

## Supporting Information

### Mechanical Properties of Organic-Inorganic Halide Perovskites, $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X=I, Br and Cl) by Nanoindentation

Shijing Sun,<sup>a</sup> Yanan Fang,<sup>b</sup> Gregor Kieslich,<sup>a</sup> Tim J. White<sup>\*b</sup> and Anthony K. Cheetham<sup>\*a</sup>

<sup>a</sup>Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS. E-mail: akc30@cam.ac.uk

<sup>b</sup>School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798. Email: tjwhite@ntu.edu.sg

**Table. S1** Summary of a number of representative nanoindentation experiments, variations between each measurement are due to the systematic error of the indenter and random errors from sample preparation procedures.

Crystals	Crystal System	Orientation	No. of Indents	Young's Modulus (GPa)	Std.Dev.	Hardness (GPa)	Std.Dev.
<b><math>\text{CH}_3\text{NH}_3\text{PbBr}_3</math></b>							
1	Cubic	010	20	17.71	0.61	0.31	0.02
2	Cubic	011	11	15.56	0.60	0.26	0.02
<b><math>\text{CH}_3\text{NH}_3\text{PbCl}_3</math></b>							
1	Cubic	100	11	19.77	0.69	0.29	0.02
2	Cubic	110	18	17.66	0.57	0.30	0.02
<b><math>\text{CH}_3\text{NH}_3\text{PbI}_3</math></b>							
1	Tetragonal	112	14	10.74	0.53	0.42	0.04
2	Tetragonal	100	14	10.44	0.77	0.43	0.04

## Indexing

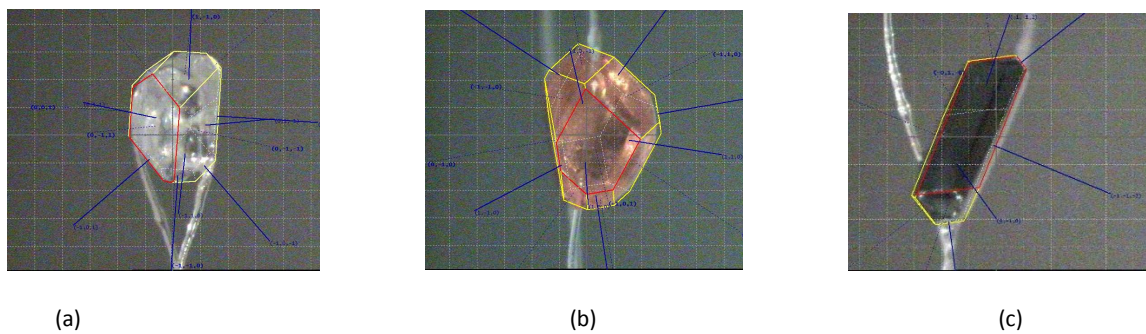


Fig.S1 Photographs of representative face-indexed single crystals, (a)  $\text{CH}_3\text{NH}_3\text{PbCl}_3$ , (b)  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  and (c)  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

## Indentation Hardness

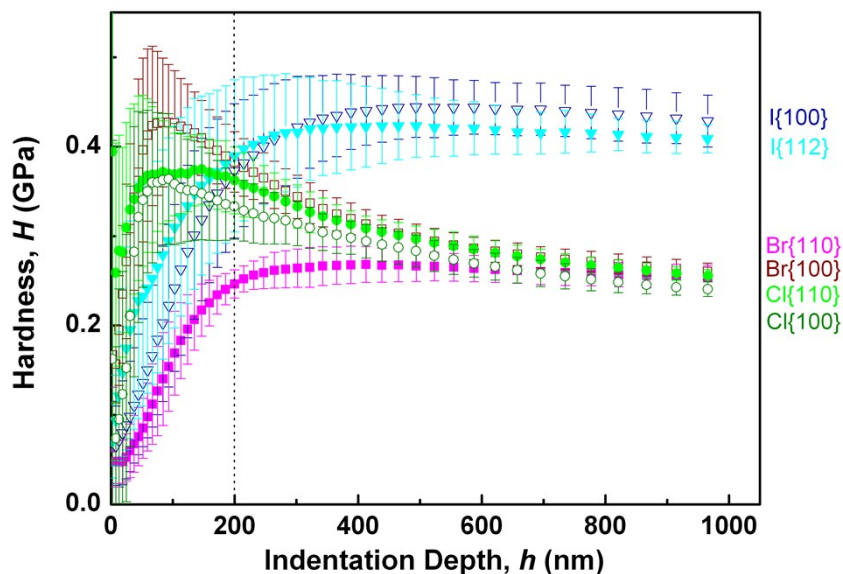


Fig. S2 Hardness as a function of the indentation depth (Each curve was obtained from one representative crystal).

## Nanoindentation Methodology

In continuous stiffness measurement (CSM) mode, where indentation is controlled by displacement, Young's modulus ( $E$ ) and hardness ( $H$ ) were measured using a three sided pyramidal sharp Berkovich tip. With a strain rate of  $0.05 \text{ s}^{-1}$ , the load,  $P$ , and the displacement,  $h$  were monitored continuously during the experiment and the indenter was held for 30 s at the maximum load before unloading at the same strain rate in order to minimize the creep effect.  $P$  was plotted as a function of indentation depth and the elastic contact stiffness,  $S$  was determined by  $dP/dh$ . The analysis of  $P$ - $h$  curves was described in the previous literature.<sup>1,2</sup> Using the standard Oliver-Pharr Method,<sup>3</sup> the reduced modulus,  $E_r$ , was obtained by:

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_c}} \quad (1)$$

Where  $A_c$  is the contact area under load based on the calibrated tip areal function and  $\beta$  is a constant that depends on the

geometry of the indenter (for a Berkovich tip  $\beta = 1.034$ ). The anisotropic elastic moduli along different crystal facets were then extracted by:

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_s^2}{E_s} \quad (2)$$

Where  $\nu$  and  $E$  are Poisson's ratio and elastic modulus, respectively; and the subscripts  $i$  and  $s$  refer to the indenter and test material, respectively.<sup>3</sup> In this study the measured Young's Modulus ( $E$ ) refers to  $E_s$ . The diamond indenter properties used are  $E_i = 1141$  GPa, and Poisson's ratio for the indenter is  $\nu_i = 0.07$ . In the main article, elastic moduli were calculated using the  $\nu_s = 0.3$ .

As a measure of materials' ability to resist local plastic deformation, indentation hardness ( $H$ ) is determined by:<sup>3</sup>

$$H = \frac{P_{\max}}{A_c} \quad (3)$$

Where  $P_{\max}$  is the maximum indentation load and  $A_c$  is the contact area between the indenter tip and the sample. In this case,  $A_c$  is calculated from the contact depth  $h_c$ , governed by the following equation:<sup>4</sup>

$$h_c = h_{\max} - 0.75 \frac{P_{\max}}{S} \quad (4)$$

Where  $P_{\max}$  refers to the maximum indentation depth and the extent of elastic recovery is represented by  $0.75(P_{\max}/S)$ .

## References

- 1 J. C. Tan, J. D. Furman and A. K. Cheetham, *J. Am. Chem. Soc.*, 2009, **131**, 14252–4.
- 2 W. Li, M. S. R. N. Kiran, J. L. Manson, J. a Schlueter, a Thirumurugan, U. Ramamurty and A. K. Cheetham, *Chem. Commun.*, 2013, **49**, 4471–3.
- 3 W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, 2004, **19**, 3–20.
- 4 W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, 1992, **7**, 1564–1583.