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CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} from non-iodide lead salts for perovskite solar cells via formation of PbI\textsubscript{2}

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We report formation of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} from more soluble, non-iodide lead salts like Pb(SCN)\textsubscript{2} and Pb(NO\textsubscript{3})\textsubscript{2}. When exposed to CH\textsubscript{3}NH\textsubscript{3}I vapours, colourless lead salts turned yellow before the formation of black perovskite. Investigation of this yellow intermediate suggests that anion exchange (converting lead salts to PbI\textsubscript{2}) precedes the perovskite formation. PCE of 7.6\%, 8.4\% are achieved for devices formed from Pb(SCN)\textsubscript{2} and Pb(NO\textsubscript{3})\textsubscript{2} respectively.

Organic inorganic hybrid perovskites have gained significant attention in last few years for their promising photovoltaic performance.\textsuperscript{1} Power conversion efficiencies approaching 20\% have already been reported with single junction perovskite solar cells and it is expected that perovskites in tandem geometry can achieve efficiencies reaching 30\%.\textsuperscript{2} Methylammonium lead iodide (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}) perovskite have been the frontrunner in these high efficiency solar cells.\textsuperscript{3} This perovskite is not difficult to access and can be formed by mixing lead iodide (PbI\textsubscript{2}) and methylammonium iodide (MAI). Perovskites made from mixture of lead chloride (PbCl\textsubscript{2}) and MAI have also shown rather high efficiencies.\textsuperscript{4} Contrary to the initial reports of having mixed halide perovskite (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3},Cl\textsubscript{2}), recent reports suggest that perovskite formed from PbCl\textsubscript{2} is chloride free (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}).\textsuperscript{5}

There are recent reports dedicated to understand this process.\textsuperscript{6} A yellow intermediate phase is observed during the formation of the perovskite through which chloride ions were replaced by iodide ions. When such an exchange of anions takes place, question arises whether other lead salts also can form the same perovskite (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}). Recent report, showed that even the lead salt such as lead acetate also tend to form CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite.\textsuperscript{7} But the mechanism through which these non-halide salts form CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} still remain unclear. In order to understand the formation of perovskite, we treated three different non-iodide lead salts, (halide: PbCl\textsubscript{2}, pseudo-halide salt: Pb(SCN)\textsubscript{2} and non-halide salt: Pb(NO\textsubscript{3})\textsubscript{2}) with methylammonium iodide vapours. Perovskite formation was attempted through sequential vapour-assist solution process.\textsuperscript{8} Through this method the perovskites were formed slowly in about two to five hours. This slow formation allows us to monitor the progress of perovskite formation. Unlike PbCl\textsubscript{2}, perovskites formed from Pb(NO\textsubscript{3})\textsubscript{2} and Pb(SCN)\textsubscript{2} clearly passed through a yellow PbI\textsubscript{2} stage before the formation of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. The perovskite films were formed from, by spin coating lead salt from DMF solution on to TiO\textsubscript{2} coated FTO substrate (solution method). PbCl\textsubscript{2} is insoluble in DMF and therefore it was vapour deposited over TiO\textsubscript{2}.\textsuperscript{9} The colourless lead salt films were then exposed to MAI vapour at around 180 °C for 5 hours in closed graphite vessel in the nitrogen filled glove box to form complete perovskite film. When exposed for shorter duration or lower temperature, a yellow intermediate state was obtained which on further exposure to the MAI vapour transforms to a black perovskite film (Figure 1). In order to understand the perovskite formation, thin film XRD was performed on lead film, yellow intermediate and black perovskite film for all three precursors. Experimental details were given in supporting information.

Figure 1: Colourless lead thiocyanate Pb(SCN)\textsubscript{2} film (A) Yellow intermediate film formed upon exposure to MAI vapours (B) and complete perovskite film (C)

