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Item Type	Article
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Citation	Retrograde solubility of formamidinium and methylammonium lead halide perovskites enabling rapid single crystal growth 2015, 51 (100):17658 Chem. Commun.
Eprint version	Post-print
DOI	<a href="https://doi.org/10.1039/C5CC06916E">10.1039/C5CC06916E</a>
Publisher	Royal Society of Chemistry (RSC)
Journal	Chemical Communications
Rights	Archived with thanks to Chem. Commun.
Download date	2024-04-17 05:29:37
Link to Item	<a href="http://hdl.handle.net/10754/583895">http://hdl.handle.net/10754/583895</a>

**Retrograde solubility of formamidinium and methylammonium lead halide perovskites  
enabling rapid single crystal growth**

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## **Experimental procedure:**

### **Chemicals and reagents**

Lead bromide ( $\geq 98\%$ ), lead iodide (99.999% trace metal basis), DMF (anhydrous, 99.8%) and GBL ( $\geq 99\%$ ) were purchased from Sigma Aldrich. MAX and FAX were purchased from Dyesol Limited (Australia). All salts and solvents were used as received, without any further purification.

### **Synthesis of FAPBX<sub>3</sub> single crystals**

***Formamidinium lead iodide:*** 0.8 M solution of FAPbI<sub>3</sub> was prepared in GBL and filtered using PTFE filters with a 0.2- $\mu\text{m}$  pore size. 2 ml of the filtrate was placed in a 4-ml vial, and the vial was placed in an oil bath, at 80 °C. Then temperature was gradually increased to 115 °C and kept for 3 h. To further increase the crystal size, the setup was kept at 117 °C for 1 h, and at 120°C for another hour. The size of the crystal can be further increased through the gradual increase of temperature.

***Formamidinium lead bromide:*** 1 M solution of FAPbBr<sub>3</sub> was prepared in DMF:GBL (1:1 v/v) and filtered using PTFE filters with a 0.2- $\mu\text{m}$  pore size. 2 ml of the filtrate was placed in a 4-ml vial, and the vial was placed in an oil bath, at 40 °C. Then temperature was gradually increased to 55°C and kept for 3 h. To further increase the crystal size, the setup was kept at 57 °C for 1 h, and 60°C for another hour. The size of the crystal can be further increased through the gradual increase of temperature.

All procedures were conducted under ambient conditions and a humidity of 55–57%.

## **Solubility test**

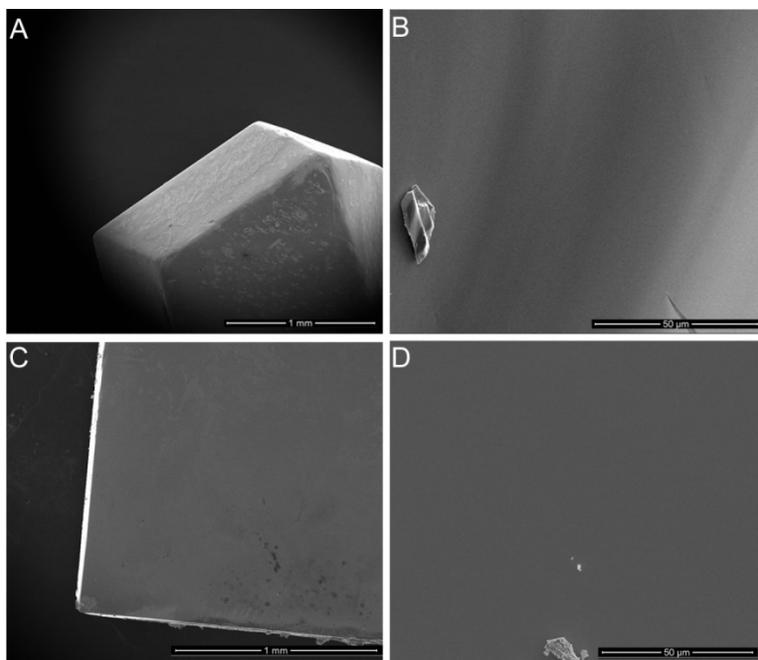
FAPbI<sub>3</sub> powder was obtained through grinding crystals prepared by inverse temperature crystallization discussed above. 3 ml of GBL was heated to required temperature while stirring and we started adding small amount of perovskite powder, 0.05 g by 0.05 g. Saturation conditions were assumed when the amount of solute did not completely dissolve within 30 minutes after being dropped into the solution. This process was repeated at different temperatures. The error bar is  $\pm 0.05$  g.

