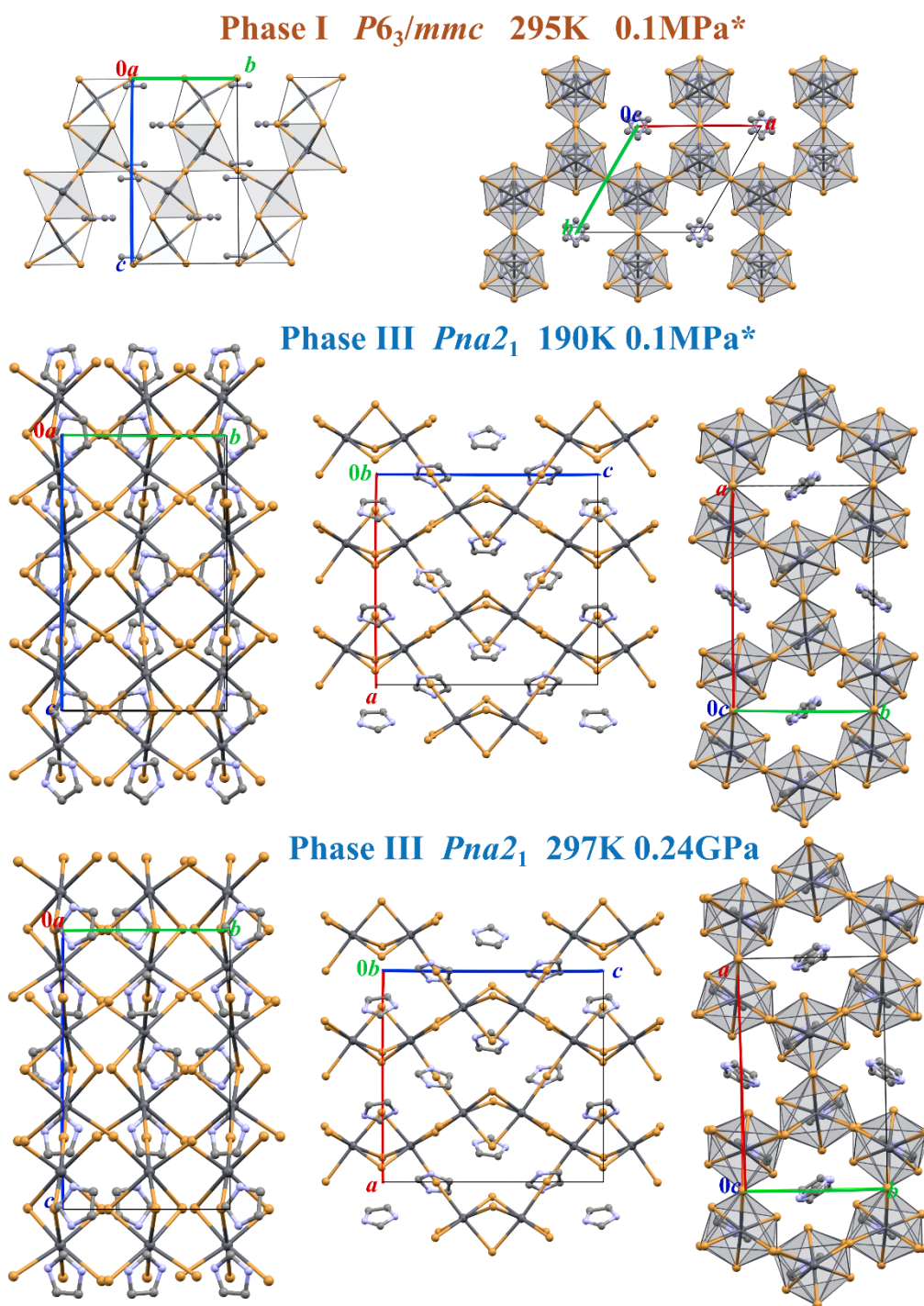


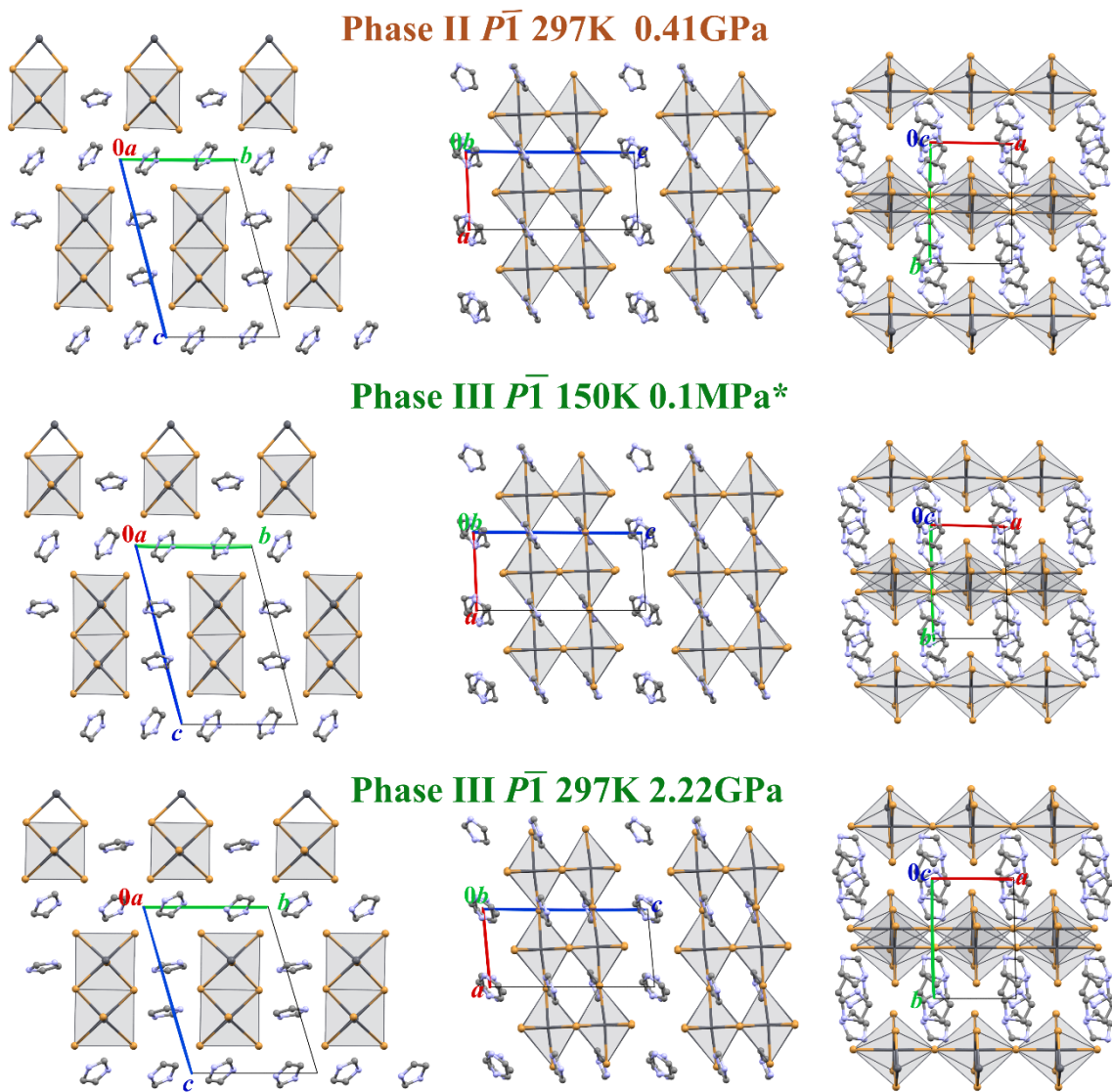
Electronic Supplementary Information

for

