A step towards environmental benign Mg/Pb based binary metal mixed halide perovskite material

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ABSTRACT

Today's the best performing perovskite solar cells utilise Pb^{2+} as a major bivalent cation source, however, the presence of toxic Pb is major issue that put its commercialization in dire straits. In this report, we unveiled the chemical synthesis and characterisation of Mg/Pb binary metal mixed halide perovskite with chemical formula $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ using $MgCl_2$ as a compositional gradient with nominal value of x from 0.1 to 0.9. The FESEM images of compositions corresponding to higher proportion of Cl^- (or $MgCl_2$) demonstrate improved particle (or grain) size of ~ 8–12 μm. There is a close resemblance of stoichiometric ratio of Pb:Mg obtained from EDX analysis with that of incorporated stoichiometric ratio of Pb:Mg. Further, Mg and Cl incorporation is strengthened by the characteristic spectral peak for core level electron of Mg(2p) and Cl(2p) other than Pb(4f) and I(3d) in the XPS survey spectrum of composition x = 0.5. These binary Mg/Pb Perovskite with bandgap in the range 1.57–1.59 eV behave as comparatively less toxic potential candidate for the single junction module. The IR studies at room temperature show observable shift in peak positions on comparing two extreme compositions i.e., x = 0.1 and x = 1.0. It is noticeable that both standard $CH_3NH_3PbI_3$ and binary Mg/Pb Perovskite with nominal value x = 0.7 have comparable thermal stability, however, the composition x = 0.1 have lower thermal stability than x = 0.7. The carrier lifetimes measurements by Microwave Detected Photoconductivity (MDP) showed an improvement of lifetime to 142 μs for nominal value x = 0.9 compared to 76 μs in case of $MAPbI_3$ film. Correspondingly we see a 160 mV improvement in open-circuit voltage (V_{OC}) in the solar cells fabricated with nominal value x = 0.9 ($V_{OC} = 1.07$ V) as compared to standard $MAPbI_3$ cells ($V_{OC} = 0.90$ V). The champion cell with nominal value x = 0.9 shows PCE of 14.2% where as the best PCE of $MAPbI_3$ cell is 14.50% under a reverse scan.

1. Introduction

The wonder material "Organic-Inorganic Lead halide perovskite" enormously astonished the photovoltaic realm by rivalling CIGS, CdTe and thin film crystalline Si solar cell with power conversion efficiency (PCE) of 22.7% reported by Yang et al. (2017), https://www.nrel.gov/pv/assets/images/efficiency-chart.png. It has phenomenal photophysical properties like high extinction coefficient, low exciton binding energies, long-range ambipolar charge transport and tunable band gap (Seo et al., 2016). Also, the affordable precursors with wide range of fabrication techniques are the prime factors for the boom in perovskite research over other photovoltaic (Cui et al., 2015). This hybrid perovskite has an ABX_3 structure with a corner sharing octahedral $[BX_6]^{4-}$ framework. Here, A is a cation like $CH_3NH_3^+$ (MA) and/or $HC(NH_2)_2^+$

(FA) and/or inorganic cation such as Rb^+ and Cs^+ (Turren Cruz et al., 2018; Yi et al., 2016; Saliba et al., 2016; Gao et al., 2014; Eperon et al., 2014). B is mostly Pb^{2+}. X is more often I^- Gao et al., 2014, Br^- Gao et al., 2014; Eperon et al., 2014, Cl^- Gao et al., 2014 or a mixture of halides (Hendon et al., 2015; Heo et al., 2014) or PF_6^- (Jiang et al., 2015), SCN^- (Nagane et al., 2014) and BF_4^- (Jiang et al., 2015; Prajongtat and Dittricht, 2015).

