Single-Source, Solvent-Free, Room Temperature Deposition of Black $\gamma$CsSnI$_3$ Films

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The presence of a nonoptically active polymorph (yellow-phase) competing with the optically active polymorph (black $\gamma$-phase) at room temperature in cesium tin iodide (CsSnI$_3$) and the susceptibility of Sn to oxidation represent two of the biggest obstacles for the exploitation of CsSnI$_3$ in optoelectronic devices. Here room-temperature single-source in vacuum deposition of smooth black $\gamma$-CsSnI$_3$ thin films is reported. This is done by fabricating a solid target by completely solvent-free mixing of CsI and SnI$_2$ powders and isostatic pressing. By controlled laser ablation of the solid target on an arbitrary substrate at room temperature, the formation of CsSnI$_3$ thin films with optimal optical properties is demonstrated. The films present a bandgap of 1.32 eV, a sharp absorption edge, and near-infrared photoluminescence emission. These properties and X-ray diffraction of the thin films confirm the formation of the orthorhombic (B-$\gamma$) perovskite phase. The thermal stability of the phase is ensured by applying in situ an Al$_2$O$_3$ capping layer. This work demonstrates the potential of pulsed laser deposition as a volatility-insensitive single-source growth technique of halide perovskites and represents a critical step forward in the development and future scalability of inorganic lead-free halide perovskites.

Pulsed laser deposition (PLD) has offered unique options for the development of complex materials thin film growth, allowing stoichiometric transfer and multicompound deposition independent of the relative volatility of the elements and ultimate control of interfaces. In the field of complex oxides, PLD opened the way to high-$T_c$ superconducting films requiring stoichiometric transfer of multiple (4–5) cations.[8] Here we present the rather unexplored but enormous potential of PLD as a unique single-source in-vacuum deposition technique of all-inorganic halide perovskites, using cesium tin iodide (CsSnI$_3$) as case example.

CsSnI$_3$ has been widely proposed in literature as a Pb-free and all-inorganic alternative to the archetypical hybrid halide solar cell absorber, CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$). The replacement of toxic Pb with Sn is a natural choice due to their similar ionic radius and lower toxicity of Sn.[9] The replacement of the organic cation (e.g., CH$_3$NH$_3$) with Cs has been proposed to enhance the thermal stability of the material.[9] While the decomposition temperature of Cs-based halide perovskites is higher than the ones containing organic cations, the size of the Cs$^+$ cation is at the limit for stability of the perovskite structure, and therefore causing phase instabilities[4–6] between the optically active (black) perovskite phase and the nonoptically active (yellow) nonperovskite phase. In CsSnI$_3$ these phases can coexist at room temperature. Black phase stabilization in all-inorganic perovskites is therefore critical to ensure their application in optoelectronic devices and has been the subject of very recent work, focused on CsPbI$_3$[7,8] and CsSnI$_3$.[9]

In terms of synthesis, solution-based processes are the most widely used techniques to fabricate these materials.[10–14] Concerns about the use of highly toxic solvents and complex device integration have recently motivated the investigation of solvent-free and vacuum-based thin film deposition processes.[11,15,16] Thermal coevaporation has been the main in-vacuum technique that enabled high quality thin film formation of a family of halide perovskites and high-efficiency devices.[11,17,18] However, the need for multiple sources due to the different volatility of the constituent elements poses a limitation for the synthesis of multication-multihalide materials and their further upscaling. Steps toward achieving a single-source deposition have sporadically been reported for laser-based techniques. This includes resonant infrared matrix assisted pulsed laser evaporation[19,20] and pulsed-laser deposition (PLD)[21–23] of MAPbI$_3$ and CsPbBr$_3$, but high material quality remains yet to
be demonstrated. An approach gaining popularity is the mechanochemical synthesis of halide perovskite powders and subsequent thin film formation following single-source vapor deposition (SSVD) of those powders.\textsuperscript{[24–26]} However, SSVD might present hurdles on the exploration of a plethora of multication-multihalides and double-perovskites due to differing volatilities, i.e., off-stoichiometric transfer and/or sticking.