The same solubility test was performed for MAPbI<sub>3</sub>.

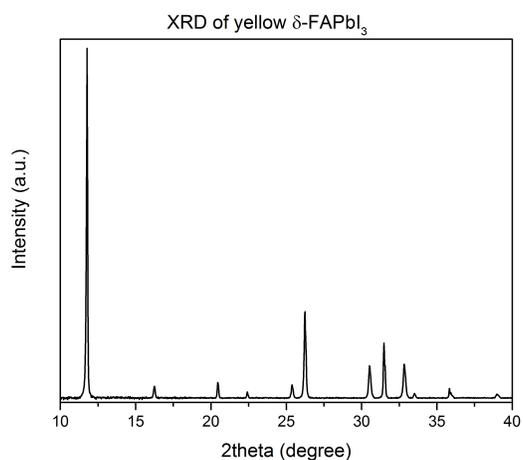
In the case of bromide-based perovskites, the analogous procedure was performed, except DMF for MAPbBr<sub>3</sub>, and DMF/GBL (1:0, 1:1 v/v) for FAPbBr<sub>3</sub> were used as solvents.

## **Measurement and characterization**

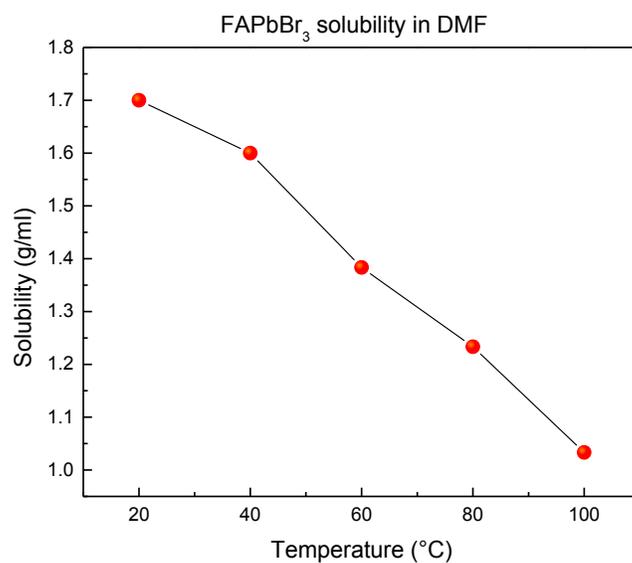
Powder X-ray diffraction was performed with a Bruker AXS D8 diffractometer using Cu-K $\alpha$  radiation. The steady-state absorptions were recorded utilizing a Cary 6000i spectrophotometer with an integrating sphere. Scanning electron microscopy was performed on Quanta 600.



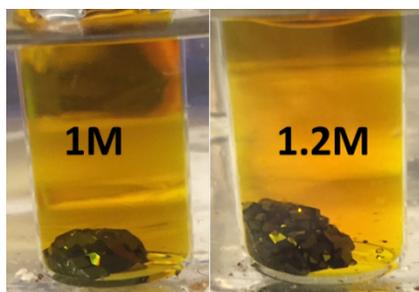
**Fig. 1. SEM images of the surface and cleaved crystals.** SEM of (A) surface of  $\text{FAPbI}_3$ , (B) cleaved  $\text{FAPbI}_3$ , (C) surface of  $\text{FAPbBr}_3$  and (D) cleaved  $\text{FAPbBr}_3$ . Excess precursors from solution can be observed on the surface of the crystals. No cracks or grain boundaries are found on the surface or core of cleaved crystals indicating the single crystalline nature of both crystals. The dust in (b,d) indicate the good focus of electron beam.



