. 4(a)). The absorption onsets of the BiI_3 film and the MBI film was observed at approximately 700 and 590 nm, respectively. However, the absorption onsets of the composite films varied with MBI content, demonstrating a phenomenon called multi-absorptions. Moreover, weakened absorption was observed in the composite films, especially for the $(BiI_3)_{0.5}(MBI)_{0.5}$ and $(BiI_3)_{0.25}(MBI)_{0.75}$ samples. The absorption mechanism can be explained by multiple factors. One explanation is the bandgap difference. The bandgap of the MBI perovskite was larger than that of BiI_3. Therefore, as the content of MBI increased in the composite films, the absorption shifted to the short-wavelength region. The other explanation is light scattering. Grain size-dependent light scattering affects spectral absorption [30,31]. Smaller grains are beneficial for more efficient light scattering in the short-wavelength region. Therefore, the nano-scale network structure in the MBI film enhanced the scattering and absorption in the short wavelength region. By contrast, the larger layer-structured MBI grains of micrometers in the $(BiI_3)_{0.5}(MBI)_{0.5}$ and $(BiI_3)_{0.25}(MBI)_{0.75}$ composite films showed weaker light scattering and absorption in the short wavelength region. The detailed bandgaps of the BiI_3 and MBI films were calculated by the Tauc equation [32]:

$$\alpha h\gamma = \beta(h\gamma - E_g)^n \tag{2}$$

where α is the absorption coefficient, $h\gamma$ is the photon energy, β is a constant, and E_g is the bandgap. Considering that BiI_3 and MBI are indirect bandgap materials, $n = \frac{1}{2}$ is used in the evaluation [12,15]. Therefore, the bandgaps of the BiI_3 and MBI films were estimated to be 1.77 and 2.15 eV, respectively (Fig. 4(b)). However, precise evaluation of bandgaps of the composite films was difficult because of the multi-absorption effects.

Energy level matching is another key factor affecting the performance of thin-film solar cells. To experimentally estimate the energetic position of the valence band, we performed PYS on the $(BiI_3)_{1-x}(MBI)_x$ films grown on the FTO substrates. As shown in Fig. S2, all of the valence bands of $(BiI_3)_{1-x}(MBI)_x$ films were approximately −6.10 eV, demonstrating slight dispersion when x varied from 0 to 1.0. This phenomenon was observed because the top of the valence band in BiI_3 and MBI materials was mainly attributed to the antibonding 6s character of the partially oxidized

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Bi^{3+} cation and I$^-$ anion, and both of the materials have a valence band of approximately −6.00– −6.10 eV [12,15]. Accordingly, no obvious dispersion was observed in the valence band in the (BiI$_3$)$_{1-x}$ (MBI)$_x$ composites. By contrast, the spin−orbit coupling, along with the large atomic weight of the Bi^{3+} cation, could lead to a more disperse conduction band and lower electron effective mass [15–19]. Moreover, a schematic energy band diagram was constructed in Fig. 5. In this diagram, the conduction band of MBI was higher than that of TiO$_2$, whereas the conduction band of BiI$_3$ was slightly lower than that of TiO$_2$. However, because the bandgaps of the composites could not be precisely qualified, their conduction bands were not quantitatively determined in this work.