Here we present single-source room temperature PLD of CsSnI\textsubscript{3} thin films with excellent optical properties achieved by the formation of the orthorhombic black (B-\textit{γ}) perovskite phase. This work introduces PLD as an enabling technology to achieve near-stoichiometric transfer of all-inorganic halide perovskites in vacuum, opening the path for controlled and reproducible growth as well as ease of integration in devices from photovoltaics to more complex architectures such as integrated photonics.

Figure 1 summarizes the fabrication process of the solid PLD target. Equimolar amounts of CsI and SnI\textsubscript{2} source powders were mixed by ball-milling in an Ar-filled vessel. We note that the mixing is done only by rotation of the cylindrical vessel containing the powder and ZrO\textsubscript{2} balls, and therefore is different from the known mechanochemical synthesis.\textsuperscript{[26]} To ensure a uniform mixture of the powders, the mixing process was left running for 3 d. The enhanced uniformity of the Cs, Sn, and I elemental distribution on the target with increasing mixing time was confirmed by energy-dispersive X-ray spectroscopy (Figure S1 and Table S1, Supporting Information). The mixed powders were then pressed into a 2 cm diameter disk-shaped pellet using a uniaxial press and subsequently exposed to an isostatic pressure of 360 MPa using a hydraulic press. A similar procedure has been applied 33 MPa and hydraulic press applying 360 MPa isostatically, and final target.

The target was loaded into the PLD chamber, which was then evacuated to a base pressure of \( \approx 1 \times 10^{-7} \) mbar. CsSnI\textsubscript{3} thin films were deposited onto Si (with native SiO\textsubscript{2}), fused silica, and glass substrates at room temperature using a KrF (248 nm) laser and a fluence of 0.2 J cm\textsuperscript{-2}. The growth rate was 0.05 nm per pulse such that for a laser repetition frequency of 5 Hz, the total duration to grow 100 (200) nm CsSnI\textsubscript{3} was only 400 (800) s. An Ar working pressure of \( 1.3 \times 10^{-3} \) mbar was kept constant during deposition and no additional reactive gasses were introduced. Following CsSnI\textsubscript{3} deposition, an amorphous Al\textsubscript{2}O\textsubscript{3} capping layer was applied in situ by PLD. Steady-state photoluminescence (PL) spectra and absorption coefficient measurements were performed on 100 nm thick PLD-grown CsSnI\textsubscript{3} films on fused silica substrates (Figure 2). The PL emission is centered at 1.38 eV (900 nm). Consistently, the absorption coefficient determined by photothermal deflection spectroscopy (PDS) shows a sharp absorption edge centered at 1.32 eV. The absorption coefficient is shown with a solid black line and for comparison, the absorption coefficient (also determined by PDS) of a reference methylammonium lead halide (MAPbI\textsubscript{3}) perovskite film\textsuperscript{[28]} is shown with a dashed black line. These results highlight the high absorption coefficient at the whole visible spectral range and sharp edge, indicating a high quality absorber material, comparable to MAPbI\textsubscript{3}\textsuperscript{[28]}.

In order to extract the Urbach energy, the absorption spectrum was calculated from the PL spectrum at the band edge area via the reciprocal relation.\textsuperscript{[29]} Individually, this recalculated absorption spectra and the absorption coefficient measured by PDS both confirm an Urbach energy of 12.9 meV for the PLD grown CsSnI\textsubscript{3} films. This is only 0.4 meV higher that of MAPbI\textsubscript{3} (12.5 meV) determined by the same methods. Such a low Urbach energy indicates potential for low voltage losses in the optimized solar cell.\textsuperscript{[10]}

A bandgap of 1.32 eV extracted from the Tauc plot (Figure S3, Supporting Information) and the aforementioned optical

**Figure 1.** Illustration of PLD target fabrication process. From left to right: Stoichiometric mixture of CsI and SnI\textsubscript{2} powders, ball milling, uniaxial press applying 33 MPa and hydraulic press applying 360 MPa isostatically, and final target.