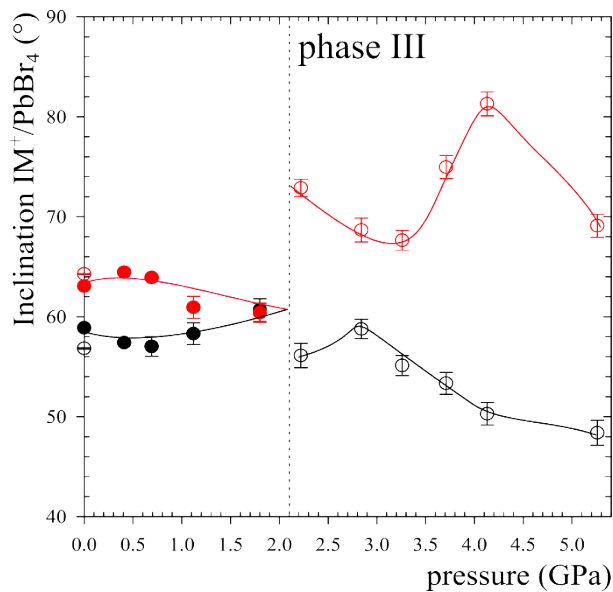
## Exploring Pressure-Induced Phase Transitions in Imidazolium Lead Bromide Hybrids



