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Optical Characterization of Lead-Free Cs$_2$SnI$_6$ Double Perovskite Fabricated from Degraded and Reconstructed CsSnI$_3$ Films

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Supporting Information

ABSTRACT: Halide perovskites have experienced a huge development in the past years, but they still have two major challenges for their massive implantation: the long-term stability and the use of lead. One of the most obvious lead-free candidates to replace these perovskites is CsSnI$_3$, but due to its poor environmental stability, it has been discarded for the fabrication of stable devices. Nevertheless, ambient degradation of CsSnI$_3$ and later reconstruction produce a relatively stable lead-free Cs$_2$SnI$_6$ double perovskite with interesting optical properties that have not been deeply characterized previously. In this work, the potential use for the optical properties of Cs$_2$SnI$_6$ is studied and compared with that of the most common halide perovskite, CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$). The Cs$_2$SnI$_6$ films stayed in a standard atmosphere for a week without showing any signs of degradation. They also demonstrated better reflective behavior than MAPbI$_3$ and higher absorption in the 650 and 730 nm spectral range, making this material interesting for the development of photodetectors in this region. This study demonstrates that Cs$_2$SnI$_6$ is a promising material for photodevices, as it highlights its main characteristics and optical parameters, giving an original view on the use of the double perovskite, but at the same time emphasizing the need to improve the electrical properties for the development of efficient optoelectronic devices.

KEYWORDS: optical characterization, lead-free, perovskite, coevaporation deposition, tin halide, full inorganic

INTRODUCTION

Lead halide perovskites (APbX$_3$, with A being an organic/ inorganic cation and X an halide anion) have experienced a huge development in past years, due to their suitability for the fabrication of solar cells, going from an initial 3.81% power conversion efficiency to the recently achieved 25.2%. These perovskites have demonstrated their great absorption capabilities, high photoluminescence quantum yield, and cheap fabrication processes. All these facts make them great candidates not only for the solar cell world but also for other optoelectronic applications such as solid light emitters or as photodetectors. However, these systems present a significant drawback facing their commercialization due to the toxicity of the lead. Consequently, a lot of studies focus on the development of lead-free perovskites with characteristics similar to those of their lead counterparts.

There are a lot of possible lead-free candidates. However, tin halide perovskites have drawn the attention of the scientific community, due to their similarities with the lead halide perovskites. In particular, the fully inorganic CsSnI$_3$ achieved 0.88% efficiency in its first use as a Schottky solar cell. Chung et al. studied the electrical properties of CsSnI$_3$, discussing its metallic behavior instead of a semiconducting one. They argued that this behavior is due to the tin vacancies produced in the structure during its formation. Following that, Marshall et al. included a 10% excess of SnI$_3$ in the formation of the film, or 20% of SnF$_2$ to cover the tin vacancies, achieving an efficiency around 2–2.76%. The main drawback of this perovskite is the poor stability in environmental conditions, because the Sn$^{II}$ is easily oxidized to Sn$^{IV}$. Lee et al. tried to avoid this oxidation using Sn$_2$F$_6$ as a reducing agent in the formation of the formamidinium tin iodide (FASnI$_3$) perovskite, achieving a power conversion efficiency of 4.8%. Recently, Chen et al. mixed the CsSnI$_3$ with germanium (Ge), making a “double perovskite” (Cs$_2$SnGeI$_6$) with 7.11% efficiency. However, a majority of these studies were carried under a nitrogen atmosphere. Under these conditions, Sn$^{IV}$ arises, transforming CsSnI$_3$ perovskite into Cs$_2$Sn$_2$I$_6$ double perovskite. Nevertheless, this material itself constitutes a more air stable candidate than its nonoxidized counterpart. It has been previously used as a hole transport layer (HTL) in dye-sensitized solar cells, and also as nanowires or quantum rods. Several synthesis methods have been employed for its preparation. However, the optical properties of this material have not been broadly studied in the literature. In this work, the optical properties of Cs$_2$Sn$_3$I$_6$ obtained as the final film stayed in a standard atmosphere for a week without showing any signs of degradation. They also demonstrated better reflective behavior than MAPbI$_3$ and higher absorption in the 650 and 730 nm spectral range, making this material interesting for the development of photodetectors in this region. This study demonstrates that Cs$_2$Sn$_3$I$_6$ is a promising material for photodevices, as it highlights its main characteristics and optical parameters, giving an original view on the use of the double perovskite, but at the same time emphasizing the need to improve the electrical properties for the development of efficient optoelectronic devices.
degradation product of CsSnI3 in air, are studied in depth. In order to compare the properties of the thin film material and of the bulk, the powder is also synthesized with a novel and easy precipitation method. Moreover, with a comparative analysis of CsSnI3, and of the widely used perovskite, the methylammonium lead iodide (MAPbI3) properties show the potential for reasonable that the material volume ratio is proportional to the is convenient to calculate the deposition rate ratio. It is, in fact, depending on the molecular weight and densities (eq 2), is equal to the thickness, and in turn to the evaporation rate. Thus, the volume ratio, and make