The (BiI$_3$)$_{1-x}$(MBI)$_x$ solar cells were fabricated to evaluate their potential applications in solar cell technology. Fig. 6 shows that the (BiI$_3$)$_{1-x}$(MBI)$_x$ solar cells consists of FTO/compact-TiO$_2$/mesoprous-TiO$_2$/absorber/HTM/Ag. The champion *I-V* data and curves of each group are shown in Table 1 and Fig. 7. In this study, all of the (BiI$_3$)$_{1-x}$(MBI)$_x$ devices showed photovoltaic outputs, in which the BiI$_3$ solar cell showed a V_{oc} of 0.44 V, a J_{sc} of 0.25 mA/cm^2, and a *PCE* of 0.045%; by contrast, the MBI solar cell showed a V_{oc} of 0.46 V, a J_{sc} of 0.13 mA/cm^2, and a *PCE* of 0.023%. The photovoltaic performance of the solar cells strongly depended on the (BiI$_3$)$_{1-x}$(MBI)$_x$ active layers. For the BiI$_3$ and MBI solar cells, the energy band diagram suggested that the photo-excited holes from the BiI$_3$ and the MBI films can be injected into the Spiro, assuming that a good separation has occurred. However, given that the conduction band of BiI$_3$ was quite proximate to that of TiO$_2$, the driving force is insufficient to inject the excited electron from the BiI$_3$ into the TiO$_2$ layer [12,20]. Moreover, the theoretical *PCE* of BiI$_3$ solar cells would probably have a relatively low maximum. Accordingly, the BiI$_3$ solar cells with PTAA/PIDT-DFBT as HTMs fabricated from a physical method were reported with only a V_{oc} of 0.22 and 0.42 V [12]. In our experiments we obtained a V_{oc} of 0.44 V, whereas the *PCE* in the BiI$_3$ solar cell remained very low. For the MBI perovskite solar cells, the *PCE* was low mainly because the bandgap of MBI was too large for the effective absorption of visible light.

Interestingly, Table S3 and Fig. S3 show that with a small amount of the MBI injected into the BiI$_3$ films, the photovoltaic performance of the composite solar cells was significantly enhanced, in which the (BiI$_3$)$_{0.8}$(MBI)$_{0.2}$ solar cells reached the optimum performance. Compared with the BiI$_3$ solar cells, the (BiI$_3$)$_{0.8}$(MBI)$_{0.2}$ solar cells showed a champion *PCE* that increased from 0.045%

to 0.076% and a V_{oc} that obviously improved from 0.44 V to 0.57 V. Regarding the enhanced photovoltaic performance of the composite solar cells, two explanations are offered. First, this phenomenon was attributed to the improved crystallization and coverage. The XRD and SEM results above showed that the introduction of MBI significantly improved the BiI_3 crystallization of the $(BiI_3)_{0.8}$ $(MBI)_{0.2}$ films and optimized the film quality, effectively reducing the recombination and leakage in the devices. Moreover, the series resistance of the $(BiI_3)_{0.8}(MBI)_{0.2}$ solar cells was relatively lower than that of the others, indicating a more effective charge transport. Second, the enhanced photovoltaic performance was attributed to band bending in the composite films. As shown in Fig. 8, band bending occurred at the MBI-BiI_3 interfaces in the $(BiI_3)_{1-x}(MBI)_x$ composites. Given that the BiI_3 and the MBI are semiconductors without doping, their Fermi levels are possibly located near the center of the bandgaps. When these two semiconductors came into contact, the Fermi levels of these materials migrated, forming a stable space charge region at the hetero-interface [33]. Therefore, compared with that of BiI_3, the conduction band of the $(BiI_3)_{1-x}(MBI)_x$ composite systems increased due to band bending. Considering that the conduction band of the BiI_3 approached that of TiO_2, the band bending could result in a more efficient injection of photon-excited electrons from the composite absorbing layers into the TiO_2. In particular, because the large amount of the MBI nano-sheets in the BiI_3 grains created numerous BiI_3-MBI interfaces, the conduction bands of the entire BiI_3-MBI systems were improved compared with that of the BiI_3 film. Accordingly, the $(BiI_3)_{0.8}(MBI)_{0.2}$ solar cells displayed obviously enhanced V_{oc} and *PCE*.

