

## Supporting Information

### The mechanical properties of the ferroelectric metal-free perovskite [MDABCO](NH<sub>4</sub>)I<sub>3</sub> (MDABCO = Methyl-1,4- diazabicyclo[2.2.2]octane)

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**Synthesis of [MDABCO](NH<sub>4</sub>)I<sub>3</sub>.** MDABCOI was synthesized as reported by Kreuer *et al.*<sup>1</sup> For the synthesis of [MDABCO](NH<sub>4</sub>)I<sub>3</sub>, MDABCOI (2.54 g, 10 mmol), NH<sub>4</sub>I (1.45 g, 10 mmol) were dissolved in 5 mL HI (57%), 2 mL H<sub>3</sub>PO<sub>3</sub> and 15 mL H<sub>2</sub>O. H<sub>3</sub>PO<sub>3</sub> acts as stabilizer for HI to avoid reduction to elemental iodine. By slow evaporation at room temperature or cooling to 2 °C colorless cubic shaped single crystals formed after a couple of days. The crystals were collected via filtration and dried at 60 °C for 24 h with Ar.

**High pressure single crystal diffraction and bulk modulus.** In total, five single crystal X-ray diffraction measurements have been performed at  $p$  = ambient, 0.23, 0.46, 0.72 and 1.28 GPa. In an initial single crystal X-ray diffraction experiment under ambient conditions, a small single crystal of [MDABCO](NH<sub>4</sub>)I<sub>3</sub> was measured on a 4-circle single crystal diffractometer equipped with a Pilatus 300K detector at beamline I19 at the Diamond Lightsource with an X-ray energy of 0.4890 Å. In this measurement, the same measurement program as for the subsequent diamond anvil cell (DAC) experiments was used, providing us with the instrument model of the diffractometer. For high pressure single crystal X-ray diffraction (HPSCXRD) at  $p$  = 0.23, 0.46, 0.72 and 1.28 GPa a single crystal of [MDABCO](NH<sub>4</sub>)I<sub>3</sub> was cut to approximately 0.140 x 0.80 x 0.050 mm size and mounted in a diamond anvil cell with a gasket opening of approximately 200 μm in diameter and Silicon oil AP100 as hydrostatic pressure medium. A ruby sphere was placed next to the crystal for pressure calibration during the experiments.<sup>2,3</sup> The error on the pressure of the experiment was estimated to 0.05 GPa based on differences of the pressure before and after the high-pressure experiment. During data integration of all measurements, twinning of [MDABCO](NH<sub>4</sub>)I<sub>3</sub> was explicitly included, finding two distinguishable twin domains in all cases with a domain ratio of approximately 3:2. Data integration was performed by using CrysAlis Pro v38.46, whilst ShelXL as integrated in Olex2 was used for structure solution.<sup>4,5</sup>

**Bulk modulus.** The bulk modulus was obtained by fitting a 2<sup>nd</sup> order Birch-Murnaghan equation of state to our  $V(p)$  data, using the program EosFit-7c.<sup>6</sup> During the fitting procedure, the errors on  $V$  and  $p$  were included using the weighting procedure as given in EosFit-7c. Since literature provides different hydrostatic limits for silicone oil, the sensitivity of the bulk modulus towards the last pressure point was tested ( $p_4 = 1.26$  GPa),<sup>7, 8</sup> to gain confidence in the obtained bulk modulus:

- (i) BM fit 2<sup>nd</sup> order to all datasets, refining  $V_0$ ,
- (ii) BM fit 2<sup>nd</sup> order to all datasets, fixing  $V_0$
- (iii) BM fit 2<sup>nd</sup> order without the last pressure point, refining  $V_0$
- (iv) BM fit 2<sup>nd</sup> order without the last pressure point and fixing  $V_0$ .

An overview of the obtained values is given in Table S1.

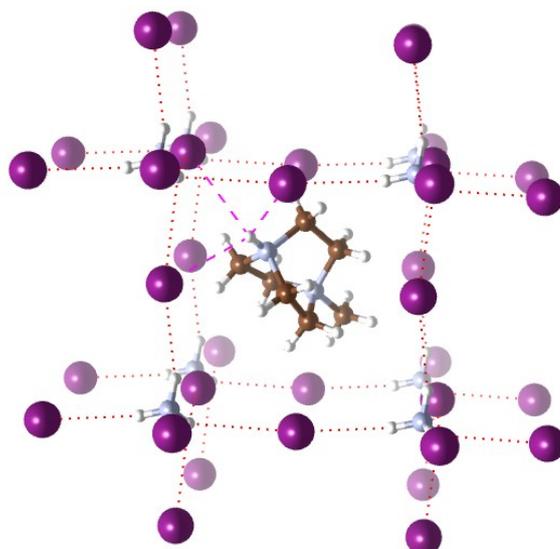
**Table S1.** Overview of the bulk moduli obtained by fitting a 2<sup>nd</sup> order Birch-Murnaghan equation of state. For the analysis, different situations were considered as given in the column “Details of the fit”, which was done by using EosFit-7c.<sup>6</sup>

