Organic-free indium-doped cesium lead iodide perovskite for solar cell application

Govindhasamy Murugadoss[1,2] ✉, Rangasamy Thangamuthu[2], Manavalan Rajesh Kumar[3], Ramamoorthy Ravishankar[4]

[1]*Centre for Nanoscience and Technology, Sathyabama Institute of Science and Technology, Chennai 600119, Tamilnadu, India*
[2]*Materials Electrochemistry Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630 003, Tamilnadu, India*
[3]*Institute of Natural Science and Mathematics, Ural Federal University, Mira 19, Yekaterinburg, Russia*
[4]*CIF Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630 003, Tamilnadu, India*
✉ *E-mail: murugadoss_g@yahoo.com*

Herein, organic-free all-solid-state based perovskite solar cells (PSCs) are successfully fabricated by one-step method. The absorption position of the non-perovskite cesium lead iodide (δ-CsPbI$_3$) was significantly shifted towards longer wavelength side by substituting indium (In) ion with different stoichiometric ratio. The authors demonstrated a facile route to achieve high efficiency by the fabrication of room temperature stable mixed-phase CsPbI$_3$ perovskite. Photovoltaic efficiency of doped perovskite is four times increased compared to pure yellow phase CsPbI$_3$. To the best of the authors' knowledge, this is the first demonstration of In-doped-CsPbI$_3$ based PSCs, which was fabricated under completely open-air atmosphere.

1. Introduction: In recent years, organic–inorganic lead halide perovskite solar cells (PSCs) have stunned the photovoltaic field, given the tremendous research interest in them, owing to the unique combination of their high performance and the low-cost fabrication process. The hybrid PSCs have attracted tremendous interest in the last six years with rapid progress in power conversion efficiencies from 3.8% to the present record of 22.1% [1–3]. The best efficiencies that have been recorded with these perovskite materials use a general formula such as AMX$_3$, where A is the organic component cation as methylammonium (MA$^+$) and formamidinium (FA$^+$), M is the metal cation (Pb) and X corresponds to the halide (I) or a mixture of halides (Cl, Br, I) anions. To date, the organic cation based MAPbI$_3$ and FAPbI$_3$ PSCs only reached high efficiency. However, one of the concerns that need to be addressed is the stability of the organic cations. The organic cations such methylammonium iodide (MAI) and formamidinium iodide (FAI) are highly moisture sensitive, because of this issue, the high-efficiency PSC still fabricated only within the clove box with inert atmosphere to protect moisture [4]. To completely remove the unstable organic component and maximally enhance the thermal stability, all-inorganic based PSCs with photoactive black phase cesium lead iodide (α-CsPbI$_3$) were successfully achieved under air-free conditions by Snaith *et al.* and the working PVs showed a preliminary PCE of 2.9% [5]. So far, various metal cations such as Sn, Bi, Ge, and Sb were used as an alloy and dopant in CsPbI$_3$ [6]. Recently, a small amount of hydro-iodic acid (HI) induced microstrain in the crystal lattice was believed to be the major reason for the stabilisation of α-CsPbI$_3$ at room temperature. Hence, we hypothesised that partially substituting Pb^{2+} (1.19 Å) with a smaller cation also could cause the lattice distortion to produce microstrain in the crystal lattice and stabilise the α-CsPbI$_3$ at room temperature [7]. Herein, we attempt to stabilise the α-CsPbI$_3$ at room temperature by partial substitution of the B-site of perovskite with 'In' ion for the first time. Furthermore, we found that by processing the material in a totally ambient environment resulted in stable perovskite. Optical and structural properties are investigated for different concentrations of the 'In' doped CsPbI$_3$ perovskite. Organic-free lead halide In-doped with Cs based PSCs (CsPb$_{1−x}$In$_x$I$_3$) fabricated on mesoporous TiO$_2$ (mp-TiO$_2$) as scaffold layer using CuSCN HTM, and the photovoltaic study was performed.

2. Experimental

2.1. Device fabrication: TiO$_2$ nanoparticles (20 nm, dyesol) were dispersed into absolute ethanol and spin-coated (4000 rpm, 30 s) onto a substrate with the architecture SnO$_2$:F (FTO) conductive glass (15 Ω cm^{-1}, Pilkington) coated with a compact TiO$_2$ layer (TiDIP 0.39 M in 2-propanol, Aldrich). CsPbI$_3$ was deposited by the one-step method. 1:1 molar ratio of PbI$_2$ and CsI were dissolved into DMF (Aldrich, 99.8%) and then spin-coated by sequential deposition at 2000 rpm and then 4000 rpm as shown in Fig. 1*a* and architecture of the fully inorganic solar cells is schematically shown in Fig. 1*b*. 300 μl of chlorobenzene was dripped (before end of the 8 s) on the film during spin coating. The entire perovskite film fabrication process was performed in the ambient atmosphere with ∼60% humidity. After spin coating, CuSCN was deposited by doctor blade technique. Propylsulphide used as solvent for CuSCN with 8 mg/ml concentration. Finally, gold (50 nm) was deposited by thermal evaporation at 10^{-6} Torr as contacts.