\[ \frac{m_{CsSnI3}}{m_{SnI2}} = \frac{117.6}{12} = 1.176 \]

This means that, to achieve the correct stoichiometry, the deposition rate of CsI must be 1.176 times bigger than that of SnI2. With this simple calculation, we can customize the ratio between the two precursors and make films with CsI or SnI2 excess, with different properties.32,33 The optimized temperature values for each crucible are ~270 °C for SnI2, and ~510 °C for CsI. All these coevaporations took place with the evaporator at 3 × 10⁻³ Torr pressure, inside a nitrogen filled glovebox.

**RECONSTRUCTION CONDITIONS.** The conversions to Cs2SnI6 were carried out in the dark, with a temperature between 21 and 23 °C and relative humidity of 28-35%. The samples were stored in aluminum wrapped boxes in laboratory conditions, in air. CsSnI3, Powder Synthesis. Pure CsSnI3 powder was synthesized with the following procedure. A 1 mmol portion of CsI (259.81 mg) was mixed with 1 mmol of SnI2 (372.52 mg) in a vial. A 1 ml portion of acetone was added to the mixture to form a black suspension, which gently stirred at 750 rpm for a couple of hours, in order to completely disperse the precursors. After the evaporation of the acetone in ambient conditions, it was possible to collect the precipitated black crystals of Cs2SnI6.

**EXPERIMENTAL SECTION**

Thin Film Fabrication. The CsSnI3 thin film was deposited using a coevaporation technique, as can be schematically seen in Figure 1. We used an MBrann thermal evaporator, filling two crucibles with precursors: one with CsI (99.9%, Sigma-Aldrich) and the other one with SnI2 (99.9%, Sigma-Aldrich). The glass substrates were previously ultrasonicated with ethanol and isopropanol (1:1), and then ultrasonicated again with ethanol and acetone. After the evaporation of the acetone in ambient conditions, the precursors were dispersed in ethanol and acetone (1:1). The coevaporation of the binary salts leads to the self-assembly of the final film, it is convenient to calculate the deposition rate ratio. It is, in fact, reasonable that the material volume ratio is proportional to the film thickness, and in turn to the evaporation rate. Thus, the volume ratio, and make films that correspond to the 24 h needed in that study. This enhanced stability of initial CsSnI3 is attributed to better quality of the deposition method employed here, as they reported a two-step sequential deposition by alternating thermal evaporation depositions, followed by a thermal annealing to provoking a solid-state reaction between the layers. This method increases the chance of getting pinholes and an inhomogeneous morphology, compared to the film obtained by thermal coevaporation.34 The absorbance spectra reported in Figure 2a, with CsI or SnI2 excess, with different properties.32,33 The optimized temperature values for each crucible are ~270 °C for SnI2, and ~510 °C for CsI. All these coevaporations took place with the evaporator at 3 × 10⁻³ Torr pressure, inside a nitrogen filled glovebox.