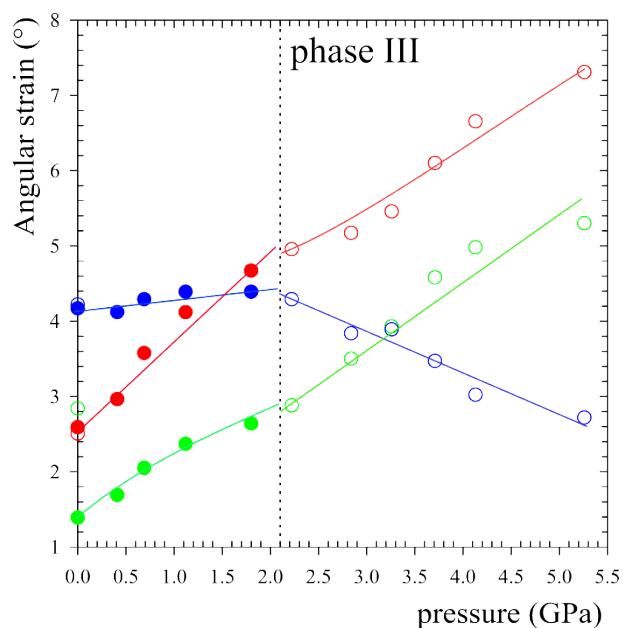
**Figure S1.** IMPbBr<sub>3</sub> structure in phases I and III along the three main crystallographic directions.



**Figure S2.**  $\text{IM}_2\text{PbBr}_4$  in phases II and III along the three main crystallographic directions.

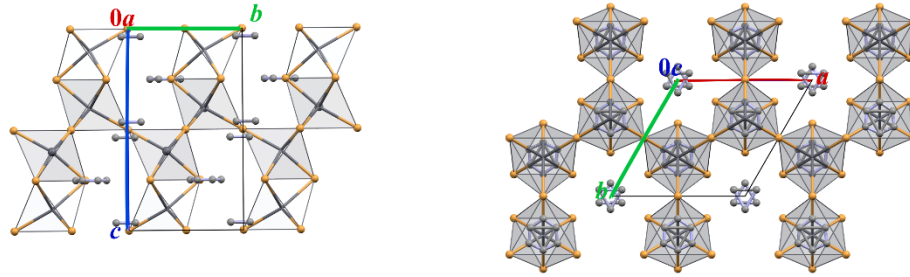


**Figure S3.** Inclination angle of the mean planes of two independent  $IM^+$  cations to the mean plane  $Pb_1-Br_3, Br_4, Br_1, Br_1$  in  $IM_2PbBr_4$ : phase II at 0.1 MPa/295 K (full circles); phase III at 0.1 MPa/150 K (open circles); at high pressure the values of suggested phases II and III are marked by open and full symbols, respectively. The vertical dashed line indicates the transition between phases II and III.

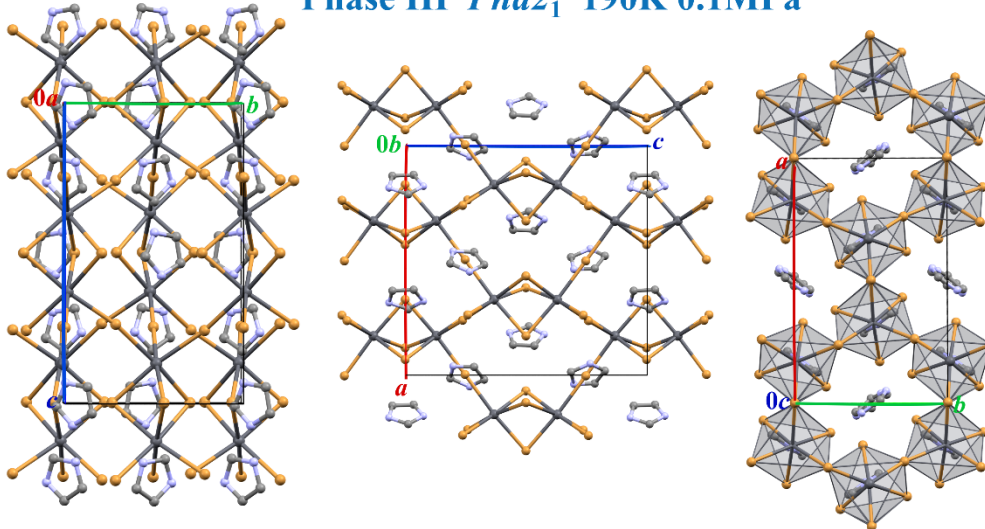


**Figure S4.** Triclinic strain calculated for the  $Im_2PbBr_4$  crystal as the deviations of the unit-cell angles for the lattices transformed into the orthorhombic phase I (according to matrix  $M^{-1}$ -see Equation 1):  $|90^\circ-\alpha_i|$  - red;  $|90^\circ-\beta_i|$  - green;  $|90^\circ-\gamma_i|$  - blue. Open and full symbols refer to phases II and III, respectively. The vertical dashed line indicated the transition between phases II and III.