Although it is an emerging paradigm in photovoltaic world, however, the Pb toxicity is one of the major concern that impedes the commercialization. Over the last couple of years, steps to decrease the Pb^{2+} content via substitution with other potential cation that retain or improve the optical and photovoltaic performance of standard $CH_3NH_3PbI_3$ have been elicited. In 2014, the pioneer work of Ogomi et al. (2014) shows tunable band gap in mixed Pb/Sn perovskite by

varying the ratio of Pb and Sn indicating Sn as a potential alternative for Pb based perovskite. Moreover, this study also shows the composition $CH_3NH_3Pb_{0.5}Sn_{0.5}I_3$ has absorption spectrum extended up to 1060 nm with PCE of 4.18% and it also reveals the significance of Pb^{2+} in stabilising the Sn^{2+} state. Hao et al. (2014a) improved this efficiency to 7.27% with J_{sc} of 20.64 mA/cm^2 and showed that $CH_3NH_3Sn_{1-x}Pb_xI_3$ solid solutions do not obey the linear trend in band gap between two extreme compositions and simultaneously portray $CH_3NH_3SnI_3$ as a potential lead free perovskite with an efficiency of 5.44%. However, the efforts to replace Pb^{2+} with its congeners Sn^{2+} or Ge^{2+} did not work well as they suffer from easy oxidation of $+2$ to $+4$ state. Oxidation of Sn^{2+} to Sn^{4+} state under ambient conditions, causes the breakdown of the perovskite unit cell structure along with the formation of wide band gap tin oxide (3.6 eV) that results in energy level mismatch between HTM and perovskite leading to decreased PCE (Hao et al., 2014b; Sabba et al., 2015; Stoumpos et al., 2015). Further in 2015, Navas et al. (2015) compared the experimental and theoretical structure of $CH_3NH_3Pb_{1-x}Cd_xI_3$ and estimated the stability of perovskite form up to x = 0.5, however with later compositions like x = 0.75 and x = 1.0 the perovskite form is unstable. Recently in 2017, Wang et al. (2016) investigated an alternative Pb–In perovskite MAPb$_{1-a}$In$_a$I$_3$Cl$_a$ where films exhibit high quality with multiple ordered crystal orientations that allow efficient charge transport along multiple directions and thus improve device performance. Further, optimizing the InCl$_3$ molar ratio, improved efficiency of 17.55% is achieved for the composition MAPb$_{0.85}$In$_{0.15}$I$_3$Cl$_{0.15}$. However, the crustal abundance of In is very low ~50 ppb and it rarely forms its own minerals.

Though literature has given various substitutes of Pb^{2+}, still they are not the suitable ones. There are issues related to stability and morphology of Sn^{2+} and Ge^{2+}, relatively low abundance of In^{2+} and toxicity concerned with Cd^{2+}. Therefore, in this article, we have substituted the Pb^{2+} with nontoxic, stable, eighth most abundant and homovalent cation Mg^{2+} based on $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ formulation by varying the nominal value of x from x = 0.1 to x = 0.9.

2. Materials and methods

2.1. Materials

Chemicals PbI$_2$, MgCl$_2$, Methylammonium iodide (MAI) and solvents anhydrous Dimethylformamide (DMF), Acetonitrile and Chlorobenzene were purchased from Sigma Aldrich. Mesoporous TiO$_2$ was obtained from Dyesol, 2,2′,7,7′-tetrakis (*N,N*-di-*p*-methoxyphenyamine)-9,9-spirobifluorene (spiro-OMeTAD) was purchased from Feiming Chemical Limited. All the materials were used as received.

2.2. Synthesis of $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ powder

Powdered $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ x = 0.1–1.0 were synthesized by using solid state reaction. Stoichiometric amounts (1:1) of CH$_3$NH$_3$I and PbI$_2$ (99%, Sigma Aldrich) was finely ground in a mortar for synthesizing standard perovskite (CH$_3$NH$_3$PbI$_3$). The binary Mg/Pb based perovskite powders were prepared by mixing stoichiometric amounts of CH$_3$NH$_3$I, anhydrous MgCl$_2$ and PbI$_2$ and homogenized in a mortar to

get black crystalline powder. These were heated at 100 °C for 15 min for complete conversion to perovskite.