2.2. Characterisation: The X-ray diffraction (XRD) spectra of CsPbI$_3$ film on FTO plate was recorded using a PW 3040/60 X'pert PRO with Cu ka radiation. UV/visible (UV/vis) absorption spectra were obtained in a Hitachi (Model U-4100) UV/vis NIR spectrophotometer. Surface morphology and the cross-sectional view of the MAPbI$_3$ and ⟨FTO/c-TiO$_2$/m-TiO$_2$/MApbI$_3$/In/CuSCN/Au⟩ device architecture were performed using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6380LV). Photocurrent–voltage (*J–V*) measurement for the PSCs was performed under AM 1.5 sun irradiation (100 mW/cm^2) using a 100–220 W small beam simulator (Photo Emission Tech., Inc., model SS80AAA) with a cell's area of 0.25 cm^2.

3. Results and discussion: Fig. 2*a* shows the XRD spectra of pure and doped CsPbI$_3$ perovskite. The pure CsPbI$_3$ shows the absolute yellow phase. However, the yellow phase was changed by doping of 'In' ions. The yellow phase CsPbI$_3$ prepared without adding Indium ion showed characteristic peaks of orthorhombic structure with a space group of *Pnma*. With an increase in 'In' content in the films, strong diffraction peaks of (0 1 2), (1 1 2), (0 1 4) and (1 2 2) planes of the orthorhombic phase gradually decreased, and (1 0 0), (1 1 0), (1 1 1), (2 0 0) and (2 1 1) peaks of cubic
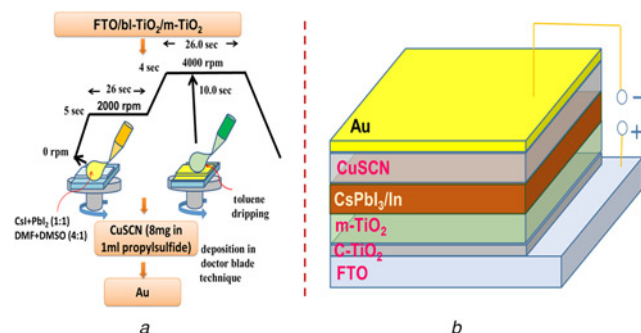
Fig. 1 *Fabrication procedure and device structure of the PSC*
a Schematic illustration of CsPbI₃ film deposition
b Device structure of the In-doped CsPbI₃ PSCs

Fig. 2 *XRD pattern, UV absorption and band gap plot*
a XRD spectra of pure and various concentrations of In-doped perovskite film on glass
b, *c* UV–vis absorption spectra and corresponding energy bandgap plot of the samples

phase emerged, which clearly demonstrating the phase transition from the δ-phase to α-phase. Moreover, a strong diffraction peak showed at 12.9°, which corresponds to unreacted PbI₂ [8]. All perovskite films were annealed only at 160°C, but the black perovskite phase (α-CsPbI₃) is normally stable above 300°C and shows the desired photovoltaic behaviour. The crystal structure of orthorhombic perovskite phase is similar to the ideal cubic phase, where PbI₆ octahedra are slightly distorted and corner-shared in three dimensions. The low temperature processed 'In' doped CsPbI₃ perovskite thin-film shows the mixed phase of orthorhombic and cubic structure until the higher doping concentration of 25%. However, the diffraction peaks of δ-phase were noticeably reduced with increasing diffraction intensity of α-phase for the $CsPb_{0.80}In_{0.20}I_3$ composition. Because of the smaller radius of In^{3+} (0.94 Å) compared to Pb^{2+} (1.19 Å), partial substitution can increase the tolerance factor from 0.81 (α-CsPbI₃) to 0.84 ($CsPb_{0.80}In_{0.20}I_3$) for the mixed phase, which is beneficial to improve the stability. Under our experimental conditions, the $CsPb_{0.80}In_{0.20}I_3$ composition was selected as an optimum level.

