Efficient solar cells based on stable, non-toxic tin(IV) perovskite materials

- Final report -

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Summary
In this project lead-free alternative materials to the promising and efficient lead halide perovskite have been explored for solar cell application, order to develop more environmentally friendly and stable photovoltaic devices compared. Tin (Sn(IV))- based double perovskite materials such as Cs_2SnI_6 were successfully synthesized, but thin films of this material were of rather poor quality and resulted in solar cells with only 0.28% efficiency.
Other lead-free double perovskites, such as $Cs_2AgBiBr_6$, were also investigated. We were able to produce good quality films and solar cells with up to 1.37% efficiency were obtained. To further improve the quality of the $Cs_2AgBiBr_6$ film, we employed the methylamine gas "healing method" that was applied to treat lead-free halide double perovskite for the first time. Interestingly, we found that methylamine gas can introduce reversible optical bleaching in lead-free perovskites, enabling them to more applications beyond photovoltaic, such as smart windows.

1. Goals and Purpose

The goal of this project is to develop environmentally friendly and stable photovoltaic devices based on lead-free perovskites, initially focusing on the tin (Sn)- based double perovskite Cs_2SnI_6. Later, most focus was given to another lead-free double perovskite, $Cs_2AgBiBr_6$.

2. Experimental results and discussion

2.1 Synthesis of crystalline Cs_2SnI_6 powders

We successfully synthesized high-quality Cs_2SnI_6 powder by using two different recipes:
Recipe 1: 0.3117g CsI (1.2 mmol) and 0.37579 g SnI_4 (0.60 mmol) were mixed in 2 ml of anhydrous ethanol and stirred for above 12 hours, followed by centrifuging the resulting precipitate and drying it at 50 °C. The black Cs_2SnI_6 powder was finally obtained.
Recipe 2: 0.08145g Cs_2Co_3 (0.5 mmol) and 0.156g SnI_4 (0.5 mmol) were mixed in 1.5 mL of HI acid and 7.5 mL of anhydrous ethanol and stirred at 60 degrees for above 12h. Subsequently, the precipitate was centrifuged and dried at 50 °C to yield the Cs_2SnI_6 powder.
Both approaches yield high-purity Cs_2SnI_6 powder, as proven by the X-ray diffraction data (Figure 1). Cs_2SnI_6 shows good environmental stability, showing no visible decomposition after storing in air for 120 days.

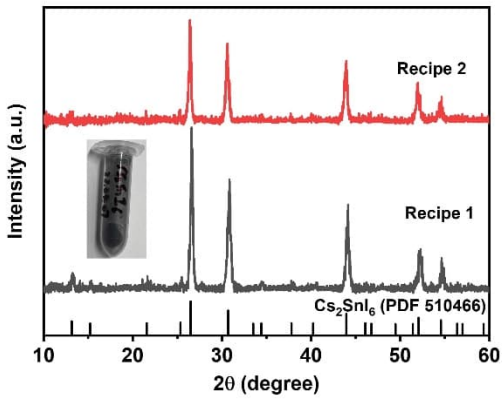

Figure 1. XRD patterns of Cs_2SnI_6 powder. The inset shows the photograph of Cs_2SnI_6 powder. The diffraction peaks are corresponding to pure Cs_2SnI_6.

2.2 Preparation of precursor solutions for solution processing

We dissolved the synthesized Cs_2SnI_6 powder in the solvent mixture (N, N-dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) is 10/1 by volume) to prepare a 0.3 M precursor solutions. For comparison, we also directly dissolved a stoichiometric amount of CsI and SnI_4 in the same solvent mixture to prepare a 0.3 M precursor solution.

2.3 Fabrication of Cs_2SnI_6 thin films

The crystallization behavior and film formation of Cs_2SnI_6 is quite different from that of lead-based halide perovskites. We have tried various methods to fabricate Cs_2SnI_6 thin films.

2.3.1 One-step spin coating

We first tried the commonly used one-step spin coating method to fabricate Cs_2SnI_6 films, but could not get the require crystal structure. Specifically, a yellow color film was achieved after one-step spin coating, which is mainly the color of SnI_4 instead of Cs_2SnI_6. This means that CsI and SnI_4 did not form the Cs_2SnI_6 directly after spin coating, which would be expected. We further annealed this film to promote the reaction and crystallization. Unfortunately, even at relatively low temperatures (80 °C or 100 °C) for a short time (several minutes), the yellow film will totally decompose into colorless, as shown in Figure 2. This could be explained by the extremely poor thermal stability of SnI_4, which can evaporate.

