ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Supporting Information

## Room-Temperature Synthesis, Growth Mechanisms and Optical Properties of Organic-Inorganic Halide Perovskite $CH_3NH_3PbX_3$ (X= I, Br and Cl) Single Crystals

Maryam Bari [a], Hua Wu [b,a], Alexei A. Bokov [a], Rana Faryad Ali [a], Hamel N. Tailor [a], Byron D. Gates [a], and Zuo-Guang Ye [a]*

[a] *Department of Chemistry and 4D LABS, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada.*
[b] *Department of Applied Physics, Donghua University, Songjiang, Shanghai, 201620, China.*
**Corresponding Author. E-mail: zye@sfu.ca*
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

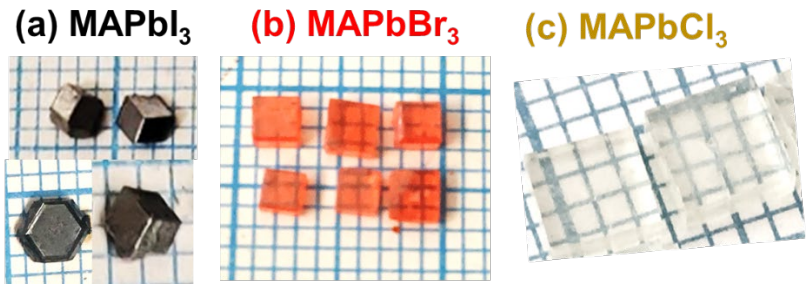


**Figure S1.** Optical images of the $MAPbX_3$ (X= I, Br, Cl) crystals grown by room temperature crystallization (RTC).

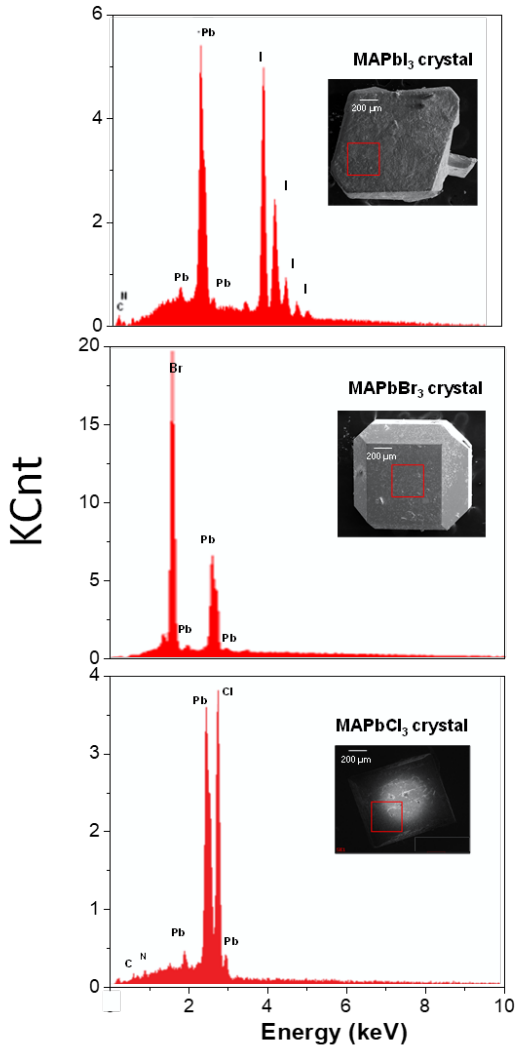


**Figure S2.** Energy dispersive X-ray spectroscopy (EDX) analyses of the $MAPbX_3$ crystals grown by RTC.

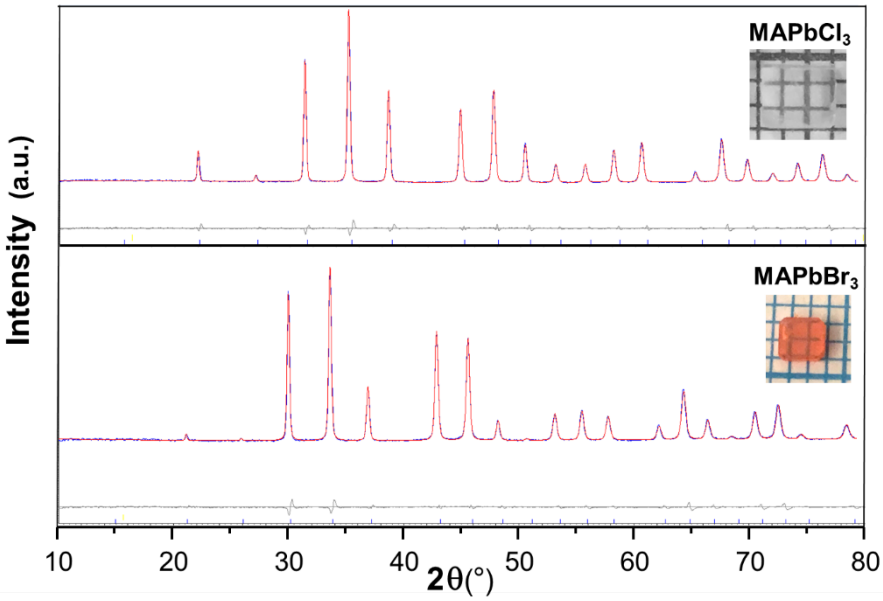


