



New class of lead free perovskite material for low-cost solar cell application



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ABSTRACT

In this paper, we fabricate a new class of perovskite sensitizer material for photovoltaic application. This is not only low-cost perovskite material but also is a non-toxic material for solar cell as compared to the conventional materials used in PSC. Detailed procedure of synthesis of $\text{CH}_3\text{NH}_3\text{SnCl}_3$ material and its application in fabrication of PSC is presented in the article. Perovskite material *i.e.* methyl ammonium tin tri-chloride ($\text{CH}_3\text{NH}_3\text{SnCl}_3$) was prepared by direct deposition of equimolar concentration of $\text{CH}_3\text{NH}_3\text{Cl}$ and tin chloride (SnCl_2) in dimethylformamide (DMF) solution. X-ray diffraction pattern (XRD) of the material confirms the formation of perovskite structure whereas, UV–vis absorption spectroscopy shows the absorption range of these material. Crystal formation of the perovskite is confirmed from the scanning electron microscope (SEM). A comparison of the crystal and powder form of perovskite material is discussed in depth in terms of structural, optical and electrical properties.

1. Introduction

Hybrid perovskite methyl ammonium lead iodide (MAPbI_3) is one the most prominent material in the field of photovoltaics and shows outstanding chemical and physical properties such as good absorption, high extinction coefficient, direct band gap, small exciton binding energy, *etc.* [1,2]. Apart from having a suitable bandgap, it also has excellent electronic properties like high carrier mobility, shallow defect levels, and high carrier diffusion lengths, *etc.* [3–5]. In 2009 the first reported perovskite-based solar cell shows 3.8% of power conversion efficiency (PCE) with liquid electrolyte [6]. Perovskite solar cell can be fabricated as n-i-p and p-i-n type of the organic inorganic metal halides. The simple perovskite formula is ABX_3 where, 'A' corresponds to organic cation (Cs^+ , Rb^+ , CH_3NH_3^+ , $\text{CH}_3\text{CH}_2\text{NH}_3^+$), 'B' corresponds to metal ion (Sn, Ge, Pb, *etc.*) and 'X' corresponds to halides (I^- , Br^- , Cl^- , BF_4^- , PF_6^- , SCN^- *etc.*). These are most promising materials for optoelectronic device application such as Light Emitting Diode [6,7], Humidity Sensor [8], Field Effect Transistors [9], LASERs [10], photodetectors [11,12] and photo active layer in photovoltaic solar cells [8]. The perovskite solar cell is developing as a new type of photovoltaic technology that can become an extensively used low-cost technology in coming future [9–11]. The crystal structure of $\text{CH}_3\text{NH}_3\text{SnX}_3$ shows different phases from cubic, tetragonal, orthorhombic, monoclinic and triclinic by varying the temperature. It forms cubic phase at

high temperature, in this phase, the $(\text{CH}_3\text{NH}_3)^+$ orientations are disordered in nature, basically, the SnX_6 structural unit has perfect cubic symmetry. The tilting and distortion of SnX_6 octahedral creates the space for the cations at low temperature. $\text{CH}_3\text{NH}_3\text{SnX}_3$ compounds crystallize into monoclinic phase at low temperature and forms tetragonal phase at room temperature. The optical band gap of $\text{CH}_3\text{NH}_3\text{SnX}_3$ can be tuned carefully by choosing the halide in this compound so that it can be useful for various applications. It is reported that adding extra Iodine (I), Chlorine (Cl) or Bromine (Br) in $\text{CH}_3\text{NH}_3\text{SnX}_3$ can tune its bandgap from IR region to visible light region. It has been also reported that tuning the bandgap of the material will certainly affect the size therefore one can control the photo response and power conversion efficiency of the device. All the hybrid perovskite materials, are made up of organic and inorganic units, therefore, shows attractive physical properties and also shows promising contribution to the technological advancement [13]. Researchers have reported various interesting properties such as metal-insulator transition, 2D magnetism [14,15], excitonic light emission properties [16] and mobility like an organic component [17]. However, due to its low-cost and easy preparation techniques for thin film deposition, these materials show potential in producing efficient devices. Commercialization of highly efficient perovskite solar cell can be archived by developing excellent encapsulation layer and materials with humidity and air resistance with high ultra violet light stable thin film on the perovskite surface. There is only

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handful of literatures available related with synthesis of methyl ammonium tin tri chloride based PSCs. Recrystallization process is one of the oldest methods known for the separation and purification of organic compounds and also one of the best methods for extracting pure molecules from the solvent. Till now researchers have reported various type of preparation method of perovskite thin film such as one step method, sequential deposition method, vapor-assisted solution processing (VASP) [18] and physical vapor deposition (PVD) [19]. However, Spin-coating is one of the low-cost thin film depositing techniques, and widely used for solution-process perovskite based solar cells [20].

