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# Ag management of rudorffites solar cells utilizing aliphatic ammonium

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#### Abstract

As environmentally friendly compounds, lead-free perovskites have gained widespread application in the fabrication of solar cells in recent years. Among these, rudorffites such as AgBiI<sub>4</sub> are considered as promising candidates owing to their favorable band structure and exceptional stability. However, the formation of Ag vacancies during the synthetic process poses a significant challenge, severely hindering carrier transport properties. To address this issue, we propose an Ag management strategy utilizing aliphatic ammonium, which serves multiple purposes: it enhances the solubility of AgI in the precursor solution, mitigates phase separation caused by stoichiometric mismatches during AgBiI<sub>4</sub> film formation, and effectively passivates Ag defects. The butylamine hydroiodide modified AgBiI<sub>4</sub> solar cells achieved a champion power conversion efficiency of 1.97%, representing a 26% enhancement over the control device.

Supplementary material for this article is available online

Keywords: perovskites, lead-free, AgBil<sub>4</sub>, Ag management, aliphatic ammonium

#### 1. Introduction

Hybrid lead-based perovskite solar cells (PSCs) have achieved a huge breakthrough, with a power conversion efficiency (PCE) of 26.95% in the single junction device, 34.6% in the perovskite/Si hybrid tandem [1]. However, lead toxicity not only poses significant risks to human health, wildlife, and ecological systems [2], but also creates substantial barriers to commercializing this innovative technology [3, 4]. To meet the environmental sustainability, various categories of lead-free perovskites have been developed for photovoltaic application [5–10]. For instance, tin halide perovskite

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with an additive engineering strategy has reached a maximum efficiency of 15.7% [11].  $Cu(In_{1-x}Ga_x)Se_2$  thin-film solar cells achieve optimal performance through precise tuning of the Ga/(Ga + In) ratio [12]. By further incorporating silver ([Ag]/[Ag]+[Cu] = 0.19) into the absorber layer, the device has reached a record efficiency of 23.64% [13].

Bismuth halide perovskites have garnered significant attention for photovoltaic applications [14], particularly in compounds such as  $A_3B_2X_9$  (A<sup>+</sup> = Cs<sup>+</sup>/MA<sup>+</sup>; B<sup>3+</sup> = Bi<sup>3+</sup>; X<sup>-</sup> = I<sup>-</sup>), which exhibit 0D or 2D structures [15], and  $A_2B^+B^{3+}X_6$  (A<sup>+</sup> = K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>; B<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ag<sup>+</sup>; B<sup>3+</sup> = Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Sb<sup>3+</sup>, Bi<sup>3+</sup>; X<sup>-</sup> = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) [16, 17]. Rudorffites, based on  $[AX_6]^{5-}$  and  $[BX_6]^{3-}$  octahedra edge shared bismuth-based perovskites, have drawn widespread attention due to their distinctive structural composition. The chemical formula for rudorffites is  $A_aB_bX_{a+3b}$  (A<sup>+</sup> = Cu<sup>+</sup> /Ag<sup>+</sup>, B<sup>3+</sup> = Bi<sup>3+</sup>, X<sup>-</sup> = I<sup>-</sup>) [18]. The AgBi<sub>2</sub>I<sub>7</sub> devices were successfully fabricated for the first time by Sargent's group, achieving a PCE of 1.22% [19]. By incorporating elements such as cesium,

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bromine or sulfur into the precursor solution, the photovoltaic devices with tunable bandgap were achieved [20–22]. Notably, the device doped with sulfur achieved the highest efficiency of 5.6%. Despite extensive modifications, the PCE of rudorffitesbased devices remains constrained by suboptimal thin-film morphology and inherent defects [23].

