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

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We report synthetic steps towards lead free manganese based perovskite  $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$  (nominal x = 0.1-1.0), photovoltaic material via solid state reaction. Further application as an excellent panchromatic light harvester involve cell fabrication with inverted planar architecture at low processing temperature. This novel perovskite offer an outstanding Voc of 1.19 V with Fill Factor 87.9%.

The last straw concerned with commercialisation of modern organic and inorganic photovoltaic is higher cost processing and overpricing.<sup>1</sup> In this regard cost effectiveness and ease of processing is the main consequence of forefront of Organic-Inorganic hybrid perovskites. It was successfully incorporated as hole transporting materials in third generation photovoltaics.<sup>2</sup> The Organic-Inorganic hybrid perovskites have ABX<sub>3</sub> structure with corner sharing BX<sub>6</sub> octahedra network. Here, A is a cation such as  $Cs^+$  or a small molecule like  $CH_3NH_3^+$ ,  $(HC(NH_2)_2^+)$ which not only maintain total charge balance but also influence the crystal structure there by tune the band gap.<sup>3,4</sup> X is likely Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or a mixture of halides. B is more oftenly Pb<sup>2+</sup> Although hazardous environmental aspects of associated lead creates additional roadblocks in the development of this yardstick CH3NH3PbI3 . Efforts have been made to substitute  $Pb^{2+}$  with same group elements like  $Sn^{2+}$ ,  $Ge^{2+5,6}$  However, Sn<sup>2+</sup> and Ge<sup>2+</sup> have addressed the stability issues due to ease of oxidation in 4+ state under ambient conditions that break down perovskite structure along with formation of oxide and hydroxide of tin metal.<sup>5</sup> This drags the research community to envaisage on other substitute of lead. Recent studies show incorporation of  $Cu^{2+},\ Ca^{2+},\ Cd^{2+}$  and  $Sr^{2+}$  metals cations as alternatives, are attracting a great intereset to the scientific communities.<sup>7,8</sup> Studies involving CH<sub>3</sub>NH<sub>3</sub>SrI<sub>3</sub> stated different bonding pattern of M-X bond that impedes intercalation of CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> which is basic framework of CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> with band gap of 3.6eV makes it inappropriate absorber.<sup>9</sup> Attempts have been made to swap the lead through split an ion approach using Bi and chalcogenide such as S, Se.<sup>10</sup> Taking this into consideration there emerges an urgent need to propose a perovskite material constituting a metal ion moiety which is stable under ambient conditions, is abundantly available and

<sup>a.</sup> Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand-247667, India. Email:kar.prasen@gmail.com does not pose toxic threat.

In this communication, we report for the first time, the synthesis, characterization and fabrication of a manganese based lead free mixed halide perovskite with chemical formula  $CH_{3}NH_{3}Pb_{x}Mn_{1\text{-}x}I_{1\text{+}2x}Cl_{2\text{-}2x}.$  In order to investigate the structure of the material synthesized, X-Ray Diffraction measurements were performed. The diffraction pattern is in good agreement with the data reported for the tetragonal conformation (Space group I4/mcm, Z=4) of the perovskite structure and the structure obtained is identical to the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> structure.<sup>11,12</sup> The measured XRD pattern indicates splitting of diffraction reflections at 13.95° and 14.06°  $2\theta$  value is due to (002) and (110) plane. Splitted peak around 28.13° and 28.40°  $2\theta$  value is assigned for (004) and (022) plane of perovskite. The peak at  $31.64^{\circ}$ ,  $31.83^{\circ}$ , 40.43 and  $43.11^{\circ} 2\theta$  value is related to (114), (310), (224) and (330) plane of perovskite (Fig. 1a and b). Presence of all these lattice plane ensures the Tetragonal CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Upon addition of manganese chloride (MnCl<sub>2</sub>) to the lead based perovskite, very slight shift in  $2\theta$  value is observed along with consistent decrease in the lattice parameter a and c which indicates the formation of a solid solution (Table.1). This slight decrease in lattice parameter leads to very meager change in volume across the series. It can be seen from Fig. 1c that the  $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$  solid solution is in agreement with Vegard's  $law^{\cdot 13}$  The lattice parameters progressively decreases with addition of MnCl<sub>2</sub> due to small ionic radius of Mn<sup>2+</sup> with respect to Pb<sup>2+</sup>. A prominent change in the peak intensity, however, is evident. This can be attributed to the loss of crystallinity of the structure upon addition of manganese. Furthermore, it can be observed that the intensity of the peaks is doubled from x = 0.8 to x = 1.0. Study of the remaining composition is shown in (Fig. S2 ESI<sup>+</sup>).