Figure 2(a) represents the XRD of different lead salts deposited over TiO\textsubscript{2} coated FTO substrate. It is worthy to highlight that the lead iodide (PbI\textsubscript{2}) showed an intense (011) peak at the 2θ values of 12.7° where as
other lead salts (PbCl₂, Pb(SCN)₂, and Pb(NO₃)₂) do not show any peak in that region. Figure 2(c) corresponds to XRD of black perovskite films. XRD peaks for perovskite formed from PbI₂ and PbCl₂ match perfectly with each other which is in line with recent reports. Interestingly, even the peaks of perovskite formed from Pb(SCN)₂ and Pb(NO₃)₂ match with the peaks of CH₃NH₃PbI₃. This suggests that irrespective of lead salt used, same perovskite is formed in vapour assist sequential deposition process. Figure 2(b) represents the XRD of yellow intermediate where, for lead thiocyanate and lead nitrate along with original lead salt peak, a new peak appeared at 20 value of 12.7°. This peak matches with the XRD peak of PbI₂ suggesting that the SCN⁻ and NO₃⁻ ions were exchanged with I⁻ (from MAI) resulting in the conversion of lead salt (Pb(SCN)₂ and Pb(NO₃)₂) to PbI₂. Formation of yellow intermediate phase during solution processed perovskite formation from PbCl₂ has already been reported and attributed to yellow phase of perovskite. However, the yellow intermediate observed in case of Pb(SCN)₂ and Pb(NO₃)₂ does not corresponds to the yellow intermediate perovskite phase rather it corresponds to PbI₂. Thiocyanate ion a pseudohalide is a polyatomic analogue of halides resembling the properties of halogen. Resemblance of their chemical properties allows them to act as a substitute for halogens in several chemical compounds. When lead thiocyanate was exposed to MAI vapours, we did not observe the formation of perovskite containing thiocyanate. Rather, it undergoes anion exchange forming PbI₂ and subsequently CH₃NH₃PbI₃.

Even the yellow intermediate from PbCl₂ shows a small peak at 20 of 12.7° (which matches with PbI₂ peak), however peaks were also observed at 21.45°, 24.10° and 29.0° which do not match with any of the peaks for PbI₂ or PbCl₂ or CH₃NH₃PbI₃ or TiO₂ or FTO. Although in case of lead thiocyanate and lead nitrate the exchange of anions at lead salt stage is clearly observed, for lead chloride exchange at lead salt stage is unclear and requires further investigation. For these yellow intermediate thin films, a small peak at 20 value of 14.1 was also observed. This peak corresponds to (110) CH₃NH₃PbI₃ which can be attributed to the partial formation of perovskite by the interaction of PbI₂ and MAI.

![Figure 3: SEM-EDS spectra of CH₃NH₃PbI₃ formed from different precursors Pb(NO₃)₂ (yellow edge), Pb(SCN)₂ (red edge) and PbCl₂ (green edge)](image)

The elemental composition of the different lead precursor perovskite films were carried out using energy dispersive spectroscopy (EDS) mapping in SEM mode. From figure 3 it is observed that EDS spectra for perovskites from all three lead precursors match with each other. For perovskites formed from different lead salts, especially lead nitrate and lead thiocyanate, EDS analysis corresponds to the signal of lead and iodine in an atomic ratio close to 1:3 (Table S1). Detailed EDS data is provided in supplementary information. Similar to recent literature reports, we could not detect any signal corresponding to chlorine in perovskite formed from PbCl₂. In similar trend, no EDS signal for sulphur atom is observed in the perovskite formed from Pb(SCN)₂. All these results suggest that same perovskite (CH₃NH₃PbI₃) is formed in vapour assisted sequential deposition method. EDS analysis was also performed on yellow intermediate state and black perovskite formed from the exposure of PbCl₂ to MAI vapours. EDS analysis of yellow intermediate state does show the presence of iodine before formation of perovskite (Table S2), but the stage at which the anions got exchanged still remains unclear and need further investigation.

![Figure 2 (A) XRD of lead precursors (B) XRD of intermediate stage (C) XRD of perovskites formed from Pb(NO₃)₂, Pb(SCN)₂, PbCl₂ and PbI₂](image)

Even the yellow intermediate from PbCl₂ shows a small peak at 20 of 12.7° (which matches with PbI₂ peak), however peaks were also observed at 21.45°, 24.10° and 29.0° which do not match with any of the peaks for PbI₂ or PbCl₂ or CH₃NH₃PbI₃ or TiO₂ or FTO. Although in case of lead thiocyanate and lead nitrate the exchange of anions at lead salt stage is clearly observed, for lead chloride exchange at lead salt stage is unclear and requires further investigation. For these yellow intermediate thin films, a small peak at 20 value of 14.1 was also observed. This peak corresponds to (110) CH₃NH₃PbI₃ which can be attributed to the partial formation of perovskite by the interaction of PbI₂ and MAI.