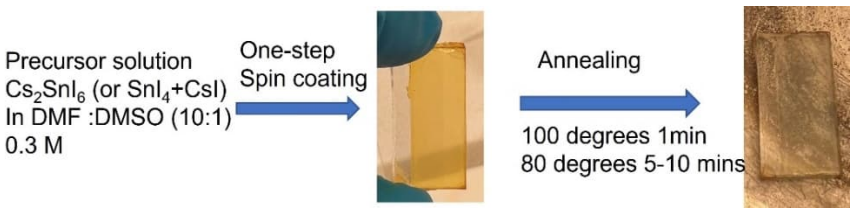

Figure 2. Optical images of the one-step spin coating process

2.3.2 Spray coating

The spray coating method was also tried in this project. The precursor solution was sprayed on a pre-heated substrate at 130 °C. Similar to one-step spin coating, the precursor material SnI_4 easily leaves the substrate during annealing.

2.3.3 Two-step dipping

Considering the difficulty of crystallization and the super unstable of SnI_4, the two-step method is worth trying. We dissolved CsI in methanol solvent (30 mg/mL) and SnI_4 in ethanol solution (150 mg/mL). The substrate was first dipped in SnI_4 (or CsI) solution and then dipped into CsI (or SnI_4) solution. Repeating this process several times to expect to achieve the Cs_2SnI_6 film. Although some black Cs_2SnI_6 (powders) can form on the substrate after dipping, the very poor and rough morphology is still not suitable for solar cell devices.

2.3.4 Two-step spin coating

Using a two-step method could form the Cs_2SnI_6 compounds, the main challenge is to get a uniform film. We then employ the two-step spin-coating method to fabricate Cs_2SnI_6 thin films since the spin-coating process usually results in a relatively uniform morphology. As shown in Figure 3, SnI_4 film was first deposed by the one-step spin coating method. In the second step, 50-100 μL CsI solution was dropped on the SnI_4 film, and the black Cs_2SnI_6 appeared immediately. To make the film more uniform, we choose to drop the CsI solvent on SnI_4 during the spin coating process. The resulting film was further annealed at 130 °C for 10 mins. We also performed the UV-Vis measurement to investigate the optical properties and then calculated its direct bandgap of around 1.63 eV.

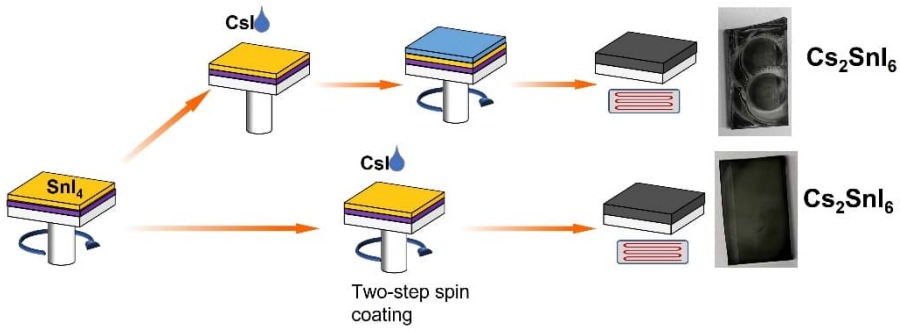

Figure 3. Schematic illustration of the two-step coating process for Cs_2SnI_6 thin film.

2.4 Fabrication of Cs_2SnI_6-based solar cells

Based on the above Cs_2SnI_6 film, we further tried fabricating the solar cell device with the structure of FTO/c-TiO_2/m-TiO_2/Cs_2SnI_6/PTB_7/Au. The device exhibited power conversion efficiency (PCE) of 0.28% with an open-circuit voltage (Voc) of 0.38 V, a short-circuit current density (Jsc) of 1.15 mA cm^{-2}, and a fill factor (FF) of 64% (Figure 4). This very poor PCE is mainly due to the poor quality of the Cs_2SnI_6 film, which still needs serious improvement. We also tried to employ methylamine gas healing method to modify the film morphology, but it will change the composition of Cs_2SnI_6. In other words, the key challenge for Cs_2SnI_6-based solar cells is fabricating a high-quality and pure-phase Cs_2SnI_6 film.

