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1. Introduction

Alkali-metal doping is an effective strategy to improve the device performance of thin film solar cells, such as Cu(In,Ga)(S,Se)₂ (CIGSSe),¹⁻⁴ Cu₂ZnSn(S,Se)₄ (CZTSSe),^{2,5-8} Sb₂(S,Se)₃⁹ and organicinorganic hybrid halide perovskite solar cells (PSCs).^{10–14} For instance, Li⁺, Na⁺, K⁺ and Rb⁺ doping can passivate surface or grain-boundary defects, promote crystal growth, and improve the electrical properties of CIGSSe^{3,4} and CZTSSe^{6–8} solar cells. Interestingly, Li⁺ can alloy with the kesterite phase leading to a solid solution (Li_xCu_{1-x})₂ZnSn(S,Se)₄ that offers a way of tuning the band

Alkali-metal-ion-doping strategy to improve the photovoltaic properties of Ag₂Bil₅ solar cells[†]

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Alkali-metal-ion doping is an efficient strategy to improve the device performance of thin film solar cells. Though doping with Li⁺ or Cs⁺ doping has been reported in Ag–Bi–I solar cells, the influence of doping with other alkali metal ions on Ag–Bi–I solar cells has not been systematically studied. In this work, we investigate the effects of five alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) on the structure, morphology, and optical and electrical properties of Ag₂Bil₅ absorber layers, and also their influence on the device performance. All alkali-metal-doped Ag₂Bil₅ thin films show high crystallinity and have similar suitable band gaps. Hall effect measurements demonstrate that the alkali-metal-doped Ag₂Bil₅ films show an improved electrical performance compared with the pristine Ag₂Bil₅ thin film, which is beneficial to achieving high-efficiency solar cells. Unexpectedly, Cs⁺ doping can significantly increase the grain size of Ag₂Bil₅ thin films, leading to a porous absorber that reduces the device efficiency. The device performance of Li⁺-, Na⁺-, K⁺- and Rb⁺-doped Ag₂Bil₅ is significantly improved compared with that of pristine Ag₂Bil₅. It is found that the order of the power conversion efficiency promotion ability is K⁺ > Rb⁺ > Na⁺ > Li⁺ > Cs⁺ under the same experimental conditions. The present approach can be extended to other Bi-based solar cells to improve their device performance, which is critical for applications in absorbers with poor electrical performance or low crystallinity.

gaps of the absorber layers and improving the device performance. In addition, LiOH, NaOH, KOH, RbOH and CsOH have been introduced into Sb-based precursor solutions to fabricate Sb₂S₃ solar cells.9 It is worth noting that only heavy alkali metal ions $(K^+, Rb^+, and Cs^+)$ are beneficial for absorbers to grow into large grains and form a better morphology, which facilitate the improvement of the device performance of Sb₂S₃ solar cells. Moreover, the role of alkali metal ions in halide perovskite solar cells has also been widely investigated.¹⁵⁻²¹ Low concentrations of Cs⁺ and Rb⁺ promote halide homogenization and enhance the charge-carrier lifetime, which plays a critical role in improving the photovoltaic device performance.¹⁰ Alkali metal ions with a gradient size occupy different positions in the crystal lattice of the perovskite, and they play various roles, e.g. crystallinity adjustment, defect passivation and ion migration.¹¹ Based on the above discussion, we can infer that the modes of alkali-metal doping include substitutional²² and interstitial doping.²³ In substitutional doping, the alkali metal can replace ions with a similar radius and coordination mode, which has a significant impact on the band gap and defects of the absorber layer.^{24,25} The interstitial doping is mainly to promote the growth of crystal grains, passivate the crystal surface and grain boundaries, and improve the device performance.²⁶ In the past few years, Bi-based materials, a new type of absorber, have aroused widespread interest among researchers,27-33 but the performance of Bi-based solar cells is far lower than those of CIGSSe, CZTSSe,