Phase I  $P6_3/mmc$  295K 0.1MPa\*



Phase III  $Pna2_1$  190K 0.1MPa\*



Phase III  $Pna2_1$  297K 0.24GPa

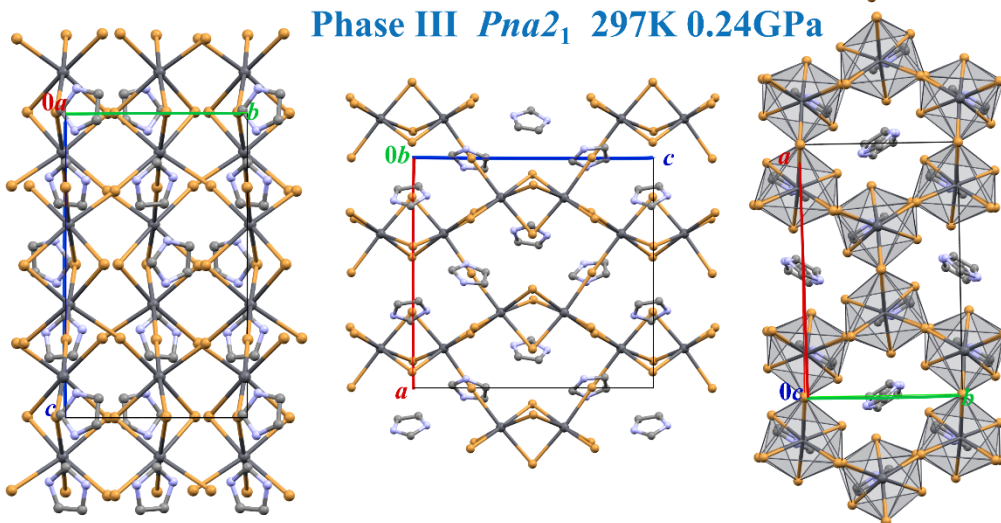
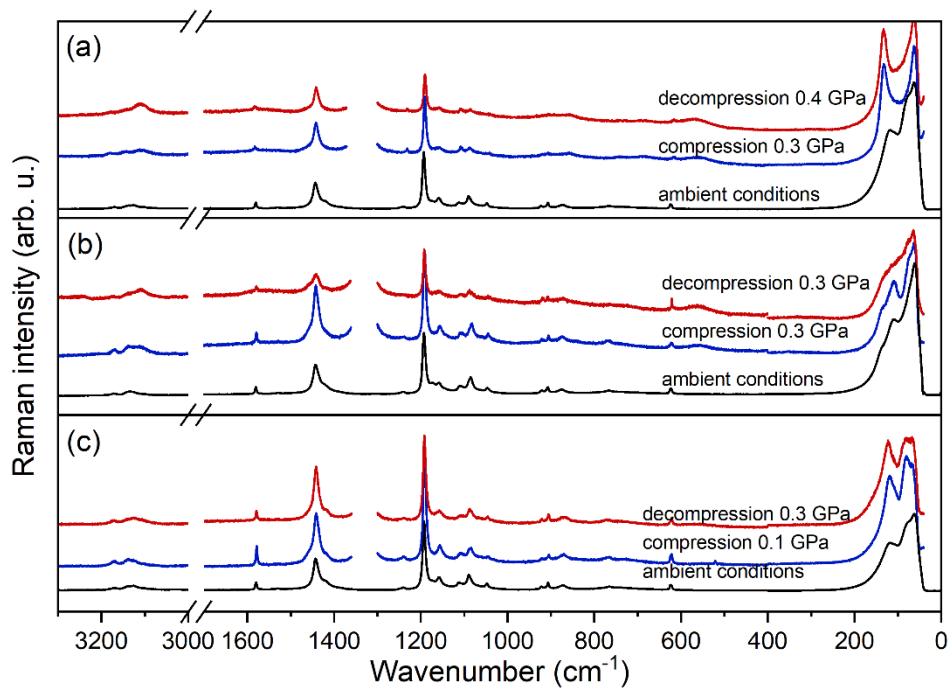
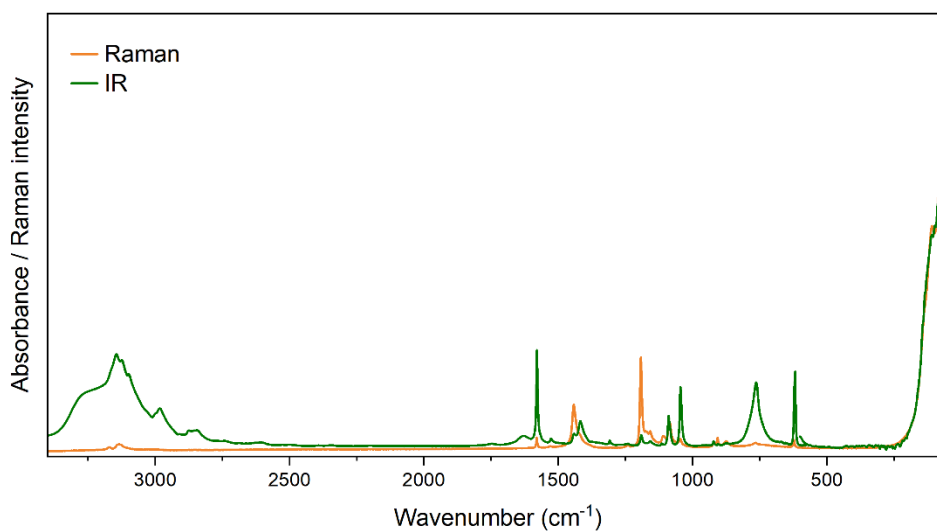