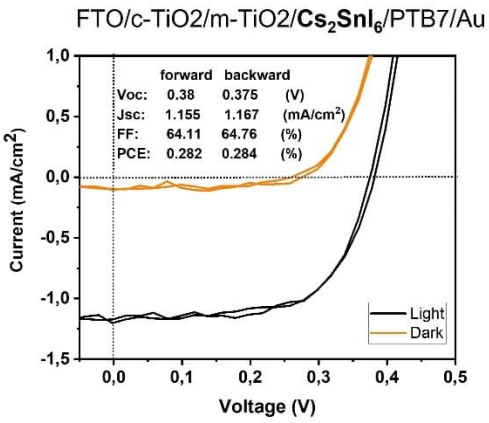

Figure 4. *J*–V curve of the Cs_2SnI_6 devices with mesoporous TiO_2 structure and the polymer PTB7 as hole conductor.

2.5 Double perovskite $Cs_2AgBiBr_6$ solar cells

Since the Cs_2SnI_6 is still challenging to fabricate a high-quality thin film, trying other double perovskites (eg. $Cs_2AgBiBr_6$) is another choice to further explore their potential in solar cells. Compared with Cs_2SnI_6, $Cs_2AgBiBr_6$ can be understood by using one monovalent cation B^+ (Ag^+) and one trivalent B^{3+} (Bi^{3+}) to replace one Sn^{4+}. $Cs_2AgBiBr_6$ easily forms uniform and high-quality films by the one-step coating method, which may be more suitable for solar cells. To prepare $Cs_2AgBiBr_6$ thin films, a 0.5 M precursor solution was made by dissolving CsBr (212.8 mg), AgBr (93.88 mg), and $BiBr_3$ (224.35 mg) powder in 1 mL of dimethyl sulfoxide (DMSO), which was then heated at 100 °C and stirred for 12 hours until a clear yellow solution was obtained. Afterward, 45 µL of the precursor solution was spin-coated onto a glass substrate at 3000 rpm for 60 s with an N_2 flown into the spin coater chamber in an ambient environment. The substrates were annealed at 280°C in air for 5 min to produce high-quality $Cs_2AgBiBr_6$ films. Based on this film, the solar cell device with the traditional mesoporous structure of FTO/c-TiO_2/m-TiO_2/ $Cs_2AgBiBr_6$/Spiro-OMeTAD/Au was fabricated. The champion device exhibits a power conversion efficiency (PCE) of 1.37 % with a Voc of 0.99 V, a *J*sc of 1.55 mA cm^{-2}, and a FF of 74%.

2.6 Optimization of $Cs_2AgBiBr_6$ films – methylamine vapor treatment

To further improve the quality of the $Cs_2AgBiBr_6$ film, we employed the methylamine gas healing method to treat lead-free halide double perovskite for the first time. Interestingly, the treated $Cs_2AgBiBr_6$ film on a glass substrate shows a significantly enhanced crystallinity with the dominant (400) diffraction peak 26 times stronger than in the raw $Cs_2AgBiBr_6$ film (Figure 4a,b). Moreover, the diffraction intensity ratio between the (400) and (220) diffraction peaks (I(400)/I(220)) is dramatically increased from 1.47 to 91.64, indicating the orientation of $Cs_2AgBiBr_6$ film becomes almost single-oriented with diffractions of the {200} peak series (Figure 4c). The combination of enhanced crystallinity and single orientation make this treated $Cs_2AgBiBr_6$ film highly attractive for high-performance photoelectronic applications. However, we noticed that this is a highly substrate-dependent behavior, as these benefits only occur on a glass substrate, which hinders its further application in solar cells. We think the main reason is the crystallinity of the substrate, as the glass is an amorphous substrate, but FTO, C-TiO_2, and

m-TiO_2 are all crystalline. So, this methylamine gas healing method could be useful for double perovskite solar cells with n-i-p structure because the hole transporting material is usually amorphous.

Interestingly, we found that methylamine gas can introduce reversible optical bleaching in lead-free perovskites, enabling them to more applications beyond photovoltaic, such as smart windows (Figure 4d). By exposure to a methylamine gas atmosphere, the color of $Cs_2AgBiBr_6$ films change from yellow to transparent. The reason is found to be the interactions between methylamine gas and Bi^{3+}, which results in forming of an amorphous liquefied transparent intermediate phase. This process is fully reversible upon removing the methylamine gas by annealing. In addition, we found that the methylamine gas-induced reversible optical bleaching also happened in other lead-free materials, such as $Cs_3Bi_2I_9$ and $Cs_3Sb_2I_9$, suggesting its universality.

