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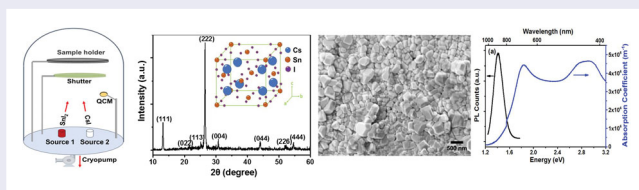
A two-step dry process for Cs_2SnI_6 perovskite thin film

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ABSTRACT

A two-step process for synthesizing stable Cs_2SnI_6 perovskite thin films is reported in this letter. The two-step process includes the co-evaporation of two precursors SnI_2 and CsI onto a glass substrate, followed by a post thermal annealing process in iodine vapor. Using this technique, pure Cs_2SnI_6 perovskite thin films were successfully synthesized without any wet process. These perovskite thin films are found to be stable under ambient conditions. They also show an electron mobility up to $509 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is higher than the mobilities of films prepared by solution processes reported in the literature.



IMPACT STATEMENT

A novel two-step dry process to synthesize phase-pure, air-stable Cs_2SnI_6 perovskite thin film with higher electron mobility than that of the films prepared by the solution process.

ARTICLE HISTORY

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KEYWORDS

Perovskite; thin film; solar cell; anneal; iodine

1. Introduction

Organic-inorganic lead halide perovskite solar cells have obtained prominent attention in recent years with certified power conversion efficiencies (PCEs) up to 22.1% [1–4]. The practical application of such perovskites, however, confronted big challenges due to their poor stability under ambient conditions and the toxic lead component. Many attempts have been made to explore lead-free and stable perovskites [5–7]. Among them, the Sn-based fully inorganic perovskites are of particular interest [8–10]. For example, γ - CsSnI_3 is a p-type perovskite and has been reported either as a hole conductor layer [11] or an absorber layer [12] in solar cells. However, the poor stability has prevented the fabrication of devices under ambient conditions and limited the PCE to below 2% when it was used as an absorber layer [12,13].

Most recently, a perovskite variant, Cs_2SnI_6 , has been shown to be more stable than γ - CsSnI_3 and has attracted

attention in the optoelectronic community. Cs_2SnI_6 belongs to the $Fm\bar{3}m$ space group with a cubic lattice parameter of $11.62 \text{ \AA}$ [14]. In comparison to CsSnI_3 , half of the octahedral Sn atoms are missing and creating discrete molecular $[\text{SnI}_6]^{2-}$ octahedra in Cs_2SnI_6 [15]. The stability of Cs_2SnI_6 has been attributed to the $4+$ state of Sn [15] or the strong Sn–I covalent bond [16]. It is a native n-type semiconductor [17] with a band gap between 1.26 and 1.62 eV, which is very close to the optimal band gap for solar cell application [18].

Although Cs_2SnI_6 has shown these promising properties for photovoltaic applications, high efficiency devices have not been realized due to its metallic conductivity. The high density of iodine vacancies and impurities such as CsI are thought to be responsible for the high conductivity behavior. Although a lot of work has been done on improving the film quality, an effective method has yet to be developed. Cs_2SnI_6 is generally synthesized

via solution process. However, the solution process often results in low film quality, such as, films with impurities introduced during the synthesis [19]. Cs_2SnI_6 can also be obtained by solid-state reactions. For example, it can be obtained by a gradual oxidation of $\gamma\text{-CsSnI}_3$, which is a two-step process, i.e. synthesis of CsSnI_3 first and followed by an oxidation process. However, the formation of SnO_2 as a second phase is inevitable in this process [20]. Alternatively, Saparov et al. reported another solid-state process to synthesize Cs_2SnI_6 , in which, a thin layer of CsI was first deposited, followed by a thermal annealing in SnI_4 vapor [21]. In this approach, the overall film thickness might be limited due to the low diffusion rate of SnI_4 molecules, and it cannot generate an iodine-rich environment. Herein, we report air stable Cs_2SnI_6 films with a much improved phase purity and mobility through a co-evaporation process followed by low-temperature annealing in iodine vapor atmosphere. The obtained pure phase Cs_2SnI_6 is stable up to two months without any protection when stored in atmosphere at room temperature, and shows a high electron mobility up to $509 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