**Figure S3.** Stability study of the halide perovskite crystals grown by RTC and stored in ambient condition for two years: PXRD patterns of $MAPbX_3$ (X= Br and Cl) (blue line), the Pawley refinement (red line) with a profile residual factor $R_{wp}$ = 0.50 for both compounds, and the difference (grey line on the bottom of the panel).

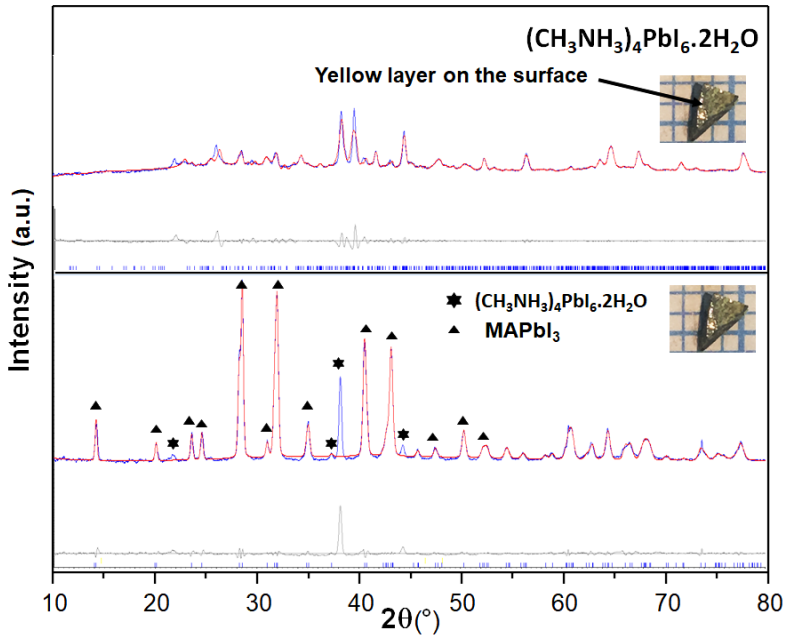


**Figure S4.** Stability study of the $MAPbI_3$ crystals grown by RTC and stored in ambient condition for one year. Bottom: PXRD pattern of an as-grown $MAPbI_3$ crystal containing a yellow layer formed on the crystal surface (blue line), the Pawley refinement (red line) with the profile residual factor $R_{wp}$ = 1.50 for $MAPbI_3$. Top: PXRD pattern of the yellow compound scratched out from the grown crystal, which matches the PXRD of $(CH_3NH_3)_4PbI_6.2H_2O$ with a $R_{wp}$ = 0.50, as previously reported. [1,2]