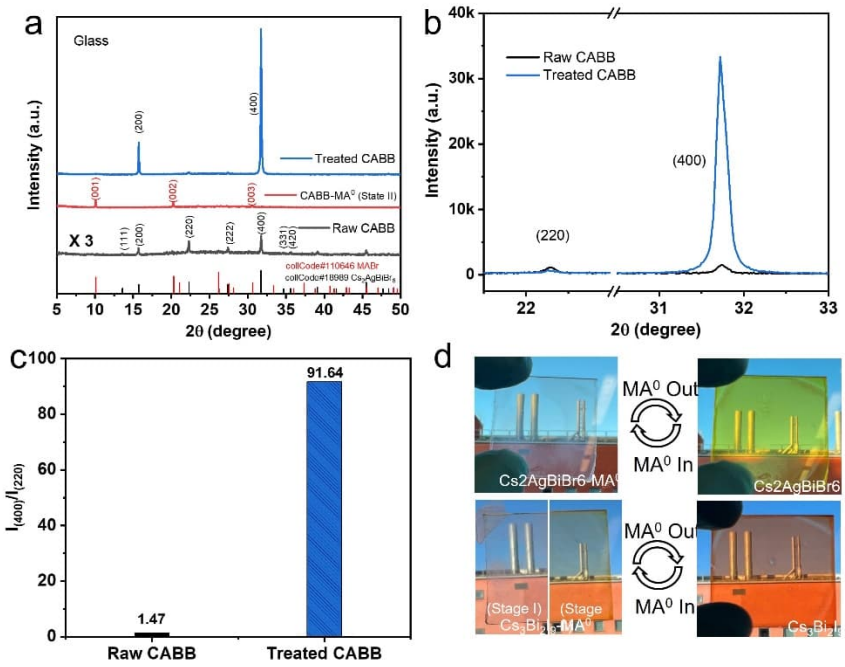

Figure 5. (a) XRD patterns of $Cs_2AgBiBr_6$ film at different stages during methylamine gas treatment. The diffraction intensity of raw $Cs_2AgBiBr_6$ film is multiplied three times for better comparison. (b) The enlarged view of the (220) and (400) diffraction peaks in the XRD patterns of raw and methylamine gas-treated $Cs_2AgBiBr_6$ films. (c) The diffraction intensity ratio between the (400) and (220) peaks in raw and methylamine gas-treated CABB films. (d) Photographs of smart windows based on $Cs_2AgBiBr_6$ film and $Cs_3Bi_2I_9$ film in their transparent and colored states. Objects are visible through the windows in both states.

3. Conclusion

We successfully synthesized pure Cs_2SnI_6 powders, which shows good environmental stability. Due to the extremely poor thermal stability of SnI_4, it is challenging to fabricate pure phase Cs_2SnI_6 thin films through the one-step spin coating and spray methods. The two-step dipping or spin coating method can form black Cs_2SnI_6 thin films, but the quality is still far from satisfactory. The resulting device shows a poor PCE of 0.28%. Currently, the key challenge is

to depose high-quality and pure phase Cs_2SnI_6 thin films, which still needs more effort. The sequential vapor deposition method could be promising for Cs_2SnI_6 and is worth investigating more.

Another lead-double perovskite $Cs_2AgBiBr_6$ was also investigated in this project, which has a similar structure as Cs_2SnI_6. We observe a reversible optical bleaching phenomenon in $Cs_2AgBiBr_6$ thin films through the absorption and release of methylamine gas molecules, resulting in a significant color change from yellow to transparent for $Cs_2AgBiBr_6$. The experimental characterizations indicate that the methylamine molecules induce a full collapse of the initial perovskite structure to a liquefied transparent intermediate phase by the interaction between the methylamine molecules with Bi^{3+}, leading to optical bleaching. This intermediate phase can recrystallize back to the perovskite phase with improved orientation and morphology after removing methylamine molecules from the film. This interesting phenomenon makes lead-free materials attractive for smart windows and other on-demand applications. Moreover, methylamine-treated $Cs_2AgBiBr_6$ film exhibits improved orientation, enhanced crystallinity, and improved uniform morphology, which is highly desirable for some optoelectronic applications.

4. Publications

(1). F. Ji, G. Boschloo, F. Wang, F. Gao, Challenges and Progress in Lead-Free Halide Double Perovskite Solar Cells, *Solar RRL* **2023**, solr.202201112.

(2) F. Ji, B. Zhang, F. Wang, W. M. Chen, I. A. Buyanova, G. Boschloo, Reversible optical bleaching of bismuth-based lead-free perovskite films, *Adv. Science, under revision.*