Numerous strategies have been developed to improve film quality, such as incorporating methylamine acetate into the precursor solution to induce the formation of an intermediate phase, effectively modulating crystallization kinetics and optimizing film morphology [24]. Additionally, interface engineering techniques have been employed, utilizing tailored ligands to passivate defects at the perovskite/hole transport layer interface, thereby enhancing charge carrier transport and overall device performance [25]. In rudorffites, the presence of vacancies facilitates the formation of films with distinct stoichiometric compositions, including AgBiI<sub>4</sub>, AgBi<sub>2</sub>I<sub>7</sub>, Ag<sub>3</sub>BiI<sub>6</sub>, and Ag<sub>2</sub>BiI<sub>5</sub> [26]. Our investigation focuses on the AgBiI<sub>4</sub> system, where deviations from ideal stoichiometric ratios induce alterations in film properties, thereby critically determining their structural integrity. However, the available research study overlooked the fact that the poor solubility of AgI itself influences the formation of Ag vacancies. Previous approaches have merely postponed the deterioration of preexisting silver defects via post-processing methods, rather than suppressing their initial generation.

In this study, we systematically investigated the preparation of AgBiI<sub>4</sub> thin films and their optoelectronic properties. By incorporating aliphatic ammonium, we achieved Ag management (AM) in perovskite films. Specifically, AM refers to the addition of appropriate aliphatic ammonium to: (1) enhance the solubility of AgI in the precursor solution, (2) mitigate Ag vacancies caused by stoichiometric mismatches, and (3) passivate Ag defects through molecular coordination. Therefore, AgBiI<sub>4</sub> modified by aliphatic ammonium additives (e.g. butylamine hydroiodide (BAI)) exhibited oriented growth of crystals, reduced non-radiative recombination and mitigated film defects. The solar cells based on BAI treated AgBiI<sub>4</sub> achieve a champion PCE of 1.97%, which was enhanced by 26% compared with that of the control device.

#### 2. Methods

**Materials.** SnO<sub>2</sub> colloid precursor (tin (IV) oxide, 15% in  $H_2O$  colloidal dispersion), N, N-dimethylformamide (DMF, 99.99%) anhydrous dimethyl sulfoxide (DMSO,99.8%), were purchased from Alfa Aesar. AgI (99.99%), BiI<sub>3</sub> (99.99%) were purchased from Aladdin. Isopropanol (IPA) was purchased from Concord Technology. BAI and poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) were purchased from Xi'an Polymer Light Technology Corp. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS, Clevios PVP AI 4083) was purchased

from Heraeus. Deuterated dimethyl sulfoxide (DMSO- $d_6$ , 99.8%) was purchased from J&K. All these commercially available materials were used as received without any further purification.

Perovskite Device Fabrication. 140.8 mg AgI, 353.8 mg BiI<sub>3</sub> and 0.01 mmol ml<sup>-1</sup> BAI were dissolved in 0.75 ml DMSO and 0.25 ml DMF as precursor solution and stirring at 65 °C for 2 h, and then filtered by a 0.22 mm poresize filter. The indium tin oxide (ITO) glass was sequentially cleaned in deionized water, acetone, and ethanol under ultrasonic each for 30 min, and then treated with oxygen plasma for 15 min. The SnO<sub>2</sub> electron transport layer was prepared by spin-coating dispersed SnO<sub>2</sub> colloid in deionized water (volume ratio of 1:6) at a speed of 3000 rpm for 30 s, then annealed at 150 °C for 30 min. AgBiI<sub>4</sub> precursor solution was spin-coated on the substrate at 500 rpm for 3 s and then 5000 rpm for 30 s. At the 10 s before the end of the spincoating process, 300 uL IPA was dropped on the substrate center. Then the sample was annealed at 110 °C for 15 min and then at 150 °C for 15 min on a hot plate. 10 mg ml<sup>-1</sup> PTAA was spin-coated onto the AgBiI<sub>4</sub> film with 3000 rpm for 30 s after the sample cooled down. Finally, Ag electrode was deposited by thermal evaporation through a shadow mask to pattern the electrode. The active area of solar cell is  $0.09 \text{ cm}^2$ .

