Supporting Information

The mechanical properties of the ferroelectric metal-free perovskite $[MDABCO](NH_4)I_3$ (MDABCO = Methyl-1,4-diazabicyclo[2.2.2]octane)

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Synthesis of $[MDABCO](NH_4)I_3$. MDABCOI was synthesized as reported by Kreuer *et al*.[1] For the synthesis of $[MDABCO](NH_4)I_3$, MDABCOI (2.54 g, 10 mmol), NH_4I (1.45 g, 10 mmol) were dissolved in 5 mL HI (57%), 2 mL H_3PO_3 and 15 mL H_2O. H_3PO_3 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 $[MDABCO](NH_4)I_3$ 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 $[MDABCO](NH_4)I_3$ 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.[2, 3] 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 $[MDABCO](NH_4)I_3$ 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.[4, 5]

Bulk modulus. The bulk modulus was obtained by fitting a 2nd order Birch-Murnaghan equation of state to our $V(p)$ data, using the program EosFit-7c.[6] 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),[7, 8] to gain confidence in the obtained bulk modulus:

(i) BM fit 2nd order to all datasets, refining V_0,
(ii) BM fit 2nd order to all datasets, fixing V_0
(iii) BM fit 2nd order without the last pressure point, refining V_0
(iv) BM fit 2nd 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 2nd 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.[6]

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

The final bulk modulus of [MDABCO]$(NH_4)I_3$ is obtained to 15.19 ± 0.70 GPa, when averaging over all four different bulk moduli.

Nanoindentation experiments on [MDABCO]$(NH_4)I_3$. Nanoindentation experiments were performed using an MTS Nanoindenter XP instrument equipped with a continuous stiffness measurement module. The [MDABCO]$(NH_4)I_3$ 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 [MDABCO]$(NH_4)I_3$ 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.

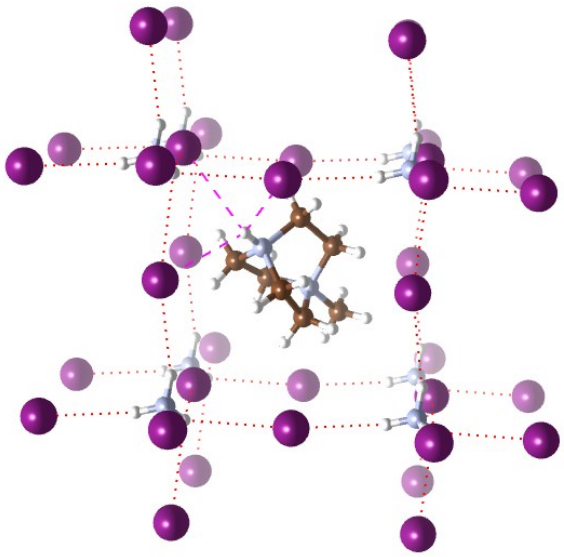

Figure S1. Shown is the structure of [MDABCO]$(NH_4)I_3$ with emphasis on the extended hydrogen bonding network. Within the 3D network of $[(NH4)I3]^{2-}$, three strong and three weak hydrogen bonding (HBs) interactions between $(NH_4)^+$ cations and I^- exists (red dotted line) and three additional HBs exist between $[MDABCO]^{2+}$ and the negatively charged framework (purple dashed line).

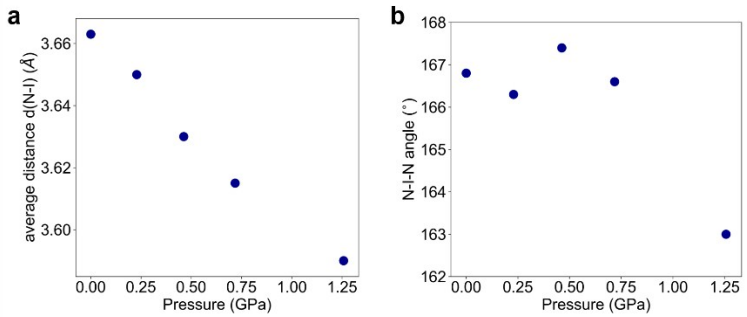

Figure S2. Average nitrogen iodine bond distances within $[(NH_4)I_6]$-octahedra (a) and N-I-N angle (b) as function of pressure.

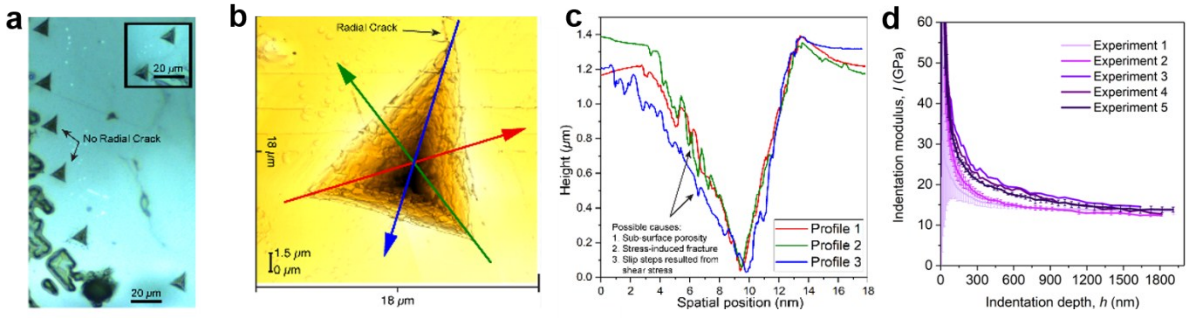

Figure S3. (a) Optical image of eight representative residual indents, two of which are shown in the inset. (b) An AFM topographic image of a residual indent corresponding to the profile lines marked in the 3 D height image in panel (c). In (d)