**RESULTS AND DISCUSSION.**

CsSnI3 samples prepared on glass substrates by coevaporation (see Experimental Section) inside the glovebox were characterized under ambient conditions. After 10 min of ambient air exposure, samples experienced a fast degradation to their precursors (Figure 2a) with a decrease of the absorbance (Figure 2b). Accordingly, their color changed from dark brown (CsSnI3, left) to yellow (CsI + SnI2, center). The poor stability of the CsSnI3 in air is mainly due to the decomposition (eq 3) and oxidation (eq 4) mechanisms.

\[ \text{CsSnI3} + \text{environmental conditions} \rightarrow \text{CsI} + \text{SnI2} \quad (3) \]

\[ \text{2SnI2} + \text{O}_2 \rightarrow \text{SnI2} + \text{SnO3} \quad (4) \]

The oxidation from Sn2⁺ to Sn4⁺ leads to the phase conversion to Cs2SnI6 in which half of the tin atoms are missing, because they form tin oxide. The complete reaction is shown in eq 5.

\[ 2\text{CsSnI3} + \text{O}_2 \rightarrow \text{Cs}_2\text{SnI}_6 + \text{SnO}_2 \quad (5) \]

This CsSnI3 degradation and Cs2SnI6 reconstruction has been demonstrated by Qiu et al.35 but with some differences. In our case, the degradation and reconstruction take between 3 and 5 days to get the film completely dark (Figure 2a, right) as compared to the 24 h needed in that study. This enhanced stability of initial CsSnI3 is attributed to better quality of the deposition method employed here, as they reported a two-step sequential deposition by alternating thermal evaporation depositions, followed by a thermal annealing to provoking a solid-state reaction between the layers. This method increases the chance of getting pinholes and an inhomogeneous morphology, compared to the film obtained by thermal coevaporation.34
show that the film recovers its capacity to absorb the wavelengths between 700 and 800 nm completely, but it loses the absorption capacity in shorter wavelengths and has a planar response with two humps, instead of the original ramp shape. This characteristic behavior, resulting in an average visible transmittance (AVT) of 42.1%, doubling the value of the AVT reported for 150 nm MAPI films, is attractive for a semitransparent application. In this case the thickness, measured using a profilometer and by SEM cross section, giving a result of 230 nm (Figure S1a,b), was not sacrificed to obtain a high transmittance value, avoiding the problems related to the contact between the deposited layer above and below the perovskite, leading to a short circuit in optoelectronic devices. Note that slower degradation of CsSnI3 is observed in the inferior side of the analyzed sample, Figure 2a, where FTO (fluorine doped SnO2) is exposed in the substrate. This fact points to a possible effect of fluorine in FTO as a reducing agent in the enhanced stability of CsSnI3 in this region. However, deep analysis of this observation is beyond the scope of this work.

To compare the properties in bulk, we synthesized the Cs2SnI6 powder following the procedure explained in the Experimental Section. The X-ray diffraction (XRD) patterns of the powder and of the thin film are shown in Figure 3a. Here, we considered the powder (Figure 3b) as a reference pure material, with characteristic peaks at 13.16, 26.52, 30.72, 44, 52.04, and 54.68, all of them representing lattice planes of Cs2SnI6. After comparing these peaks with a film exposed to ambient air for 5 days, it is possible to recognize similar patterns in the degraded and reconstructed samples. However, 3 days after this, another two peaks have arisen, at 27.6 and 48.76, both belonging to CsI, one of the precursors. This fact implies that the films maintain their air stability for 1 week, approximately. Then, they start decomposing into their...
precursors again. This highlights that, despite the Cs₂SnI₆ double perovskite presenting an enhanced stability compared with most of its perovskite counterparts, it also requires encapsulation for long-term stability.