Structural similarity of this novel perovskite with standard perovskite  $CH_3NH_3PbI_3$  opens the area for further analysis. Optical characterization of the synthesized perovskite was performed by UV-Vis spectroscopy and Photoluminescence measurements. It is observed that the film exhibits a broad absorption spectrum in the NIR spectral range therefore is a strong panchromatic absorber. The absorption onset for x = 1 lies at 816 nm and successive addition of MnCl<sub>2</sub> leads to blue shift of the absorption onset with wavelength 796 nm for x = 0.1(Fig. 2a). It can be seen from UV-Vis data that the bandgap increases upon increasing the MnCl<sub>2</sub> content in the perovskite.

Electronic Supplementary Information (ESI) available: [Experimental method and characterization data]. See DOI: 10.1039/x0xx00000x

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#### а b X=0.2 X=0.2 10.14 12.82 C 12.80 X=0.4 10.12 X= 0.4 12.78 X= 0.6 10.10 Intensity 2 Intensit 12.76 X= 0.6 10.08 a(A) (A) 12.74 X=08 10.06 12.72 X=0.8 12.70 10.04 12.68 X= 1.0 X= 1.0 10.02 12.6 1.0 0.6 0.8 1.0 0.2 27.5 30.0 325 16 20 24 28 32 36 48 25.0 35.0 12 40 44 2 theta 2 theta

Fig. 1 (a) X- Ray Diffraction plots of the MAPb<sub>x</sub>Mn<sub>1-x</sub>I<sub>1+2x</sub>Cl<sub>2-2x</sub> system as a function of x. (b) Enlarge view from 25-35  $2\theta$  value. (c) Variation in lattice parameter a as a function of x.

The increase in the bandgap can also be associated with the substitution of iodine ions by chlorine ions. A marginal increase in the bandgap has an associated advantage of reduced quantity of lead which is  $1/10^{\text{th}}$  of the initial. Hence change in elemental composition accompanied by crystal distortion which is responsible for tuning of band gap as compared to standard CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.

The room temperature photoluminescence peak of the standard CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> is centered at 753nm. The peak maxima occur at approximately the same value of wavelength irrespective of the composition (Fig. 2b). It should be observed that the substitution of iodide ions by chlorine ions, according to the previous reports, is expected to increase the bandgap of the perovskite. But the emission peak does not face a shift upon addition of manganese chloride as one of the initial compounds. Change in the composition is not well reflected in the Photoluminescence spectra. Study of the remaining composition is shown in (Fig. S4b ESI†).

In case of polycrystalline material UV-Vis absorption spectra does not give precise band gap measurement. Here transmitted radiation intensity not only depend on absorption due to optical band gap but also on light scattered by material & absorption due to intrinsic defect in semiconductor. Therefore we have performed Diffusion Reflectance Spectra (DRS) (Fig. 2c) to calculate the optical absorption coefficient ( $\alpha$ ) using Kubelka-Munk relationship according to the equation K/S = $(1-R)^2/2R = F(R) = \alpha$ . Here, K and S are the Kubelka-Munk absorption and scattering coefficient respectively. F(R) is the Kubelka-Munk function and R is the percentage of reflected light. The optical bandgap is depicted by the transformed Kubelka-Munk function<sup>14</sup>  $[F(R)hv]^p = A(hv - E_g)$ . Here  $E_g$  is the bandgap energy. In case of a direct allowed transition, p (transition probability) attains a value of 2 or 2/3 where indirect allowed transition considers 1/2 or 3/2 values for p. The optical bandgap is obtained by extrapolating the linear part of the  $[F(R)hv]^2$  plot, also known as the Tauc plot.

