Inorganic and Lead-free CsBi₃I₁₀ Thin Film Solar cell Prepared by Single-source Thermal Evaporation

Huabin Lan (✉ lanhuabin@sztu.edu.cn)

Shenzhen Technology University <https://orcid.org/0000-0003-0729-2053>

Xingye Chen

Shenzhen University

Ping Fan

Shenzhen University

Guangxing Liang

Shenzhen University

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Abstract

All inorganic lead-free halide perovskites have attracted much attention due to their non-toxic and good band gap. In this paper, we first prepared all inorganic lead-free perovskite $\text{CsBi}_3\text{I}_{10}$ thin films by single source thermal evaporation deposition. The results show that $\text{CsBi}_3\text{I}_{10}$ thin films prepared by single source thermal evaporation have layered structure, high purity hexagonal phase and high crystallinity, which are consistent with the theoretical calculation results. The surface of the thin film was compact and uniform, and had high homology with the crystal structure of the evaporation source material. After annealing, the crystallinity of the film was further improved. The band gap of the $\text{CsBi}_3\text{I}_{10}$ thin film calculated was 1.83 eV, Perovskite solar cells based on $\text{CsBi}_3\text{I}_{10}$ thin films exhibit an efficiency of up to 0.84%. These results indicate that the proposed single source thermal evaporation method has the potential to prepare high efficiency inorganic lead-free perovskite solar cells.

1. Introduction

In recent years, organic-inorganic perovskite materials have attracted great attention in the photovoltaic field all over the world due to its simple production process, low cost and high photoelectric performance. These excellent properties make it have a huge application market in photodetectors, optical converters, light-emitting diodes and solar cells [1–4]. In particular, perovskite solar cells are developing rapidly. At present, the highest photovoltaic conversion efficiency (PCE) of perovskite solar cells has reached 25.5% [5]. This efficiency is comparable to that of Si, CdTe and CIGS solar cells already commercially available [6]. However, the organic-inorganic perovskite solar cells have poor stability, lead based perovskite materials are highly toxic and pollute the environment, which seriously hinder the commercialization of perovskite solar cells [7, 8]. Therefore, it is necessary to find other metals to replace lead in order to solve the problem of environmental pollution. At this time, non-toxic inorganic non-lead perovskite materials have attracted the attention of researchers and related exploration has been carried out [9, 10]. It is of great significance to replace Pb^{2+} with all-inorganic non-lead perovskite materials that are narrower, more chemically stable and more environmentally friendly, such as $\text{Sn}^{2+}/\text{Ge}^{2+}$ base perovskite, $\text{Bi}^{3+}/\text{Sb}^{3+}$ base double perovskite and halide perovskite added with S^{2-} . However, Sn^{2+} is easily oxidized to Sn^{4+} , leading to Sn based perovskite instability in the air, which greatly limits its development as a light absorbing layer [11–14]. CsGeI_3 has a stable diamond crystal structure, but the maximum photoelectric conversion efficiency of CsGeI_3 solar cells is only 0.11%, and its manufacturing cost is high. Bismuth-based ternary iodide is used as perovskite solar cell absorbing materials [15]. The low power conversion efficiency of these materials limits the practical application of bismuth-based solar cells. Bi-based total inorganic perovskite $\text{A}_a\text{B}_b\text{X}_x$ ($\text{A} = \text{Cs, Ag, Cu}$; $\text{B} = \text{Bi, Sb}$; $\text{X} = \text{I, Br}$; $\text{X} = \text{a} + 3\text{b}$), such as $\text{Cs}_3\text{Sb}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{CsBi}_3\text{I}_{10}$, CuBiI_4 and Ag_3BiI_6 become new choices of absorption layers for solar cells [16, 17]. Its stability can be improved by replacing MA^+ or FA^+ with Cs^+ . In the bismuth-based perovskite material $\text{CsBi}_3\text{I}_{10}$, Bi^{3+} has the same potential as lead cation to obtain high efficiency $6\text{S}^26\text{P}^0$ electron configuration to form the perovskite conduction band and valence band, and $\text{CsBi}_3\text{I}_{10}$ band gap width of about 1.77eV is suitable