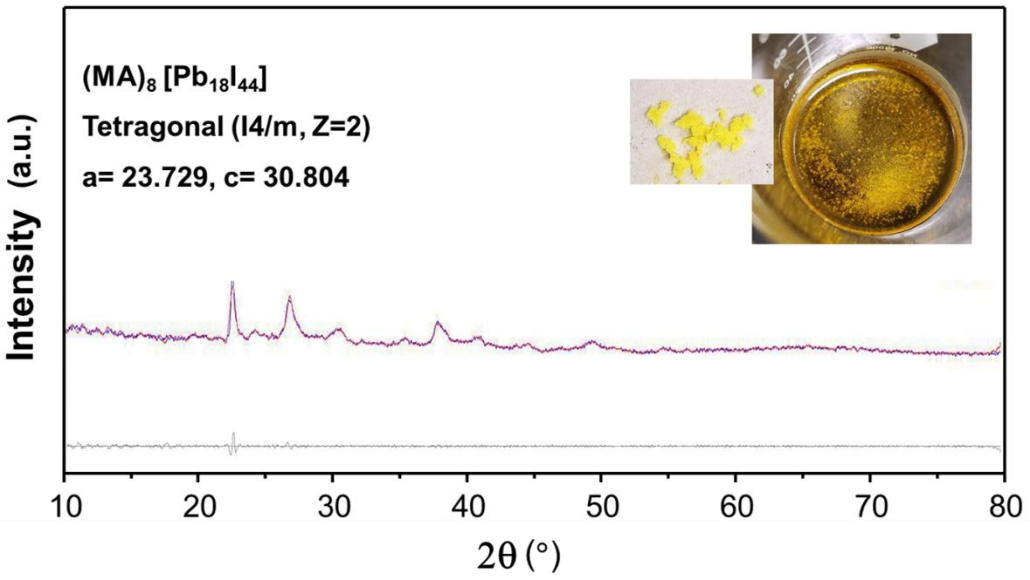


**Figure S5.** Powder XRD pattern of the yellow crystals obtained from 1 M solution of $MAPbI_3$ in GBL, which was saturated at 60 °C and cooled down to room temperature (blue line), and the Pawley refinement (red line) with the profile residual factor $R_{wp}$ = 0.35 for $(MA)_8[Pb_{18}I_{44}]$ intermediate adduct.[3]

## Calculation of the Nucleation Parameters from Interfacial Energy

Based on the homogeneous nucleation theory,[4] the change in Gibbs free energy ($\Delta G$) for the formation of spherical nuclei can be calculated by the following equation:

$$\Delta G = -\frac{4}{3}\pi r^3 \left|\Delta G_v\right| + 4\pi r^2 \sigma, \quad \text{(S1)}$$

where $\sigma$ is the interfacial energy, $r$ is the nucleus radius and $\Delta G_v$ represents the volume free energy, which can be expressed as:

$$\Delta G_v = -\left(\frac{K_B T \ln S_r}{v}\right), \quad \text{(S2)}$$

where $v$ is the specific volume of solute, $T$ is the temperature, $S_r$ is the supersaturation ratio and $k_B$ is the Boltzmann constant. Based on Eqs. (S1) and (S2), the critical nucleus radius $r_c = -\frac{2\sigma}{\Delta G_v}$ and the critical free energy barrier ($\Delta G_c$) can be determined using the following relations:

$$\frac{d(\Delta G)}{dr} = -4\pi {r_c}^2 |\Delta G_v| + 8\pi r_c \sigma = 0, \quad \text{(S3)}$$

$$\Delta G_c = \frac{16\pi\sigma^3 v^2}{3{k_B}^2 T^2 (\ln S_r)^2} \quad \text{(S4)}$$

According to the above equations, the nucleation parameters such as critical radius of nuclei ($r_c$), Gibbs free energy per volume unit ($\Delta G_v$), and critical free energy barrier ($\Delta G_c$) have been calculated and the results are listed in Table 1. Figure S6 shows the critical radii of the grown $MAPbCl_3$ crystals as a function of supersaturation ratio at 25 °C and 110 °C.