It is assumed that the synthesized perovskite is having direct bandgap. It can be observed from (Fig. 2d) that band gap for all compositions of  $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$  (i.e., x=0.1-1.0) ranges from 1.56eV to 1.54eV compared to 1.56eV for standard

 $CH_3NH_3PbI_3$ . Study of the remaining composition is shown in (Fig. S3 ESI<sup>+</sup>)



Fig. 2 a) Absorption Spectra b) Photoluminescence Spectra (c) Diffusion Reflectance Spectra d) Tauc plot e) Fourier Transform Infrared Spectroscopy of  $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$  as a function of x.

Fourier Transform Infrared Spectroscopy (FTIR) of the perovskite materials for different values of x is performed at ambient temperature shown in Figure (2e). Literature review evaluate that low temperature orthorhombic form is preferred over tetragonal and cubic form due to less angular fluctuation.<sup>16</sup> Shift in peak position for different composition as a function of varying degree of interaction between organic moiety and inorganic cage can be well

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explained by taking region  $800 \text{cm}^{-1}$   $3100 \text{cm}^{-1}$ .<sup>17</sup> This region is primarily used for internal vibration of Methyl ammonium cation. The peak at around 913 cm<sup>-1</sup>and 1268 cm<sup>-1</sup> assigned for CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> rocking vibration. The peak centered at 1374 cm<sup>-1</sup> and 1465 cm<sup>-1</sup> denoted for symmetric CH<sub>3</sub> and NH<sub>3</sub><sup>+</sup> bending respectively. The peak corresponds to 1624 cm<sup>-1</sup> in due to asymmetrical NH<sub>3</sub><sup>+</sup> bending. The peak broadening from 2800 cm<sup>-1</sup>-3600 cm<sup>-1</sup> comprise symmetric and asymmetric NH<sub>3</sub><sup>+</sup> stretching. The peak for symmetric NH<sub>3</sub><sup>+</sup> stretching around 3136 cm<sup>-1</sup> is more prominent for CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. It can be clearly seen that there is no observable change in the IR spectra on decreasing the polarisibility by successive decrease in values of x or Iodide ion (according to Lorentz-Lorenz shift).<sup>18</sup> Study of the remaining composition is shown in (Fig.S4 ESI<sup>†</sup>)

Table. 1 Nominal value for Manganese in contrast to the experimental value obtained by the EDX analysis, lattice parameter

Nominal Value (1-x)	Experime- ntal Value (1-x)	Lattice Parameters a (Å)	Lattice Parameter c (Å)	E <sub>g</sub> (DRS)
0	0	10.1243	12.8067	1.56
0.2	0.183	10.0866	12.7589	1.56
0.4	0.3605	10.0491	12.7115	1.54
0.6	0.575	10.0367	12.6958	1.56
0.8	0.788	10.0201	12.6749	1.55

EDX analysis was performed for different values of x in the perovskite  $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$  shown in Table S1. It state that upon decreasing the value of x from 1.0 to 0.2, the amount of lead incorporated in the material decreases from 30.58 weight percent to 0.72 weight percent. Thus, the amount of lead incorporation in the perovskite material has been reduced by a factor of 43. Furthermore, it can be seen that the amount of manganese incorporation increases from 0 to 21.41 weight percent in x=1 and x=0.2 samples respectively. The abundance of manganese incorporation is depicted by EDX mapping (Fig. 3).

A consistent trend in the particle size, however, cannot be observed from the FESEM images of the perovskite powder. Clearly resolved crystals can be observed from the FESEM images of perovskites corresponding to x = 1.0 - 0.5respectively. But, as the amount of manganese in the perovskite material increases beyond x=0.5, i.e, for x= 0.4 to 0.1, separate crystals are no longer observed and infact highly diffused crystals were obtained with sharing common boundaries. Study of the remaining composition is shown in (Fig.S5 and S6 ESI<sup>†</sup>) Furthermore, it must be noted, that for x=0, a stable perovskite structure is not obtained by the aforementioned procedure. Thus, it can be concluded that beyond x=0.5, the addition of increasing amounts of manganese chloride decreases the stability of the proposed material under ambient conditions. The results, however, may prove to be different under inert conditions for preparation of the material. Table (1) shows the manganese incorporation in few samples, i.e., x=0.2, 0.4, 0.6 0.8, 1.0 that have the experimental value for (1-x) is close or less than the nominal value derived form weight% depicted EDX analysis.