as the perovskite solar cell absorption layer [18]. However, the highest photoelectric conversion efficiency of $\text{Cs}_3\text{Bi}_2\text{I}_9$ based perovskite solar cells prepared by traditional spinning coating method is only 3.2%. Therefore, the preparation of high-quality $\text{CsBi}_3\text{I}_{10}$ thin films by traditional solution method has become a new challenge [19, 20].

At present, there are few studies on $\text{CsBi}_3\text{I}_{10}$ thin film solar cells, which are generally prepared by non-vacuum solution method. $\text{CsBi}_3\text{I}_{10}$ thin films are obtained by heat treatment after spinning the precursor solutions of CsI and BiI_3 [18]. However, the non-vacuum film forming environment is difficult to ensure the repeatability of the process, and it is difficult to grow a continuous and uniform film on a large area, resulting in low film quality. In addition, dual-source thermal evaporation method requires precise control of the evaporation sources of organic and inorganic materials at the same time, so it is difficult to effectively control the film composite process, and it is easy to deviate from the stoichiometric ratio [21]. Therefore, the development of large area, high quality, non-toxic and high stability perovskite film is an important topic for future application, especially for the prospect of non-lead inorganic perovskite film. As far as we know, single-source thermal evaporation has been very mature in the preparation of high quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films [22]. However, there have been few reports of this approach in $\text{CsBi}_3\text{I}_{10}$ thin film solar cells.

In this work, the first principle density functional theory (DFT) was used to calculate the crystal structure and electronic structure of $\text{CsBi}_3\text{I}_{10}$. Inorganic lead-free perovskite $\text{CsBi}_3\text{I}_{10}$ thin films were prepared by vacuum single source thermal evaporation method. The $\text{CsBi}_3\text{I}_{10}$ powder was directly heated and then deposited on the substrate to form the $\text{CsBi}_3\text{I}_{10}$ film. Meanwhile, the microstructure, composition, energy band structure, optical and electrical properties of the $\text{CsBi}_3\text{I}_{10}$ film were analyzed. The photoelectric conversion efficiency of $\text{CsBi}_3\text{I}_{10}$ thin film solar cells based on single source thermal evaporation is 0.84%, which provides a new method for preparing inorganic lead-free perovskite.

2. Experimental Procedures

2.1. $\text{CsBi}_3\text{I}_{10}$ crystals and powder preparation

The 0.3997g CsI (99.99%, Xi'an Polymer Light Technology) and 2.718g BiI_3 (99.99%, Sigma-Aldrich) were mixed in N,N -dimethylformamide (DMF) (99.0%, MaterWin, China)/dimethyl sulfoxide (DMSO) ($\geq 99.0\%$, MaterWin, China) and stirred in a closed magnetic beaker for 24 hours. Then, the $\text{CsBi}_3\text{I}_{10}$ precursor solution was transferred to the petri dish, and the temperature was kept at 200°C on the hot plate until all the precursor solution volatilized to obtain the $\text{CsBi}_3\text{I}_{10}$ crystal as shown in Fig. 1. Then, the prepared $\text{CsBi}_3\text{I}_{10}$ crystal was ground into powder and used as film evaporation material.