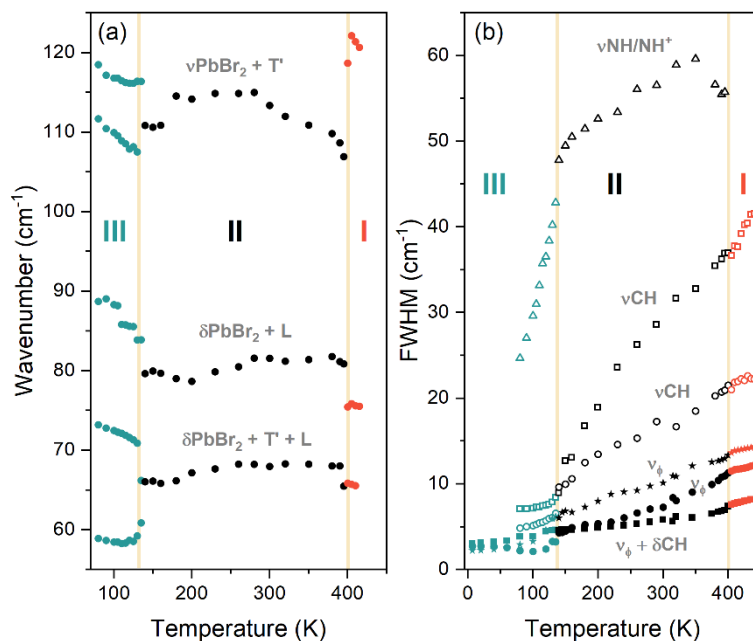
Figure S5.  $IM_3PbBr_5$  in phases I and III along  $a$ ,  $b$ , and  $c$  directions.