**Space-charge-limited current (SCLC) Device Fabrication** 100uL PEDOT:PSS was spin-coated on the cleaned ITO substrate center at a speed of 4000 rpm for 30 s, then annealed at 150 °C for 30 min. The AgBiI<sub>4</sub> film preparation, HTL perparation, and electrode deposition were the same as above.

Characterization. The XRD patterns were measured using xray diffraction (XRD) system (PANalytical Inc.) with monochromatic Cu K  $\alpha$  irradiation ( $\lambda = 1.5418$  Å). The scanning electron microscope (SEM) images were recorded using a high-resolution scanning electron microscopy (Hitachi S-4800). The absorption spectrum was recorded with a UVvisible spectrophotometer (UV3600Plus). Photoluminescence (PL) and time-resolved PL (TRPL) spectra were measured by Lifetime and Steady-state Spectrometer (FLS1000 Edinburgh Instruments Ltd.). The Fourier transform infrared spectra (FTIR) results were collected by a FTIR spectrometer from Nicolet iS50. The XPS was measured by a Thermo Scientific ESCALAB 250Xi. The ultraviolet photoelectron spectroscopy (UPS) measurement was carried out by a Thermo Fisher Nexsa. Dynamic light scattering (DLS) analysis was conducted using a Malvern Zetasizer Nano ZS to determine particle size distribution in the precursor solutions. Photovoltaic performances were measured by using a Keithley 2611 source meter at AM 1.5 G illumination (100 mw cm<sup>-2</sup>) under a Newport Thermal Oriel 69911300 W solar simulator. All the measurements of the solar cells were performed under ambient atmosphere at room temperature without encapsulation.



**Figure 1.** (a) Schematic illustration of the fabrication processes of the AgBiI<sub>4</sub> perovskite film. (b) PCE distribution of 20 individual PSCs fabricated separately under different post-treatment processes. (c) J-V curves of the champion PSCs. (d) IPCE spectra and integrated current density of the devices.

#### 3. Results and discussion

We fabricated n–i–p perovskite devices with the planar structure of ITO/SnO<sub>2</sub>/AgBiI<sub>4</sub>/PTAA/Ag, where the active layer AgBiI<sub>4</sub> was prepared by one-step spin-coating method assisted by antisolvent, as illustrated in figure 1(a). AM was realized by incorporating aliphatic ammonium with varying carbon chain lengths into the precursor solution, including methylamine hydroiodide (MAI, CH<sub>5</sub>NI), ethylamine hydroiodide (EAI, C<sub>2</sub>H<sub>8</sub>NI), propylamine hydroiodide (PAI, C<sub>3</sub>H<sub>10</sub>NI), BAI(C<sub>4</sub>H<sub>12</sub>NI) and amylamine hydroiodide (AAI, C<sub>5</sub>H<sub>14</sub>NI).

Firstly, we fabricated various devices incorporating different additives and the efficiency of these devices was statistically analyzed, which is depicted in figure 1(b). It was evident that short-chain additives provided only negligible enhancement to device performance. In contrast, additives with carbon counts of three or more, including PAI, BAI and AAI, exhibited substantial improvements in device efficiency, as illustrated in figure 1(c), and the average data from multiple devices is presented in table S1. The PCE of the control device is 1.56% with a short-circuit current density  $(J_{SC})$ of 4.12 mA cm<sup>-2</sup>, open-circuit voltage ( $V_{OC}$ ) of 0.694 V and a fill factor (FF) of 58.6%. In comparison, the champion device modified by BAI achieved a PCE of 1.97%, with  $J_{SC}$ of 5.07 mA cm<sup>-2</sup>,  $V_{OC}$  of 0.720 V and FF of 58.4%. To verify the  $J_{SC}$  of the devices, incident-photon-to-electron conversion efficiency (IPCE) measurement was conducted as shown in figure 1(d). Among the entire photon conversion range, devices treated with BAI exhibited higher external quantum efficiency (EQE), resulting in a higher integrated *J*sc. The integrated *J*sc for PSCs treated with PAI, BAI and AAI were 4.79, 5.06 and 4.66 mA cm<sup>-2</sup>, respectively, which matched well with the data obtained from J-V curves (with an error margin of less than 5%).