The optical properties of orthorhombic (δ-CsPbI₃) and mixed-phase of orthorhombic–cubic (δ–α phase) thin films with different concentrations of 'In' doped CsPbI₃ layers were characterised by the absorption spectra. Figs. 2*b* and *c* show the absorption and corresponding bandgap curves (Tauc plots) of the samples. The absorption onset shows for undoped CsPbI₃ (Fig. 2*b*) at around 470 nm, corresponding bandgap of 2.62 eV (Fig. 2*c*). The higher bandgap with longer wavelength confirms yellow phase of CsPbI₃; the low range absorption is insignificant for photovoltaic application. However, the absorption was tuned towards long wavelength by doping indium ion with various concentrations. When introducing 'In' ion from 0.05 to 0.25 stoichiometric ratio, the absorption wavelength is significantly shifted towards longer wavelength side about 70 nm. The absorption shifting indicates a phase change of δ-CsPbI₃ to α-CsPbI₃ by doping the 'In' ions. However, a black α-CsPbI₃ exhibited the absorption in the visible light region, extending up to ~730 nm with band gap of 1.70 eV [9]. Hence, the obtained optical result revealed that phase transition was not completely occurred from orthorhombic to cubic phase; it formed only a mixed structure. However, the observed significant shifting in absorption as mentioned above can be used as photoactive materials in solar cells.

To confirm the benefits of 'In' substitution on device performance, FTO/c-TiO₂/mp-TiO₂/CsPb₁₋ₓInₓI₃/CuSCN/Au photovoltaic devices were fabricated. The device fabrication and device performance were done in an ambient air atmosphere. Surface image of CsPbI₃ with different magnifications and cross-sectional image of the ⟨FTO/c-TiO₂/mp-TiO₂/$CsPb_{0.80}In_{0.20}I_3$/CuSCN/Au⟩ are shown in Figs. 3*a*–*c*, respectively. The surface morphology of CsPbI₃ shows full coverage with the homogenous growth of the mesoporous TiO₂ layer. Fig. 3 and Table 1 show the current
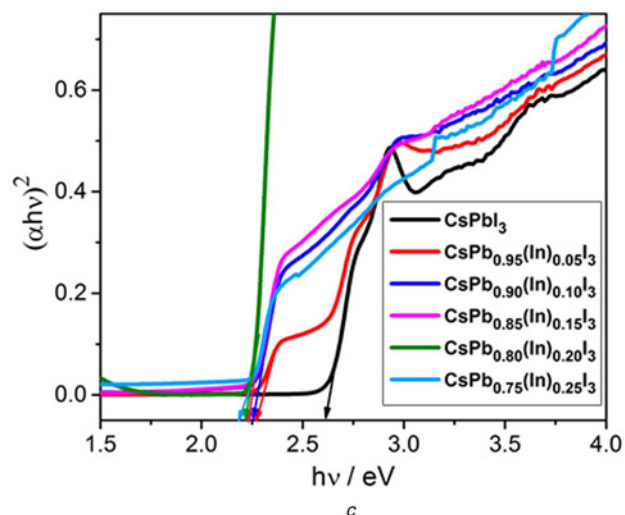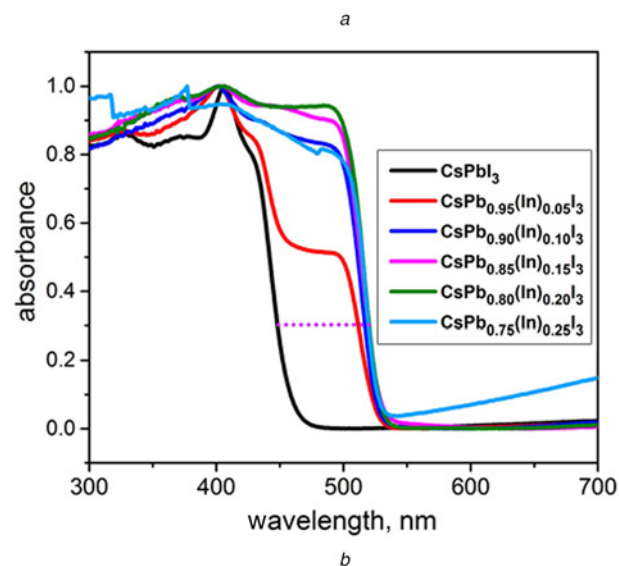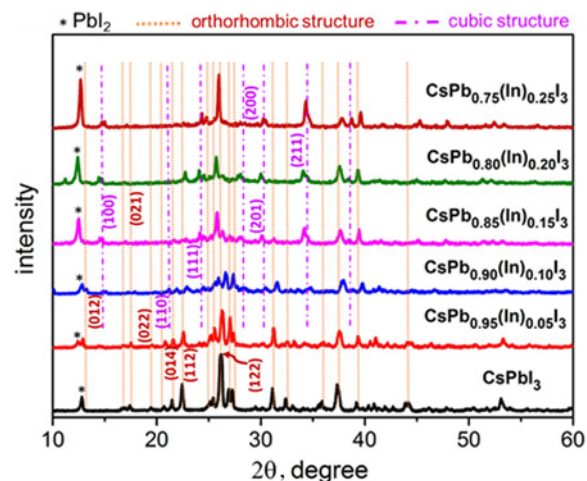
density–voltage curve and the photovoltaic parameters of the devices. The photovoltaic study was performed for all the concentrations of 'In' incorporated perovskite. Using precursors with 20% 'In' substitution ($CsPb_{0.80}In_{0.20}I_3$), the resultant devices gave the
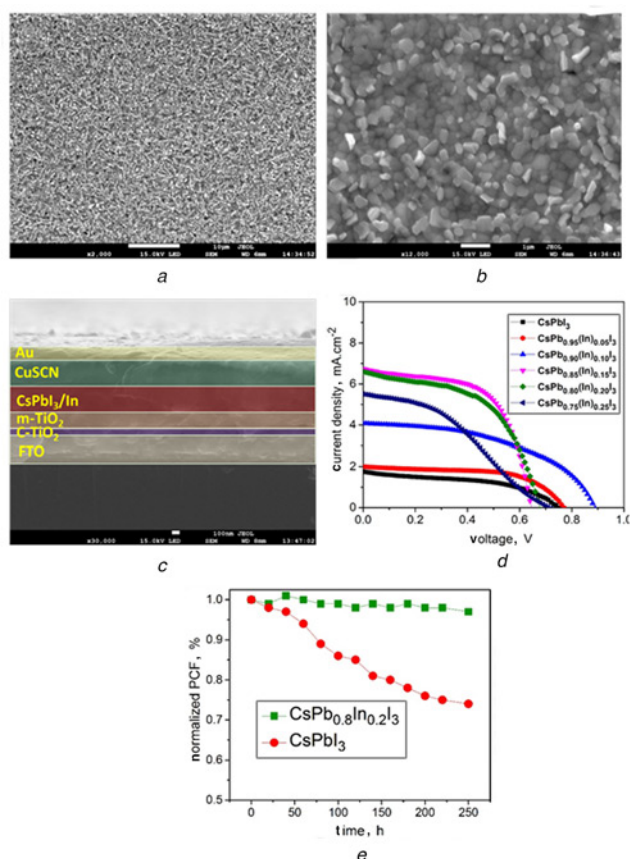
Fig. 3 *FE-SEM images of surface view of perovskite layer, cross-sectional view of device, I-V curves and stability result*
a, *b* Surface images of $CsPb_{0.80}In_{0.20}I_3$ perovskite film with different magnifications
c Cross-sectional view of the device. The scale bar represents 100 nm
d J–V curves of pure and various concentrations of In-doped $CsPbI_3$ perovskite
e Stability results of the device for 250 h under a similar measurement condition