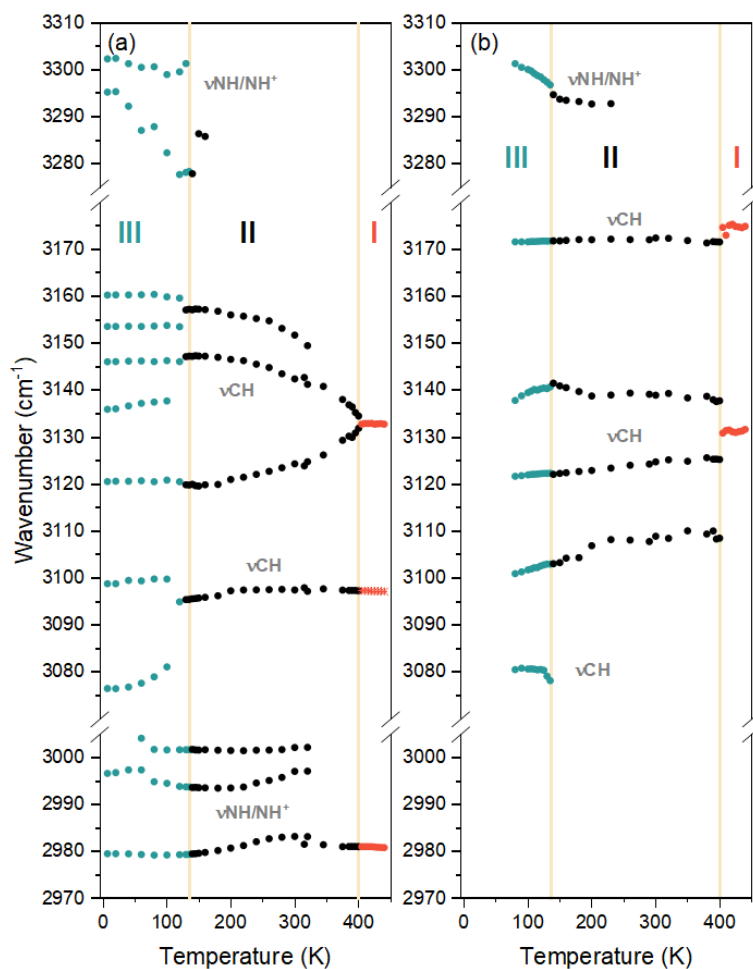
**Figure S6.** Comparison of the Raman spectra at ambient conditions, at the lowest pressure in cell and after decompression for  $\text{IMPbBr}_3$  (a),  $\text{IM}_2\text{PbBr}_4$  (b), and  $\text{IM}_3\text{PbBr}_5$  (c).



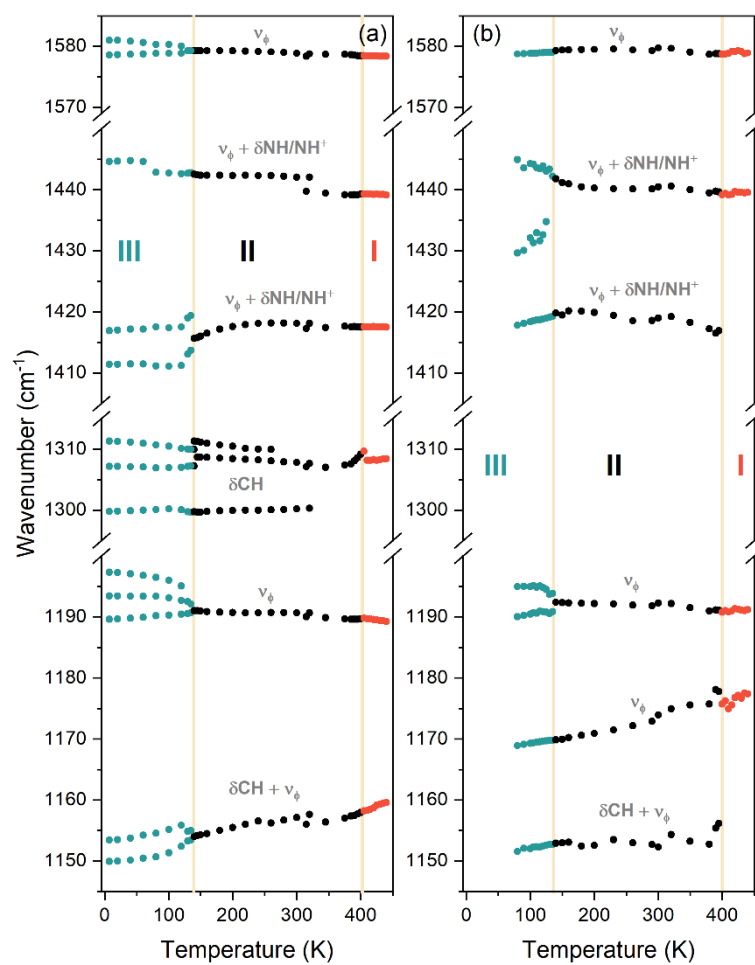
**Figure S7.** Comparison between infrared and Raman spectra at ambient conditions.