In order to investigate the impact of additives on solubility, DLS experiment was carried out with AgBiI<sub>4</sub> solutions at various concentrations [27]. When the concentration of the precursor solution without additive was reduced from 0.7 to  $0.6 \text{ mmol ml}^{-1}$ , the number of large particles in the solution slightly decreased. When the concentration was further reduced to 0.5 mmol ml<sup>-1</sup>, most of the large particles disappeared, indicating further dissolution of perovskite. Therefore, when the concentration reached 0.6 mmol  $ml^{-1}$ , the precursor remained undissolved as shown in figure 2(a). By comparing the difference of solubility between AgI and BiI<sub>3</sub>, we determined that most of the undissolved precursor was AgI. Then, the same concentration of PAI, BAI and EAI additives was added into 0.6 mmol  $ml^{-1}$  precursor solution as shown in figure 2(b). A significant reduction in the intensity of large particles was observed, indicating that the additives enhanced the solubility of the precursors and facilitated the formation of thin films with relatively precise chemical stoichiometry. Moreover, we utilized energy dispersive x-ray analysis to investigate the elemental distribution on the surface of the thin films. We calculated the Ag/Bi and relative anion/metal ratios summarized in table 1. The Ag/Bi ratio



**Figure 2.** (a) DLS of the precursor solutions with different concentrations. (b) DLS of the precursor solutions added with different aliphatic ammonium. (c)–(f) Top view SEM of the control, PAI, BAI, AAI AgBiI<sub>4</sub> films. (g)–(j) AFM images of the control, PAI, BAI, AAI AgBiI<sub>4</sub> films.

Table 1.	Atomic ratios	of the	different	AgBiL <sub>4</sub>	devices.
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Sample	Ag (%)	Bi (%)	I (%)	Ag/Bi	Relative anion/ metal ratio <sup>a</sup>
Control	19.60	14.36	66.04	1.36	1.05
PAI	17.77	15.19	67.04	1.17	1.06
BAI	17.47	15.84	66.69	1.10	1.02
AAI	17.46	15.36	67.18	1.14	1.06

<sup>a</sup> Relative anion/metal ratio refers to the ratio of I/(Ag + 3Bi).

deviated from the precursor ratio of 1.00-1.36 in the control film, while the ratio in the modified films balanced at  $\sim$ 1.10, implying the alleviation of Ag<sup>+</sup> occupation at grain surface modified by the aliphatic ammonium. Moreover, we investigated the morphological effects on AgBiI<sub>4</sub> thin films through top-view SEM and atomic force microscope (AFM), as shown in figures 2(c)-(j). The control film exhibited small and disordered grains with noticeable pores, and AgI particles could be observed in the pores, which darkened over time under electron microscopy. The AFM images also revealed a rough and uneven surface for the control film. In contrast, the films treated with PAI and AAI showed clearer grain boundaries, larger average grain size, fewer pores and unobservable AgI, resulting in a smoother film. The films treated with BAI at the same concentration exhibited more larger and ordered grains, leading to an effective optimization in surface flatness and smoothness. All the results indicated that the addition of the above aliphatic ammonium could regulate the solubility of the precursors and enhance the quality of the thin films.