2. Methods

2.1. Material synthesis

Cs_2SnI_6 thin films were grown through a two-step process, i.e. vacuum co-evaporation of two precursors SnI_2 and CsI , followed by thermal annealing in iodine vapor ambient. SnI_2 (purity 99.9%) and CsI (purity 99.999%) powders were purchased from SIGMA-ALDRICH. Both were used as received without any purification. The vacuum evaporation was a co-deposition process, that is, SnI_2 and CsI were deposited onto pre-cleaned glass substrates simultaneously, as shown in Figure 1(a). The base pressure was 1×10^{-7} Torr. The molar ratio between SnI_2 and CsI was maintained at 1.0:2.0 during deposition, which was well controlled through the deposition rate of each precursor. The substrate temperature was around 60°C without intentional heating during deposition. The average growth rate was $1 \text{ \AA/s}$ and the thickness of the as-deposited films ranged from 300 to about 600 nm. After the deposition, the iodine vapor thermal annealing process was conducted in a tube furnace, which was purged with N_2 before annealing. In addition to the as-deposited

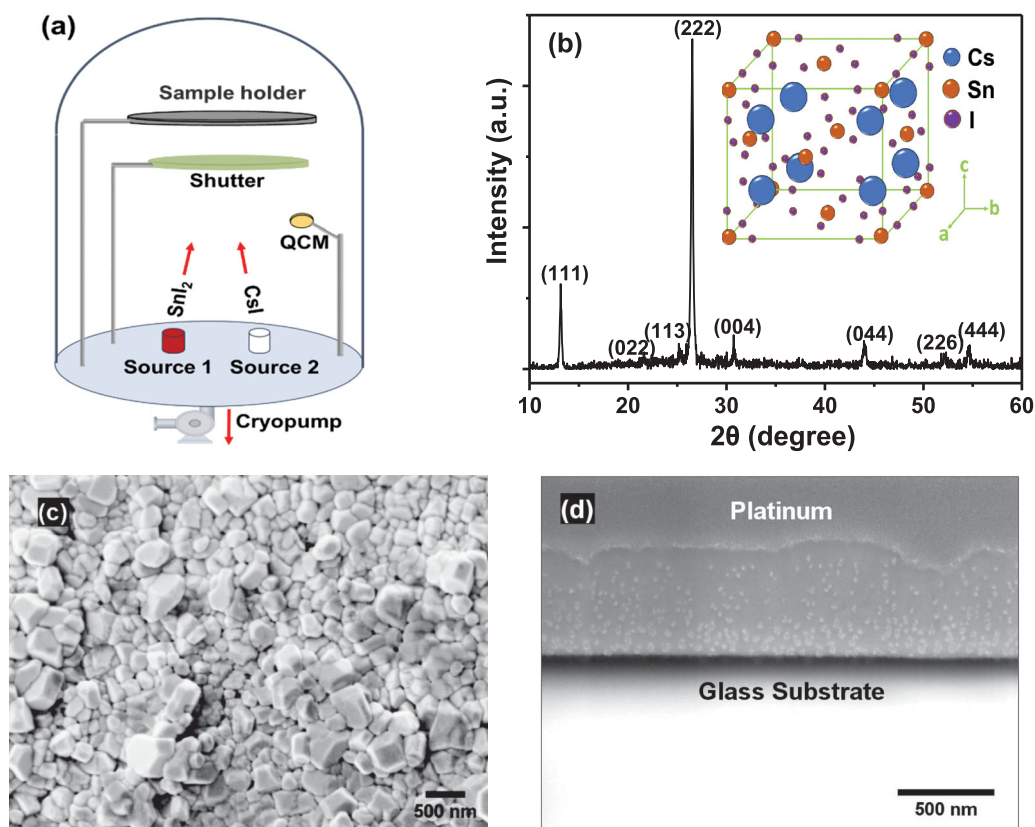


Figure 1. (a) A schematic diagram showing the vacuum system with two evaporation sources. (b) The X-ray θ - 2θ spectrum of a 600 nm thick Cs_2SnI_6 film deposited on glass substrate by the two-step dry process. The inset shows the crystal structure of Cs_2SnI_6 . (c) The top view SEM image of the Cs_2SnI_6 film. (d) A cross section SEM image of the Cs_2SnI_6 film on glass substrate.