2.2. $\text{CsBi}_3\text{I}_{10}$ thin films preparation

Figure 1 shows the preparation process of $\text{CsBi}_3\text{I}_{10}$ thin film, including crystal preparation, single source thermal evaporation and annealing. TiO_2 dense layer and mesoporous layer were prepared before deposition of thin film $\text{CsBi}_3\text{I}_{10}$. Fluorine doped tin oxide (FTO) (Square resistance $< 15\Omega$, South China Xiangcheng Tech., China) conductive glass was used in the experiment. First, the FTO glass is cleaned with isopropanol, acetone, desolvent and ethanol, and treated with UV/O_3 before use. According to the steps described in the references [26], TiO_2 dense layer solution was rotated-coated on After cooling, the TiO_2 paste (30NR-D, Dyesol, Queanbeyan, Australia) diluted with ethanol (mass ratio 1:6) was used as the mesoporous layer solution, and then it was spin coated on the dense TiO_2 layer and sintered at 500°C for 30 min to form the mesoporous structure of TiO_2 . FTO glass, and then sintered at 450°C for 30 minutes to form TiO_2 dense layer. Put glass/FTO/c- TiO_2 /m- TiO_2 into vacuum chamber, weigh 300mg $\text{CsBi}_3\text{I}_{10}$ perovskite powder, put the powder into the evaporation boat, the distance between the substrate and the evaporation source is 25cm, the substrate does not need to be heated, the substrate rotation speed is 40r/ min, when the vacuum degree reaches $6\times 10^{-4}\text{pa}$, turn on the evaporation power supply, and quickly increase the working current of the evaporation boat from 0A to 140A until the powder was completely evaporated to form a 250 nm thick $\text{CsBi}_3\text{I}_{10}$ thin film. Slowly adjust the evaporation current to 0A, turn off the molecular pump and mechanical pump in turn, and finally fill the vacuum chamber with nitrogen to take out the film sample and put it into the glove box.

2.3. Device fabrication

The perovskite solar cells with a device structure of glass/FTO/c- TiO_2 /m- TiO_2 / $\text{CsBi}_3\text{I}_{10}$ /spiro-OMeTAD/Ag was fabricated. The prepared glass/FTO/c- TiO_2 /m- TiO_2 / $\text{CsBi}_3\text{I}_{10}$ was annealed at 160°C for 20 minutes in a glove box filled with nitrogen. After that, 72.3 mg of Spiro-OMeTAD (99%, ChemBoron, China) in 1 mL of chloridobenzene solution was used as hole transport materials with the addition of $28\mu\text{L}$ of 4-tert-butylpyridine (96%, Macklin) and $19\mu\text{L}$ of bis(trifluoromethane) sulfonimide lithium salt actronitel (520 mg/mL). It rotates the coating on $\text{CsBi}_3\text{I}_{10}$ film at a speed of 3000 rpm 30s. Finally, 60 nm silver film was prepared by thermal evaporation method.

2.4. Characterization

The crystal orientation and structure of the films were determined by X-ray diffraction (XRD, Ultima IV) at 40 kV and 40 mA under Cu K_α radiation ($\lambda = 0.15406\text{ nm}$). Field emission scanning electron microscopy (FE-SEM, Zeiss, Supra 55) was used to analyze the surface and cross-sectional morphology of the films and battery devices. Energy dispersive X-ray spectroscopy combined with scanning electron microscopy (EDX: Bruker Quantax 200) was used to determine its composition. The valence band of $\text{CsBi}_3\text{I}_{10}$ thin films was measured by UV electron spectroscopy (UPS) using a 21.2 EV monochromatic black source and VG Scienta R4000 analyzer. Spectrophotometer (lambda 950) was used to evaluate the light absorption characteristics. Thermogravimetric analysis (TGA) was carried out in N_2 atmosphere by thermogravimetric analyzer (TGA Q50, TA instruments). The current density -voltage (J-V) characteristics of planar $\text{CsBi}_3\text{I}_{10}$ perovskite solar cells were measured with Keithley 2400 source meter under the

condition of standard analog light source AM 1.5G (100 mW/cm²). Two masks are used to precisely set the illumination of the device area to 0.1 cm².