Table 1 Photovoltaic result of pure and different concentration of In-doped $CsPbI_3$ perovskite

Perovskite	Jsc, mAcm^{-2}	Voc, V	FF	Efficiency, %
$CsPbI_3$	1.7	0.75	0.47	0.62
$CsPb_{0.95}In_{0.05}I_3$	2.0	0.77	0.60	0.92
$CsPb_{0.90}In_{0.10}I_3$	4.1	0.88	0.46	1.74
$CsPb_{0.85}In_{0.15}I_3$	6.6	0.67	0.53	2.39
$CsPb_{0.80}In_{0.20}I_3$	6.7	0.64	0.60	2.61
$CsPb_{0.75}In_{0.25}I_3$	5.5	0.71	0.36	1.44

best performance of 2.61%. Without 'In' substitution, the reference devices have photon to current conversion efficiency (PCE) of only 0.62%. The significant improvement in PCE in In-incorporated devices comes from the improved Jsc and FF due to phase changes and good surface coverage. The PCE results confirm that lower and higher concentrations 'In' in the precursor are insufficient to bring about any benefits and results in poorer device performance. The solar cells were stored in ambient atmosphere at

room temperature without encapsulation and measured every day for over 250 h under one sun illumination, and the corresponding PCEs changes were plotted as shown in Fig. 3*e*. Compared to the pure $CsPbI_3$, In-doped CsPbI3 solar cells show high stability. The increasing stability of the doped PSCs is due to dual performance of the In ions, tuning optical absorption and stability. Luo *et al.* recently reported an efficient $CsPbI_3$ cell with a PCE of 4.13% by employing mesoporous structure and adding organic-based Spiro-OMeTAD HTM [10]. Thus, we can continue to improve solar cell performance by using different device structures and/or optimising the electron transport and hole transport layers in future work.

4. Conclusion: In summary, we have proved for the first time that the incorporation of 'In' in $CsPbI_3$ could partially develop α-phase along with δ-phase at room temperature. We also demonstrated that the mixed-phase is suitable for the fabrication of all-inorganic based PSCs with reasonable PCE. At an optimal condition ($CsPb_{0.80}In_{0.20}I_3$), PSCs with CuSCN as the HTM demonstrated PCE of 2.61%. Further research will help to identify the exact mechanism of stabilisation and the incremental role of Sn-replacing. The result here reported could have an important implication to obtain less-Pb perovskite materials with enhancement of efficiency and stability.

6 References

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