samples, iodine particles were also put into the tube furnace to provide iodine vapor. Iodine vapor was generated by heating iodine particles to the desired annealing temperatures under ambient pressure. There was no gas flow during thermal annealing in order to maintain the iodine vapor pressure. A wide range of annealing temperatures were used in this work varying from 50°C to 270°C. Accordingly, the time needed to obtain Cs_2SnI_6 films varied from tens of hours to 30 s, depending on the annealing temperature. For comparison, Cs_2SnI_6 films were also synthesized by a gradual oxidation of CsSnI_3 . For this, CsSnI_3 was synthesized by sequential deposition of multilayer of SnI_2 and CsI with a molar ratio of 1.0:1.0, followed by a rapid thermal annealing at 280°C [9]. When these CsSnI_3 films were kept under ambient conditions, they gradually turn into Cs_2SnI_6 films in a few days, through an oxidation process [11].

2.2. Material characterizations

X-ray diffraction (XRD) spectra of samples were obtained at room temperature using a PANalytical Xpert diffractometer system with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.1541$ nm, 40 kV and 20 mA) and a point detector. The step size for 2θ scan is 0.03°. The surface morphologies were characterized with a Zeiss SUPRA 55 scanning electron microscope (SEM). Cross-section SEM sample was prepared by a Zeiss focused ion beam milling and imaged by SEM. The absorption spectra were measured with a Varian Cary 6000i UV–Vis–NIR Spectrometer with an InGaAs detector. Raman shift was measured with a LabRAM HR800 micro-Raman system (Horiba Jobin Yvon) equipped with a confocal microscope attachment and a charge-coupled detector. The excitation laser wavelength was 785 nm. The laser beam was focused onto the samples through a $\times 50$ magnification lens. The measurement used a laser power of 2 mW and the beam diameter was 2 μm . Photoluminescence (PL) was measured with a home-built system with a 532 nm CW laser and a Si photodetector. For time-resolved PL (TRPL) measurement, an Avalanche Photodiode Detector (PDM series, made by Micro Photon Devices) was used. A Trigger Diode Assembly (TDA, made by PicoQuant) was used to generate the pulsed excitation light. The excitation laser wavelength for TRPL measurement was 514 nm. For both PL and TRPL measurements, the laser power was 500 μW with a beam diameter of 1 μm . Hall effect measurements were carried out using a home-built 4-point probe system controlled by a LabVIEW program. The set-up was capable of applying a magnetic field up to 4.5 kG and varying the sample temperature in the range of 200–350 K. The Hall measurements were taken at room temperature using indium as contacts on the sample.

3. Results and discussions

Sequential or co-evaporation of two precursors in a vacuum is a convenient way to produce Cs_2SnI_6 thin films. In principle, CsI and SnI_4 with a molar ratio of 2.0:1.0 could produce stoichiometric Cs_2SnI_6 films without any second phase. However, SnI_4 is not suitable for thermal evaporation because it is susceptible to thermal decomposition on heating and does not form a continuous film. Alternatively, SnI_2 was selected as one of the precursors. By annealing the co-evaporated ($\text{SnI}_2 + \text{CsI}$) film with a molar ratio of 1.0:2.0 in iodine vapor, a pure phase of Cs_2SnI_6 was achieved under a relatively low annealing temperature. The iodine vapor annealing process plays two key roles in synthesizing Cs_2SnI_6 perovskite, i.e. to achieve the correct stoichiometry and to provide excess iodine to suppress defect density, which will be discussed in later sections.

Figure 1(b–d) shows the structural characteristics of the synthesized Cs_2SnI_6 thin film, which was obtained through annealing at 50°C for one hour in iodine vapor. XRD was performed on the sample to check for the crystallinity. Figure 1(b) shows XRD spectrum of this sample. The peaks at the 2θ values: 13.1°, 21.5°, 26.5°, 30.7°, 43.9°, 52.0°, 54.5°, correspond to the atomic planes of (111), (022), (222), (004), (044), (226), (444), respectively. It can be clearly seen from Figure 1(b) that all the peaks came from Cs_2SnI_6 and there was no peak from CsI . The existence of an extra CsI component as impurity is very common in Cs_2SnI_6 by other synthesis process [19]. The crystals of Cs_2SnI_6 can be clearly seen from the SEM image shown in Figure 1(c), with an average grain size of 150 nm. The cross-section SEM image is shown in Figure 1(d).

