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Solid state transformation of the crystalline monohydrate (CH₃NH₃)PbI₃(H₂O)) to the (CH₃NH₃)PbI₃ perovskite

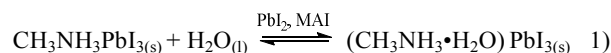
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Colorless crystals of (CH₃NH₃•H₂O)PbI₃ spontaneously lose water at 298K which triggers a transformation to the black (CH₃NH₃)PbI₃ perovskite in the solid state as a porous microcrystalline solid with nanoscale substructure, but the dihydrate (CH₃NH₃)₄PbI₆•2H₂O requires much more forcing conditions to produce (CH₃NH₃)PbI₃.

The optoelectronic properties of methyl ammonium lead tri-iodide (CH₃NH₃PbI₃ (**1**)) with a 3-D perovskite type structure have permitted fabricating several solar cell architectures that have high conversion efficiencies¹⁻²² which has sparked a surge of research on this material. Aqueous solutions of PbI₂ and CH₃NH₃I can alternately produce crystals of the black anhydrous 3-D perovskite CH₃NH₃PbI₃ (**1**)²³, a nearly colorless monohydrate ((CH₃NH₃)PbI₃•H₂O) (**2**)²⁴ and a light yellow dihydrate ((CH₃NH₃)₄PbI₆•2H₂O) (**3**)²⁵ depending on the temperature and solution composition. The optoelectronic properties of **1** are of far greater interest than **2** and **3** because of the relatively small band gap of ~1.5 - 1.6 eV^{23,26-28} and broad electronic absorption spectrum of the black compound (**1**) compared to **2** and **3** with band gaps of 3.1 eV²⁹ and 3.8eV^{24,30} respectively. Several recent studies have addressed the stability of **1** and the effects on solar cell performance that result from exposure to water and oxygen.^{29,31-34} This article reports on aspects of the conversions of crystals of the mono and dihydrates (**2,3**) into **1** in the solid state that extend and complement recent studies of the reactions of **1** with water vapor.²⁹

Crystals of **1-3** were prepared by reported aqueous procedures²³⁻²⁵ and the structures verified using powder and single crystal X-ray diffraction (SI). Aqueous solutions of PbI₂ and CH₃NH₃I provide a facile route through which the solids of **1**, **2** and **3** are able to interconvert. An equilibrium mediated by the aqueous solution is established between the solids of **1** and **2** when they are both in contact with an aqueous solution saturated with the PbI₂/CH₃NH₃I reaction mixture (eq. 1). Placing



the black perovskite crystals back into contact with the mother liquor reaction solution at 298K resulted in **1** disappearing and crystals of **2** appearing. Crystals of **1** and **3** were also grown from solutions of PbI₂ and CH₃NH₃I in γ -butyrolactone (GBL)³⁵ in the absence and presence of water respectively, but no conditions were found that gave crystals of the monohydrate **2** in GBL.

Structures of **1**, **2** and **3** have 3-D²³, 1-D²⁴ and 0-D²⁵ arrays of PbI_n⁽ⁿ⁻²⁾⁻ respectively (figure 1), where each Pb(II) is surrounded by six iodides in octahedral-like structures. Ratios of ionic radii provide a guide for the capability of ABX₃ materials to produce perovskite-like 3-D structures.^{36,37} Applying the recently proposed procedure for estimating the effective ionic radius for polyatomic ions³⁷ to the hydrated methyl ammonium cation ([CH₃NH₃•H₂O]⁺) gives an estimated effective ionic radius (r_A) of 346nm and tolerance factor (α) of 1.13 ($\alpha = (r_A + r_X) / (\sqrt{2}(r_B + r_X))$). The tolerance factor of 1.13 is substantially outside the range of 0.8 - 1.0 where 3-D

perovskite-like structures are the most stable morphology.³⁷ Adoption of lower dimensional structures for compounds of $[\text{CH}_3\text{NH}_3\cdot\text{H}_2\text{O}]^+$ with $\text{PbI}_n^{(n-2)-}$ is consistent with the effective size of the hydrated methyl ammonium cation. Loss of water from **2** generates methyl ammonium cations ($[\text{CH}_3\text{NH}_3]^+$) which have a near ideal tolerance factor ($\alpha = 0.92$) for giving a perovskite-like 3-D structure.²⁵ The thermodynamically favored coulombic lattice energy for the 3-D structure drives the conversion of **2** into **1**.