3. Results And Discussion

The crystal structure of CsBi₃I₁₀ thin films has been predicted in previous papers [23], from rhombic structure in BiI₃ to hexagonal structure in Cs₃Bi₂I₉. Figure 2a shows the crystal and electronic structures of CsBi₃I₁₀ thin films calculated by first principles DFT, indicating that CsBi₃I₁₀ is a layered crystal structure. We calculated all the XRD spectra, and determined the crystal structure of CsBi₃I₁₀ powder, as-deposited CsBi₃I₁₀ thin film and annealed thin film by X-ray diffraction (XRD). The results are shown in Fig. 2b. It is found that the calculated XRD patterns are basically consistent with the experimental XRD patterns of as-deposited CsBi₃I₁₀ thin film and annealed thin film. From the XRD patterns, it can be seen that the most significant peaks of CsBi₃I₁₀ films are (003), (006) and (300), which can correspond to the calculated XRD peak positions. This result further indicates that CsBi₃I₁₀ has a layered crystal structure. After annealing, the characteristic peaks (003) and (006) of CsBi₃I₁₀ films are significantly enhanced, which indicates that the annealed CsBi₃I₁₀ films have higher phase purity and better crystallinity, and (003) enhanced preferred orientation can be obtained. Figure 2c shows the weight change of CsBi₃I₁₀ powder with temperature in nitrogen atmosphere. It can be seen from the figure that the weight of the sample decreases with the increase of temperature. For CsBi₃I₁₀ powder, when the temperature was higher than 300 °C, the weight of CsBi₃I₁₀ begins to lose, which indicates that the CsBi₃I₁₀ powder is thermally unstable and begins to decompose when the temperature is higher than 300°C.

Figure 3 shows the SEM images of as-deposited CsBi₃I₁₀ thin film and annealed thin film. Before annealing, the CsBi₃I₁₀ film was dense and uniform, and the surface of TiO₂ was completely covered and compact. After annealing, the CsBi₃I₁₀ thin films were compact, the grain size increases, and the layered structure can be seen, which is consistent with the observation of XRD. The reason of pinhole formation in annealed films is not clear, but it may be related to the growth process of thin films. The composition of CsBi₃I₁₀ film is an important factor affecting its structure, electrical and optical properties. Table 1 shows the composition of as-deposited CsBi₃I₁₀ thin film and annealed thin film measured by EDS. The Cs/Bi/I ratios of CsBi₃I₁₀ powder, as-deposited thin film and annealed thin film were calculated as shown in Table 1. The Cs/Bi/I ratio of powder and annealed film is very close to the stoichiometric ratio of CsBi₃I₁₀ thin film, which also indicates the formation of pure phase CsBi₃I₁₀ film.

Table 1
The composition of CsBi₃I₁₀ powder, as-deposited thin film and annealed thin film.

Sample	Cs(at%)	Bi(at%)	I(at%)	N(Cs)/N(Bi)/N(I)
CsBi ₃ I ₁₀ powder	6.71	21.96	71.22	1:3.22:10.45
As-deposited films	6.56	20.68	72.76	1:3.15:11.10
annealed films	6.77	20.53	72.70	1:3.03:10.74

The optical properties of CsBi₃I₁₀ films are strongly affected by the microstructure. Figure 4 shows the UV-visible spectra of annealed films and as-deposited films. It can be seen from Fig. 4a that the prepared CsBi₃I₁₀ films have low reflectivity, and obvious interference phenomenon occurs at the wavelength of 670 nm to 1400 nm. The transmission spectrum of annealed films is lower than that of as-deposited films, which is mainly due to the existence of grain boundaries in annealed films to reduce light scattering. Therefore, the absorption spectra calculated from reflectance and transmittance are shown in Fig. 4c, indicating that the CsBi₃I₁₀ thin films prepared by single source thermal evaporation have good absorption, and most of the absorption peaks begin at the wavelength of ~ 600 nm. Finally, according to absorption spectrum calculation, the band gap width of as-deposited film and annealed film was 1.79 eV and 1.78 eV respectively, which were close to the theoretical value of 1.77 eV reported in the literature [18].