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 $[\]dagger$ Electronic supplementary information (ESI) available: Top-view and crosssectional SEM images of as-prepared Ag–Bi–S–I films with alkali metal doping; EDS mapping of the as-prepared undoped Ag₂BiI₅ film, the element contents of the as-prepared Ag₂BiI₅ thin films doped with different alkali metal ions; XPS spectra of Ag–Bi–S–I and Ag₂BiI₅ thin films; UPS spectra of the Ag₂BiI₅ thin film; statistical efficiency distribution of 30 devices with the K⁺-doped Ag₂BiI₅ absorber; PV parameters of the Ag₂BiI₅ solar cells with and without alkali metal doping; top-view and cross-sectional SEM images of 1% (a and b) and 2% (c and d) Cs⁺doped Ag₂BiI₅ thin films; and PV parameters of 1% and 2% Cs⁺-doped Ag₂BiI₅ solar cells (PTAA as the HTL). See DOI: 10.1039/d1nj02627e

Sb₂(S,Se)₃ and PSCs. Therefore, alkali-metal doping has great potential in improving the efficiency of Bi-based solar cells.

The Bi-based solar cell is a general term for a series of solar cells containing the Bi element in the absorber layer, including Bi_2S_3 , 34,35 BiSI,³⁶ AgBiS₂,³⁷ CuBiS₂^{38,39} and Bi-based halides (binary,⁴⁰ ternary^{41–43} and quaternary⁴⁴). Ag_aBi_bI_{a+3b} is an important Bi-based absorber material, and a large number of encouraging results have been achieved.^{45–51} In the crystal structure of $Ag_aBi_bI_{a+3b}$, [AgI₆] and [BiI₆] octahedra are connected through shared edges and further increase the structural dimension. 48 AgBiI_4, 49 AgBi_2I_7, 52 Ag_2BiI_5, 45 Ag₃BiI₆⁴⁸ and AgBi₃I₁₀⁵³ demonstrate an appropriate direct band gap of 1.6-1.86 eV. AgBi₂I₇ was first reported by Sargent et al. in 2016.52 The best power conversion efficiency (PCE) of the Ag-Bi-Ibased device was achieved by Pai et al. in 2018,⁵⁴ by introducing sulfide to partially substitute iodine. The band gap is decreased and the valence band edge is upshifted by sulfide doping, which contributes to improving the device performance. Recently, Li-TFSI⁵⁵ and CsI⁵⁶ were introduced into the precursor solutions to improve the quality of AgBiI₄ thin films and to enhance the PCEs of AgBiI₄ solar cells. However, the effects of other alkali metals being incorporated into Ag-Bi-I absorbers have not been investigated.

In this work, we investigate the effects of different alkali-metal doping on the performance of Ag₂BiI₅ solar cells by introducing LiI, NaI, KI, RbI and CsI into the Ag-Bi-S-I-based precursor solutions. Compared with the traditional one-step deposition approach, our method can adjust the thickness of the asprepared films by repeating the spin-coating and annealing processes. The as-prepared film is AgBiS₂ and unknown Ag compounds. Interestingly, the XRD patterns demonstrate that alkali-metal doping does not change the crystal structure of Ag₂BiI₅, so the alkali-metal doping model is one of interstitial doping. The Li⁺-, Na⁺-, K⁺- and Rb⁺-doped Ag₂BiI₅ films show dense and continuous surface morphologies. Unexpectedly, there are a lot of pinholes in the Cs⁺-doped Ag₂BiI₅ film due to its larger grain-size composition. All the absorption edges of Ag₂BiI₅ thin films are at the wavelength of \sim 700 nm, which proves that the doping mode of the alkali metal is interstitial. Hall effect measurements indicate that alkali-metal doping can increase the carrier concentration, thus leading to a high conductivity. Finally, we fabricate Ag₂BiI₅ solar cells with the structure of glass/ITO/ SnO₂/Ag₂BiI₅/PTAA/Ag. The device performance of Li⁺-, Na⁺-, K⁺- and Rb⁺-doped Ag₂BiI₅ is significantly improved compared with that of pristine Ag₂BiI₅. As a result, we achieve a PCE of 0.75% for the K⁺-doped Ag_2BiI_5 solar cell, with an open circuit voltage $(V_{\rm OC})$ of 0.68 V, a short circuit current density $(J_{\rm SC})$ of 1.95 mA/cm², and a fill factor (FF) of 56.20%, which is significantly higher than that of other devices. Moreover, it is found that the order of the power conversion efficiency promotion ability is K^+ > $Rb^+ > Na^+ > Li^+ > Cs^+$ under the same experimental conditions.

