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Supporting Information

Towards Removal of toxicity from Lead based perovskite Solar Cell by Compositional Gradient using Manganese Chloride

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1. Experimental Section

1.1 Synthesis of MAI

CH_3NH_3I was synthesized by reacting 38 ml (0.3 mol) of methyl amine (33 wt.% in absolute ethanol, Sigma Aldrich), and 40 ml of hydroiodic acid (57 wt.% in water, Aldrich) in a 250ml round bottom flask at 0° for 2 hr .The prepcepitated was collected by rotatary evaporator at 60°C, followed by recrystallisation with Ethanol . Recrystallisation is necessary to remove the stabilizer H_3PO_2 and its product with MA (MAH_2PO_2), Ordinary washing diethyl ether unable to remove these impurities. Presence of these impurities imparts insoluable Pb complexes formation with H_3PO_2 leads to cloudy precursor solution.[1]

1.2 Synthesis of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$

Samples of general formula $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ (where MA = Methyl Ammonium and x= 0.1 - 1.0 were synthesized using the procedure involving solid state reaction of the involved compounds. Standard perovskite with chemical formula $CH_3NH_3PbI_3$ was prepared by mixing stoichiometric amounts (1:1) of CH_3NH_3I and PbI_2 (99%, Sigma Aldrich) finely homogenized in a mortar. The approach was extended to synthesize the Manganese based perovskite. Stoichiometric amounts of CH_3NH_3I, PbI_2 and anhydrous $MnCl_2$ were mixed and homogenized in a mortar to obtain a black crystalline powder. To ensure a complete conversion into perovskite and ensuring absence of impurities, the powder was then heated to 120°C .

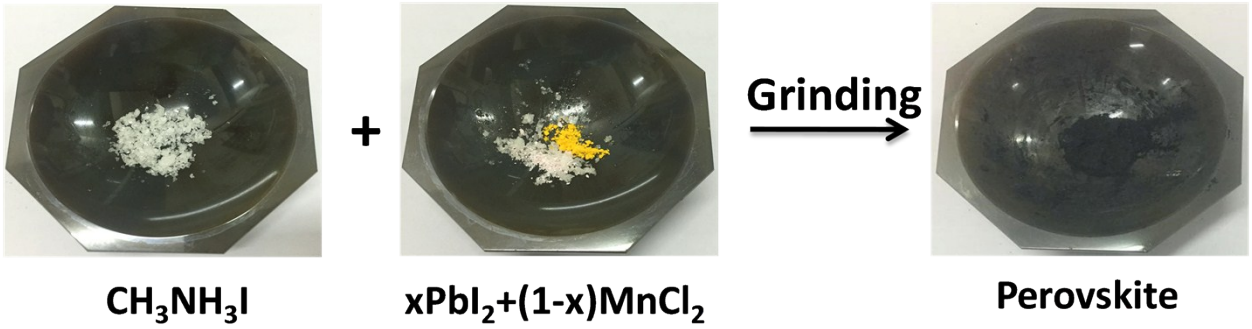

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Fig. S1 Synthesis procedure of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x.}$

2. Characterization

2.1 X-Ray diffraction

The crystal structure of the powder was analyzed at room temperature Cu- K radiation Powder X-Ray Diffraction (Bruker D8 Advance Diffractometer). The set included perovskite powders which were heat treated to 120C.

2.2 UV Vis Absorption Spectroscopy and Photoluminescence Spectroscopy

Shimadzu UV-Vis 2450 spectrophotometer was used for recording UV-Vis absorption spectra. Horiba scientific Fluoromax-4C spectrophotometer was used for recording photoluminescence spectra . Photoluminescence and UV-VIS measurements were performed by preparing films of the perovskite material on quartz substrate. 0.88M solution of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x.}$ was prepared in Dimethylformamide (DMF). The films were deposited on the TiO2 coated quartz samples using Doctor Blading of the solutions followed by heating the samples at 120°C. TiO2 was coated on the quartz samples using spin coating. Uniform black films of the perovskite material were obtained on the quartz substrate. The samples were then used for performing the UV-VIS and PL measurements.

2.3 Diffusion Reflectance Spectroscopy (DRS)

The Diffusion Reflectance Spectra of different perovskites was measured from 350-1000nm (1.24eV to 3.54eV with steps of 1nm, Varian Cary 5000 UV-VIS-NIR spectrophotometer). For performing these measurements, a reference of $BaSO_4$ was used and pellets of the perovskite powder were prepared according to the sample holder.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The pellets for FTIR analysis were prepared by grinding manganese based perovskite with previously dried KBr. Thermo scientific Nicolet 6700 was used for recording spectra.