To double-check the presence of the CsI, we measured the morphology by scanning electron microscopy (SEM) (Figure 4). The pure powder presents crystals with tiny bright dots in the secondary electron image but not in the backscattered one. In

Figure 4. Scanning electron microscopy (SEM) images of (a) pure powder sample and (b) Cs₂SnI₆ samples. (c) After 11 days on the SEM, the top view of the Cs₂SnI₆ CsI crystals became visible. (d) Zoom-in of the CsI crystal detail.

Figure 5. Optical characterization of Cs₂SnI₆ thin films: (a) reflection, transmission, and absorption measurements; (b) refractive index and extinction coefficient values; (c) Tauc plot determining the band gap; and (d) photoluminescence peak matching with the band gap.
fact, the crystal and the bright dots were analyzed using energy-dispersive X-ray spectroscopy (EDS) measurements, with both giving the same result, Cs ≈ 22%, Sn ≈ 11%, and I ≈ 66%, matching the CsSnI₃ structure (Figure S2a). Figure 4b shows that the surface of the thin film before the final decomposition is rough. Although it was not possible to measure the CsSnI₃ film, because of the fast degradation, we are confident that the morphology is homogenous, as the coevaporation gives a perfect mirror-like film (Figure S3). Consequently, the roughness observed in CsSnI₃ is likely generated during the oxidation and reconstruction process, as briefly mentioned above.

In Figure 4c,d, we can see the surface of the CsSnI₃ thin film starting the degradation process, because crystals of CsI start appearing. The composition of the crystals was confirmed by EDS measurements (Figure S2b).

Optical properties of the Cs₂SnI₆ thin films prepared by degradation and reconstruction were systematically analyzed. We measured and calculated the absorption coefficient, band gap, refractive index, and extinction coefficient.

The absorption, reflection, and transmission of the films were measured (Figure 5a), and the corresponding values were used to obtain the absorption coefficient, α, using the relation below:

$$\alpha = \frac{1}{t} \log \left( \frac{1 - R}{T} \right) \approx 2.303 \frac{A}{t}$$

Here, t is the thickness of the film, and R, T, and A are reflectance, transmittance, and absorbance of the film, respectively. The approximation showed in eq 6 is accepted if the reflectance is close to zero. In this study, the approximation matches the real case, due to the low reflection of the film (Figure 5a).

The values of refractive index and extinction coefficient as a function of wavelength, see Figure 5b, were obtained following eqs 7 and 8:

$$\kappa = \frac{\alpha}{4\pi}$$

$$n = -2(R + 1) \pm \sqrt{(2(R + 1))^2 - 4(R - 1)^2(1 + \varepsilon^2)}$$

In these equations, λ is the wavelength, R the measured reflectance, n the refractive index, and κ the extinction coefficient.

Cs₂SnI₆ thin films presented a band gap of 1.63 eV, see Figure 5c, as it was calculated using the linear interpolation of the Tauc plot. This plot compares (hν)² (α = 2, considering Cs₂SnI₆ as a direct band gap material) against the energy of the photons (hν), where h is Planck’s constant and ν the photon’s frequency. Previous literature studies provide a wide range of band gap values for Cs₂SnI₆, between 1.2 and 1.6 eV. Our work is in good agreement with studies pointing to a high band gap in this range. Regarding the optical band gap, the photoluminescence (PL) of the thin films results in the emission peak (Figure 5d) at 792 nm. Translated to energy, this value is 1.57 eV, which matches with the result obtained from the Tauc plot, with a relatively small Stokes shift. No significant PL quantum yield was measured for these samples, pointing to a high nonradiative recombination of the material.