The Fermi energy (E_f) and valence band energy (E_v) of CsBi₃I₁₀ thin films were measured by ultraviolet photoelectron spectroscopy (UPS). Figure 5a,b depict the determined valence band levels. The energy of monochromatic light source (He I light) was 21.22eV and the secondary cut-off edge was 16.33eV. We can find that E_f was 4.89 eV, according to the equation $E_f = 21.22 \text{ eV (HeI)} - E_{cutoff}$ [24]. The E_v value was determined by linear extrapolation ($E_v - E_f$) in the low binding-energy region, calculated E_v was 6.43 eV. Figure 5c shows a sharp absorption edge, indicating a high light absorption coefficient in the visible light range. The relationship between the band gap and optical absorption conforms to the Tauc relation, and the formula is $ah\nu = C(h\nu - E_g)^{1/2}$, where a is the absorption coefficient, h is the Planck constant, C is the constant, and ν is the photon frequency [18]. The calculated energy band gap (E_g) of CsBi₃I₁₀ film is 1.83 eV, which is close to the previous band gap (E_g) of 1.79 eV calculated from the absorption spectrum. The conduction band energy (E_c) is estimated according to $E_v + E_g$, and the band diagram as shown in Fig. 5d. The CsBi₃I₁₀ thin films deposited by single source thermal evaporation may be an N-type semiconductors, because E_f is higher than the median value of band gap.

In order to evaluate the potential application of CsBi₃I₁₀ thin films prepared by single source thermal evaporation method in solar cells, we prepared all inorganic perovskite solar cells with the device structure of glass/FTO/c-TiO₂/m-TiO₂/ CsBi₃I₁₀/spiro-OMeTAD/Ag, as shown in Fig. 6a. Figure 6b show the SEM cross section images of solar cell based on annealed CsBi₃I₁₀ thin film. It can be seen from the Fig. 6b and S1 that the cross section of the cell device based on annealed CsBi₃I₁₀ thin film was more

compact and smooth without pinholes. TiO_2 and spiro-OMeTAD were used as electron transport materials and hole transport materials (ETM and HTM), respectively. The annealed $\text{CsBi}_3\text{I}_{10}$ film has compact and uniform cross-section, which is mainly due to the infiltration of some $\text{CsBi}_3\text{I}_{10}$ films into the mesoporous TiO_2 layer after annealing and the further growth of the grains. Figure 6c depicts the energy level arrangement of the battery device. It can be seen from the structure energy band of TiO_2 and perovskite battery, TiO_2 is used to transfer electrons to FTO and spiro-OMeTAD is used to transport holes, it is easy for electrons to transfer continuously from perovskite to TiO_2 layer, thus forming photocurrent [25]. Figure 6d,e show the $J - V$ curves of as-deposited and annealed $\text{CsBi}_3\text{I}_{10}$ thin film solar cells, and Table 2 shows the device parameters (J_{sc} , V_{oc} , FF , PCE). It can be found that as-deposited $\text{CsBi}_3\text{I}_{10}$ thin film solar cell exhibit J_{sc} of 1.07 mA/cm^2 , V_{oc} of 0.47 V , FF of 47.36% , leading to a low PCE of 0.24% (Forward). $\text{CsBi}_3\text{I}_{10}$ thin film after annealing, the PCE of $\text{CsBi}_3\text{I}_{10}$ thin film solar cell was significantly improved, J_{sc} was significantly increased to 4.86 mA/cm^2 , and the final device efficiency reaches 0.84% (Forward). However, $\text{CsBi}_3\text{I}_{10}$ thin film after annealing, V_{oc} decreases to 0.38V , which may be due to the small pinhole defects in the annealing process, resulting in uneven HTM rotation coating and leakage, which may reduce the maximum voltage of the device, this phenomenon also leads to hysteresis effect. Figure 6f shows the statistics efficiency of solar cell based on as-deposited and annealed $\text{CsBi}_3\text{I}_{10}$ thin film. It can be seen from the Fig. 6f that the solar cell based on annealed $\text{CsBi}_3\text{I}_{10}$ thin film, although V_{oc} drops to 0.38V , the solar cell efficiency was significantly improved. Although the photoelectric conversion efficiency of $\text{CsBi}_3\text{I}_{10}$ thin film solar cell prepared by single source thermal evaporation is still lower than that of ordinary Pb-based perovskite solar cells. However, the inorganic Pb-free $\text{CsBi}_3\text{I}_{10}$ thin films prepared by single-source thermal evaporation have a potential application prospect in the field of photovoltaic.