2.5 Field Emission Scanning Electron Microscopy (FESEM)

The compositional analysis was performed using energy dispersive X-Ray spectroscopy (EDX) imaging was performed using Field Emission Scanning Electron Microscope (FESEM)(Carl Zeiss Ultra Plus). A cobalt standard was used for the calibration of the quantitative elemental analysis. Inert atmosphere was not used for the sample manipulations and the experiments were conducted in ambient conditions.

Device fabrication and characterization

Pretreated Patterned ITO glass having sheet resistance of 15 Ω sq-1 was cleaned through the following sequential steps such as ultrasonics in detergent, deionized water, acetone, isopropanol, and finally treated with UV-ozone for 10 min. A poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS, CleviosTM P VP AI 4083) layer was spin coated on a ITO substrates at 4000rpm for 30 sec and then substrate was anneled at 150 °C for 10 min . $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ precursor solution (15 wt%) in Dimethyl formamide (DMF) was spin-cast at 2500 rpm for 60 s and heated at 120 °C for 30 sec. $PC_{61}BM$ solution (20 mg/mL in chlorobenzene) was then spin-coated onto the surface of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ layer at 1500 rpm for 30 s. The trace amount of solvent (chlorobenzene)in the film will continuously infilterate PCBM to form a close contact with the perovsite film underneath. Finally aluminum was deposited on $PC_{61}BM$ layer through a shadow mask under vacuum (ca. 10^{-6} Pa).