Details of fit	K (Gpa)	K' (GPa)
BM 2 <sup>nd</sup> order, all pressure points, refining $V_0$	14.91 ± 0.49	4
BM 2 <sup>nd</sup> order, all pressure points, fixing $V_0$	14.86 ± 0.41	4
BM 2 <sup>nd</sup> order, first 4 pressure points, refining $V_0$	15.66 ± 0.89	4
BM 2 <sup>nd</sup> order, first 4 pressure points, fixing $V_0$	15.34 ± 0.58	4

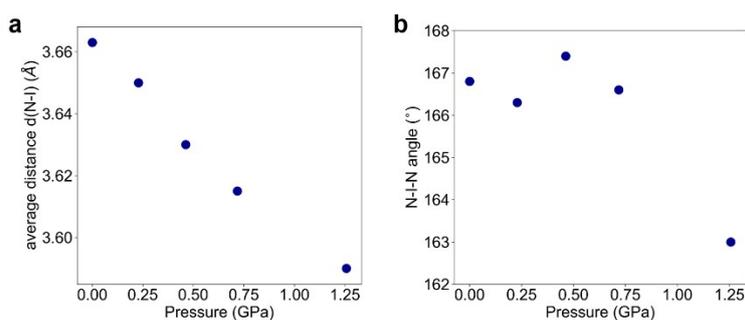
The final bulk modulus of  $[\text{MDABCO}](\text{NH}_4)\text{I}_3$  is obtained to  $15.19 \pm 0.70$  GPa, when averaging over all four different bulk moduli.

**Nanoindentation experiments on  $[\text{MDABCO}](\text{NH}_4)\text{I}_3$ .** Nanoindentation experiments were performed using an MTS Nanoindenter XP instrument equipped with a continuous stiffness measurement module. The  $[\text{MDABCO}](\text{NH}_4)\text{I}_3$  single crystals were positioned on aluminum stubs and the peripheries of the crystals were mounted using super glue for immobilizing the lateral movement. The prepared samples were secured in a desiccator under the vacuum condition to avoid the hygroscopic decomposition of the crystal surface, which was observed under ambient conditions. For nanoindentation experiments, a Berkovich diamond tip was employed to indent the  $[\text{MDABCO}](\text{NH}_4)\text{I}_3$  single crystals to a penetration depth of approximately 1900 nm from the crystal surface (**Figure S2a**).

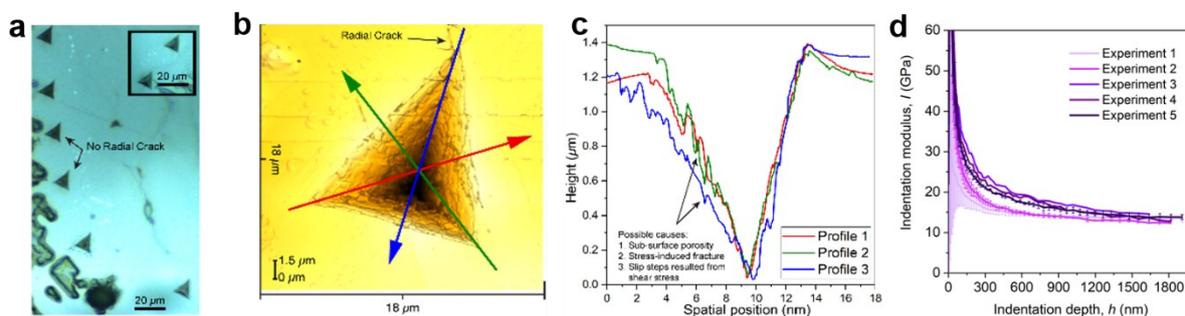
Nanoindentation experiments were performed along the [111] direction. Comparing the change of the [111] direction from high pressure single crystal diffraction studies with the main directions, i.e. [111] = 2.4 %, [100] = 2.5 % and [001] = 2.2%, only minor anisotropic contributions are expected for nanoindentation experiments along other directions. However, as given in the main manuscript, the morphology of the grown crystals only allows for probing the [111] direction by nanoindentation.



**Figure S1.** Shown is the structure of  $[\text{MDABCO}](\text{NH}_4)\text{I}_3$  with emphasis on the extended hydrogen bonding network. Within the 3D network of  $[(\text{NH}_4)\text{I}_3]^{2-}$ , three strong and three weak hydrogen bonding (HBs) interactions between  $(\text{NH}_4)^+$  cations and  $\text{I}^-$  exists (red dotted line) and three additional HBs exist between  $[\text{MDABCO}]^{2+}$  and the negatively charged framework (purple dashed line).



**Figure S2.** Average nitrogen iodine bond distances within  $[(\text{NH}_4)\text{I}_6]$ -octahedra (a) and N-I-N angle (b) as function of pressure.



**Figure S3.** (a) Optical image of eight representative residual indents, two of which are shown in the inset. (b) An AFM topographic image of a residual indent corresponding to the profile lines marked in the 3 D height image in panel (c). In (d)

**Table S2.** Comparison of bulk moduli and Young's moduli of various HOIPs, perovskites and related ferroelectric materials.