Table 2
The device parameters of solar cell based on as-deposited and annealed $\text{CsBi}_3\text{I}_{10}$ thin film.

Sample	$V_{oc}(\text{V})$	$J_{sc}(\text{mA/cm}^2)$	FF	PCE
As-deposited	0.47	1.07	47.36%	0.24%
Annealed	0.38	4.86	45.48%	0.84%

4. Conclusions

In summary, we report a facile, efficient and reproducible new method for the fabrication of all inorganic Pb-free perovskite $\text{CsBi}_3\text{I}_{10}$ thin film prepared by single-source thermal evaporation. Firstly, we prepared $\text{CsBi}_3\text{I}_{10}$ crystal powder with layered structure. Secondly, $\text{CsBi}_3\text{I}_{10}$ thin films were prepared by single-source thermal evaporation. $\text{CsBi}_3\text{I}_{10}$ films had high purity hexagonal phase and crystallinity, which were consistent with the theoretical calculation results. $\text{CsBi}_3\text{I}_{10}$ thin film was uniform, smooth and non

porous. The surface of TiO_2 was completely covered and the chemical composition was similar to that of precursor powder. In the visible light range, $\text{CsBi}_3\text{I}_{10}$ thin film had high optical absorption coefficient, and the band gap of the film is 1.83eV, which is close to the theoretical value. The PCE of $\text{CsBi}_3\text{I}_{10}$ perovskite thin film solar cells prepared by single source thermal evaporation is 0.84%, which has good performance and reproducibility. The results show that the inorganic Pb-free $\text{CsBi}_3\text{I}_{10}$ thin film prepared by single source thermal evaporation method have potential applications in photovoltaic field.

Declarations

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References

- [1] D. Moghe, L. Wang, C. J. Traverse, A. Redoute, M. Sponseller, P. R. Brown, V. Bulović, R. R. Lunt, All Vapor-deposited Leadfree Doped CsSnBr_3 Planar Solar Cells, *Nano Energy*. 28, 469– 474 (2016)
- [2] M. Habibi, F. Zabihi, M. R. Ahmadian-Yazdi, M. Eslamian, Progess in emerging solution-processed thin film solar cells-Part II: Perovskite solar cells, *Renewable Sustainable Energy Rev.* 62, 1012 (2016)
- [3] A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Toxicity of organometal halide perovskite solar cells, *Nat. Mater.* 15, 247– 251 (2016)
- [4] A. H. Slavney, T. Hu, A. M. Lindenberg, H. I. Karunadasa, A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications, *J. Am. Chem. Soc.* 138, 2138–2141 (2016)
- [5] R. Nishikubo, H. Kanda, I. García-Benito, A. Molina-Ontoria, G. Pozzi, A. M. Asiri, M. K. Nazeeruddin, A. Saeki, Optoelectronic and Energy Level Exploration of Bismuth and Antimony-Based Materials for Lead-Free Solar Cells, *Chemistry of Materials*. 32, 6416 (2020)
- [6] C. C. Vidyasagar, B. M. Muñoz Flores, V. M. Jiménez, Recent Advances in Synthesis and Properties of Hybrid Halide Perovskites for Photovoltaics, *Nano-Micro Lett.* 10, 68 (2018)
- [7] T. Ma, S. Wang, Y. Zhang, K. Zhang, and L. Yi, The development of all-inorganic CsPbX_3 perovskite solar cells. *J Mater Sci* 55:464–479 (2020)