2. Experimental section

2.1. Materials

Silver oxide (Ag₂O, 99.7%), bismuth hydroxide (Bi(OH)₃, 90%), iodine (I2, 99.8%), lithium iodide (LiI, 99%), sodium iodide

(NaI, 99.5%), potassium iodide (KI, 99%), rubidium iodide (RbI, 99.9%), cesium iodide (CsI, 99.9%), tin chloride dihydrate (SnCl₂·2H₂O, 98%), n-butylamine (CH₃(CH₂)₃NH₂, 99%) and carbon disulfide (CS2, 99.9%) were purchased from Aladdin. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) was purchased from Luminescence Technology Corp. N,N-Dimethylformamide (HCON(CH₃)₂, 99.8%) and chlorobenzene (C₆H₅Cl, 99.5%) were obtained from Alfa Aesar. Dimethyl sulfoxide ((CH₃)₂SO, AR) and ethanol (CH₃CH₂OH, AR) were bought from Beijing Chemical Works. All chemicals were used directly without any further treatment.

2.2. Deposition of Ag₂BiI₅ thin films

First, 2 mL of *n*-butylamine and 1.2 mL of carbon disulfide were slowly mixed in a DMF/DMSO (2.5:1.5 volume ratio) solution with magnetic stirring at room temperature. Butylamine reacted with carbon disulfide and formed butyldithiocarbamic acid. Then, 289.675 mg (1.25 mmol) of Ag₂O, 325.025 mg (1.25 mmol) of $Bi(OH)_3$ and 158.63 mg (0.625 mmol) of I_2 were dissolved in the solution by heating at 80 °C. For the respective alkali-metal-doping precursor solution, 0.1125 mmol of LiI, NaI, KI, RbI or CsI was added to the precursor solution. The molar ratio of alkali/(Ag + Bi) was set as 3%. After cooling down, the precursor solution was centrifuged and spun at 5000 rpm for 30 s on the SnO₂ electron-transport layers. The as-prepared thin films were obtained after annealing at 230 °C for 1 min and the spin-coating/annealing process was repeated 5 times to obtain the required thickness (~ 300 nm) of the as-prepared films. To obtain Ag₂BiI₅ thin films, the as-prepared thin films and 507.62 mg (2 mmol) of iodine were added to a weighing bottle (Ø 60 \times 40 mm). Then, the bottle was placed on a 155 $^{\circ}$ C heating plate for 40 min. After this iodization procedure, the Ag₂BiI₅ thin films were formed. Note that all procedures were performed in the air.

2.3. Fabrication of Ag₂BiI₅ solar cell devices

The Ag₂BiI₅ solar cell devices with an architecture of ITO/SnO₂/ Ag₂BiI₅/PTAA/Ag were constructed. First, the patterned ITO glass substrates (20 \times 20 \times 0.5 mm) were washed successively with detergent, deionized water, acetone and isopropanol by ultrasonic treatment for 20 min, dried under a fast nitrogen flow, and then treated with UV-ozone for 15 min. Next, 415.3 mg (2 mmol) of SnCl₂·2H₂O was dissolved in a mixture of 2 mL of butyric acid and 2 mL of n-butylamine. Subsequently, the dissolved solution was diluted to a total volume of 10 mL by using ethanol, and spun on the ITO glass substrates at a speed of 3000 rpm for 30 s, followed by thermal annealing at 180 °C for 30 min on the hot plate in ambient air. The PTAA was dissolved in chlorobenzene at a concentration of 10 mg mL⁻¹ and was spun onto the obtained ITO/SnO₂/Ag₂BiI₅ substrates at 3000 rpm for 30 s. Finally, the top Ag electrodes were thermally deposited using steel shadow masks, and devices with an area of 9 mm² were achieved.

