Supporting Information

Single Crystal of Two-Dimensional Mixed-Halide Copper-based Perovskites with Reversible Thermochromism

Amr Elattar^a, Hiroo Suzuki^a, Ryuji Mishima^a, Kodai Nakao^a, Hiromi Ota^b, Takeshi Nishikawa^a, Hirotaka Inoue^a, Aung Ko Ko Kyaw^c, and Yasuhiko Hayashi^a *



Fig. S1 Crystal growth of 2D-centimeter-sized Cu-based perovskites at (water/air) interface: C4 (a) BB (b). Bulk crystals of mixed-halides Cu-perovskites (c).



Fig. S2 2D-Cu perovskite crystals after grinding with mortar where (CC: yellow, C6.5: orange, C5: red, C4: dark red, C3: reddish-brown, C2: dark brown, C0.5 and BB: dark green)



Fig. S3 Scanning electron microscope (SEM) images show the two-dimensional structures of Cuperovskites. Elemental mapping of halides though perovskite crystals where blue and green spots for Brand Cl-distributions respectively.



Fig. S4 Crystal structures of $(CH_3NH_3)_2CuCl_4^{-1}$ (a), $(CH_3NH_3)_2CuCl_2Br_2^{-2}$ (b). Green Cu, blue N, gray C, red Cl, brown Br and pink H.



Fig. S5 (a) Powder XRD of Cu-perovskite crystals after grinding with mortar. (b) Expansion of XRD-first peak.



Fig. S6 (a) Thermogravimetric analysis (TGA) of Cu-perovskites. (b) Decomposition temperature values of Cu-perovskites extracted from TGA analysis.



Fig. S7 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C6.5** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S8 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C5** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S9 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C4** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S10 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C3** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S11 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C2** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S12 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **C0.5** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S13 Exfoliation effect (a) Optical microscopic images of different mechanically exfoliated **BB** flakes, scale bar (10 μ m). (b), (c) Raman spectra of exfoliated flakes in the range of 50-500 cm-1 and 2500-3000cm-1, respectively.



Fig. S14 Temperature-induced XRD of CC for one heating/cooling cycle.



Fig. S15 (a) and (b) Temperature-induced color change of C6.5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C6.5: (c) Expansion of $2\Theta = 42.6^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S16 Temperature-induced XRD of C6.5 for one heating/cooling cycle.



Fig. S17 (a) and (b) Temperature-induced color change of the C5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C5: (c) Expansion of $2\Theta = 49.7^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S18 Temperature-induced XRD of C5 for one heating/cooling cycle.



Fig. S19 (a) and (b) Temperature-induced color change of the C4 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C4: (c) Expansion of $2\Theta = 49.7^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S20 Temperature-induced XRD of C4 for one heating/cooling cycle.



Fig. S21 (a) and (b) Temperature-induced color change of the C3 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C3: (c) Expansion of $2\Theta = 28.5^\circ$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S22 Temperature-induced XRD of C3 for one heating/cooling cycle.



Fig. S23 (a) and (b) Temperature-induced color change of the C2 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C2: (c) Expansion of $2\Theta = 42.6^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S24 Temperature-induced XRD of C2 for one heating/cooling cycle.



Fig. S25 (a) and (b) Temperature-induced color changes of the C0.5 crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of C0.5: (c) Expansion of $2\Theta = 73.4^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S26 Temperature-induced XRD of C0.5 for one heating/cooling cycle.



Fig. S27 (a) and (b) Temperature-induced color change of the BB crystal with heating and cooling cycles, respectively. Temperature-dependent XRD of BB: (c) Expansion of $2\Theta = 36.9^{\circ}$ reflection at different temperatures. (d) d-spacing calculated from the 2 Θ values extracted from the XRD patterns at different temperatures.



Fig. S28 Temperature-induced XRD of BB for one heating/cooling cycle.



Fig. S29 Differential scanning calorimetry (DSC) of CC (a), C6.5 (b), C5 (c), and C4 (d) with scan rate of 10 K/min.



Fig. S30 Differential scanning calorimetry (DSC) of C3 (e), C2(f), C0.5 (g), and BB (h) with scan rate of 10 K/min.



Fig. S31 Temperature dependence of transmittance spectra of CC and C6.5 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.

Fig. S32 Temperature dependence of transmittance spectra of C5 and C4 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.

Fig. S33 Temperature dependence of transmittance spectra of C3 and C2 samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.

Fig. S34 Temperature dependence of transmittance spectra of C0.5 and BB samples for heating (a, d) /cooling cycle (b, e) with hysteresis loops (c, f), respectively.

Supplementary note:

Comparison between d-space and transmittance hysteresis loops

Consider

The transmittance of the sample at 30 ^oC before heating and after cooling are T30H and T30C, respectively.

The d-space of the sample at 30 ^oC before heating and after cooling are d30H and d30C, respectively.

Two probabilities are observed:

1. T30H > T30C

According to this behavior, the sample color, after cooling, is darker than its color before heating. Thus, d30H < d30C and the crystal lattice is still in its expanded form. This means that the sample just requires more time to return-back to its normal color. This behavior was observed for CC, C6.5, C5, C3, C0.5 and BB samples.

2. T30H < T30C

According to this behavior, the sample color after cooling is lighter than its color before heating. Thus, d30H > d30C. This means that the sample has lighter color than its initial color after heating/cooling cycle, i.e. the crystal lattice is more compressed than its initial one. This behavior was observed for C2 and C4 samples.

References

- 1 I. Pabst, H. Fuess and J. W. Bats, Acta Crystallogr. Sect. C, 1987, 43, 413–416.
- 2 R. D. Willett, *Acta Crystallogr. Sect. C*, 1991, **47**, 1081–1082.