

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

CH₃NH₃PbI₃ from non-iodide lead salts for perovskite solar cells *via* formation of PbI₂

Cite this: DOI: 10.1039/x0xx00000x

Ganapathy Balaji^{a*}, Pranav H. Joshi^b, Hisham A. Abbas^b, Liang Zhang^b, Ranjith Kottokkaran^a, Mehran Samiee^b, Max Noack^a, Vikram L. Dalal^a

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

We report formation of CH₃NH₃PbI₃ from more soluble, non-iodide lead salts like Pb(SCN)₂ and Pb(NO₃)₂. When exposed to CH₃NH₃I 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 PbI₂) precedes the perovskite formation. PCE of 7.6 %, 8.4 % are achieved for devices formed from Pb(SCN)₂ and Pb(NO₃)₂ respectively.

Organic inorganic hybrid perovskites have gained significant attention in last few years for their promising photovoltaic performance.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%.² Methylammonium lead iodide (CH₃NH₃PbI₃) perovskite have been the frontrunner in these high efficiency solar cells.³ This perovskite is not difficult to access and can be formed by mixing lead iodide (PbI₂) and methylammonium iodide (MAI). Perovskites made from mixture of lead chloride (PbCl₂) and MAI have also shown rather high efficiencies.⁴ Contrary to the initial reports of having mixed halide perovskite (CH₃NH₃PbI_{3-x}Cl_x), recent reports suggest that perovskite formed from PbCl₂ is chloride free (CH₃NH₃PbI₃).⁵

There are recent reports dedicated to understand this process.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 (CH₃NH₃PbI₃). Recent report, showed that even the lead salt such as lead acetate also tend to form CH₃NH₃PbI₃ perovskite.⁷ But the mechanism through which these non-halide salts form CH₃NH₃PbI₃ still remain unclear. In order to understand the formation of perovskite, we treated three different non-iodide lead salts, (halide: PbCl₂, pseudo-halide salt: Pb(SCN)₂ and non-

halide salt: Pb(NO₃)₂) with methylammonium iodide vapours. Perovskite formation was attempted through sequential vapour-assist solution process.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 PbCl₂, perovskites formed from Pb(NO₃)₂ and Pb(SCN)₂ clearly passed through a yellow PbI₂ stage before the formation of CH₃NH₃PbI₃.

The perovskite films were formed from, by spin coating lead salt from DMF solution on to TiO₂ coated FTO substrate (solution method). PbCl₂ is insoluble in DMF and therefore it was vapour deposited over TiO₂.⁹ 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)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 TiO₂ coated FTO substrate. It is worthy to highlight that the lead iodide (PbI₂) showed an intense (011) peak at the 2θ values of 12.7° where as

other lead salts (PbCl_2 , $\text{Pb}(\text{SCN})_2$ and $\text{Pb}(\text{NO}_3)_2$) do not show any peak in that region.¹⁴ Figure 2(c) corresponds to XRD of black perovskite films. XRD peaks for perovskite formed from PbI_2 and PbCl_2 match perfectly with each other which is in line with recent reports.¹⁰ Interestingly, even the peaks of perovskite formed from $\text{Pb}(\text{SCN})_2$ and $\text{Pb}(\text{NO}_3)_2$ match with the peaks of $\text{CH}_3\text{NH}_3\text{PbI}_3$. This suggests that irrespective of lead salt used, same perovskite is formed in vapour assisted 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 2θ value of 12.7° . This peak matches with the XRD peak of PbI_2 suggesting that the SCN^- and NO_3^- ions were exchanged with I^- (from MAI) resulting in the conversion of lead salt ($\text{Pb}(\text{SCN})_2$ and $\text{Pb}(\text{NO}_3)_2$) to PbI_2 . Formation of yellow intermediate phase during solution processed perovskite formation from PbCl_2 has already been reported and attributed to yellow phase of perovskite.¹¹ However, the yellow intermediate observed in case of $\text{Pb}(\text{SCN})_2$ and $\text{Pb}(\text{NO}_3)_2$ does not correspond to the yellow intermediate perovskite phase rather it corresponds to PbI_2 . Thiocyanate ion a pseudohalide is a polyatomic analogue of halides resembling the properties of halogens. 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 PbI_2 and subsequently $\text{CH}_3\text{NH}_3\text{PbI}_3$.