2.4. Characterization

The powder XRD patterns were measured using a Bruker D8 FOCUS X-ray diffractometer. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 electron microscope equipped with an energy dispersive X-ray (EDX) analyzer (Bruker AXS XFlash detector 4010). X-ray photoelectron spectroscopy (XPS) spectra were collected using a Thermo ESCALAB 250 X-ray photoelectron spectrometer with an Al Ka X-ray source. The binding energy was calibrated using the C 1s peak at 284.6 eV. UV-vis absorption spectra were recorded using a Shimadzu UV-3600 spectrometer. Ultraviolet photoelectron spectroscopy (UPS) was carried out using an Axis Ultra DLD, with an emission line of HeI (21.22eV). The thicknesses of the thin films were measured using a step profiler (AMBIOS, XP-100). Current density-voltage (J-V) measurements were conducted under standard AM 1.5G, 100 mW cm⁻² illumination conditions using a Keithley 2400 source meter. External quantum efficiency (EQE) spectra were acquired using a Zolix SCS100 QE system. Hall effect measurements were obtained using an ET9000 Hall effect system (Eastchanging Technologies Inc.) via the van der Pauw method.

3. Results and discussion

Herein, Ag₂O, Bi(OH)₃ and iodine were dissolved together in butyldithiocarbamic acid solution.^{57,58} It should be noted that the traditional silver bismuth iodide precursor solution can only be deposited once,^{45,47,49,50} and it is hard to fabricate highquality Ag–Bi–I thin films with adjustable thicknesses. In this work, the thicknesses of the as-prepared films were easily adjusted by repeating the spin-coating and annealing processes. Subsequently, we use the iodization process to convert S^{2-} in the as-prepared film to I⁻. By choosing 155 °C and 40 min as the iodization conditions, large-grain Ag₂BiI₅ thin films were obtained. The procedure for the deposition of Ag₂BiI₅ thin films is summarized in Fig. 1.

The XRD pattern (Fig. 2a) demonstrates that the as-prepared film is mainly $AgBiS_2$ (PDF #21-1178). It should be noted that since the ratio of Ag to Bi in the precursor solution is 2:1, there



Fig. 1 Schematic illustration of the fabrication of Ag₂Bil₅ films.

should be some amorphous or low-crystallinity Ag compounds (marked with the * sign) in the as-prepared film. However, we cannot accurately determine the structure of the Ag compounds by the XRD pattern. Moreover, the as-prepared thin film consists of nanoparticles and has no penetrating holes from the cross-sectional scanning electron microscopy (SEM) images (Fig. 2b and c). Compared with the traditional one-step approach, our deposition method can prepare high-quality thin films with adjustable thicknesses, which are beneficial to improve the morphology of absorber layers. Though the surface of the as-prepared thin film is discontinuous, the subsequent iodination process can convert small particles into large grains, thereby eliminating these small pores. The top-view and crosssectional SEM images of the as-prepared Ag-Bi-S-I thin films with alkali-metal doping are shown in Fig. S1 and S2 (ESI⁺), and all films consist of small, cluster-like nanoparticles. There are some holes present on the surface, but no penetrating holes exist. In addition, some white components appear on the surface, which may be amorphous or low-crystallinity Ag compounds. Energy dispersive spectroscopy (EDS) mapping of the as-prepared undoped Ag₂BiI₅ film is shown in Fig. S3 (ESI⁺), and it shows that the composition in the prefabricated film is uniform. Furthermore, to confirm the presence of the alkalimetal elements in the Ag₂BiI₅ films, the compositions of the asprepared Ag₂BiI₅ films doped with different alkali-metal ions were measured by surface EDS measurement. The values in Table S1 (ESI[†]) represent the median and standard deviation of each element's atomic percentage, which was calculated from five different points within each film. The EDS results confirm the lateral uniformity and homogeneous nature of the absorber layers.

After the iodization process, the diffraction peak intensities increase markedly (Fig. 3), which demonstrates the crystallinity enhancement. Hexagonal Ag2BiI5 (PDF #35-1025) with the space group $R\bar{3}m$ is formed after iodization. The strongest diffraction peak is located at 12.8°, corresponding to the (003) plane, and indicating that the Ag2BiI5 thin film is highly orientated along the c-axis of the unit cell. It should be noted that the two peaks with a similar intensity at 41.5° and 42.2° from the (110) and (108) planes confirm the existence of Ag₂BiI₅ without other Ag-Bi-I phases.⁵⁹ By introducing 3 mol% LiI, NaI, KI, RbI, or CsI into the precursor solution, the almost constant XRD peak positions demonstrate that the doping alkali metal ions do not change the crystal structure of Ag₂BiI₅, and the alkali-metal doping model is one of interstitial doping (Fig. 3a). In previously reported studies, the Li⁺ and Cs⁺ ions undergo substitutional doping. Differently, the alkali metal ions in our work undergo interstitial doping, which may be attributed to the difference in the preparation method of the absorber layers. Furthermore, the enhanced XRD peak intensities of the alkali-metal-doped samples indicate that the doping can increase the crystallinity of the Ag₂BiI₅ thin films, especially for the main peak (003), following the sequence of $Cs^+ > K^+ > Rb^+ > Na^+ > Li^+$ (Fig. 3b).