It is believed that the co-evaporation and annealing in iodine vapor are the two main reasons that are responsible for producing the Cs_2SnI_6 pure phase. In order to verify this, several Cs_2SnI_6 films from different processes were made and compared by checking the structures from XRD spectra. In Figure 2(a), a Cs_2SnI_6 film was obtained through the oxidation of CsSnI_3 . This film was deposited by a sequential deposition with a molar ratio of 1.0:1.0. In addition to the Cs_2SnI_6 peaks, two strong peaks from CsI (110) and CsI (200) appeared at $2\theta = 27.6^\circ$ and 39.4° , respectively. This indicates that the film is not as pure as that obtained by the two-step process. Moreover, the inset SEM image shows a substantially different morphology implying poorer crystallinity compared to that of the SEM image shown in Figure 1(c).

Another sample obtained from the sequential deposition with a molar ratio of 1.0:2.0 was annealed in iodine vapor. This process could achieve the right Cs_2SnI_6 stoichiometry, but compared to the co-evaporation

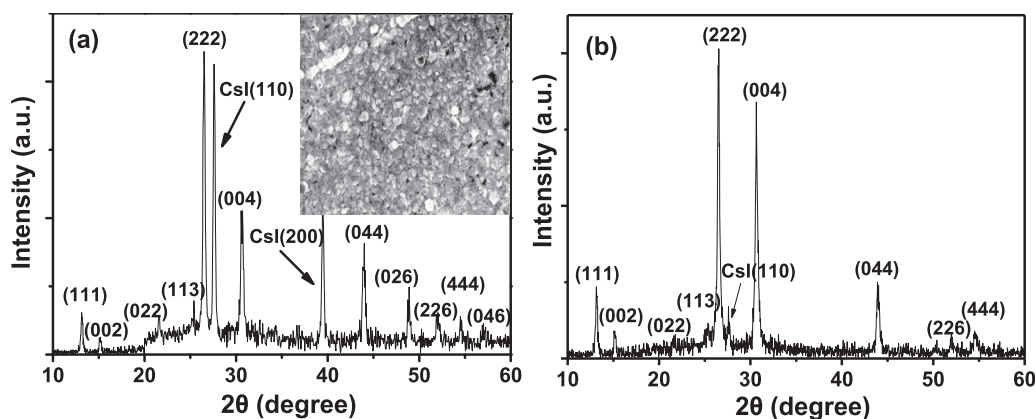


Figure 2. Comparison of the Cs_2SnI_6 films deposited on glass substrates by different processes. (a) An XRD spectrum of a Cs_2SnI_6 film obtained from the oxidation of CsSnI_3 . CsI (110) and (200) impurity peaks at $2\theta = 27.6^\circ$ and 39.4° , respectively, can be seen. The inset shows an SEM top view image of the same film. (b) An XRD spectrum from a Cs_2SnI_6 film obtained by a sequential deposition process followed by annealing in iodine vapor. A CsI(110) peak can be seen at 27.6° .

strategy, the two precursors were not uniformly mixed. Therefore, the solid-state reaction during thermal annealing may not be complete. As can be seen from Figure 2(b), one peak from CsI (110) at 27.6° was clearly observed. All Cs_2SnI_6 peaks observed in Figure 2(a) were observed in Figure 2(b) except (026) and (046). These results indicated the importance of co-evaporation and annealing in iodine vapor to obtain a pure Cs_2SnI_6 phase.

To determine the optical properties, the absorbance spectra of Cs_2SnI_6 thin film were measured in the wavelength range of 200–1000 nm. The absorption coefficient α was calculated based on the absorbance spectra and was shown in Figure 3(a). In the visible range up to 700 nm, the absorption coefficient α is around $5 \times 10^6 \text{ m}^{-1}$, which is comparable to that of the $\text{CH}_3\text{NH}_3\text{PbI}_3$'s absorption coefficient [22]. The Tauc plot was used to estimate the energy gap of Cs_2SnI_6 . As a direct band gap material, the variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ is plotted in Figure 3(b). The energy gap is determined from the intersection of the linear regression (red line) on the energy axis. A band gap of $1.40 \pm 0.01 \text{ eV}$ was determined from the Tauc plot.

The optical band gap was further verified by PL spectroscopy. Figure 3(a) shows the room temperature PL spectrum (black curve) excited by 514 nm CW laser in a vacuum. A broad but pronounced PL peak ranging from 700 to 900 nm with the peak centered at 880 nm was observed, suggesting a band gap of $1.41 \pm 0.01 \text{ eV}$. This is consistent with the band gap obtained from the Tauc plot shown in Figure 3(b). Based on the PL and absorption measurements, it can be concluded that the synthesized Cs_2SnI_6 has a direct band gap of $1.41 \pm 0.01 \text{ eV}$, which is consistent with literature reports, where the bandgap values vary from 1.26 to 1.6 eV [15,20,21]. TRPL was performed to characterize the carrier lifetime.

