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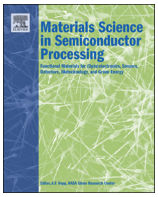

Recrystallization and phase stability study of cesium tin iodide for application as a hole transporter in dye sensitized solar cells

Lekha Peedikakkandy [a], Parag Bhargava [b,*]

[a] *Centre for Research in Nanotechnology and Science, Indian Institute of Technology, Bombay 400076, India*
[b] *Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay 400076, India*

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A B S T R A C T

In this work, we report synthesis and stability analysis of cesium tin iodide ($CsSnI_3$) prepared through solid state and solution route methods for its application as a hole transport layer in dye sensitized solar cells (DSSC). Phase formation, chemical stability and degradation mechanism of $CsSnI_3$ were studied using X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Optical band gap of the material was studied using UV–vis spectroscopy and photoluminescence studies. $CsSnI_3$ synthesized through solid state route was used as a hole transport material (HTM) for dye sensitized solar cells with cell efficiency up to 3%. Temperature dependent excitonic emission studies shows that B-γ-$CsSnI_3$ shows a linear increase in band gap with increasing temperature.

1. Introduction

$CsSnI_3$ belongs to a class of semiconducting perovskites of the composition $CsSnX_3$ (X=Cl, Br, I or mixed halides) first reported to be synthesized in 1926 by Karantassis [1–3]. Tri-iodide of this compound ($CsSnI_3$), because of its optical and electronic properties, has generated a lot of interest for its application in dye sensitized solar cells (DSSCs), Schottky solar cells and other optoelectronic devices [2,5–8]. At room temperature, two polymorphs of $CsSnI_3$ are reported: a one-dimensional double-chain structure which is yellow in color (Y-$CsSnI_3$) and the second polymorph has a three-dimensional perovskite structure and is black in color (B-$CsSnI_3$). The orthorhombic black polymorph, B-γ-$CsSnI_3$ (space group Pnma), is the material of interest for application in optoelectronic devices because of its high p-type metal-like conductivity (200 S cm^{-2}) and high hole mobility (585 $cm^2\,V^{-1}\,s^{-1}$) at room temperature. B-γ-$CsSnI_3$ has a direct band gap of ~1.3 eV and strong near-infrared photoluminescent emission at 950 nm [2–5]. $CsSnI_3$ undergoes a series of phase changes from cubic (152 °C) to tetragonal phase (77 °C) and orthorhombic phase upon gradual cooling to room temperature and at room temperature two polymorphs of $CsSnI_3$ exist, metastable B-$CsSnI_3$ and Y-$CsSnI_3$. Scaife and Yamada reported the earliest study on the phase change and structural information of $CsSnI_3$ compounds [2,3,5].

DSSC is a cheaper alternate for the conventional semiconductor solar cells, but durability of DSSC remains an issue due to the use of iodine based corrosive liquid electrolyte. To solve this problem and make DSSCs commercially viable several solid and semi-solid hole transport materials were used in lieu of corrosive liquid electrolytes [5]. Kanatzidis et al. replaced the liquid electrolyte with an inorganic hole transport material, $CsSnI_3$, that can be deposited as a liquid and ends up as solid hole transport layer as the solvent dries

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* Corresponding author. Tel.: +91 22 25767628.
E-mail address: pbhargava@iitb.ac.in (P. Bhargava).

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off, with cell conversion efficiencies up to 10.2% [5]. One of the interesting properties of $CsSnI_3$ for its application as hole transport material (HTM) in DSSC is its solubility in polar organic solvents allowing for better permeation into the porous titania matrix and thus improving hole transport between dye and HTM layer. One of the reasons reported for low performance of other organic (e.g.: spiro-OMeTAD) and inorganic (e.g.: NiO, CuSCN, CuI) HTMs is poor pore filling of mesoporous titania photo-anode in DSSC leading to inefficient hole transport between dye and HTM [5,7]. The solubility of inorganic $CsSnI_3$ in organic solvents makes it penetrate easily into the titanium oxide pores. When dried, the compound recrystallizes forming an intimate contact with the dye molecules allowing for better hole conduction. These properties along with high hole mobility in $CsSnI_3$ make it an excellent replacement of liquid electrolytes for solar cell applications.

The dissolution and recrystallization of $CsSnI_3$ as conducting B-γ-$CsSnI_3$ phase are crucial for its application as an HTM in DSSC. The chemical stability of conducting B-γ-$CsSnI_3$ under ambient conditions remains to be understood [5,8]. A better understanding of phase changes and degradation mechanism of B-γ-$CsSnI_3$ under ambient conditions is crucial for its application in opto-electronic devices. The present study reports, synthesis, stability and recrystallization analysis of $CsSnI_3$ prepared using two different routes – solid state and solution route for its application as HTM in DSSCs.