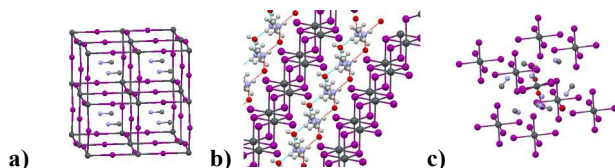


Figure 1: a) 3-D perovskite-like material $\text{CH}_3\text{NH}_3\text{PbI}_3$ (**1**) b) 1-D chains of $[\text{PbI}_3]_2^{2-}$ and cationic $[\text{CH}_3\text{NH}_3\cdot\text{H}_2\text{O}]^+$ units. (2) Hydrogen bonding network between CH_3NH_3 and H_2O shown with blue lines. c) 0-D structure of $(\text{CH}_3\text{NH}_3\cdot 2\text{H}_2\text{O})\text{PbI}_6$ (**3**) with isolated PbI_6 octahedra.

The near colorless crystals of the monohydrate **2** in air or vacuum spontaneously lose water in a period of minutes to form a black material shown to be perovskite **1** by the powder x-ray diffraction pattern (Figure 2, eq. 2).

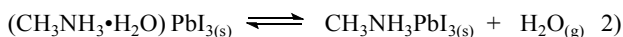


Figure 3 shows images from an optical microscope that illustrate how the change from colorless to black propagates for a crystal of **2** converting to **1**. The conversion is retarded by a coating of paratone oil to permit observation of this transformation over a period of two hours. Inspection of the conversion from a single crystal of **2** to **1** is illustrated in figure 3 and a video in the SI indicates that the conversion is initiated from points of nucleation which then propagate through the entire crystal. The complete loss of the characteristic diffraction peaks at 8.35° and 10.31° of the monohydrate **2** and appearance of powder diffraction peaks at 14.18° and 28.46° corresponding to reflections from the 110 and 220 crystal planes of **1**^{23,31} show that the conversion process is quantitative and exclusively produces the 3-D perovskite $(\text{CH}_3\text{NH}_3\text{PbI}_3)$ (**1**) as a polycrystalline material (Figure 2).

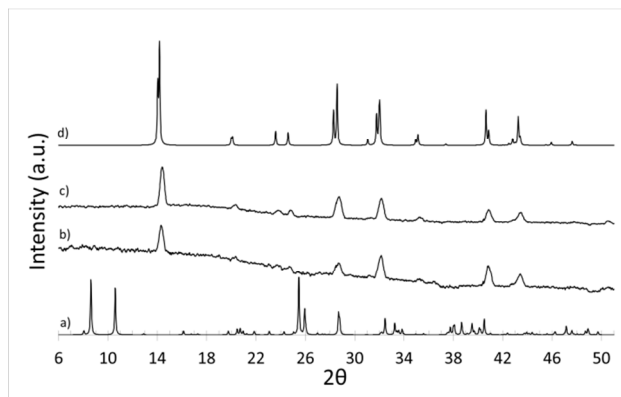


Figure 2: a) Calculated powder pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{H}_2\text{O}$ b) Powder pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{H}_2\text{O}$ crystal after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ c) Powder pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{H}_2\text{O}$ crystal after conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ and crushed to fine powder d) Calculated powder pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$.



Figure 3: Observation of a single crystal of $\text{CH}_3\text{NH}_3\text{PbI}_3\cdot\text{H}_2\text{O}$ (**2**) immersed in paratone oil at 298K in air and the spontaneous conversion to $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite (**1**) recorded at different times a) $t = 4$ minutes b) $t = 48$ minutes c) $t = 104$ minutes.

Light yellow crystals of **3** ($(\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot 2\text{H}_2\text{O}$) in air developed a black surface characteristic of the perovskite **1** over a period of 12 hours. The bulk interior of the crystal of **3** is unchanged (figure 4). Formation of **1** from **3** removes the components of CH_3NH_2 , HI and water (eq. 3) and is much slower than forming **1** by loss of water from **2** (eq. 1). A video showing the formation of **1** on the surface of **3** is given in the SI. Every effort should be made to avoid formation of **3** in the preparation of perovskite-like **1** because **3** cannot be easily removed or converted to **1**. This is best achieved by using rigorously dried solvents and using a minimal ratio of $\text{CH}_3\text{NH}_3\text{I}$ to PbI_2 .

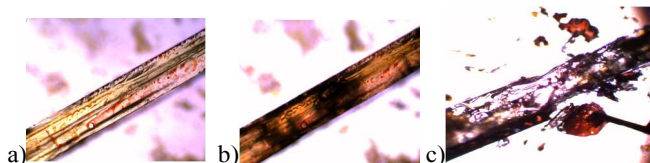


Figure 4: Single crystal of $((\text{CH}_3\text{NH}_3)_4\text{PbI}_6\cdot 2\text{H}_2\text{O})$ (**3**) placed on a glass slide and observed under optical microscope at a) 5 minutes b) 12 hours and c) surface of crystal removed with spatula to reveal intact interior of **3**.