For comparison, a Cs_2SnI_6 sample from the oxidation of CsSnI_3 film was also measured. As shown in Figure 3(c), the sample from the two-step process (curve 2) has a longer lifetime than the one from CsSnI_3 oxidation (curve 1), suggesting that the defect density is less in the sample grown by the two-step process. From a curve fitting using two exponential decay functions, the lifetime of the sample from the two-step process has a fast component of 0.07 ns and a slow component of 0.30 ns. The fast and slow lifetimes of the sample from CsSnI_3 oxidation are 0.04 and 0.28 ns, respectively. These are relatively short lifetimes compared to other perovskites reported in the literature, and may be related to the grain size. To probe the vibration property of the film, room temperature Raman spectrum of Cs_2SnI_6 film was collected using 785 nm excitation wavelength and shown in Figure 3(d). There were three first-order Raman modes below 150 cm^{-1} , $\nu(A_1g)$ at 127 cm^{-1} , $\nu(E_g)$ at 92 cm^{-1} , and $\delta(F_2g)$ at 78 cm^{-1} , corresponding to Sn-I symmetric stretch, Sn-I asymmetric stretch, and I-Sn-I asymmetric bending modes in the $[\text{SnI}_6]^{2-}$ octahedra, respectively. Two higher order modes were also observed at 248 and 348 cm^{-1} . These observed peaks agree well with the Raman spectrum of synthesized polycrystalline Cs_2SnI_6 powders using 785 nm excitation wavelength reported in the literature [23,24].

One of the main challenges for perovskite materials is their long-term stability, which is compromised because these materials are extremely sensitive to moisture and oxygen. To study the stability of Cs_2SnI_6 , the synthesized sample was kept at room temperature under ambient conditions without any protections and was checked with XRD periodically. The Cs_2SnI_6 reported here was stable up to two months without any protection. Figure 4(a) summarizes the XRD spectra of the pristine sample, as