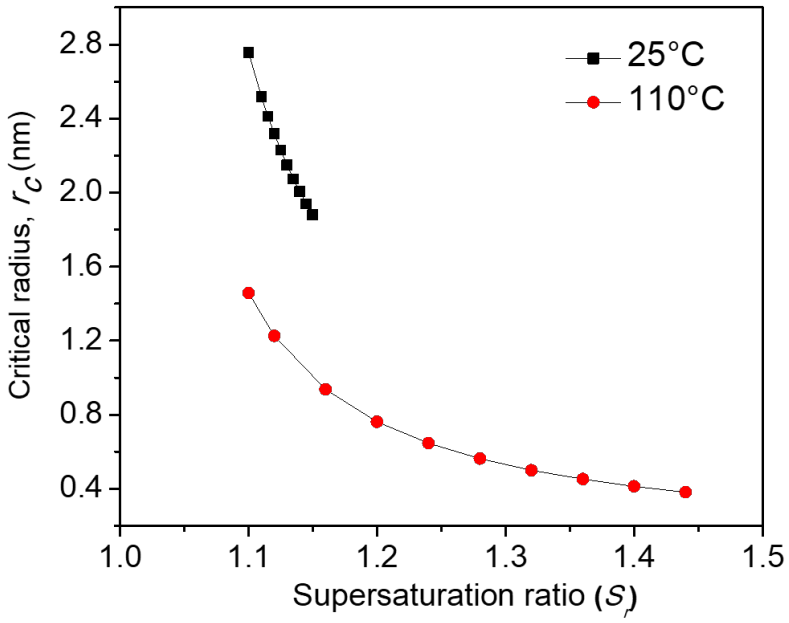


**Figure S6.** Critical radii as a function of the supersaturation ratio for the growth of $MAPbCl_3$ crystals at 25 °C and 110 °C.

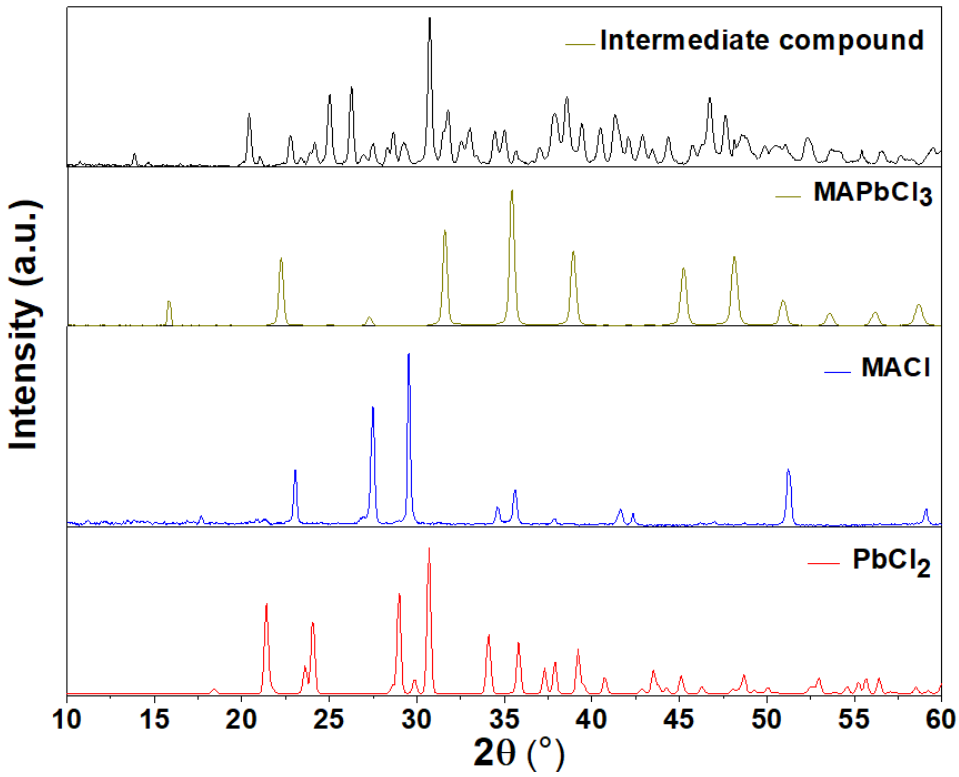


**Figure S7.** PXRD pattern of the intermediate compound formed during RTC, shown together with the patterns of pure $MAPbCl_3$ and the precursors (MACl and $PbCl_2$) as reference.