Fig 4 shows photovoltaic performance of fabricated device based on inverted planar architecture ITO/PEDOT:PSS/MAPb<sub>x</sub>Mn<sub>1</sub>.  $_xI_{1+2x}Cl_{2-2x}/PC_{61}BM/Al (x=0.9)$  under Air Mass 1.5 Global with an irradiation intensity of 100 mW/cm<sup>2</sup>. It displays an alarming open circuit voltage V<sub>oc</sub> and Fill factor (FF) of 1.19V and 87.9% respectively. Unfortunately the obtained energy conversion efficiency of 0.32% is a cause of flat short-circuit current of 15.146  $\mu$ A which is consistent with previous reports.<sup>19</sup>

# (a)



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Fig. 3 (a) Photograph of $MAPb_xMn_{1-x}I_{1+2x}Cl_{2-2x}$ with	Х				
decreasing from 1 - 0.1. (b) FESEM images of the synthesize	ed				
perovskite for different values of x along with the EDX plo	ots				
and EDX mapping showing the incorporation of lead an	nd				
manganese in MAPb <sub>x</sub> Mn <sub>1-x</sub> $I_{1+2x}Cl_{2-2x}$ .					

The cross section of fabricated cell shows ~45nm thick layer of hole transporting material (HTM) PEDOT:PSS just above the ITO film followed by ~125nm thin layer of MAPb<sub>x</sub>Mn<sub>1-x</sub>I<sub>1+2x</sub>Cl<sub>2-2x</sub> perovskite which was completely covered by around 150nm thick layer of PC<sub>61</sub>BM as a electron tansporting material (ETM).

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Fig. 4. (a) Device architecture of ITO/PEDOT:PSS/ MAPb<sub>x</sub>Mn<sub>1-x</sub>I<sub>1+2x</sub>Cl<sub>2-2x</sub>/PC<sub>61</sub>BM/Al (b) Cross-sectional SEM image showing the device structure of MAPb<sub>x</sub>Mn<sub>1-x</sub>I<sub>1+2x</sub>Cl<sub>2-2x</sub> perovskite solar cells. (c) Current–voltage curves of MAPb<sub>x</sub>Mn<sub>1-x</sub>I<sub>1+2x</sub>Cl<sub>2-2x</sub> perovskite solar cells  $\mathbf{x} = \mathbf{0.9}$  (d) Top morphology of perovskite film on ITO/PEDOT:PSS substrates.

We have used only 15wt% of perovskite (1:1 ratio) solution for device fabrication that give a very thin layer of perovskite ~125nm. This gives insufficient charge carrier generation as a consequence low short circuit current  $I_{sc}$  is observed. In this way there is less charge carrier generation due to insufficient thickness of absorber layer which greatly suppress the device efficiency. Here the outastanding fill factor is achieved due to complete surface coverage of perovskite layer which leads to high shunt resistance ( $R_{sh}$ ). The device surged in term of  $V_{oc}$  (1.19V) which is attributed to pin hole free morphology of top layer that inturn reduce recombination to an appreciable extent (Fig 4d). It may be one of the highest  $V_{oc}$  reported yet via inverted planar architecture over other bilayered HTM that incorporate polymer additive to increase the work function of HTM in order make perfect ohmic contact.<sup>20</sup>

Experiments with other composition is in their preliminary stage. we have fabricated cell considering composition X=0.8 achieved  $\eta$  0.83%, V<sub>oc</sub> 0.88 V, fill factor 19.2% but is still under optimisation. There is plenty of room available for further invesigation such as to explore the interfacial engineering of synthesized perovskite and HTM/ETM interfaces. This communication may lead to deeper insight due to presence of observable amount of Chlorine which is one of the most debatable among scientific community. Since we have used one step precursor deposition method, modification by other processing method for the growth of high quality crystal under inert condition makes it unprecedented absorber.

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# The graphical and textual abstract



Here we put a step toward swapping of toxic lead from lead based perovskite solar cell through compositional change using Manganese Chloride as a substitute with a formula of MAPb<sub>x</sub>Mn<sub>1</sub>.  $_xI_{1+2x}Cl_{2-2x}$  (nominal x = 0.1-1.0). Further cell fabrication with inverted planar architecture at low processing temperature shows potential application towards future perovskite solar cell.