In order to put this material in context with other materials of the perovskite family, we compared it with the most studied perovskite, MAPbI₃. Figure 6a,b shows the comparison of refractive index and extinction coefficient between both materials. Two main aspects are remarkable here: the first one, regarding n, is the huge difference between the MAPbI₃ (around 2.5) and the Cs₂SnI₆ (around 1.5) values. This fact can make Cs₂SnI₆ better than MAPbI₃ in terms of reflection and interface index matching, depending on the surrounding layers. The second important fact is regarding κ, as MAPbI₃ can be considered a better absorber than Cs₂SnI₆; nevertheless, between 650 and 730 nm, Cs₂SnI₆ has a higher extinction coefficient than MAPbI₃, which implies that it is a better absorber in this spectral interval. This fact points to a good potential for Cs₂SnI₆ for the development of photodetectors in this range.

With these results it is also possible to calculate the ideal short-circuit current density that a solar cell made with Cs₂SnI₆ could have. We have done this using the generation rate and by supposing an ideal case with no electrical losses.
thickness of the film, r the reflectance, and \( \text{Irr} \) the irradiance value of the incident light.

Using this equations, under the sun spectrum (AM1.5G), we obtain a \( \text{J}_\text{sc} \) value of 18.86 mA/cm^2 in a device with an active layer thickness of 230 nm. The maximum value is obtained by supposing ideal conditions (zero reflectance and an optimum optical thickness), and it equals 33.68 mA/cm^2. So, making thicker devices will give us higher current density values (e.g., 26.01 mA/cm^2 at 500 nm thickness). In thicker cases, several problems start appearing, due to the increase in the distance that the carriers have to travel to reach the electrodes. Nevertheless, these electrical issues are far away from our actual study.

**CONCLUSIONS**

In summary, we have prepared a CsSnI\(_3\) thin film from the degradation and reconstruction of CsSnI\(_3\) first prepared by coevaporation. The structural properties of the CsSnI\(_3\) samples were compared with Cs\(_2\)SnI\(_6\) powders, prepared by a novel method, obtaining a good agreement. CsSnI\(_3\) thin films exposed to ambient standard conditions of oxygen and moisture do not exhibit degradation for 1 week. We have successfully characterized the powder and films to obtain their crystaline structure, band gap, morphology, and optical properties (PL, absorption coefficient, band gap, refractive index and extinction coefficient). These values have been compared with MAPbI\(_3\), perovskite, revealing that CsSnI\(_3\) presents better reflective properties than MAPbI\(_3\). In addition, despite MAPbI\(_3\) presenting higher absorption than CsSnI\(_3\), in most of the visible wavelength range, this is not the case in the spectral range between 650 and 730 nm, where CsSnI\(_3\) presents higher light absorption, making this material interesting for the development of photodetectors in this specific range or for semitransparent applications. Further research will be needed to improve the electrical properties of this material limited by high nonradiative recombination as we confirm by PL characterization. All these facts make this lead-free double perovskite, CsSnI\(_3\), a great candidate as an absorber for photodevices from an optical point of view and stress the need for further work on the improvement of the electrical properties.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at [pubs.acs.org/doi/10.1021/acsaem.9b01827](https://pubs.acs.org/doi/10.1021/acsaem.9b01827).

Scanning electron microscopy cross section, energy-dispersive X-ray spectroscopy results, and pictures of the evaporated films (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**

1. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131, 6043−6045.

2. Dissado, L. A.; Nigmatullin, R. R.; Hilb, R. M. The Fading of Memory During the Regeneration of Structural Fluctuations. Adv. Chem. Phys. 2007, 133, 523.

3. Wang, J.; Wang, N.; Jin, Y.; Si, J.; Tan, Z.-K.; Du, H.; Cheng, L.; Du, X.; Bai, S.; He, H.; Ye, Z.; Lei, M. L.; Friend, R. H.; Huang, W. Interfacial Control Toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes. Adv. Mater. 2018, 27, 2311−2316.

4. Fakharmirdad, A.; Shibli, U.; Quo, W.; Ijgh, T.; Sultan, M.; Heremans, P.; Schmidt-Mendels, L. Intrinsically and Layered Perovskites for Optoelectronic Devices. Adv. Mater. 2019, 31, 1807095.