**Figure 2.** Absorption coefficient (left axis) and steady state PL (right axis) of 100 nm CsSnI\textsubscript{3} PLD grown films. To highlight the sharp absorption edge of the CsSnI\textsubscript{3}, the absorption coefficient of a reference MAPbI\textsubscript{3} film is presented.
properties are characteristics of the black orthorhombic phase of CsSnI$_3$ (B-$\gamma$-CsSnI$_3$). The formation of polycrystalline B-$\gamma$-CsSnI$_3$ thin films is confirmed by XRD. Figure 3 displays the XRD patterns of the target and the thin films shown in this paper. Panel (a) indicates that the target is an unreacted mixture of CsI and SnI$_2$ powders, whereas panel (b) demonstrates that thin films grown from this target by PLD at room temperature crystallize in the perovskite structure and very well match the reference pattern of B-$\gamma$-CsSnI$_3$ following reference. No difference between thin (100 nm) and thicker films (200 nm) was noticed, indicating that the B-$\gamma$-CsSnI$_3$ phase remains stable with doubled thickness (solid lines in Figure 3b). The dashed lines in Figure 3b are measurements taken four months ($\approx$ 3000 h) after fabrication of the films, where the films were stored in a glove box filled with argon gas, demonstrating that the B-$\gamma$-CsSnI$_3$ phase of both film thicknesses remains stable even months after thin film fabrication. After these XRD measurements the same films were kept in open air for 72 h, measured again, and still showed no structural changes (dotted lines in Figure 3b). The Al$_2$O$_3$ capping layer with a thickness of 13 and 40 nm for the 100 and 200 nm thick CsSnI$_3$ films, respectively, is amorphous and therefore not present in the XRD spectra. Information about thin films grown from targets with different mixing times is found in Figure S2 in the Supporting Information.

Figure 3. a) X-ray diffraction (XRD) pattern of the solid PLD target shown in Figure 1. b) XRD patterns of 100 and 200 nm thick CsSnI$_3$ films deposited at room temperature by PLD. The solid lines are measurements directly after the deposition, the dashed lines after 3000 h in Ar atmosphere, and the dotted lines after additional 72 h in air. For comparison, the same B-$\gamma$-CsSnI$_3$ reference spectrum is plotted below in both graphs. The plots indicate that while the source target does not present the CsSnI$_3$ phase but a mixture of the CsI and SnI$_2$ powders, the resulting thin films present the single black orthorhombic phase of CsSnI$_3$, which is stable over long time thanks to the Al$_2$O$_3$ capping layer.

Scanning transmission electron microscopy (STEM) results (Figure 4) confirm uniform sticking of the ablated elements and the formation of a smooth and dense film with large elongated grains along the thickness of the film (Figure 4a). Zoomed-in area of Figure 4a with enhanced contrast is shown in Figure S5

Figure 4. a) Cross-section bright-field TEM image of a PLD-grown B-$\gamma$-CsSnI$_3$ film on Si. The image shows the formation of a dense film with elongated crystalline grains. b–g) High-angle annular dark-field (HAADF) image and EDX mapping of the constituent elements of CsSnI$_3$ and the Al$_2$O$_3$ capping layer. EDX confirms uniform distribution of Cs, Sn, and I along the thickness of the layer and conformal coating of the Al$_2$O$_3$ capping layer.
in the Supporting Information. The distribution of cesium (Cs), tin (Sn), and iodide (I) in the films was evaluated by cross-section energy-dispersive X-ray spectroscopy (EDX) mapping (Figure 4b–d). The EDX maps show a uniform distribution of the three elements across the thickness of the film and quantitative analysis indicate an overall Cs/Sn ratio of 1. Combining Rutherford back scattering (RBS) and particle induced X-ray emission (PIXE), we determined an iodide content in the films of ≈65 at% (Figure S4, Supporting Information). Figure 4f also shows conformal coating and uniformity of the amorphous Al2O3 protective layer. The low roughness of the CsSnI3 + capped Al2O3 films was furthermore confirmed by atomic force microscopy (Figure S6, Supporting Information).