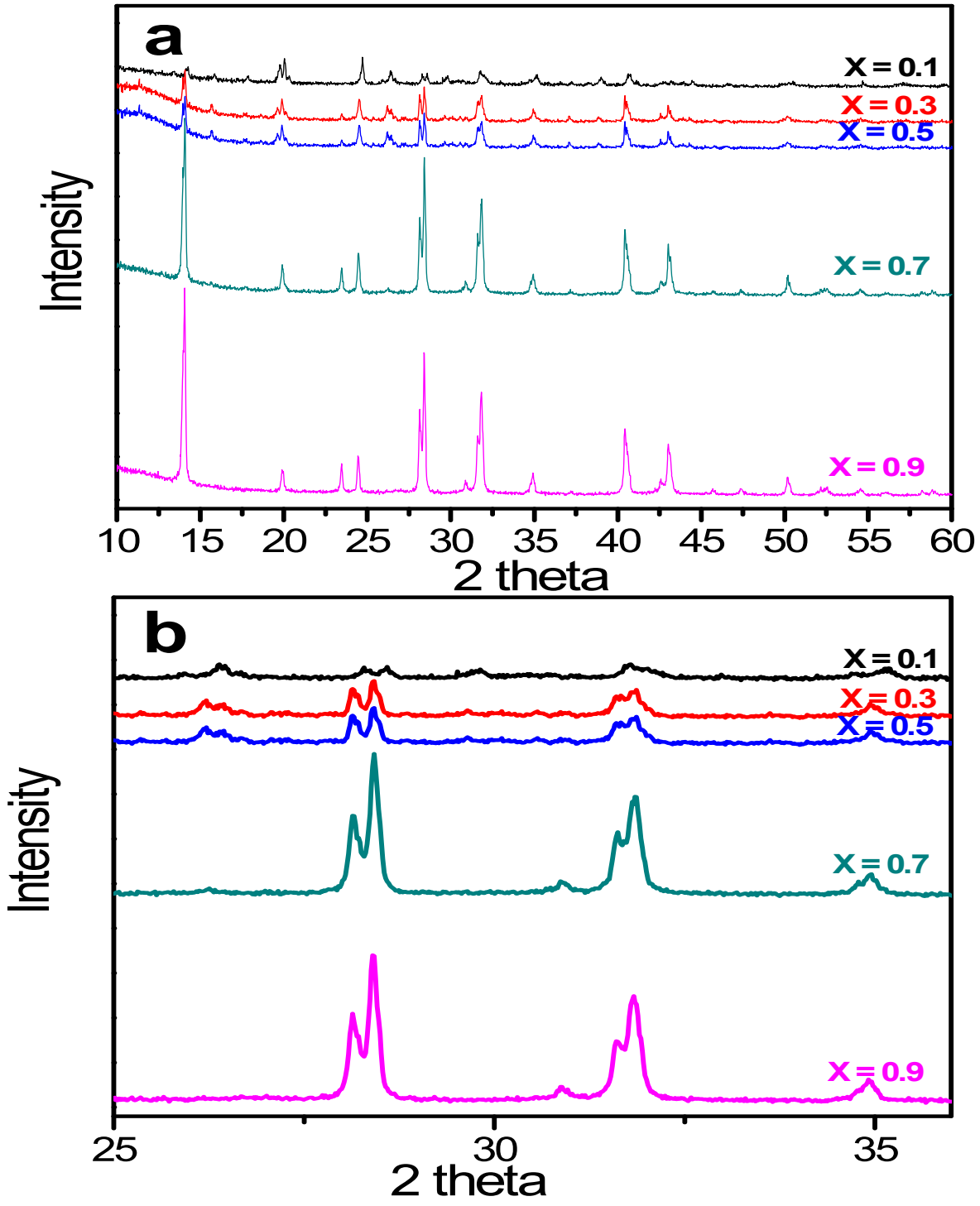
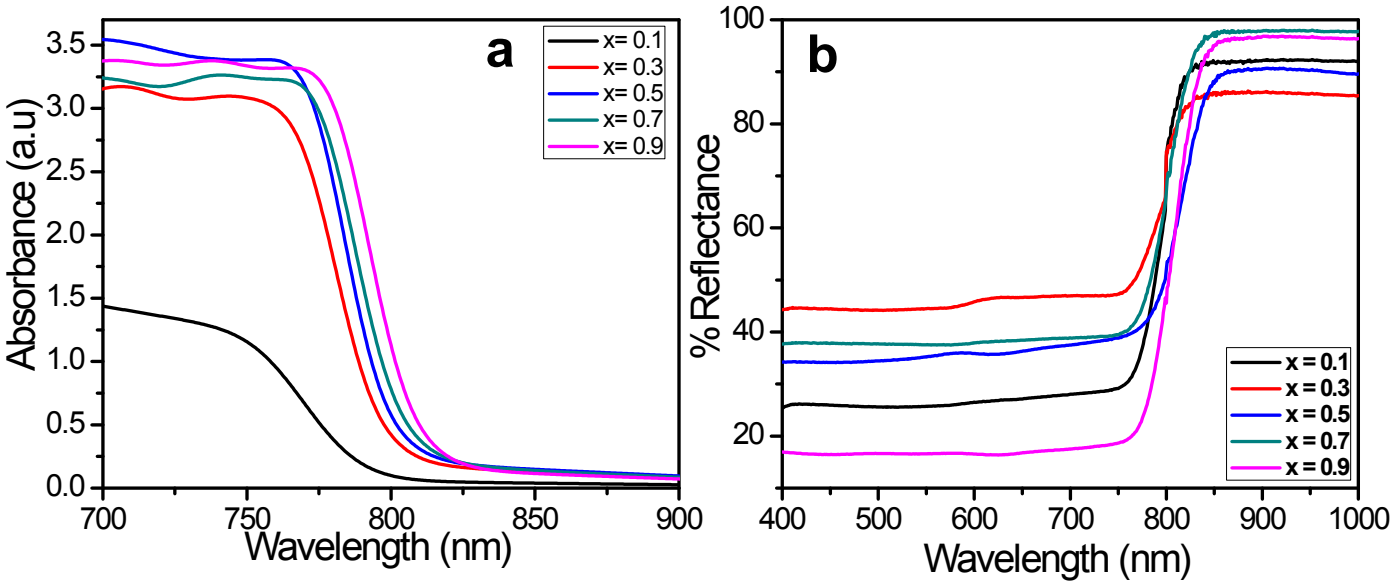


Fig. S2 (a) X- Ray Diffraction plots of the $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ system as a function of x (b) Enlarge view from 25-35 2θ value