2.3. Device fabrication

Commercial FTO coated glass substrates are used to fabricate the devices. Substrates are sequentially cleaned by Acetone, 2-Propanol and DI water (10 min each). This is followed by UV light exposure for 10 min to modify the work function of FTO. A 45 nm compact TiO$_2$ layer is deposited by atomic layer deposition followed by spin coating of mesoporous-TiO$_2$ at 4000 rpm for 30 s. The samples are then annealed at 500 °C for 1 h. The thin films of $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ perovskite are deposited by spin coating of 1:1 stoichiometric ratio of MAI and metal halide i.e., PbI$_2$/MgCl$_2$ in DMF on pre heated TiO$_2$ substrate at 2000 rpm for 35 s with an acceleration of 10 s followed by heating at 100 °C for 15 min in an inert atmosphere. The solution for hole transporting layer is prepared by dissolving 73 mg of Spiro-OMeTAD in 1 mL of Chlorobenzene. The additive preparation for Spiro-OMeTAD involve the solution of Li-TFSI (lithium bis(trifluoromethane) sulfonimide), prepared by dissolving 520 mg in 1 mL acetonitrile, followed by mixing of 18 μL of this stack solution and 28 μL of 4-tertbutylpyridine in previously prepared 1 mL solution of Spiro-OMeTAD, finally, the resulting solution is spin-coated at 4000 rpm for 50 s. For the top contact, patterned 100 nm thick gold (area = 4 mm^2) is deposited by thermal evaporation.

2.4. Device characterization

The J-V characterization of the cells is done by using a Keysight B2901A source-meter under AM1.5 illumination maintained by a Wavelabs SINUS-70 Solar simulator. The solar simulator is calibrated against a SOL3A-E23-02 standard. Other characterisations like XRD, FESEM, XPS, UV-PL, DRS, IR, RAMAN, TGA/DTA, MDP are detailed in SI.

3. Results and discussion

The study involves detailed analysis of novel $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ perovskite material.

3.1. X-Ray diffraction analysis

The structural analysis of powdered $CH_3NH_3Pb_xMg_{1-x}I_{3-y}Cl_y$ perovskites were performed using powder X-ray diffraction technique (Figs. 1 and 2). The observed diffraction pattern for various compositions with nominal values from x = 0.1 to x = 0.9 is in good agreement with the data reported for the tetragonal crystal structure of standard CH$_3$NH$_3$PbI$_3$ (Space group I4/mcm, Z = 4) (Fig. 2) Manser et al., 2015; Dang et al., 2015. The measured diffraction pattern for standard CH$_3$NH$_3$PbI$_3$ (x = 1.0) shows split diffraction peak for (0 0 2) and (1 1 0) plane at 13.88 and 13.89 2θ values respectively. Further, split peak at 28.00 and 28.23 2θ values corresponds to (0 0 4) and (2 2 0) planes respectively. Moreover, the planes (0 0 6) and (3 3 0) in CH$_3$NH$_3$PbI$_3$ occur at 2θ values of 42.88 and 42.99. The presence of all these characteristic lattice planes in a series of compositions with a

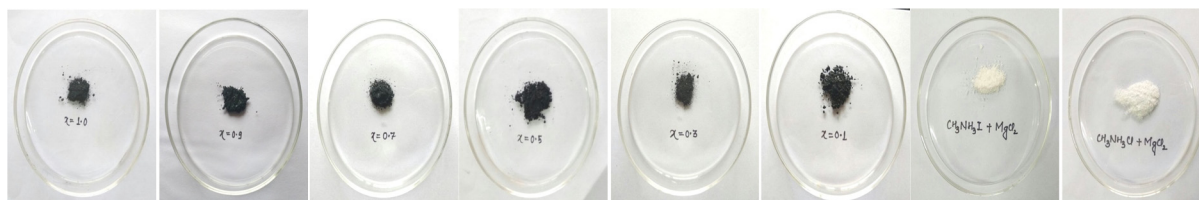**Fig. 1.** Photograph of CH$_3$NH$_3$Pb$_x$Mg$_{1-x}$I$_{3-y}$Cl$_y$ (x = 1.0 to 0.1) perovskite powder obtained from 1:1 stoichiometric ratio of MAI and Metal halide i.e., PbI$_2$/MgCl$_2$ precursors.