Concluding, we have demonstrated the feasibility of single-source in-vacuum deposition of B-γ-CsSnI3 films by PLD. The high optical quality of the films and black phase confirmation by optical and structural characterization shows the enormous potential of PLD for the single source growth of halide perovskites even at room temperature. In comparison with recently reported SSVD, PLD presents the advantage of nonequilibrium ablation of a solid target, therefore allowing near-stoichiometric transfer insensitive to the different volatilities of the elements. Another demonstrated advantage of PLD is the possibility of depositing multilayers without breaking vacuum, in this case the application of the Al2O3 layer allowing the stabilization of the black phase and protection against oxidation. This work motivates further exploration of the electrical properties of the material as well as its integration in complex devices, such as absorbers in solar cell devices, monolithic tandem solar cells or efficient light emitters in integrated photonic circuits.

**Experimental Section**

**Target Source Materials:** CsI and SnI2 source powders were purchased from Sigma-Aldrich (99.9% purity) and TCI (>97.0% purity). For the Al2O3 deposition, an Al2O3 single crystal with rough surfaces to enhance laser absorption was used as source target.

**PLD:** The vacuum chamber was evacuated to a base pressure of ≈1 × 10−7 mbar. A KrF (248 nm) laser was used to ablate the fabricated CsSnI3 target. Thin films were deposited onto Si (with native SiO2) fused silica, and glass substrates at room temperature. An Ar working pressure of 1.3 × 10−3 mbar was kept constant during deposition and no additional reactive gases were introduced. The laser frequency was kept at 5 Hz, target-to-substrate distance at 50 mm, and a fluence of 0.2 J cm−2 was used. The deposition of the Al2O3 capping layer was performed under Ar atmosphere and room temperature as the CsSnI3 film. Al2O3 is a large bandgap material (~7 eV) with insignificant absorption in the measured spectral region, therefore, the measured optical properties are unaffected by the Al2O3 thin film.

**PDS:** Photothermal deflection spectroscopy directly measures the optical absorption of thin films with sensitivity of up to four orders of magnitude. The light absorption is determined via a sample heating effect, by measuring the deflection of a probe laser beam with a position-sensitive detector. The PDS spectrophotometer uses a 150 W Xe lamp as a light source and a monochromator equipped with grating blazed at 750 nm operating in a broad spectral range from ultraviolet to infrared region 400–1200 nm.

**PL:** Photoluminescence spectra are measured using an excitation laser at 442 nm in a Renishaw in-Via REFLEX spectroscopy. The intensity of the excitation light is reduced in order to prevent any structural degradation during measurements.

**Concluding:**

The authors declare no conflict of interest.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

V.M.K. and Y.A.B. contributed equally to this work. The authors acknowledge Frank Roesthuis for support with the PLD system, Mark Smithers for high-resolution scanning electron microscopy, and Max Dobeli for RBS and PIXE measurements. M.M.-M. acknowledges the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (CREATE, Grant Agreement Number 852722) and UTWIST program of the University of Twente. M.L. acknowledges the support of Czech Science Foundation Project No. 17-26041Y.

**Keywords**

halide perovskites, laser ablation, lead-free perovskites, single-source in vacuum deposition, solvent-free deposition