![Scheme 1. Reaction of lead salts (lead nitrate, lead thiocyanate, and lead chloride) with aqueous methylammonium iodide](image)

It is important to note that, in this study, during formation of perovskite, substrate was heated up to higher temperature (>100 °C). This high temperature will favour the diffusion of ions leading to exchange of anions. Such an exchange is also observed in solution state, where lead salts (PbCl₂ or Pb(NO₃)₂ or Pb(SCN)₂) when treated with colourless aqueous solution of methylammonium iodide resulted in the immediate formation of golden yellow precipitate of PbI₂ (Figure S3). This double displacement reaction is analogous to the well-known reaction of lead salts with KI to form PbI₂ (scheme 1). Thus, irrespective of the lead salts used, because of anion exchange we end up with the same CH₃NH₃PbI₃ perovskite.
Perovskites formed from all these lead precursors were used to fabricate solar cell in FTO/TiO₂/Perovskite/P3HT/Au architecture (Figure S4). Undoped P3HT was used as hole transporting layer as it can also help to passivate the defects formed on the surface of perovskite. 15

Experimental details are mentioned in the supporting information. Figure 4 depicts the illuminated JV and external quantum efficiency (EQE) for the perovskite film formed from different lead precursor. As reported in table 1, CH₃NH₂PbI₃ perovskite solar cells formed from different lead precursors showed comparable photovoltaic behaviour. The high fill factor in PbCl₂ can be attributed to the fabrication condition, where the PbCl₂ perovskite was sequentially vapour deposited unlike Pb(NO₃)₂ and Pb(SCN)₂ perovskites which were formed by vapour assist solution process. EQE onsets from all three perovskites are at similar energies, which also supports that the perovskites formed from all lead precursors are same.

Table 1. Photovoltaic properties of CH₃NH₂PbI₃ perovskite solar cells formed from different lead precursors under ELH lamp.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Vₘₐₓ (V)</th>
<th>Jₘₐₓ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(NO₃)₂</td>
<td>0.87</td>
<td>18.17</td>
<td>53.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Pb(SCN)₂</td>
<td>0.91</td>
<td>15.14</td>
<td>55.3</td>
<td>7.6</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>0.93</td>
<td>16.91</td>
<td>69.4</td>
<td>10.9</td>
</tr>
</tbody>
</table>

It is important to note that, in our work the lead nitrate perovskite formed through vapour assisted sequential deposition showed impressive photovoltaic performance compared to the lead nitrate perovskite reported by single solvent approach. 14 Power conversion efficiencies (PCE) of 8.4 % and 7.6 % for perovskite formed from lead nitrate and lead thiocyanate precursors were achieved respectively, with photocurrent and open circuit voltage comparable to that of perovskite formed from PbCl₂. The SEM images of lead precursor and the perovskites are given in the supporting information (Figure S5 & 6). Although nitrate and thiocyanate salts of lead form perovskite through common intermediate (PbI₂), their difference in photovoltaic properties can be due to the difference in morphology and residual ions which might influence the defect states affecting the device outcome. 15 Hysteresis of the I-V curves were also studied. The hysteresis is shown in the figure S7. In our hysteresis curve the short circuit current does not change significantly upon hysteresis. The major change in hysteresis is in the fill factor. The fill factor decreased by ~ 10 % for all the three perovskite formed from the different lead precursor. All these devices were fabricated with the procedure optimized for PbCl₂. More optimization is required for Pb(SCN)₂ and Pb(NO₃)₂ to achieve higher efficiencies and the research towards that direction is currently under progress in our lab.

Conclusions
In conclusion, we report the formation of perovskite from inexpensive and more soluble lead precursors (lead thiocyanate and lead nitrate). XRD and EDS analysis of these perovskites indicate the formation of same CH₃NH₂PbI₃ perovskite. Analysis of yellow intermediate state suggests that perovskite formation takes place through the formation of lead iodide by exchange of anions between lead precursor and methylammonium iodide. Lead chloride also forms a yellow intermediate state, but whether the chloride precursor undergoes such an anion exchange before perovskite formation remains unclear and needs further investigation. PCE of 8.4 % was achieved for perovskite devices formed from lead nitrate, which to our knowledge is highest efficiency till date. We also report the first ever successful perovskite solar cell from lead thiocyanate with PCE of 7.6 %.

Acknowledgements
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Notes and references