5. López-Fraguas, E.; Arredondo, B.; Vega-Collado, C.; Pena, G. I.; Najafi, M.; Martin-Martín, D.; Galagan, Y.; Sánchez-Pena, J. M.; Vergaz, R.; Romeo, B. Visible Light Communication System Using an Organic Emitter and a Perovskite Photodetector. Org. Electron. 2019, 73, 292−298.

6. Suarez, L.; Hasunabadi, E.; Musa, A.; Carlino, N.; Masiert, C. A.; Latifi, M.; Bettotti, P.; Mora-Seró, I.; Martínez-Faston, J. P. Integrated Optical Amplifier−Photodetector on a Wearable Nanocellulose Substrate. Adv. Opt. Mater. 2018, 6, 1800201.

7. Miao, J.; Zhang, F. Recent Progress on Highly Sensitive Perovskite Photodetectors. J. Mater. Chem. C 2019, 7, 1741−1791.

8. Chatterjee, S.; Pal, A. J. Influence of Metal Substitution on Hybrid Halide Perovskites: Towards Lead-Free Perovskite Solar Cells. J. Mater. Chem. A 2018, 6, 3793−3823.

9. Sun, F.; Shatse, S.; Lam, H. N.; Miao, A. O. Advancement on Lead-Free Organic-Inorganic Halide Perovskite Solar Cells: A Review. Materials 2018, 11 (6), 1008.

10. Wang, X.; Zhang, T.; Lou, Y.; Zhao, Y. All-Inorganic Lead-Free Perovskites for Optoelectronic Applications. Mater. Chem. Front. 2019, 3, 365−375.

11. Fu, H. Review of Lead-Free Halide Perovskite as Light Absorbers for Photovoltaic Applications: From Materials to Solar Cells. Sol. Energy Mater. Sol. Cells 2019, 193, 107−132.

12. Travis, W.; Glover, E. N. K.; Bronstein, H.; Scanlon, D. O.; Polgar, P. G. On the Application of the Tolerance Factor to Inorganic and Hybrid Halide Perovskites: a Revised System. Chem. Sci. 2016, 7, 4548−4556.

13. Konstantakou, M.; Stengopolous, T. A Critical Review on Tin Halide Perovskite Solar Cells. J. Mater. Chem. A 2017, 5, 15118−15149.

14. Shams, K.; Chen, Z.; Qureshi, J.; Yu, C.; Wang, J.; Jie, X.; Penninger, W.; Vockic, N.; Midgley, J.; Kenney, J. T. Synthesis and Characterization of CsSnI3 Thin Films. Appl. Phys. Lett. 2010, 96 (22), 221903.

15. Chen, Z.; Wang, J.; Ren, Y.; Yu, C.; Shams, K. Schottky Solar Cells Based on CsSnI3 Thin Films. Appl. Phys. Lett. 2012, 101, 093901.

16. Chung, L.; Song, J.; He, J.; Androulidakis, J.; Maltakos, C. D.; Li, H.; Freeman, A. J.; Kenney, J. T.; Kamati, M. G. CsSnI3 Semiconductor or Metal? High Electrical Conductivity and Strong Near-Infrared Photoresponse from a Single Material. High Hole Mobility and Phase-Transitions. J. Am. Chem. Soc. 2012, 134, 8579−86.

17. Xiao, Z.; Zhou, Y.; Houros, M.; Kamati, T. Intrinsic Defects in a Photovoltaic Perovskite Variant Cs2SnI6. Phys. Chem. Chem. Phys. 2015, 17, 19890−3.

18. Maughan, A. E.; Ganose, A. M.; Jhang, D. J.; Scott, K. J.; Nelson, R. J. Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors. Chem. Mater. 2019, 31, 1184−1195.
ACS Applied Energy Materials

19. Trouw, G.; Katsonis, M.; Kontos, A. G.; Stoumpos, C. C.; Tsai, T.; Kaltzoglou, A.; Guo, L.; Xue, Z.; Raptis, Y. S.; Kanatzidis, M. G.; Falaras, P. Defect Perovskites under Pressure: Structural Evolution of Cs2SnX6 (X = Cl, Br, I). J. Phys. Chem. C 2012, 116, 24004–24013.