A single crystal of the monohydrate ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) (**2**) was stabilized for x-ray structure studies by immediately coating with paratone oil followed by mounting in the XRD instrument at 100K. The overall structure of **2** consists of 1-D chains of $[\text{PbI}_3]_2^{2-}$ and 1-D chains of $[\text{CH}_3\text{NH}_3 \cdot \text{H}_2\text{O}]^+$ cations with alternating methyl ammonium and water molecules held together by hydrogen bonding (Figure 1). Each Pb^{2+} interacts with six iodides in a highly distorted octahedral-like array that includes one terminal iodide (figure 1). The crystal of **2** at 100K shows a diffraction pattern for a single crystal (figure 2). When the crystal of **2** is warmed to 298K the spontaneous conversion to **1** occurs and the spots associated with a single crystal of **2** are replaced by the circles associated with a powder diffraction pattern for **1** (figure 5).

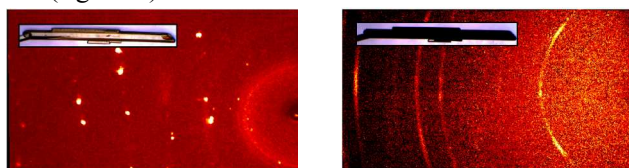


Figure 5 a) Sample single crystal diffraction frame of $(\text{CH}_3\text{NH}_3 \cdot \text{H}_2\text{O})\text{PbI}_{3(s)}$ b) Powder pattern from single crystal of **2** converted to $\text{CH}_3\text{NH}_3\text{PbI}_{3(s)}$ and mounted for powder XRD with no further manipulation.

The perovskite material (**1**) obtained from single crystals of **2** retains the bulk shape of the reactant crystals, but X-ray diffraction (figure 5) and SEM (Figure 6) indicate that a microcrystalline powder-like material is produced. The loss of one water molecule from **2** in forming **1** results in a 6% decrease in the unit cell volume. The SEM images show a porous micron scale substructure for particles of **1** formed by loss of water from a single crystal of **2** (figure 6a, figure S1, S2). Probing the substructure further by TEM suggests that 5-10 nm particles of **1** are initially produced in the solid state conversion of crystalline **2** which agglomerate into larger particles (figure 6 b, c, figure S3, S4).

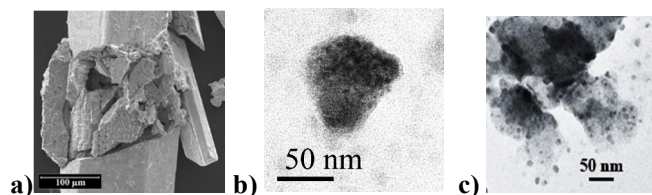


Figure 6: a) SEM of the perovskite material (**1**) obtained from single crystals of **2** retains the bulk shape of the reactant crystal, and shows the interior structures on the micron scale. b), c) TEM reveals the solid state conversion of crystal of **2** produces aggregates of 5 - 10 nm particles of **1**.

Solid state conversion for crystals of **2** to **1** is spontaneous at 298, but formation of **1** from **3** requires more forcing conditions. It is important to avoid the formation of **3** during the preparation of the perovskite **1** because the dihydrate **3** cannot be easily removed or converted to **1**. The large structural changes and the expulsion of water that occur in the transformation from the 1-D to the 3-D arrays of PbI_3^- units in the solid state conversion of crystals of **2** to the perovskite **1** destroys the long range order and produces a porous microcrystalline form of **1**. The material reported here complements the single crystal and films of **1** previously utilized in solar voltaic applications.

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Notes and references

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- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- (2) Im, J.-H.; Lee, C.-R.; Lee, J.-W.; Park, S.-W.; Park, N.-G. *Nanoscale* **2011**, *3*, 4088.
- (3) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Gratzel, M.; Park, N.-G. *Sci. Rep.* **2012**, *2*.
- (4) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. *Science* **2012**, *338*, 643.
- (5) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. *Science* **2013**, *342*, 341.
- (6) Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C.-S.; Chang, J. A.; Lee, Y. H.; Kim, H.-j.; Sarkar, A.; Nazeeruddin, K.; Gratzel, M.; Seok, S. I. *Nat Photon* **2013**, *7*, 486.
- (7) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. *Nano Lett.* **2013**, *13*, 1764.
- (8) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg. Chem.* **2013**, *52*, 9019.
- (9) Liu, M.; Johnston, M. B.; Snaith, H. J. *Nature* **2013**, *501*, 395.
- (10) Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.-S.; Wang, H.-H.; Liu, Y.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2013**, *136*, 622.
- (11) Liu, D.; Kelly, T. L. *Nat Photon* **2014**, *8*, 133.
- (12) Christians, J. A.; Fung, R. C. M.; Kamat, P. V. *J. Am. Chem. Soc.* **2013**, *136*, 758.