2. Experimental

2.1. Synthesis and characterization

As a first steps towards solid state reaction synthesis of $CsSnI_3$, a stoichiometric mixture of CsI (99.999%, Sigma-Aldrich) and SnI_2 (99.99%, Sigma-Aldrich) was sealed in a quartz tube which was evacuated at 10^{-6} Torr vacuum. The sealed glass tube was annealed at 550 °C for 30 min followed by cooling down to room temperature in 6 h [2,3,5]. The precursors melt to form a shiny black ingot which was taken out by breaking the glass tube and was ground into powder using mortar and pestle. Synthesized $CsSnI_3$ was processed under glove box conditions. For solution route synthesis, 0.05 mole of CsI powder was added to 30 g of deionized water to form a CsI solution which was mixed with 0.02 mole of $SnCl_2$ powder (99.99%, Aldrich) in 20 g of anhydrous ethanol. Phase formation, possibly $CsSnI_3$, was observed immediately as black grains in solution. The formed black crystals were washed and stored inside the glove box and were further characterized. Structure and composition of prepared $CsSnI_3$ were studied using X-ray diffraction (XRD), Raman spectroscopy and Energy-dispersive X-ray spectroscopy (EDS). Band gap of the material was estimated from the diffuse reflectance spectroscopy using Kubelka–Munk equation. Photoluminescence (PL) spectra of prepared $CsSnI_3$ were measured at 514 nm excitation wavelength. To study temperature dependence of excitonic band gap, PL spectra were recorded by varying sample temperatures from 470 to 100 K. $CsSnI_3$ as recrystallized from different solvents was also studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2.2. Preparation of dye sensitized solar cells (DSSC) with $CsSnI_3$ as HTM

$CsSnI_3$ prepared through a solid state reaction method and solution route was used as a hole transport layer replacing the liquid iodine/tri-iodide redox couple in DSSCs. For making DSSC, fluorine doped tin oxide (FTO ~ 10 Ω/square) glass substrates were cleaned by ultra-sonication in soap solution, distilled water and iso-propyl alcohol and was dried in a hot air oven. To prepare the photoanode, titania paste (P20, Dyesol) was doctor bladed on to the FTO substrates and annealed at 500 °C for one hour. Titania photoanodes were dipped in 0.3 mM ethanolic solution of dye, cis-bis(4,4′-dicarboxy-2,2′-bipyridine)-bis(isothiocyanato)ruthenium(II) (N3 dye, Solaronix) for 12 h and was washed with ethanol to remove the excess dye. Counterelectrode was prepared by sputter coating Pt on to the FTO glass substrate. Dye sensitized titania photo-anode and Pt coated counterelectrode were assembled with a spacer of 60-μm thickness (Solaronix). Performance of cells prepared with $CsSnI_3$ as the solid HTM was compared with cells prepared using liquid electrolyte (0.5 M LiI, 0.05 M of I_2, in a solution of acetonitrile and tert-butylpyridine). For depositing $CsSnI_3$ as an HTM layer, 30 mg of $CsSnI_3$ was dissolved in 1 ml mixture of methoxyactonitrile (MeAc), dimethylformamide (DMF) and acetonitrile (ACN) taken in 1:3:2 volumetric proportion. For a part of the samples $CsSnI_3$ solution was doped with SnF_2 (99.99%, Sigma-Aldrich), by adding 5 wt% of SnF_2 into the $CsSnI_3$ solution [8]. Both the liquid electrolyte and $CsSnI_3$ solution were injected into the cell using a micropipette; $CsSnI_3$ injected cells were dried overnight inside the glovebox. *I–V* characteristics of cells (area 0.25 cm^2) were measured under one sun illumination.

3. Results and discussion

XRD analysis of $CsSnI_3$ synthesized through solid state route as in Fig. 1(a) shows formation of pure B-$\gamma$$CsSnI_3$ [5,9,14], whereas XRD in Fig. 1(b) of $CsSnI_3$ synthesized through solution route shows peaks of B-γ-$CsSnI_3$ and Y-$CsSnI_3$ along with peaks of mixed halides $CsSnI_{3-x}Cl_x$ ($x=0$, 1, 2, and 3). Raman analysis of powder samples of $CsSnI_3$ synthesized through solid state reaction as shown in Fig. 1 (c) shows the characteristic peaks at 200 cm^{-1} which corresponds to the first order-LO phonon scattering and the broad second peak at 400–600 cm^{-1} corresponding to the triply enhanced second order Raman scattering [10]. Raman spectra for samples prepared using solution route, shown in Fig. 1(d), are similar to those for samples prepared by solid state route Fig. 1(c) except for minor difference in peak beyond 650 cm^{-1} which may be due to the presence of mixed halides.

For estimation of optical band gap and phase stability of B-$CsSnI_3$ and Y-$CsSnI_3$ phase pure material synthesized through solid state reaction was used. Diffuse reflectance spectra were acquired for black films of B-$CsSnI_3$.These films were prepared by coating solution of B-$CsSnI_3$, obtained through solid state reaction, in DMF on glass substrate followed by heat treatment at 150 °C under inert atmosphere. A band gap of 1.3 eV was estimated from plot Fig. 2(a) which was obtained on the basis of Kubelka–Munk function $f(R)=(1-R)^2/(2R)$, where '*R*' is the reflectance for B-$CsSnI_3$ films [5].