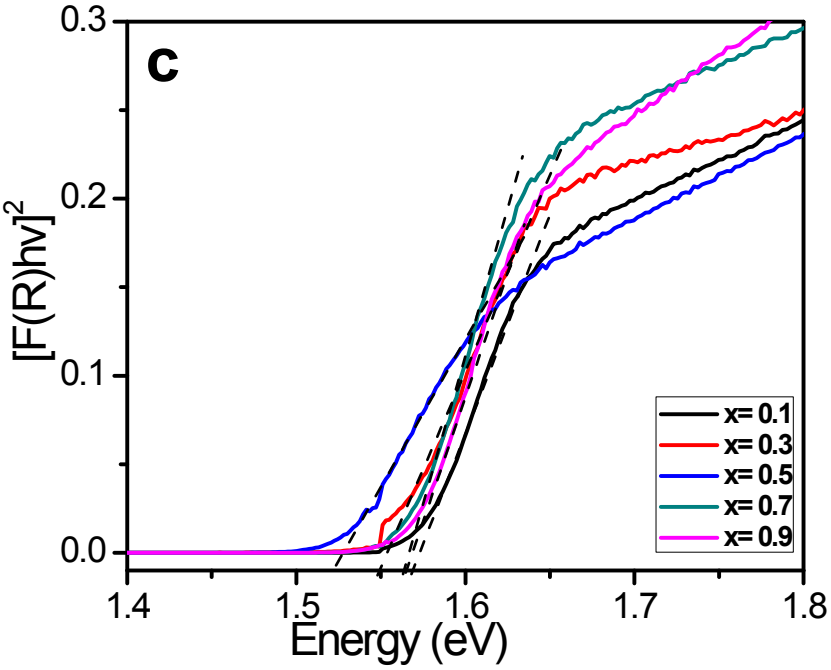


Fig. S3 a) Absorption Spectra of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ (b) Diffusion Reflectance Spectra

of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ (d) Tauc plot of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$.

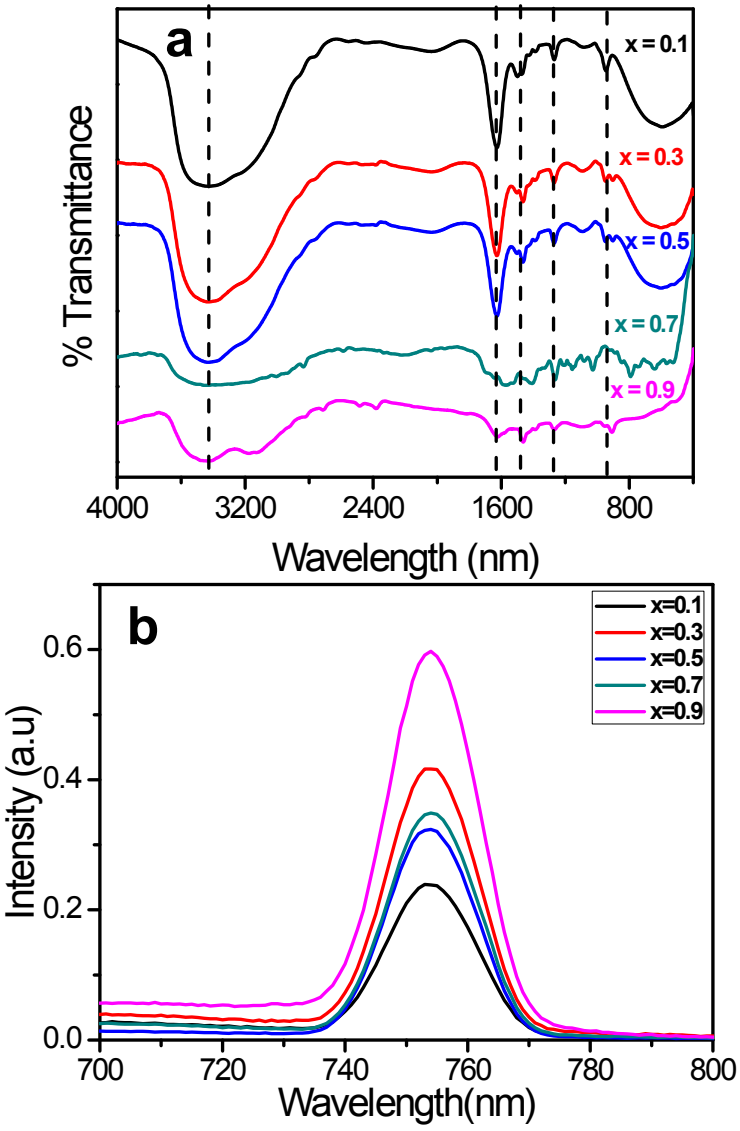


Fig. S4 (a) Fourier Transform Infrared Spectroscopy.(b) Photoluminescence Spectra of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ as a function of x.