Moreover, XPS spectra are also provided to check whether the as-prepared Ag–Bi–S–I film converts to Ag_2BiI_5 completely



Fig. 2 (a) XRD pattern, and (b) top-view and (c) cross-sectional SEM images of as-prepared Ag-Bi-S-I films.



Fig. 3 (a) XRD patterns of Ag₂Bil₅ films with and without alkali metal doping and (b) enlarged peaks at approximately 12.8°.

after the iodization process. As shown in Fig. S4a (ESI[†]), both the as-prepared film and the Ag₂BiI₅ thin film exhibit two peaks of Ag $3d_{3/2}$ and $3d_{5/2}$, and the corresponding binding energies are nearly consistent. The peaks located at approximately 374.1 eV and 368.1 eV indicate the existence of Ag⁺ cations. In addition, the two peaks at 164.1 eV and 158.8 eV, as shown in Fig. S4b (ESI[†]), can be attributed to Bi $4f_{5/2}$ and Bi $4f_{7/2}$, respectively, which confirm that Bi³⁺ remains unchanged during the iodization process. It is worth noting that the intensities of the I 3d peaks

of Ag₂BiI₅ (Fig. S4c, ESI[†]) are obviously enhanced compared with the as-prepared film. The I 3d XPS peaks can be fitted into two individual peaks at 630.5 eV and 619.1 eV, corresponding to the binding energies of I 3d_{3/2} and I 3d_{5/2}, which are the characteristic peaks of I⁻. In addition, the S 2s peak at 225.4 eV (Fig. S4d, ESI[†]) completely disappears after iodization, which illustrates that S²⁻ is removed. As a result, Ag⁺, Bi³⁺, I⁻ and S²⁻ are confirmed to coexist in the as-prepared film before iodization. After the iodization process, S²⁻ is completely converted to I⁻.



Fig. 4 Top-view and cross-sectional SEM images of the (a_1 and a_2) pristine Ag_2Bi_5 thin film; (b_1 and b_2) Li^+ -doped Ag_2Bi_5 thin film; (c_1 and c_2) Na^+ -doped Ag_2Bi_5 thin film; (d_1 and d_2) K^+ -doped Ag_2Bi_5 thin film; (d_1 and $d_$

The absorber morphology is of vital importance to the device performance of Ag_2BiI_5 solar cells. In Fig. 4, the obtained films after iodization are composed of large grains with a size of nearly 1 µm, and the average thickness of the Ag_2BiI_5 thin films is nearly 300 nm. The pristine Ag_2BiI_5 and the Li^+ , Na^+ , K^+ , Rb^+ -doped Ag_2BiI_5 thin films present dense morphologies. Nevertheless, the Cs⁺-doped Ag_2BiI_5 thin film shows pinholes, which may be attributed to a larger grain size than for the other Ag_2BiI_5 films, which is detrimental to the device performance.

To examine the optical properties of the Ag₂BiI₅ thin films, the UV-vis absorption spectra and Tauc plots of alkali-metaldoped and pristine Ag₂BiI₅ thin films are shown in Fig. 5. All thin films show absorption edges at the wavelength around 700 nm (Fig. 5a). Analysis of the Tauc plots (Fig. 5b) indicates the direct band gap characteristic of Ag₂BiI₅. From a linear fit to the Tauc plots, the band gap values are evaluated to be 1.78–1.81 eV, close to those in previously reported studies.^{47,48} In the previous studies reported in the literature, similar doping concentrations can significantly affect the band gap values, so the alkali metal should undergo interstitial doping in this work. To further examine the position of the energy level, ultraviolet photoelectron spectroscopy (UPS) spectra of the pristine Ag₂BiI₅ thin film were obtained, as shown in Fig. S5 (ESI⁺). As can be observed from the cut-off region, the cutoff energy (E_{cutoff}) is 15.9 eV. Therefore, the Fermi energy (E_F) is estimated to be 5.32 eV from the equation $E_{\rm F}$ = 21.22 eV (He I) – $E_{\rm cutoff}$. Combined with the onset linear extrapolation, the $E_{\rm onset}$ value is 0.85 eV, which is the value of $(E_{VBM}-E_F)$, where the $E_{\rm VBM}$ represents the valence band maximum energy. Therefore, the E_{VBM} is regarded as being 6.17 eV. With the band gap of the pristine Ag₂BiI₅ film of 1.81 eV, the conduction band minimum energy (E_{CBM}) is calculated to be 4.36 eV.