20. Kumar, M. H.; Dharm, S.; Seo, J.; Shin, D.; Hill, I. G.; Yan, Y.; Mitzi, D. B. Thin-Film Process for Cs2SnI6 Perovskite Thin Film. J. Mater. Chem. A 2016, 4, 11214–11220.

21. Koh, T. M.; Krishnamoorthy, T.; Yantara, N.; Shi, C.; Leong, W. L.; Binn, P. P.; Grondal, A. C.; Mihaisalik, S. G.; Mathews, N. Formation of Perovskite Tin-Based Perovskite with Low Eg for Photovoltaic Applications. J. Mater. Chem. A 2015, 3 (29), 14996–15000.

22. Marshall, K. F.; Walton, R. L.; Hatton, R. A. Tin Perovskite/Fullerene Planar Layer Photovoltaics: Improving the Efficiency and Stability of Lead-Free Devices. J. Mater. Chem. A 2015, 3, 11631–11640.

23. Lee, S. J.; Shin, S. S.; Kim, Y. C.; Kim, D.; Ahn, T. K.; Noh, J. H.; Seo, J.; Seok, S. T. Fabrication of Efficient Formamidinium Tin Iodide Perovskite Solar Cells through SnF2-Pyrazine Complex. J. Am. Chem. Soc. 2016, 138, 9741–7.

24. Chan, M.; Ju, M. G.; Garces, H. F.; Carl, A. D.; Otn, L. K.; Hawash, Z.; Zhang, Y.; Shen, T.; Qiu, Y.; Gimm, R. I.; Pasic, D.; Zeng, X. C.; Zhou, Y.; Padture, N. P. Highly Stable and Efficient All-Inorganic Lead-Free Perovskite Solar Cells with Native-Oxide Passivation. Nat. Commun. 2019, 10 (1), 1–8.

25. Kue, J. C.-R.; Lewis, D. J.; Walton, A. S.; Spencer, B. F.; O’Brien, P.; Thomas, A. G.; Flavell, W. B. Ambient Air-Stable Inorganic Cs2SnI6 Double Perovskite Thin Films Via Aerosol-Assisted Chemical Vapour Deposition. J. Mater. Chem. A 2018, 6, 11205–11214.

26. Lee, B.; Stoumpos, C. C.; Zhou, N.; Hao, F.; Malliakas, C.; Yeh, C. Y.; Marks, T. J.; Kanatzidis, M. G.; Chang, R. P. Air-Stable Molecular Semiconducting Inorganic Cs2SnI6 Thin Films: Toward Inorganic Lead-Free Perovskite Solar Cells. ACS Energy Lett. 2019, 4, 10052–10055.

27. Shin, H.; Kim, B. M.; Jung, T.; Kim, K. M.; Roh, D.-H.; Nam, J. S.; Kim, J. S.; Kim, U.-Y.; Lee, B.; Pang, Y.; Koem, T.-H. Surface State-Mediated Charge Transfer of Cs2SnI6 and Its Application in Dye-Sensitized Solar Cells. Adv. Energy Mater. 2019, 9 (3), 1803243.

28. Kaltzoglou, A.; Antoniadou, M.; Kontos, A. G.; Stoumpos, C. C.; Pergantis, D.; Tsarev, V.; Psychanta, M.; Kanatzidis, M. G.; Falaras, P. Optical-Vibrational Properties of the CsSnX6 (X = Cl, Br, I) Defect Perovskites and Hole-Transport Efficiency in Dye-Sensitized Solar Cells. J. Phys. Chem. C 2016, 120, 11777–11785.