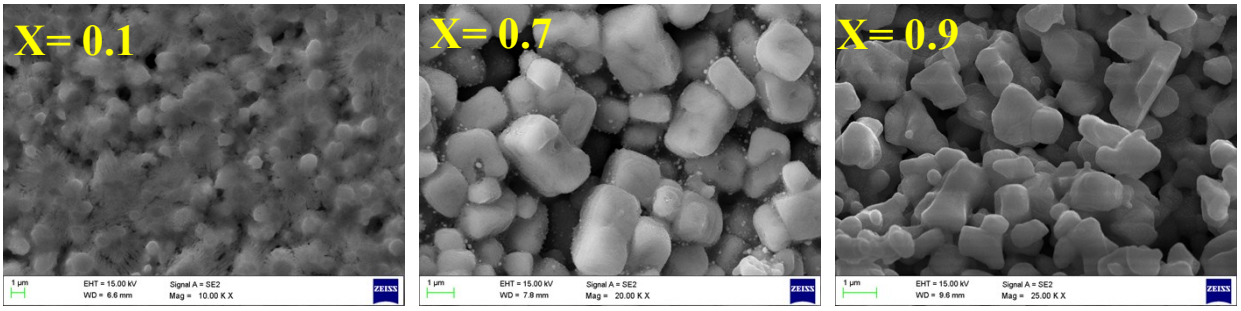


Fig. S5 FESEM images of the synthesized perovskite for different values of x = 0.1, 0.7, 0.9.

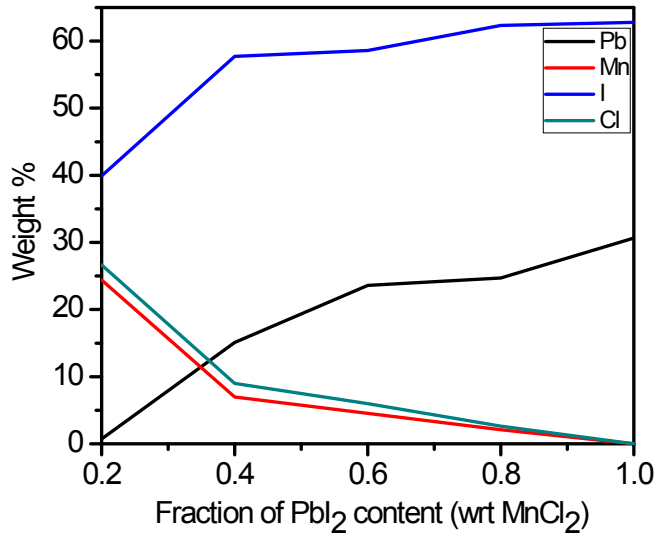


Fig. S6 Weight % of constituent element in $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ system as a function of x .

Table. S1 Elemental analysis of different composition of Perovskite.

Perovskite	Pb wt(%)	Mn wt(%)	I wt(%)	Cl wt(%)
X=1	30.58		64.15	
X=0.8	24.70	2.10	62.33	2.62
X=0.6	23.60	4.55	58.61	5.99
X=0.4	15.08	6.98	51.70	9.0
X=0.2	0.72	21.63	39.92	26.63

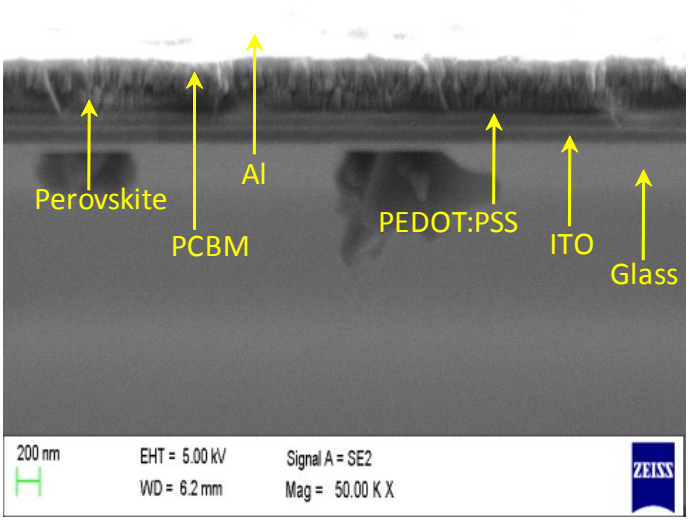


Fig S7 Cross-sectional FESEM image showing the device structure of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ (x=0.9) perovskite solar cells.

Reference

1. Y. Deng, E. Peng, Y. Shao, Z. Xiao, Q. Dong and J. Huang, *Energy Environ. Sci.,* 2015, **8**, 1544.