In addition, we examine the electrical properties of these Ag_2BiI_5 thin films to investigate the influence of alkali-metal doping. Hall effect measurements indicate that after doping with alkali metal ions, the concentration of free carriers is increased, and thus a higher conductivity is achieved. The higher carrier-density levels can be attributed to the better crystallinity. As can be observed in Table 1, K⁺-doping is the most effective strategy to enhance the carrier concentration. The carrier concentration value of K⁺-doped Ag_2BiI_5 is

Table 1 $\,$ Hall effect measurements of ${\rm Ag}_2{\rm BiI}_5$ thin films with and without alkali-metal doping

| Doping ion | Carrier concen- tration $(10^{14} \text{ cm}^{-3})$ | Electrical resis- tivity $(10^3 \Omega \cdot cm)$ | Hall mobility $cm^2 (V \cdot s)^{-1}$ |
|---------------|--|--|---------------------------------------|
| w/o | 1.33 | 7.87 | 4.87 |
| Li^+ | 2.02 | 7.71 | 3.93 |
| Na^+ | 4.36 | 5.70 | 2.61 |
| K^+ | 6.51 | 3.74 | 1.71 |
| Rb^+ | 4.39 | 5.62 | 2.51 |
| Cs^+ | 5.48 | 4.37 | 3.80 |

 $6.51 \times 10^{14} \text{ cm}^{-3}$, which is 4.9 times that of pristine Ag₂BiI₅ thin films. At the same time, the electrical resistivity of the ${
m K}^+$ -doped Ag₂BiI₅ thin film shows the lowest value of 3.74 imes $10^3 \Omega \cdot cm$, indicating the best conductivity. However, the high carrier concentration increases the carrier scattering and decreases the carrier mobility. Therefore, the Hall mobility of the K⁺-doped Ag₂BiI₅ thin film is only 1.71 cm² (V·s)⁻¹, lower than that of the Li⁺-, Na⁺-, Rb⁺-, Cs⁺-doped and pristine Ag₂BiI₅ films. Therefore, we speculate that doping K⁺ in the precursor solution is the most conducive approach to improve the performance of the Ag₂BiI₅ solar cell. In addition, Xin et al. have demonstrated that lithium doping in CZTSSe can change the polarity of the electric field at the grain boundary (GB) such that minority carrier electrons are repelled from the GB.60 Therefore, we speculate that alkali-metal doping can play a similar role for Ag₂BiI₅ films.

Considering the locations of $E_{\rm VBM}$ and $E_{\rm CBM}$ of the Ag₂BiI₅ absorber layer, we construct Ag₂BiI₅ solar cells with an n-i-p planar structure using SnO₂ and PTAA as the electrontransport and hole-transport layers, respectively (Fig. 6a). It should be noted that all procedures are conducted in air. The energy level alignment of the pristine Ag₂BiI₅ solar cell is illustrated in Fig. 6b. The Ag₂BiI₅ absorber is deposited on the 30-nm-thick SnO₂ layer. Then, PTAA and silver are sequentially deposited by spin-coating and thermal evaporation, respectively. The devices are tested under standard AM 1.5G illumination. The current density-voltage (J-V) curves of the pristine and different alkali-metal-doped Ag₂BiI₅ solar cells are presented in Fig. 6c. The detailed photovoltaic parameters are summarized in Table S2 (ESI†). The PCEs of



Fig. 5 UV-vis absorption spectra (a) and Tauc plots (b) of Ag_2Bil_5 films with and without alkali-metal doping.