In this article, we have focused our attention on the synthesis of perovskite sensitizer materials and elemental change in the behaviour of perovskite after crystallization of $\text{CH}_3\text{NH}_3\text{Cl}$. We have implemented a series of experiments to study the comparative behaviour of $\text{CH}_3\text{NH}_3\text{Cl}$ powder and crystal. The sandwiched type fabricated PSSC of perovskite powders and crystal used as sensitizers and also discussed in detail. In this paper, we have tried to make toxic free Sn based perovskite solar cell. The structure of the cell is Glass/FTO/b-TiO₂/n-TiO₂/CH₃NH₃SnCl₃/Electrolyte/Pt/FTO/Glass. Spiro-OMeTAD based conventional PSCs degrade very fast under ambient environmental condition, therefore reduces the durability and reliability of the device. Generally, spiro-OMeTAD hole conductor is most expensive material for PSC. Poly ethylene oxide (PEO) polymer is used as an organic hole conductor for perovskite solar cells which is cost effective and highly transparent. PEO is amorphous in nature and shows good solubility, smooth film forming, weak absorption in the visible region, high conductivity and low-cost hole conductor could further reduce the cost of PSC. PEO based electrolyte have great potential to replace the expensive spiro-OMeTAD because of their easy and low-cost synthesis, which enhances the technological advancement of cost-effectiveness and commercialization of perovskite solar cells [21–24].

2. Materials and methods

Ti(IV) bis(acetoacetato)-diisopropoxide, tin chloride (SnCl_2), polyethylene oxide (PEO), FTO coated glass substrate, Dimethylformamide (DMF), and Hexachloroplatinic acid (H_2PtCl_6) were purchased from Sigma Aldrich, USA while methylamine, hydrochloric acid (HCl, 57 wt. % in DI-water), diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$), acetone ($\text{C}_3\text{H}_6\text{O}$) and acetonitrile ($\text{C}_2\text{H}_3\text{N}$) from Thomas Baker (Chemicals) Pvt Ltd, India. Ti-Nanoxide D/SP (TiO₂) paste was purchased from Solaronix, Switzerland. Whereas, potassium iodide (KI) and iodine (I₂) from Himedia, India. Ethanol was purchased from Qualikems, India. All chemicals were used without any further purification.

The semiconductor light sensitizer methyl ammonium tin tri-chloride ($\text{CH}_3\text{NH}_3\text{SnCl}_3$ or MASnCl_3) was synthesized by the procedure previously reported [25]. In a common process, initially methyl ammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$) was synthesized by mixing 32.3 ml of HCl acid in 30 ml of methylamine using a round bottle flask of 250 ml. The prepared solution was passed through by ice-bath treatment maintaining temperature of reaction around 0 °C for 2 h. Whereas, extracted product was kept inside the vacuum oven for overnight at 60 °C for complete vaporization. The di-ethyl ether was used for washing the prepared precipitate of $\text{CH}_3\text{NH}_3\text{Cl}$ for several times until whitish color was appeared followed by drying at 100 °C in vacuum oven for 24 h. Now for the synthesis of $\text{CH}_3\text{NH}_3\text{Cl}$ crystal, powder of $\text{CH}_3\text{NH}_3\text{Cl}$ was dissolved in the ethanol and heated this solution at 60 °C for four hours and this solution was frozed in the refrigerator for three days and until recrystallization of our product took place. This product was filtered out and kept in vacuum oven at 80 °C for 48 h. In an ordinary crystallization procedure, we have to wait ~3–5 days for complete crystallization. The $\text{CH}_3\text{NH}_3\text{SnCl}_3$ solution of both powder and crystal were synthesized by mixing of 0.395 gm of the synthesized $\text{CH}_3\text{NH}_3\text{Cl}$ powder with 1.157 gm of SnCl_2 in 2 ml DMF and kept for stirring at 60 °C for 8 h. Finally, the prepared lead-free solution was used as a sensitizer for making Sn based devices [26,27].