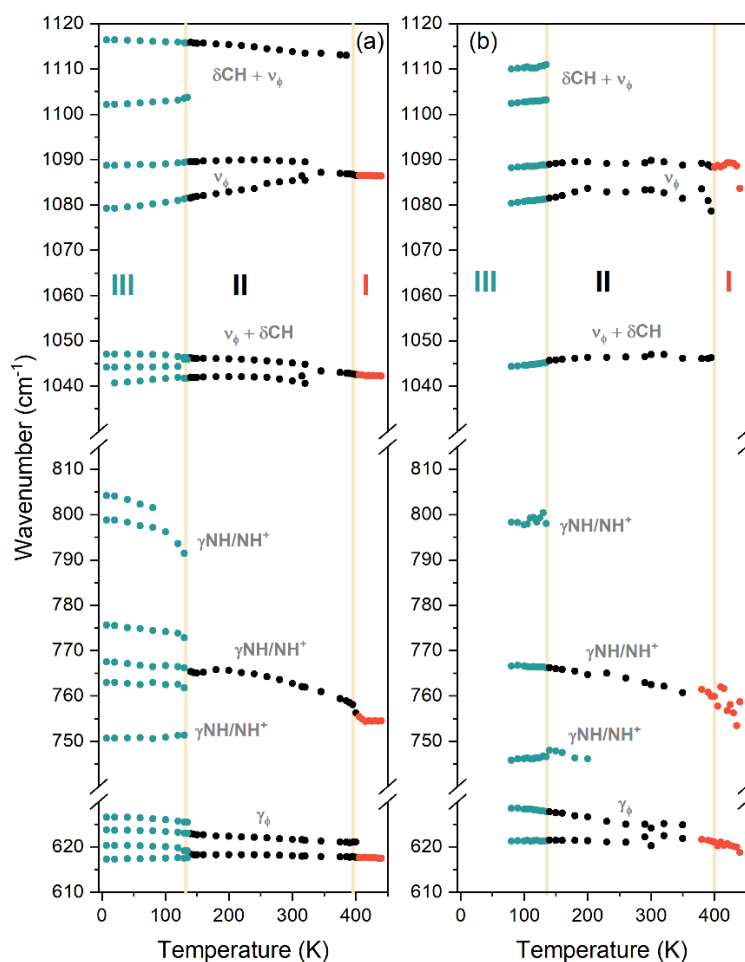
**Figure S8.** Thermal evolution of positions of low-wavenumber Raman bands (a) and changes of the full width at half maximum (FWHM) for selected IR (full symbols) and Raman bands (open symbols) (b) for  $\text{IM}_3\text{PbBr}_5$ ; Peak-fitting uncertainties are within the symbol size.



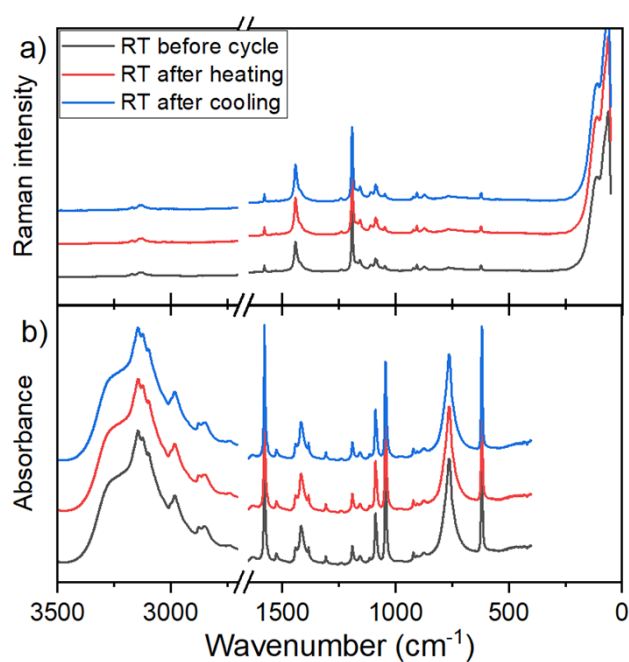
**Figure S9.** Thermal evolution of IR (a) and Raman (b) bands positions in the  $2970\text{--}3310\text{ cm}^{-1}$  range for  $\text{IM}_3\text{PbBr}_5$ ; Peak-fitting uncertainties are within the symbol size.



**Figure S10.** Thermal evolution of IR (a) and Raman (b) bands positions in the 1145-1585  $\text{cm}^{-1}$  range for  $\text{IM}_3\text{PbBr}_5$ ; Peak-fitting uncertainties are within the symbol size.



**Figure S11.** Thermal evolution of IR (a) and Raman (b) bands positions in the 610-1120  $\text{cm}^{-1}$  range for  $\text{IM}_3\text{PbBr}_5$ ; Peak-fitting uncertainties are within the symbol size.