Table S2. Overview of the mechanical properties of various ferroelectrics, and related HOIPs. References given in the last column relate to references given in the main text.

Compound	*K* [GPa]	*E* [GPa]	Ref
$[MDABCO](NH_4)I_3$	15.19±0.70	14.7 [111]	This work
$BaTiO_3$	162	128	[41]
$LiNbO_3$	110	248	[42]
KH_2PO_4	27	39	[43]
PVDF (all *trans*)	11	287	[44]
$[CH_3NH_3]PbI_3$	12	14	[36]
$[NH_3NH_2]Zn(HCOO)_3$	19	27-25	[10]
$[(CH_3)_2NH_2]Mn(HCOO)_3$	25	19	[24, 45]
$CsPbBr_3$	16	16	[36]

Table S3. Comparison of bulk moduli and Young's moduli of various HOIPs, perovskites and related ferroelectric materials.

ABX_3	B	E	Ref
Hybrid perovskites			
$NH_4[Co(HCOO)_3]$		35	9
$NH_4[Zn(HCOO)_3]$	33	18 35	10
$Me_2NH_2[Mn(HCOO)_3]$	25	19	11, 12
$Me_2NH_2[Fe(HCOO)_3]$	27		11
$Me_2NH_2[Co(HCOO)_3]$		22	12
$Me_2NH_2[Ni(HCOO)_3]$		24	12
$Me_2NH_2[Cu(HCOO)_3]$	24		11
$Me_2NH_2[Zn(HCOO)_3]$		19	12
$C(NH_2)_3[Mn(HCOO)_3]$	21	24 25 29	13, 14
$C(NH_2)_3[Co(HCOO)_3]$	27		14
$C(NH_2)_3[Cu(HCOO)_3]$	26	16 18 21	15
$C(NH_2)_3[Zn(HCOO)_3]$	30	24 27 29	15
$(CH_2)_3NH_2[Mn(HCOO)_3]$		12 13	13
$NH_2NH_3[Zn(HCOO)_3]$	19	25 27	16
$MeNH_3PbBr_3$	19.7	11 30	17
$CsPbBr_3$	16	16	18
$MeNH_3PbI_3$	14 20	14 16	18
$MeNH_3SnI_3$	13		19
$(HC(NH_2)2)SnI3$	8.0		19
$(MeNH_3)_2KGdCl_6$	20	26	20
$(MeNH_3)_2KYCl_6$	20	27	20
$(MeNH_3)_2KBiCl_6$	19	24	20
$(MeNH_3)(HC(NH_2)_2)SnI_6$	12		19
Oxide Perovskites			
$KTaO_3$	212	321	21
$KNbO_3$	147	249	21
$SrTiO_3$	173	245	22, 23
$SrZrO_3$	151	269	22, 23
$SrSnO_3$	164		22
$SrVO_3$	182		22
$SrNbO_3$	173		22
$SrCeO_3$		107	23
$SrMoO_3$		180	23
$SrHfO_3$		220	23
$SrRuO_3$		161	23
$BaUO_3$		113	23
$BaNbO_3$	171	209	24
$BaSnO_3$	146	244	25, 26
$BaZrO_3$	156	186 243	23, 24
$BaTiO3$	161	254	24
$BaCeO_3$		154	23
$BaMoO_3$		235	23
$BaHfO_3$	147	221	27
$PbTaO_3$	191	133	28
$MgSiO_3$	253		29
$MnSnO_3$	257		30
$FeTiO_3$	218		30
$BiAlO_3$	219 223	347	31
$LaCoO_3$		48	32
$La_{0.8}Ca_{0.2}CoO_3$		112	32
$La_{0.8}Sr_{0.2}CoO_3$		64	32
$YBa_2Cu_3O_7$	42 56	78 116	33
Other Perovskites			
$ScBRh_3$	197		34
$TaThN_3$	236	350	35
$NaMgH_3$	37	69	36
$MgCNi_3$	171	168	37
$ZnCNi_3$	177	167	37
$CdCNi_3$	153	164	37
$KMgF_3$	76		38
$RbMnF_3$	67		38
Ferroelectrics			
HCl	4.5		39
PVDF (all trans)	11	287	40
$NaNO_2$	22		41
KH_2PO_4	27	39	42
SbSI	19		43
$BaTiO_3$	162	128	24
$PbTiO_3$	180		44
$LiTaO_3$	134	302	45
$LiNbO_3$	110	248	45
$KNbO_3$	147	249	21

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