Fig. 6 Schematic diagram (a) and the energy level alignment (b) of the pristine Ag_2BiI_5 solar cell; J-V curves (c) and EQE spectra (d) of the Ag_2BiI_5 solar cells with and without alkali-metal doping.

the devices are increased to different extents by doping with Li⁺, Na⁺, K⁺, and Rb⁺, respectively. Due to the enhancement of crystallinity, all alkali metal ions, including Cs^+ , increase the J_{SC} value of the devices. The increased integrated J_{SC} in the external quantum efficiency (EQE) spectra (Fig. 6d) matches well with the enhanced J_{SC} results in the J-V curves. However, doping with Cs⁺ cannot improve the device performance due to the poor morphology in the SEM images. Furthermore, since the band gaps are nearly unchanged by doping with alkali metal ions, the V_{OC} remains practically unchanged for the Li⁺-, Na⁺-, K⁺- and Rb⁺-doped devices. The best performance is achieved by the introduction of K^+ , which is consistent with the previous evaluation of electrical properties. The obtained PCE is 0.75% with a V_{OC} of 0.68 V, a J_{SC} of 1.95 mA/cm², and an FF of 56.20%. Moreover, Fig. S6 (ESI⁺) shows the statistical efficiency distribution of 30 devices with the Ag_2BiI_5 absorber doped with K^+ , which indicates a good reproducibility of efficiency. Besides, there are some pinholes on the surface of the Cs⁺-doped Ag₂BiI₅ film, and this may damage the device performance. Therefore, the doping concentrations of 1% and 2% for Cs⁺-doped Ag₂BiI₅ films are used to investigate the effect of doping concentration on the film properties (Fig. S7, S8 and Table S3, ESI[†]). As shown in Fig. S7 (ESI[†]), the 1% Cs⁺-doped Ag₂BiI₅ film shows a dense and continuous morphology. In addition, some pinholes are still presented on the surface of the 2% Cs⁺-doped Ag₂BiI₅ film. Furthermore, the *J–V* curves and PV parameters of the 1% and 2% Cs⁺-doped Ag₂BiI₅ solar cells are shown in Fig. S8 (ESI[†]) and Table S3 (ESI[†]), and the 1% Cs⁺-doped Ag_2BiI_5 solar cell achieves an improved device performance (PCE = 0.49%).

4. Conclusion

In summary, an effective alkali-metal (Li⁺, Na⁺, K⁺, Rb⁺, or Cs⁺) doping strategy is applied to improve the photovoltaic performance of Ag₂BiI₅ solar cells. The introduction of alkali metal ions improves the film crystallinity and carrier concentration, which leads to an increase of the J_{SC} of the corresponding solar cells. The band gaps remain practically unchanged because the alkali-metal-doping model is one of interstitial doping. Large-grain and high-quality Ag2BiI5 thin films are obtained using our new deposition approach. It should be noted that different alkali metal ions can improve the crystallinity and increase the carrier concentration to various degrees. For instance, the Cs⁺-doped Ag₂BiI₅ thin film shows pinholes in the top-view SEM images, which may be attributed to the larger grain size compared with the other alkali-metal-doped films. In addition, the carrier concentration value of K⁺-doped Ag₂BiI₅ is higher than that of the other alkali-metal-doped films, which indicates the most conducive tendency of K⁺ to improve the device performance. Subsequently, devices with the structure of ITO/SnO₂/Ag₂BiI₅/PTAA/Ag were fabricated. The highest PCE of 0.75% is achieved after introducing K⁺. The order of the power conversion efficiency promotion ability is $K^+ > Rb^+ > Na^+ > Li^+ > Cs^+$ under the same experimental conditions. Based on a systematic understanding of the effects of doping with different alkali metals, our work provides a feasible avenue to improve the photovoltaic performance of Ag₂BiI₅ solar cells.

Author contributions

Yuxiang Wang contributed to the investigation, data curation, formal analysis, visualization, and writing – original draft. Yue Liu contributed to the investigation. Xinan Shi contributed to the investigation and resources. Lijian Huang contributed to the investigation. Gang Wang contributed to the conceptualization, project administration, and writing – review and editing. Daocheng Pan contributed to the conceptualization, funding acquisition, resources, supervision, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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