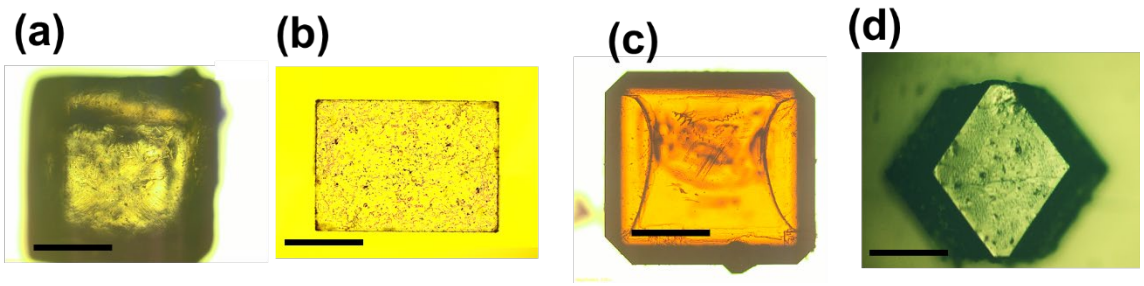


**Figure S8.** Optical micrographic images of the (001)-oriented $CH_3NH_3PbX_3$ crystals: (a) $CH_3NH_3PbCl_3$ crystal prepared via the seeded ITC; and (b) $CH_3NH_3PbCl_3$ and (c) $CH_3NH_3PbBr_3$ crystals prepared via RTC. Photographs of a-c were taken by transmitted PLM. (d) $CH_3NH_3PbI_3$ crystal via RTC, as observed by the reflected-PLM. Scale bars: 1 mm.

**Table S1.** The fluorescence decay time of the old and fresh $MAPbBr_3$ and $MAPbI_3$ crystals acquired with a time-correlated single-photon counting (TCSPC) setup using an excitation wavelength of 370 nm. *

| Compound | PL lifetime ($\tau_1$) ns | $\tau_1$ contribution to PL | PL lifetime ($\tau_2$) ns | $\tau_2$ contribution to PL | PL lifetime ($\tau_3$) ns | $\tau_3$ contribution to PL | PL lifetime ($\tau_4$) ns | $\tau_4$ contribution to PL |
|---|---|---|---|---|---|---|---|---|
| $MAPbBr_3$ (Old crystal) | 0.2 | 11.5% | 2.75 | 12.3% | 22.6 | 28% | 115.0 | 48.15% |
| $MAPbBr_3$ (Fresh crystal) | 0.35 | 10 % | 6.31 | 13% | 47.4 | 28 % | 153.3 | 49 % |
| $MAPbI_3$ (Old crystal) | 0.12 | 15.06 % | 2.40 | 16.82% | 12.4 | 31.82 % | 111.0 | 36.31 % |
| $MAPbI_3$ (Fresh crystal) | 0.15 | 15 % | 3.20 | 17% | 14.0 | 32 % | 117 | 36 % |

* The photoluminescence (PL) plots were fitted with a four-exponential decay.

**References**


1 X. Guo, C. McCleese, C. Kolodziej, A. C. Samia, Y. Zhao, C. Burda, *Dalton Trans.* **2016**, 45, 3806-3813.
2 J. A. Christians, P. A. Miranda Herrera, P. V. Kamat, *J. Am. Chem. Soc.* **2015**, 137, 1530-1538.
3 S. A. Fateev, A. A. Petrov, V. N. Khrustalev, P. V. Dorovatovskii, Y. V. Zubavichus, E. A. Goodilin, A. B. Tarasov, *Chem. Mater.* **2018**, 30, 5237−5244.
4 D. Elwell, H. J. Scheel, *Crystal Growth from High-Temperature Solutions,* Academic Press Inc, London - New York 1975.