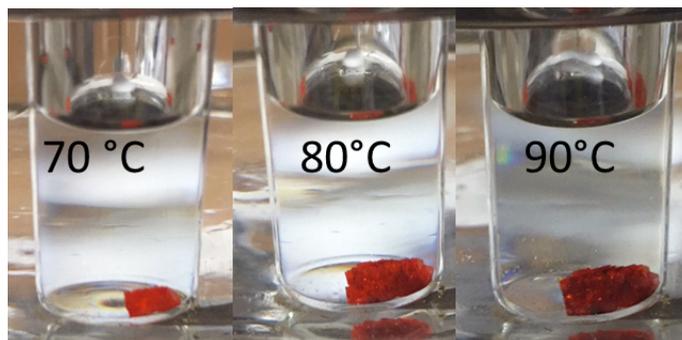
**Fig. 2. Transformation FAPbI<sub>3</sub> crystal from black polymorph to yellow.** Top - picture of fresh FAPbI<sub>3</sub> (left), and FAPbI<sub>3</sub> after 12 h (center) and 24 h (right) in air. Bottom - XRD of the yellow phase of FAPbI<sub>3</sub>.



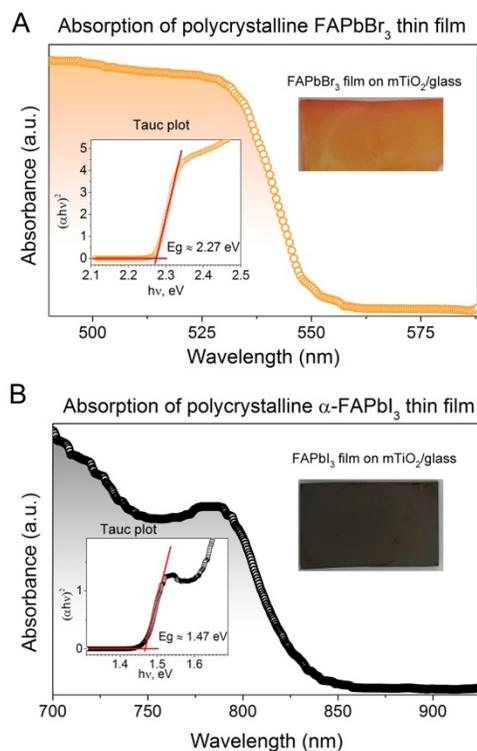
**Fig. 3. Temperature-dependent solubility of FAPbBr<sub>3</sub> in DMF.** FAPbBr<sub>3</sub> demonstrates retrograde solubility behavior in DMF. Solubility drops 1.7 times through the increasing the temperature from 20 °C to 100 °C.



**Fig. 4. Effect of the precursors concentration on the crystallization yield.** FAPbI<sub>3</sub> crystals grown from 1 M (left) and 1.2 M (right) solutions in 3 h at 120 °C. The size of the crystal is bigger from higher concentrated solution. Note that the crystals are mosaic due to fast heating of solution. In order to get well-shaped crystals, the conditions described in the Synthesis section should be used.



**Fig. 5. Effect of the crystallization temperature on the crystallization yield.** FAPbBr<sub>3</sub> grown at 70 °C (left), 80 °C (center) and 90 °C (right) for 3 h. The bigger size crystal can be grown through increasing the temperature of crystallization. Note that the crystals are mosaic due to fast heating of solution. In order to get well-shaped crystals, the conditions described in the Synthesis section should be used.



**Fig. 6. Absorption of polycrystalline FAPbX<sub>3</sub> films.** (a) Absorption of FAPbBr<sub>3</sub> polycrystalline film. (b) Absorption of  $\alpha$ -FAPbI<sub>3</sub> polycrystalline film. Insets are the picture of the film and Tauc plot to extract the bandgap. Polycrystalline films were prepared in accordance to the reported method (G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz and H. J. Snaith, *Energ. Environ. Sc.*, 2014, **7**, 982-988). Briefly, 0.88M FAPbX<sub>3</sub> in DMF was spin-coated at 2000 rpm for 40 s on a cleaned glass and annealed at 170 °C for 25 min in a nitrogen-filled glove-box. FAPbI<sub>3</sub> polycrystalline film first forms yellow phase, which gradually transforms to black phase during the annealing.