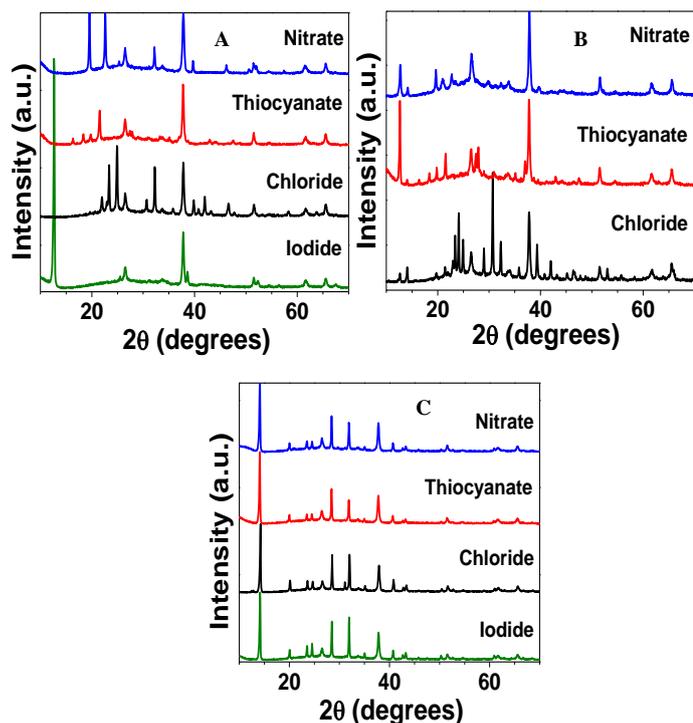


Figure 2 (A) XRD of lead precursors (B) XRD of intermediate stage (C) XRD of perovskites formed from $\text{Pb}(\text{NO}_3)_2$, $\text{Pb}(\text{SCN})_2$, PbCl_2 and PbI_2

Even the yellow intermediate from PbCl_2 shows a small peak at 2θ of 12.7° (which matches with PbI_2 peak), however peaks were also observed at 21.45° , 24.10° and 29.0° which do not match with any of the peaks for PbI_2 or PbCl_2 or $\text{CH}_3\text{NH}_3\text{PbI}_3$ or TiO_2 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 2θ value of 14.1 was also observed. This peak corresponds to (110) $\text{CH}_3\text{NH}_3\text{PbI}_3$ which can be attributed to the partial formation of perovskite by the interaction of PbI_2 and MAI.

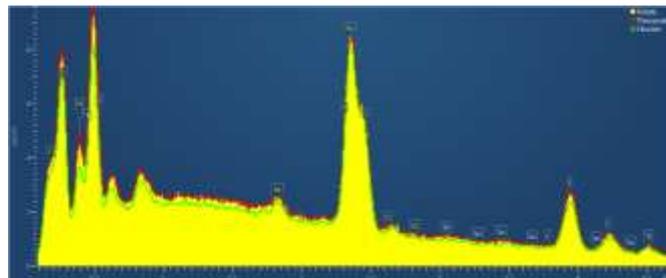
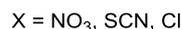


Figure 3: SEM-EDS spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ formed from different precursors $\text{Pb}(\text{NO}_3)_2$ (yellow edge), $\text{Pb}(\text{SCN})_2$ (red edge) and PbCl_2 (green edge)

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 PbCl_2 .¹⁰ In similar trend, no EDS signal for sulphur atom is observed in the perovskite formed from $\text{Pb}(\text{SCN})_2$. All these results suggest that same perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) 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 PbCl_2 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.



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

It is important to note that, in this study, during formation of perovskite, substrate was heated up to higher temperature ($>100^\circ\text{C}$). 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 (PbCl_2 or $\text{Pb}(\text{NO}_3)_2$ or $\text{Pb}(\text{SCN})_2$) when treated with colourless aqueous solution of methylammonium iodide resulted in the immediate formation of golden yellow precipitate of PbI_2 (Figure S3). This double displacement reaction is analogous to the well-known reaction of lead salts with KI to form PbI_2 (scheme 1).¹² Thus, irrespective of the lead salts used, because of anion exchange we end up with the same $\text{CH}_3\text{NH}_3\text{PbI}_3$ 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.¹³

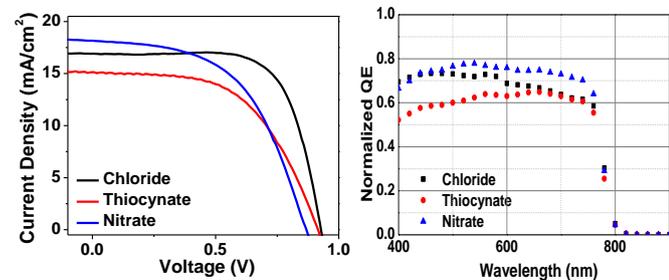


Figure 4. (a) JV characteristics and (b) EQE spectra of CH₃NH₃PbI₃ perovskite formed from different lead precursors

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, CH₃NH₃PbI₃ 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 CH₃NH₃PbI₃ perovskite solar cells formed from different lead precursors under ELH lamp.

Precursor	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
Pb(NO ₃) ₂	0.87	18.17	53.3	8.4
Pb(SCN) ₂	0.91	15.14	55.3	7.6
PbCl ₂	0.93	16.91	69.4	10.9

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 CH₃NH₃PbI₃ 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

This work was supported in part by NSF grants ECCS-1232067, CBET-1336134 and Iowa Energy Center.

Notes and references

^a Microelectronics Research Centre, Iowa State University, Ames, Iowa.

^b Department of Electrical and Computer Engineering, Iowa State University, Ames, Iowa.