- (13) Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y. *Science* **2014**, *345*, 542.
- (14) Sum, T. C.; Mathews, N. *Energy & Environmental Science* **2014**, *7*, 2518.
- (15) Kazim, S.; Nazeeruddin, M. K.; Grätzel, M.; Ahmad, S. *Angewandte Chemie International Edition* **2014**, *53*, 2812.
- (16) Gao, P.; Gratzel, M.; Nazeeruddin, M. K. *Energy & Environmental Science* **2014**, *7*, 2448.
- (17) Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. *Energy & Environmental Science* **2014**, *7*, 982.
- (18) Cui, X.-P.; Jiang, K.-J.; Huang, J.-H.; Zhou, X.-Q.; Su, M.-J.; Li, S.-G.; Zhang, Q.-Q.; Yang, L.-M.; Song, Y.-L. *Chem. Commun.* **2015**, *51*, 1457.
- (19) Lee, J.-H.; Bristowe, N. C.; Bristowe, P. D.; Cheetham, A. K. *Chem. Commun.* **2015**, *51*, 6434.
- (20) Weller, M. T.; Weber, O. J.; Henry, P. F.; Di Pumpo, A. M.; Hansen, T. C. *Chem. Commun.* **2015**, *51*, 4180.
- (21) Wu, X.; Trinh, M. T.; Niesner, D.; Zhu, H.; Norman, Z.; Owen, J. S.; Yaffe, O.; Kudisch, B. J.; Zhu, X. Y. *J. Am. Chem. Soc.* **2015**, *137*, 2089.
- (22) Choi, J. J.; Yang, X.; Norman, Z. M.; Billinge, S. J. L.; Owen, J. S. *Nano Lett.* **2014**, *14*, 127.
- (23) Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Gratzel, M.; White, T. J. *Journal of Materials Chemistry A* **2013**, *1*, 5628.
- (24) Hao, F.; Stoumpos, C. C.; Liu, Z.; Chang, R. P. H.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2014**, *136*, 16411.
- (25) Vincent, B. R.; Robertson, K. N.; Cameron, T. S.; Knop, O. *Can. J. Chem.* **1987**, *65*, 1042.
- (26) Ball, J. M.; Stranks, S. D.; Horantner, M. T.; Huttner, S.; Zhang, W.; Crossland, E. J. W.; Ramirez, I.; Riede, M.; Johnston, M. B.; Friend, R. H.; Snaith, H. J. *Energy & Environmental Science* **2015**, *8*, 602.
- (27) Lin, Q.; Armin, A.; Nagiri, R. C. R.; Burn, P. L.; Meredith, P. *Nat Photon* **2015**, *9*, 106.
- (28) Löper, P.; Stuckelberger, M.; Niesen, B.; Werner, J.; Filipič, M.; Moon, S.-J.; Yum, J.-H.; Topič, M.; De Wolf, S.; Ballif, C. *The Journal of Physical Chemistry Letters* **2015**, *6*, 66.
- (29) Leguy, A. M. A.; Hu, Y.; Campoy-Quiles, M.; Alonso, M. I.; Weber, O. J.; Azarhoosh, P.; van Schilfgaarde, M.; Weller, M. T.; Bein, T.; Nelson, J.; Docampo, P.; Barnes, P. R. F. *Chem. Mater.* **2015**.
- (30) Koutselas, I. B.; Ducasse, L.; Papavassiliou, G. C. *J. Phys.: Condens. Matter* **1996**, *8*, 1217.
- (31) Christians, J. A.; Miranda Herrera, P. A.; Kamat, P. V. *J. Am. Chem. Soc.* **2015**, *137*, 1530.
- (32) Niu, G.; Guo, X.; Wang, L. *Journal of Materials Chemistry A* **2015**, *3*, 8970.
- (33) Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfgaarde, M.; Walsh, A. *Nano Lett.* **2014**, *14*, 2584.
- (34) Bass, K. K.; McAnally, R. E.; Zhou, S.; Djurovich, P. I.; Thompson, M. E.; Melot, B. C. *Chem. Commun.* **2014**, *50*, 15819.
- (35) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M. *Science* **2015**, *347*, 519.
- (36) Goldschmidt, V. M. *Naturwissenschaften* **1926**, *14*, 477.
- (37) Kieslich, G.; Sun, S.; Cheetham, A. K. *Chemical Science* **2014**, *5*, 4712.