- [8] T. Singh, A. Kulkarni, M. Ikegami, T. Miyasaka, Effect of electron transporting layer on bismuth-based lead-free perovskite (CH₃NH₃)₃Bi₂I₉ for photovoltaic applications, *ACS Appl. Mater. Interfaces* 8, 14542–14547 (2016)
- [9] M. Ghasemi, L. Zhang, J. H. Yun, M. Hao, D. He, P. Chen, Y. Bai, T. Lin, M. Xiao, A. Du, M. Lyu, L. Wang, Dual-Ion-Diffusion Induced Degradation in Lead-Free Cs₂AgBiBr₆ Double Perovskite Solar Cells, *Advanced Functional Materials* 30, 2002342 (2020)
- [10] B. W. Park, B. Philippe, X. Zhang, H. Rensmo, G. Boschloo, E. M. J. Johansson, Bismuth Based Hybrid Perovskites A₃Bi₂I₉ (A: Methylammonium or Cesium) for Solar Cell Application, *Adv. Mater.* 27, 6806–6813 (2015)
- [11] T. Krishnamoorthy, H. Ding, C. Yan, W. L. Leong, T. Baikie, Z. Y. Zhang, M. Sherburne, S. Z. Li, M. Asta, N. Mathews, et al, Lead-free germanium iodide perovskite materials for photovoltaic applications, *J. Mater. Chem. A* 3, 23829–23832 (2015)
- [12] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A. A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, et al, Lead-free organic-inorganic tin halide perovskites for photovoltaic applications, *Energy Environ. Sci.* 7, 3061–3068 (2014)
- [13] W. Q. Liao, D. W. Zhao, Y. Yu, C. R. Grice, C. L. Wang, A. J. Cimarili, P. Schulz, W. W. Meng, K. Zhu, R. G. Xiong, et al, Lead-free inverted planar formamidinium tin triiodide perovskite solar cells achieving power conversion efficiencies up to 6.22%, *Adv. Mater.* 28, 9333–9340 (2016)
- [14] M. Lyu, J. H. Yun, M. L. Cai, Y. L. Jiao, P. V. Bernhardt, M. Zhang, Q. Wang, A. J. Du, H. X. Wang, G. Liu, et al, Organic–inorganic bismuth (III)-based material: A lead-free, air-stable and solution-processable light-absorber beyond organolead perovskites, *Nano Res.* 9, 692–702 (2016)
- [15] B. Ghosh, B. Wu, H. K. Mulmudi, C. Guet, K. Weber, T. C. Sum, S. Mhaisalkar, N. Mathews, Limitations of Cs₃Bi₂I₉ as Lead-Free Photovoltaic Absorber Materials, *ACS Appl. Mater. Interfaces* 10, 35000–35007 (2018)
- [16] P. Zhu, C. Chen, S. Gu, R. Lin, J. Zhu, CsSnI₃ Solar Cells via an Evaporation-Assisted Solution Method, *Sol. RRL* 2, 1700224 (2018)
- [17] R. L. Z. Hoyer, R. E. Brandt, A. Osherov, V. Stevanović, S. D. Stranks, M. W. B. Wilson, H. Kim, A. J. Akey, J. D. Perkins, R. C. Kurchin, Methylammonium bismuth iodide as a lead-free, stable hybrid organic-inorganic solar absorber, *Chem.-Eur. J.* 22, 2605 (2016)
- [18] G. X. Liang, X. Y. Chen, Z. H. Chen, H. B. Lan, Z. H. Zheng, P. Fan, X. Q. Tian, J. Y. Duan, Y. D. Wei, and Z. H. Su, Inorganic and Pb-Free CsBi₃I₁₀ Thin Film for Photovoltaic Applications, *J. Phys. Chem. C* 123, 27423–27428 (2019)