ABX <sub>3</sub>	B	E	Ref
<b>Hybrid perovskites</b>			
NH <sub>4</sub> [Co(HCOO) <sub>3</sub> ]		35	9
NH <sub>4</sub> [Zn(HCOO) <sub>3</sub> ]	33	18 35	10
Me <sub>2</sub> NH <sub>2</sub> [Mn(HCOO) <sub>3</sub> ]	25	19	11, 12
Me <sub>2</sub> NH <sub>2</sub> [Fe(HCOO) <sub>3</sub> ]	27		11
Me <sub>2</sub> NH <sub>2</sub> [Co(HCOO) <sub>3</sub> ]		22	12
Me <sub>2</sub> NH <sub>2</sub> [Ni(HCOO) <sub>3</sub> ]		24	12
Me <sub>2</sub> NH <sub>2</sub> [Cu(HCOO) <sub>3</sub> ]	24		11
Me <sub>2</sub> NH <sub>2</sub> [Zn(HCOO) <sub>3</sub> ]		19	12
C(NH <sub>2</sub> ) <sub>3</sub> [Mn(HCOO) <sub>3</sub> ]	21	24 25 29	13, 14
C(NH <sub>2</sub> ) <sub>3</sub> [Co(HCOO) <sub>3</sub> ]	27		14
C(NH <sub>2</sub> ) <sub>3</sub> [Cu(HCOO) <sub>3</sub> ]	26	16 18 21	15
C(NH <sub>2</sub> ) <sub>3</sub> [Zn(HCOO) <sub>3</sub> ]	30	24 27 29	15
(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> [Mn(HCOO) <sub>3</sub> ]		12 13	13
NH <sub>2</sub> NH <sub>2</sub> [Zn(HCOO) <sub>3</sub> ]	19	25 27	16
MeNH <sub>3</sub> PbBr <sub>3</sub>	19.7	11 30	17
CsPbBr <sub>3</sub>	16	16	18
MeNH <sub>3</sub> PbI <sub>3</sub>	14 20	14 16	18
MeNH <sub>3</sub> SnI <sub>3</sub>	13		19
(HC(NH <sub>2</sub> ) <sub>2</sub> )SnI <sub>3</sub>	8.0		19
(MeNH <sub>3</sub> ) <sub>2</sub> KGdCl <sub>6</sub>	20	26	20
(MeNH <sub>3</sub> ) <sub>2</sub> KYCl <sub>6</sub>	20	27	20
(MeNH <sub>3</sub> ) <sub>2</sub> KBiCl <sub>6</sub>	19	24	20
(MeNH <sub>3</sub> )(HC(NH <sub>2</sub> ) <sub>2</sub> )SnI <sub>6</sub>	12		19
<b>Oxide Perovskites</b>			
KTaO <sub>3</sub>	212	321	21
KNbO <sub>3</sub>	147	249	21
SrTiO <sub>3</sub>	173	245	22, 23
SrZrO <sub>3</sub>	151	269	22, 23
SrSnO <sub>3</sub>	164		22
SrVO <sub>3</sub>	182		22
SrNbO <sub>3</sub>	173		22
SrCeO <sub>3</sub>		107	23
SrMoO <sub>3</sub>		180	23
SrHfO <sub>3</sub>		220	23
SrRuO <sub>3</sub>		161	23
BaUO <sub>3</sub>		113	23
BaNbO <sub>3</sub>	171	209	24
BaSnO <sub>3</sub>	146	244	25, 26
BaZrO <sub>3</sub>	156	186 243	23, 24
BaTiO <sub>3</sub>	161	254	24
BaCeO <sub>3</sub>		154	23
BaMoO <sub>3</sub>		235	23
BaHfO <sub>3</sub>	147	221	27
PbTaO <sub>3</sub>	191	133	28
MgSiO <sub>3</sub>	253		29
MnSnO <sub>3</sub>	257		30
FeTiO <sub>3</sub>	218		30
BiAlO <sub>3</sub>	219 223	347	31
LaCoO <sub>3</sub>		48	32
La <sub>0.8</sub> Ca <sub>0.2</sub> CoO <sub>3</sub>		112	32
La <sub>0.8</sub> Sr <sub>0.2</sub> CoO <sub>3</sub>		64	32
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	42 56	78 116	33
<b>Other Perovskites</b>			
ScBRh <sub>3</sub>	197		34
TaThN <sub>3</sub>	236	350	35
NaMgH <sub>3</sub>	37	69	36
MgCNI <sub>3</sub>	171	168	37
ZnCNI <sub>3</sub>	177	167	37
CdCNI <sub>3</sub>	153	164	37
KMgF <sub>3</sub>	76		38
RbMnF <sub>3</sub>	67		38
<b>Ferroelectrics</b>			
HCl	4.5		39
PVDF (all trans)	11	287	40
NaNO <sub>2</sub>	22		41
KH <sub>2</sub> PO <sub>4</sub>	27	39	42
SbSI	19		43
BaTiO <sub>3</sub>	162	128	24
PbTiO <sub>3</sub>	180		44
LiTaO <sub>3</sub>	134	302	45
LiNbO <sub>3</sub>	110	248	45
KNbO <sub>3</sub>	147	249	21

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