To study the promotion of crystallinity, XRD measurement was carried. As shown in figure 3(a), the peak intensity of the samples treated with aliphatic ammonium was significantly enhanced, and BAI-modified sample exhibited 1.86 times higher than that of the control. By examining the full width at half maximum (FWHM) of the (111) characteristic peak around 12.7°, the BAI-treated sample employed the smallest FWHM as shown in figure 3(b), indicating a higher crystallinity and larger grains according to the Scherrer equation, as corroborated by SEM images. By calculating the peak ratio (311)/(111) and (400)/(111) of the crystal planes, the AM treatment promoted the preferential growth of AgBiI<sub>4</sub> towards (111) plane, resulting in a more uniform



**Figure 3.** (a) XRD patterns of the control, PAI, BAI and AAI AgBiI<sub>4</sub> films. (b) XRD patterns of the (111) peak of the control, PAI, BAI and AAI AgBiI<sub>4</sub> films. (c) The XRD peak ratio (311)/(111) and (400)/(111) of control, PAI, BAI and AAI AgBiI<sub>4</sub> films. (d) XRD patterns of BAI film before antisolvent process. (e) FTIR spectra of AgBiI<sub>4</sub>, BAI and BAI-AgBiI<sub>4</sub> mixed solutions. (f) Ag 3d core-level XPS spectra of control, PAI, BAI and AAI AgBiI<sub>4</sub> films.

orientation (figure 3(c)). Moreover, the mesophase of film formation was also studied as shown in figure 3(d). XRD was also conducted on the perovskite films without antisolvent. The characteristic peak appeared at less than 10°, indicating an intermediate phase during film formation. Aliphatic ammonium could bind with AgI in precursor solution, thus promoting the dissolution of AgI and balance the stoichiometric ratio. FTIR was conducted as shown in figure 3(e). The N-H signal shifted from 3220 to 3190 cm<sup>-1</sup>, while the C-H signal shifted from 2992 and 2910  $cm^{-1}$ -2984 and 2903 cm<sup>-1</sup> after binding with AgBiI<sub>4</sub>. X-ray photoelectron spectroscopy (XPS) revealed that the Ag 3d core levels shifted towards higher binding energies due to the interaction, with the degree in the order of BAI > AAI > PAI, indicating that BAI exhibited the strongest interaction with Ag<sup>+</sup> as shown in figure 3(f).

The ultraviolet-visible absorption spectra showed negligible enhancement compared to the control (figures S1, S2). Despite the same bandgap, the Urbach energy ( $E_u$ ) decreased from 0.12 to 0.10 eV according to the linear fitting of the Urbach tail region (figure S3), and the decreased  $E_u$  in the BAI film indicated the higher structural quality, as well as a lower voltage loss between  $V_{oc}$  and the bandgap [28]. To further investigate the carrier dynamics of the different films on glass substrates, we examined the PL and TRPL spectra. As shown in figure 4(a), PL intensity of the films treated with aliphatic ammonium was significantly higher than that of the control, indicating a reduction in defect density and

non-radiative recombination. The TRPL results and the fitting curves are presented in figures 4(b) and S4. The double exponential decay equation was fitted as  $I(t) = A_1 \exp(-\frac{t}{\tau_1}) +$  $A_2 \exp(-\frac{t}{\tau_2})$ , where  $\tau_1$  and  $\tau_2$  denote the decay time constants. The average lifetime can be calculated using the formula:  $\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$  [29]. The  $\tau$  values of the modified films increased, revealing an enhancement of overall crystalline quality (table S2). Figure 4(c) shows the TRPL lifetimes of different devices of glass/AgBiI<sub>4</sub>/PTAA. The modified films exhibited faster carrier extraction rates, which effectively suppressed carrier accumulation and recombination at the interface. We further fabricated photovoltaic devices with the configuration of ITO/PEDOT:PSS/AgBiI<sub>4</sub>/PTAA/Ag and measured the SCLC. The relationship between the trapfilling limit voltage  $(V_{\text{TFL}})$  and defect density is described by the formula:  $n_{\text{trap}} = 2(\varepsilon \varepsilon_0 V_{\text{TFL}}) / (qL^2)$ , where  $\varepsilon$  is the relative dielectric constant,  $\varepsilon_0$  is the vacuum permittivity, L is the thickness of the perovskite film, and q is the elementary charge [30]. Compared with the  $V_{\text{TFL}}$  (1.30 V) of the control device, the  $V_{\text{TFL}}$  of the modified devices was decreased (figure 4(d)), which indicated the lower defect density. UPS revealed a similar VBM between the control and other modified AgBiI<sub>4</sub> films (figures 4(e), S5(a)–(h). Both the control and PAI, BAI and AAI devices showed the similar interfacial band structure. Finally, the stability of the devices was studied at the temperature of 20 °C-35 °C and a relative humidity of 20%-40%. The BAI-modified device maintained an initial PCE of over 90% after 480 h, while the