- [19] F. Bai, Y. Hu, Y. Hu, T. Qiu, X. Miao, S. Zhang, Lead-free, air-stable ultrathin $\text{Cs}_3\text{Bi}_2\text{I}_9$ perovskite nanosheets for solar cells, *Solar Energy Materials and Solar Cells*.184, 15 (2018)
- [20] R. E. Brandt, R. C. Kurchin, R. L. Z. Hoyer, J. R. Poindexter, M. W. B. Wilson, S. Sulekar, F. Lenahan, P. X. T. Yen, V. Stevanovic, J. C. Nino, et al, Investigating of bismuth triiodide (BiI_3) for photovoltaic applications, *J. Phys. Chem. Lett.* 6, 4297–4302 (2015)
- [21] G. X. Liang, P. Fan, D. Gu, et al, Enhanced Crystallinity and Performance of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Thin Film Prepared by Controlling Hot $\text{CH}_3\text{NH}_3\text{I}$ Solution Onto Evaporated PbI_2 Nanocrystal, *IEEE journal of photovoltaic.* 6, 1537-1541 (2016)
- [22] G. X. Liang, P. Fan, J. T. Luo, et al, A promising unisource thermal evaporation for in situ fabrication of organolead halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film, *Prog, Photovolt: Res. Appl.* 23, 1901-1907 (2015)
- [23] M. B. Johansson, H. M. Zhu, E. M. J. Johansson, Extended photo-conversion spectrum in low-toxic bismuth halide perovskite solar cells, *J. Phys. Chem. Lett.* 7, 3467–3471 (2016)
- [24] Y. Kim, Z. Yang, A. Jain, O. Voznyy, G. H. Kim, M. Liu, L. N. Quan, F. P. Arquer, J. Z. Fan, E. H. Sargent, Pure Cubic-Phase Hybrid Iodobismuthates AgBi_2I_7 for Thin-Film Photovoltaics, *Angew. Chem. Int. Ed.* 55, 9586–9590 (2016)
- [25] J. Shin, M. Kim, S. Jung, C. Su, J. Park, A. Song, K. B. Chung, S. H. Jin, J. H. Lee, M. Song, Enhanced efficiency in lead-free bismuth iodide with post treatment based on a hole-conductor-free perovskite solar cell, *Nano Res.* 11, 6283–6293 (2018)
- [26] C. Lan, J. Luo, S. Zhao, C. Zhang, W. Liu, S. Hayase, T. Ma, Effect of lead-free $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ perovskite addition on spectrum absorption and enhanced photo-voltaic performance of bismuth triiodide solar cells, *J. Alloys Compd.* 701, 834–840 (2016)

Figures

Figure 1

The preparation process of $\text{CsBi}_3\text{I}_{10}$ thin film includes crystal preparation, single source thermal evaporation and annealing

Figure 2

Calculated crystal structure of CsBi₃I₁₀ (a). Calculated and experimental XRD patterns of the CsBi₃I₁₀ thin film (b). TGA curves of CsBi₃I₁₀ powders from room temperature to 800°C (c).

Figure 3

Top-view SEM images of CsBi₃I₁₀ thin film: as-deposited film (a), annealed film (b).

Figure 4

UV-vis spectra of as-deposited films and annealed films: Reflectance (a), Transmittance (b), Absorptions (c).

Figure 5

Ultraviolet photoelectron spectroscopy (UPS) measurements (a,b). $h\nu$ and $(\alpha h\nu)^2$ diagrams of CsBi3I10 thin films (c). The energy band diagram of CsBi3I10 thin film was obtained according to UPS results (d).

Figure 6

Structure diagram of CsBi₃I₁₀ thin film solar cell (a). SEM cross section images of solar cell based on annealed CsBi₃I₁₀ thin film (b). Energy level diagram of CsBi₃I₁₀ thin film solar cell (c). J-V curves of solar cell based on as-deposited and annealed CsBi₃I₁₀ thin film (d,e). PCE statistics of solar cell (total of 20 cells) based on as-deposited and annealed CsBi₃I₁₀ thin film (f).