Received: January 31, 2020
Revised: March 17, 2020
Published online:
V. Dyadkin, D. Chernyshov, V. Van Speybrouck, E. H. Sargent, J. Hofkens, M. B. J. Roelfsers, Science 2019, 365, 679.
[8] D. B. Straus, S. Guo, R. J. Cava, J. Am. Chem. Soc. 2019, 141, 11435.
[9] I. Chung, J.-H. Song, J. Im, J. Androulakis, C. D. Malliakas, H. Li, A. J. Freeman, J. T. Kenney, M. G. Kanatzidis, J. Am. Chem. Soc. 2012, 134, 8579.
[10] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, Nano Lett. 2015, 15, 3692.
[11] W. A. Dunlap-Shohl, Y. Zhou, N. P. Padture, D. B. Mitzi, Chem. Rev. 2019, 119, 3193.
[12] Q. Tai, K.-C. Tang, F. Yan, Energy Environ. Sci. 2019, 12, 2375.
[13] F. Liu, C. Ding, Y. Zhang, T. S. Ripolles, T. Kamisaka, T. Toyoda, S. Hayase, T. Minemoto, K. Yoshino, S. Dai, M. Yanagida, H. Noguchi, Q. She, J. Am. Chem. Soc. 2017, 139, 16708.
[14] J.-P. Correa-Baena, M. Saliba, T. Buonassisi, M. Grätzel, A. Abate, W. Tress, A. Hagfeldt, Science 2017, 358, 739.
[15] M. Chen, M.-G. Ju, H. F. Garces, A. D. Carl, L. K. Ono, Z. Hawash, Y. Zhang, T. Shen, Y. Qi, R. L. Grimm, D. Pacifici, X. C. Zeng, Y. Zhou, N. P. Padture, Nat. Commun. 2019, 10, 16.
[16] Z. Hong, D. Tan, R. A. John, Y. K. E. Tay, Y. K. T. Ho, X. Zhao, T. C. Sum, N. Mathews, F. García, H. S. Sos, iScience 2019, 16, 312.
[17] J. Ávila, C. Momblon, P. P. Boix, M. Sessolo, H. J. Bolink, Joule 2017, 1, 431.
[18] Z. Li, T. R. Klein, D. H. Kim, M. Yang, J. J. Berry, M. F. A. M. van Hest, K. Zhu, Nat. Rev. Mater. 2018, 3, 18017.
[19] E. T. Barraza, W. A. Dunlap-Shohl, D. B. Mitzi, A. D. Stiff-Roberts, J. Electron. Mater. 2018, 47, 917.
[20] W. A. Dunlap-Shohl, E. T. Barraza, A. Barrette, K. Gundogdu, A. D. Stiff-Roberts, D. B. Mitzi, ACS Energy Lett. 2018, 3, 270.
[21] U. Bansode, R. Naphade, O. Game, S. Agarkar, S. Ogale, J. Phys. Chem. C 2015, 119, 9177.
[22] Y. Huang, L. Zhang, J. Wang, B. Zhang, L. Xin, S. Niu, Y. Zhao, M. Xu, X. Chu, D. Zhang, C. Qu, F. Z. Zhao, Opt. Lett. 2019, 44, 1908.
[23] H. Wang, Y. Wu, M. Ma, S. Dong, Q. Li, J. Du, H. Zhang, Q. Xu, ACS Appl. Energy Mater. 2019, 2, 2305.
[24] Y. El Ajjouri, F. Palazon, M. Sessolo, H. J. Bolink, Chem. Mater. 2018, 30, 7423.
[25] M. J. Crane, D. M. Kroupa, J. Y. Roh, R. T. Anderson, M. D. Smith, D. R. Gamelin, ACS Appl. Energy Mater. 2019, 2, 4560.
[26] F. Palazon, Y. El Ajjouri, H. J. Bolink, Adv. Energy Mater. 2020, 10, 1902499.
[27] B. Yang, W. Pan, H. Wu, G. Niu, J.-H. Yuan, K.-H. Xue, L. Yin, X. Du, X.-S. Miao, X. Yang, Q. Xie, J. Tang, Nat. Commun. 2019, 10, 1989.
[28] S. De Wolf, J. Holovský, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum, C. Ballif, J. Phys. Chem. Lett. 2014, 5, 1035.
[29] D. E. McCumber, Phys. Rev. 1964, 136, A954.
[30] M. Ledinsky, T. Schöpfeldová, J. Holovský, E. Aydin, Z. Hájková, L. Landová, N. Neyková, A. Fejar, S. De Wolf, J. Phys. Chem. Lett. 2019, 10, 1368.