29. Chen, J.; Luo, Z.; Fu, Y.; Wang, X.; Cai, K.; Shen, S.; Guo, L.; Wright, J. C.; Pan, A.; Jin, S. Tin-IV: Tolerant Vapor-Phase Growth and Photophysical Properties of Aligned Cesium Tin Halide Perovskite (CsSnX3; X = Br, I) Nanowires. ACS Energy Lett. 2019, 4, 1045–1052.

30. Chen, L. J.; Luo, Z.; Chang, Y. J.; Wu, Z. H.; Chen, C. Synthesis and Optical Properties of Lead-Free Tin Cesium Tin Halide Perovskite Quantum Rods with High-Performance Solar Cell Application. J. Phys. Chem. Lett. 2016, 7, 5024–5035.

31. Guo, F.; Liu, Z.; Mehantsi, D.; Wang, T.; Blat, L. B.; Zhang, S.; Shi, S.; Washington, M. A.; Wang, G.-C.; Lu, T.-M. A Two-Step Dry Process for Cs2SnI6 Perovskite Thin Film. Mater. Res. Lett. 2017, 5, 540–546.

32. Saparov, B.; Sun, J.-P.; Meng, W.; Xiao, Z.; Duan, H.-S.; Gunawan, O.; Shin, D.; Hill, I. G.; Yan, Y.; Mitzi, D. B. Thin-Film Deposition and Characterization of a Sn-Deficient Perovskite Derivative Cs2SnI5. Chem. Mater. 2016, 28, 2315–2322.

33. Xiong, T.-B.; Yokoyama, T.; Aramaki, S.; Kanatzidis, M. G. Performance Enhancement of Lead-Free Tin-Based Perovskite Solar Cells with Reducing Atmosphere-Assisted Dispersible Additive. ACS Energy Lett. 2017, 2, 897–903.

34. Qu, X.; Cao, B.; Yuan, S.; Chen, X.; Qin, Z.; Jiang, Y.; Ye, Q.; Wang, H.; Zeng, H.; Lin, J.; Kanatzidis, M. G. From Unstable CsSnI5 to Air-Stable Cs2SnI6: A Lead-Free Perovskite Solar Cell Light Absorber with Bandgap of 1.48 eV and High Absorption Coefficient. Sol. Energy Mater. Sol. Cells 2017, 150, 227–234.

35. Dalla Gaspera, E.; Peng, Y.; Heu, Q.; Spiccia, L.; Buch, U.; Justenak, J. J.; Cheng, Y.-B. Ultra-Thin High Efficiency Semi-transparent Perovskite Solar Cells. Nano Energy 2015, 13, 249–257.

36. Mao, S.; Rizzon, A.; Munir, R.; Liotti, A.; Grant, A.; Esposito Corcione, C.; Trew, N. D.; Gagli, G.; Amassian, A.; Stingelin, N.; Colella, S. Organic Gelators as Growth Control Agents for Stable and Reproducible Hybrid Perovskite-Based Solar Cells. Adv. Energy Mater. 2017, 7, 1602600.

37. Eperon, G. E.; Bursakov, V. M.; Goriely, A.; Stroh, H. J. Neutral Color Semi-transparent Microstructured Perovskite Solar Cells. ACS Nano 2014, 8, 591–598.

38. Hecht, E.; Sziro, A. Optics; Addison-Wesley Pub. Co., 1974.

39. Phillips, L. J.; Rashed, A. M.; Tredarwoo, R. E.; Kay, J.; Yates, P.; Mitrovic, E. Z.; Woerlakosky, A.; Hall, S.; Durwe, K. Dispersion Relation Data for Methylammonium Lead Triiodide Perovskite Deposited on a (100) Silicon Wafer Using a Two-Step Vapour-Phase Reaction Process. Data in Brief 2015, 3, 926–928.

40. Luque, A.; Hagfeldt, A. Handbook of Photovoltaic Science and Engineering; Wiley, 2003.