In addition to V_{oc} and *PCE*, the hysteresis properties of the $(BiI_3)_{1-x}(MBI)_x$ solar cells with the champion performance were investigated. As shown in Fig. 9, comparison between the forward and reverse scanning of the solar cells clearly revealed the hysteresis-less properties of the $(BiI_3)_{0.8}(MBI)_{0.2}$ composite solar cells. The hysteresis of halide perovskite solar cells was speculated to be related to ionic or vacuum defects [34]. Therefore, the hysteresis-less phenomenon in $(BiI_3)_{0.8}(MBI)_{0.2}$ composite solar cells implied that small amount of MBI served as active materials rather than agents of defects in the composite films. In summary, the multiplicative effects between BiI_3 and MBI in the composites enhanced the photovoltaic performance of some composite solar devices.

Furthermore, our study showed that some other composite solar cells performed worse than pure solar cells as demonstrated by the low *PCE* and V_{oc} of these devices or the failure of some

devices (e.g., $(BiI_3)_{0.5}(MBI)_{0.5}$ solar cells). Based on the XRD and SEM results, the failures in the $(BiI_3)_{0.5}(MBI)_{0.5}$ group were likely due to the amorphous substances in the composite films. The low *PCE* and V_{oc} of the $(BiI_3)_{0.25}(MBI)_{0.75}$ composite solar cells were more likely caused by the disconnection in the composite films. Moreover, the weakened spectral absorption in the $(BiI_3)_{0.5}(MBI)_{0.5}$ and the $(BiI_3)_{0.25}(MBI)_{0.75}$ films resulted in low power conversion. Regarding the MBI solar cells, the network structure of the MBI films easily led to the failure of the devices. Furthermore, the J_{sc} of the devices remained low. One of the reasons can be attributed to the HTM used in the $(BiI_3)_{1-x}(MBI)_x$ devices because PTAA and PIDT-DFBT have a higher hole mobility than the Spiro, which was used in this study [12,13]. Another reason for the low FF and low V_{oc} was the high carrier density of the MBI (approximately 10^{16} cm^{-3}) [14,35]. The high background carrier densities in the light absorber could contribute to bulk recombination and in reduced FFs and V_{oc}.

4. Conclusions

We have developed a new method to tune the optical properties of lead-free materials by forming a composite of BiI_3 and MBI perovskite for solar cell applications. The active layers of $(BiI_3)_{1-x}(MBI)_x$ showed the gradient in the colors, crystallization and surface morphologies. The introduction of MBI into BiI_3 resulted in multi-absorption, which affected the photovoltaic performance of the composites. Compared with the BiI_3 solar cells and MBI perovskite solar cells, some $(BiI_3)_{1-x}(MBI)_x$ composite solar cells demonstrated an optimized photovoltaic output. In particular, V_{oc} and *PCE* of the $(BiI_3)_{0.8}(MBI)_{0.2}$ composite solar cells significantly increased from 0.44 V to 0.57 V and from 0.045% to 0.076%, respectively. This phenomenon was mainly attributed to two reasons. One was the enhanced crystallization and improved coverage of BiI_3 after introduction of a small amount of MBI, which effectively reduced recombination. The other was band bending at the BiI_3-MBI interfaces in the composites, and this phenomenon optimized the energy level matching between the absorbing layers and TiO_2, resulting in a more efficient electron injection from the absorbing layers into TiO_2. Our results indicated that the use of properly designed composites of lead-free materials with different absorption and energy levels can be an effective strategy to design new solar cells.

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Table 1. *I-V* characteristic of the champion $(BiI_3)_{1-x}(MBI)_x$ solar cells.

	0	0.10	0.20	0.50	0.75	1
J_{sc} (mA/cm^2)	0.25	0.25	0.27	0.20	0.12	0.13
V_{oc} (V)	0.44	0.51	0.57	0.47	0.37	0.46
FF	0.42	0.45	0.50	0.39	0.30	0.37
PCE (%)	0.045	0.058	0.076	0.035	0.013	0.023
Series resistance (Ω)	3953	3975	3075	2984	9429	8153
Shunt resistance (Ω)	36938	43781	56962	35790	18777	33303