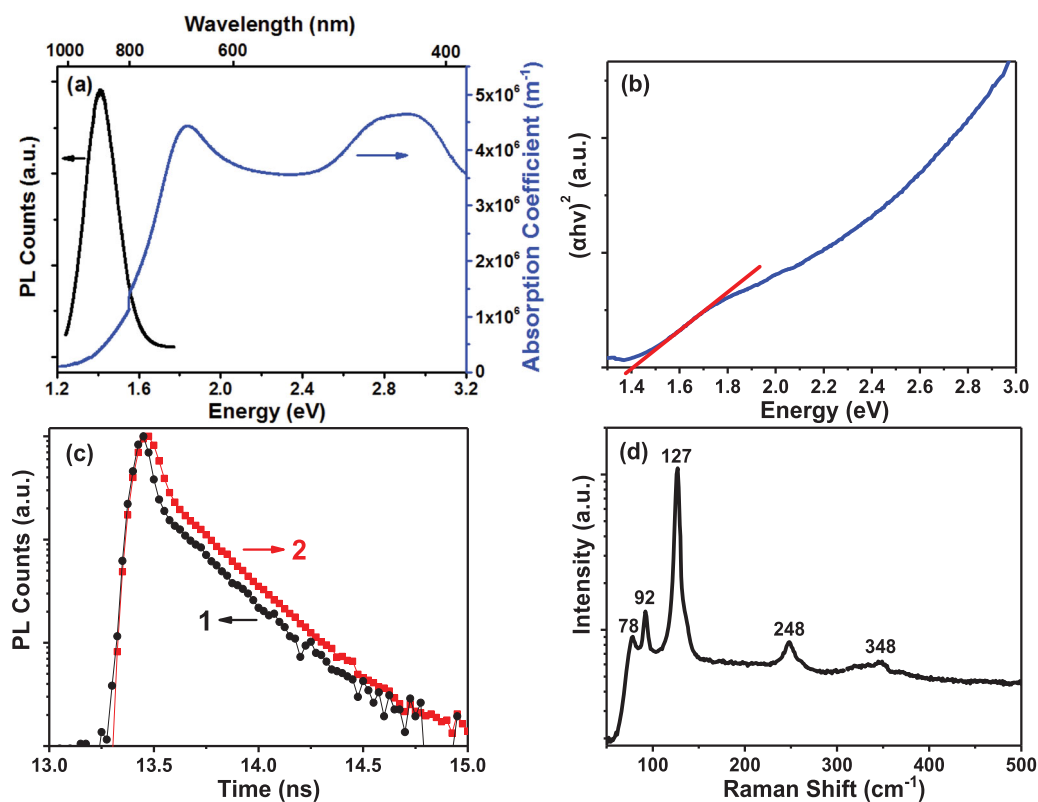


Figure 3. Optical characterization of the Cs_2SnI_6 thin films grown on glass substrates. (a) PL (left) and absorption coefficient (right) of the 600 nm thick Cs_2SnI_6 thin film grown by the two-step process. (b) The Tauc plot from the absorption spectrum shown in (a). (c) TRPL measured at room temperature. Curve (1) is for the 600 nm thick Cs_2SnI_6 sample made from the oxidation of CsSnI_3 ; Curve (2) is for the 600 nm thick Cs_2SnI_6 sample made from the two-step process. (d) Raman spectrum of 600 nm thick Cs_2SnI_6 film on glass substrate.

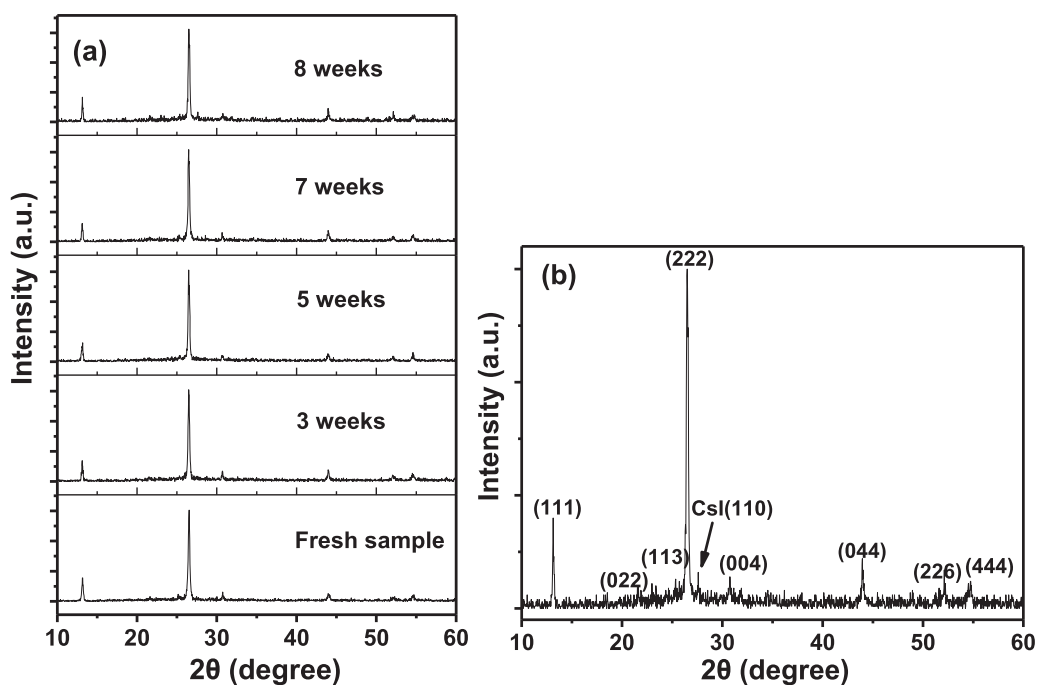


Figure 4. XRD spectra showing the stability of a Cs_2SnI_6 film grown on glass substrates by the two-step process when stored at room temperature under ambient environment. (a) Comparison of XRD spectra measured at 3 weeks, 5 weeks, 7 weeks, and 8 weeks later as well as the fresh sample. (b) XRD spectrum measured 2 months after growth shows a CsI(110) peak at 27.6°.

well as the film measured at 3 weeks, 5 weeks, 7 weeks, and 8 weeks later. The curves are vertically shifted for clarity. The peaks in each spectrum taken at different weeks are almost identical, implying that the film is stable up to two months. After that time frame, as shown in Figure 4(b), a small CsI(110) peak appeared at 27.6° due to the decomposition of Cs_2SnI_6 under the ambient conditions. Nevertheless, this is a stable material rarely observed as compared to other perovskite materials reported so far.