**Figure 4.** (a)–(b) PL spectra (a) and TRPL spectra (b) of the control, PAI, BAI and AAI films. (c)TRPL spectra of films based on the Glass/AgBiI<sub>4</sub>/PTAA structure. (d) SCLC of the control, PAI, BAI and AAI devices. (e) Energy level diagram. (f) Stability of the control and BAI modified devices.

PCE of the control device decreased to 87%. The stability of PAI and AAI-modified devices also showed a slight improvement (figure 4(f)).

#### 4. Conclusions

In this work, we conducted a systematic exploration of the fabrication and optoelectronic characteristics of AgBiI<sub>4</sub>. Through the incorporation of aliphatic ammonium, we implemented an effective AM strategy in the perovskite films. This AM approach involves the introduction of suitable aliphatic ammonium compounds to achieve three key objectives: (1) improve the solubility of AgI in the precursor solution, (2) address Ag vacancies resulting from stoichiometric imbalances, and (3) passivate Ag defects via coordination. As a result, AgBiI<sub>4</sub> films modified with aliphatic ammonium additives, such as BAI, demonstrated enhanced crystallographic orientation, suppressed non-radiative recombination, and reduced film defects. Solar cells fabricated with BAI-treated AgBiI<sub>4</sub> achieved a champion PCE of 1.97%, representing a 26% improvement over the control device.

#### 5. Future perspectives

Through the aforementioned experiments and associated characterizations, we observed that aliphatic ammonium with varying chain lengths exhibited distinct modulation effects on AgBiI<sub>4</sub>. Among these, BAI demonstrated the most pronounced enhancement in both film quality and photovoltaic performance. We ascribe this phenomenon to BAI's remarkable enhancement of AgI solubility. However, larger molecules of aliphatic ammonium aggregated within the precursor solution, thereby reducing its homogeneity. The intermolecular van der Waals forces between aliphatic ammonium could tightly bind adjacent grains, promoting favorable crystal orientation in perovskites. On the other hand, longerchain salts possess larger molecular volumes, which introduced steric hindrance during the crystallization process of perovskite films, impeding orderly crystal growth. This could result in increased grain boundary defects and discontinuities within the film, ultimately degrading the crystal quality. Therefore, an optimal chain length for aliphatic ammonium is crucial to achieving the most beneficial effects on film properties. Although the introduction of AM has effectively mitigated the stoichiometric ratio mismatch in AgBiI<sub>4</sub> systems while enhancing film quality, there remains substantial potential for further improvements in device efficiency. In the future, we aim to pursue the following strategies to further enhance device performance: (1) Utilize the synergistic effects of multiple additives to optimize defect passivation and improve film quality; (2) Incorporate an interfacial modification layer between the active layer and the PTAA to minimize interfacial recombination and achieve optimal energy-level alignment; (3) Adjust the bandgap of AgBiI<sub>4</sub> via precise elemental doping to approach the optimal bandgap for enhancing light absorption and optimizing photovoltaic properties.

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#### Author contributions

Xinyu Guo: Fabricated the samples and solar cells, manipulated the characteristics and wrote the first draft of the manuscript. Wenjin Yu: Supported in some characteristics, reviewed and revised the manuscript. Xiangdong Li, Hantao Wang, Yu Zou, Qinyun Liu and Yunan Gao:Supported in some characteristics. Lixin Xiao and Zhijian Chen: Reviewed and revised the manuscript. Bo Qu: Conceived of the idea, supervised the project, provided guidance for the work, and revised the manuscript.

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