Fluorine-doped tin oxide (FTO) conducting glass as the substrate was used for fabricating perovskite solar cell. Firstly, spin coating method was used for coating a Titania based blocking layer (b-TiO₂) onto the surface of the FTO substrate followed by annealing at 500 °C for 30 min. Doctor blade method was used for preparing thin film of titanium dioxide (n-TiO₂) paste onto the FTO/b-TiO₂ substrate. The thickness of the n-TiO₂ thin film was adjusted by the adhesive scotch tape, whose thickness was optimized for producing few 25 μm layer for device. Programmable muffle furnace was used for sintering the n-TiO₂ layer at 500 °C for 30 min followed by cooling naturally to room temperature resulting in uniform nanoporous thin film with thickness < 10 μm. The prepared solution of $\text{CH}_3\text{NH}_3\text{SnCl}_3$ was spin coated onto the surface of FTO/b-TiO₂/n-TiO₂ at 3000 rpm for 15 s. Hexa-chloroplatinic acid (H_2PtCl_6) solution was spin-coated onto the surface of conductive glass followed by sintering at 400 °C for 30 min. Polymer electrolyte consisting of PEO + 20% KI and I₂ (10% of KI) was prepared in acetonitrile. Polymer based hole transport layer was coated on TiO₂/Perovskite electrode using two-step casting method. The 'Pt' electrode and the perovskite coated active layer electrode containing solid polymer electrolyte were stacked together [28].

3. Results & discussions

3.1. UV-vis absorption

UV-vis measurement was carried out to calculate the optical band gap of the tin based perovskite material. The UV-vis absorption spectrum of the $\text{CH}_3\text{NH}_3\text{SnCl}_3$ powder and crystal is measured using a UV-vis spectrophotometer (Model no. UV-1800, SHIMADZU). Optical band gap energy (E_g) powder perovskite is analyzed from the absorption spectra graph as shown in Fig. 1(a) and for crystal perovskite shown in Fig. 1(b). The maximum absorption peak value for the powder perovskite of methyl ammonium tin tri-chloride is 490 nm and for the crystal perovskite of methyl ammonium tin tri-chloride is 560 nm [29]. The band gap energy of the perovskite was evaluated from the following Relation (1) using absorption wavelength.

$$E_g = \frac{hc}{\lambda_{\text{max}}} \quad (1)$$

Where E_g is band gap energy of the nanoparticles. From the related absorption peak, h is the Planck's constant ($h = 6.626 \times 10^{-34}$ Js), c is the velocity of light (3×10^8 m/s) and λ_{max} is the maximum absorption wavelength of the sample. The estimated band gap energy values of the sensitizer $\text{CH}_3\text{NH}_3\text{SnCl}_3$ powder perovskite is 2.5 eV and for the $\text{CH}_3\text{NH}_3\text{SnCl}_3$ crystal perovskite is 2.1 eV. It is clearly observed from the graph that the sharp onset region in the absorption spectra from the absorption edge of the perovskite layer that indicates the absence of deep states. According to the Shockley–Queisser limit of the solar cell too high band gap in any system such as SnCl based perovskite solar cell will be having lower efficiency as compare to the PbI or SnI based perovskite solar cell.

3.2. Scanning electron microscopy (SEM)

The surface topographies and morphological view of the $\text{CH}_3\text{NH}_3\text{SnCl}_3$ powder perovskite and crystal perovskite investigated using SEM (Nova NanoSEM 450). Fig. 2(a) shows SEM micrograph of one distinctive sample of powder while Fig. 2(b) shows the SEM image of crystallized perovskite at same magnification. It is clearly observed that powdered sample shows small crystal whereas, crystallized perovskite sample shows large crystals throughout the surface as compare with powdered sample. Uniformity of perovskite crystals is one of the important parameter for producing pin hole free surface with highly crystalline nature material for efficient device performance [30].

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