Carrier mobility plays a significant role in optoelectronic devices. The synthesized Cs_2SnI_6 film was characterized at room temperature by Hall Effect measurement to determine the mobility. Table 1 summarizes relevant electrical properties of four Cs_2SnI_6 films (S1–S4) with different annealing conditions. Also shown are two results (R1 and R2) from the literature with different film synthesis processes. The Hall Effect measurement indicated the Cs_2SnI_6 films are an n-type semiconductor with an electron mobility of $509 \pm 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the 600 nm thick film annealed at 50°C , which is higher than the reported value of $310 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by a solution technique [15]. The corresponding carrier concentration of sample S4 was found to be on the order of 10^{15} cm^{-3} .

It was observed that the electron mobility varied among different samples, ranging from 40 to $509 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This could be explained by the film quality in terms of impurities, defects density and morphology. Sample S1 was obtained through the oxidation of CsSnI_3 . It has a smooth morphology. However, the inevitable impurities, such as CsI, has lowered the carrier mobility to $53 \pm 5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Samples S2, S3, and S4 were all processed through the co-evaporation and thermal annealing in iodine vapor. Sample S2 is 300 nm thick and is not uniform. It should be noted that the nonuniformity of film S2 causes the Hall measurement not to be as reliable as other more uniform S1, S3, and S4 samples. Both S3 and S4 have a thickness of $\sim 600 \text{ nm}$

and are more uniform than S2. The highest mobility came from sample S4, which was annealed in iodine vapor at a lower temperature (50°C) compared to sample S3 (260°C), indicating better annealing conditions, i.e. lower annealing temperature with longer annealing time can improve film quality. Sample S4 has a higher mobility than the solution processed sample R1 reported in reference [15], probably due to the denser film by thermal deposition in comparison to the solution processed film. Sample R2 also came from solid-state reactions [21]; however, an appreciable difference between the Hall mobilities of R2 and S4 was observed. This is because the R2 film was annealed in SnI_4 vapor and free iodine was not available during annealing process to compensate the iodine vacancy in the Cs_2SnI_6 film. According to first-principles density functional theory calculation reported by Xiao et al. [17], the dominant defects that are responsible for the intrinsic n-type behavior in Cs_2SnI_6 are iodine vacancies and tin interstitial. An iodine-rich synthesis condition would be beneficial to suppress the iodine vacancy defects. This is consistent with our experimental results. In short, the Hall effect measurement results clearly indicated improved electrical properties through the iodine vapor annealing process.

4. Conclusions

In comparison to the solution-based method, the two-step all dry process reported here shows substantial advantages in preparing pure phase of Cs_2SnI_6 thin films. Particularly, the annealing process in iodine vapor ambient provides a synthesis condition which can significantly reduce the defects in the film. This iodine vapor annealing process opens a new avenue for dealing with iodine vacancy-related defects in materials, not limited to Cs_2SnI_6 itself.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Table 1. Comparison of electrical properties of Cs_2SnI_6 films from Hall effect measurements.

Cs_2SnI_6 sample	S1	S2	S3	S4	R1	R2
Type	n	n	n	n	n	n
Carrier concentration (cm^{-3})	$2 \text{ E}16$	$4 \text{ E}17$	$6 \text{ E}15$	$2 \text{ E}15$	$1 \text{ E}14$	$6 \text{ E}16$
Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	53	40	180	509	310	2.9
Resistivity ($\Omega \text{ cm}$)	4.6	0.5	5.6	9.1	100	N/A

Notes: S1 is from a 600 nm thick Cs_2SnI_6 film through the oxidation of CsSnI_3 ; S2 is a 300 nm thick Cs_2SnI_6 film from the two-step process by co-evaporation of SnI_2 and CsI followed by iodine vapor annealing at 260°C ; S3 is from a 600 nm thick Cs_2SnI_6 film by the two-step process annealing in iodine vapor at 260°C ; S4 is a 600 nm thick Cs_2SnI_6 film by the two-step process annealing in iodine vapor at 50°C ; R1 is a Cs_2SnI_6 film with an unknown thickness grown by a solution process from Ref. [15]; R2 is a 350 nm thick Cs_2SnI_6 film by annealing CsI in SnI_4 vapor from Ref. [21].

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