*g.balaj@gmail.com

Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

- (a) A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, 131, 6050. (b) H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J.-E. Moser, M. Grätzel and N.-G. Park, *Sci. Rep.*, 2012, 2, 591. (c) M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, 501, 395. (d) J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, 499, 316. (e) M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nature Photonics*, 2014, 8, 506.
- (a) H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, 345, 542. (b) P. Gao, M. Grätzel and M. K. Nazeeruddin, *Energy Environ. Sci.*, 2014, 7, 2448. (c) H. J. Snaith, *J. Phys. Chem. Lett.*, 2013, 4, 3623. (d) M. Grätzel, *Nature Materials*, 2014, 13, 838. (e) N.-G. Park, *Materials Today*, doi:10.1016/j.mattod.2014.07.007.
- (a) H.-S. Kim, J.-W. Lee, N. Yantara, P. P. Boix, S. A. Kulkarni, S. Mhaisalkar, M. Grätzel and N.-G. Park, *Nano Lett.*, 2013, 13, 2412. (b) S. Ryu, J. H. Noh, N. J. Jeon, Y. C. Kim, W. S. Yang, J. Seo and S. I. Seok, *Energy Environ. Sci.*, 2014, 7, 2614. (c) F. Huang, Y. Dkhissi, W. Huang, M. Xiao, I. Benesperi, S. Rubanov, Y. Zhu, X. Lin, L. Jiang, Y. Zhou, A. Gray-Weale, J. Etheridge, C. R. McNeill,

- R. A. Caruso, U. Bach, L. Spiccia and Y.-B. Cheng, *Nano Energy*, 2014, 10, 10.
4. (a) M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, 338, 643. (b) E. Edri, S. Kirmayer, S. Mukhopadhyay, K. Gartsman, G. Hodes and D. Cahen *Nature Communications*, 2013, 5, 3461. (c) J. You, Z. Hong, Y. M. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen, S. Lu, Y. Liu, H. Zhou and Y. Yang, *ACS Nano*, 2014, 8, 1674. (d) M. Jiang, J. Wu, F. Lan, Q. Tao, D. Gao and G. Li, *J. Mater. Chem. A*, 2015, 3, 963.
5. (a) S. T. Williams, F. Zuo, C.-C. Chueh, C.-Y. Liao, P.-W. Liang and A. K.-Y. Jen, *ACS Nano*, 2014, 10, 10640. (b) S. Colella, E. Mosconi, G. Pellegrino, A. Alberti, V. L. P. Guerra, S. Masi, A. Listorti, A. Rizzo, G. G. Condorelli, F. D. Angelis and G. Gigli, *J. Phys. Chem. Lett.*, 2014, 5, 3532.
6. (a) E. L. Unger, A. R. Bowring, C. J. Tassone, V. L. Pool, A. Gold-Parker, R. Cheacharoen, K. H. Stone, E. T. Hoke, M. F. Toney and M. D. McGehee, *Chem. Mater.*, 2014, DOI: 10.1021/cm503828b. (b) P. Pistor, J. Borchert, W. Fränzel, R. Cusk, R. Scheer, *J. Phys. Chem. Lett.* 2014, 5, 3308.
7. (a) W. Zhang, M. Saliba, D. T. Moore, S. K. Pathak, M. T. Hörantner, T. Stergiopoulos, S. D. Stranks, G. E. Eperon, J. A. Alexander-Webber, A. Abate, A. Sadhanala, S. Yao, Y. Chen, R. H. Friend, L. A. Estroff, U. Wiesner, H. J. Snaith, *Nature Communications*, 2015, 6, 6142. (b) F. K. Aldibaja, L. Badia, E. Mas-Marzá, R. S. Sánchez, E. M. Barea, I. Mora-Sero, *J. Mater. Chem. A*, 2015, DOI:10.1039/C4TA06198E.
8. Q. Chen, H. Zhou, Z. Hong, S. Luo, H-S. Duan, H-H. Wang, Y. Liu, G. Li, Y. Yang, *J. Am. Chem. Soc.*, 2014, 136, 622.
9. H. A. Abbas, R. Kottokaran, B. Ganapathy, M. Samiee, L. Zhang, A. Kitahara, M. Noack, V. L. Dalal, *APL Mat.*, 2015, 3, 016105.
10. M. I. Dar, N. Arora, P. Gao, S. Ahmad, M. Grätzel, M. K. Nazeeruddin, *Nano. Lett.*, 2014, DOI: 10.1021/nl503279x.
11. (a) C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, 52, 9019. (b) K. W. Tan, D. T. Moore, M. Saliba, H. Sai, L. A. Estroff, T. Hanrath, H. J. Snaith and U. Wiesner, *ACS Nano*, 2014, 5, 4730.
12. P. Patnaik. "Handbook of Inorganic Chemicals" McGraw-Hill, 2002.
13. N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely and H. J. Snaith, *ACS Nano*, 2014, 10, 9815.
14. N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely and H. J. Snaith, *ACS Nano*, 2014, 10, 9815.
15. D. T. Moore, H. Sai, K. W. Tan, L. A. Estroff, U. Wiesner, *APL Mat.*, 2014, 2, 081802.