**Figure S12.** Room-temperature Raman (a) and IR spectra (b) of  $\text{IM}_3\text{PbBr}_5$  recorded before and after a thermal-cycling protocol: RT (black lines)  $\rightarrow$  440 K  $\rightarrow$  RT (red lines)  $\rightarrow$  80 K  $\rightarrow$  RT (blue lines). The samples were equilibrated for 30 min at each temperature step.

**Table S1.** Detailed crystallographic data for IMPbBr<sub>3</sub> at high-pressure.

Pressure		0.24 GPa	0.63 GPa	0.88 GPa	1.24 GPa	1.65 GPa	2.00 GPa
CCDC numbers		2473957	2473958	2473959	2473960	2473961	2473962
Crystal system		orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group		<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>
Unit cell dimensions	<i>a</i> (Å)	14.1683(9)	13.9667(7)	13.8183(7)	13.6717(6)	13.5158(6)	13.4525(7)
	<i>b</i> (Å)	8.852(11)	8.759(8)	8.712(6)	8.661(4)	8.588(3)	8.549(4)
	<i>c</i> (Å)	14.8432(9)	14.8128(7)	14.7579(7)	14.7132(5)	14.6421(5)	14.6220(6)
Unit cell angles	$\alpha$ (°)	90	90	90	90	90	90
	$\beta$ (°)	90	90	90	90	90	90
	$\gamma$ (°)	90	90	90	90	90	90
Volume (Å <sup>3</sup> )		1862(2)	1812.2(16)	1776.6(11)	1742.1(8)	1699.5(7)	1681.6(7)
Z/Z'		8/2	8/2	8/2	8/2	8/2	8/2
Molecular volume (V/Z)		232.75	226.525	222.075	217.763	212.438	210.2
Calculated density (g/cm <sup>3</sup> )		3.682	3.783	3.858	3.935	4.033	4.076
Absorption (mm <sup>-1</sup> )		30.932	31.774	32.411	33.053	33.882	34.242
F(000)		1792	1792	1792	1792	1792	1792
Crystal size (mm)		0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.30 × 0.20 × 0.04	0.20 × 0.20 × 0.04
$\theta$ -range for data collection (°)		4.8670 to 23.6650	4.6180 to 25.6200	4.6460 to 25.0130	4.6750 to 25.7300	4.7070 to 25.2380	4.7280 to 25.3250
Min/max indices: <i>h, k, l</i>		-17 ≤ <i>h</i> ≤ 17, -2 ≤ <i>k</i> ≤ 2, -18 ≤ <i>l</i> ≤ 18	-17 ≤ <i>h</i> ≤ 17, -2 ≤ <i>k</i> ≤ 2, -18 ≤ <i>l</i> ≤ 18	-17 ≤ <i>h</i> ≤ 17, -3 ≤ <i>k</i> ≤ 3, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 17, -3 ≤ <i>k</i> ≤ 3, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16, -3 ≤ <i>k</i> ≤ 3, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16, -4 ≤ <i>k</i> ≤ 4, -18 ≤ <i>l</i> ≤ 18
Reflect. Collected/unique		7698/1022	7811/1090	7528/1224	7227/1226	6662/1160	7258/1230
Data/restraints/parameters		1022/178/155	1090/165/148	1224/165/148	1226/171/148	1160/194/148	1230/165/148
Goodness-of-fit on F <sup>2</sup>		1.104	0.995	1.026	0.996	0.925	1.035
Final <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>l</i> >2σ <sub>1</sub> )		0.0655/0.1641	0.0467/0.0947	0.0405/0.0652	0.0415/0.0630	0.0404/0.0504	0.0389/0.0615
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)		0.1016/0.1933	0.1147/0.1397	0.0754/0.0767	0.0824/0.0757	0.0836/0.0615	0.0753/0.0715
Largest diff. peak/hole (e.Å <sup>-3</sup> )		1.00/-0.60	1.01/-0.99	0.79/-0.63	1.23/-0.90	0.85/-0.67	1.01/-0.76

$$w=1/(\sigma^2F_o^2+w_1^2*P^2+w_2*P), \text{ where } P=(\text{Max}(F_o^2,0)+2*F_c^2)$$

**Table S2.** Detailed crystallographic data for IMPbBr<sub>3</sub> at high-pressure.

Pressure		2.35 GPa	2.65 GPa	3.06 GPa	3.58 GPa	4.29 GPa	4.88 GPa
CCDC numbers		2473963	2473964	2473965	2473966	2473967	
Crystal system		orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group		<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>
Unit cell dimensions	<i>a</i> (Å)	13.3713(10)	13.2728(8)	13.2201(7)	13.1813(17)	13.086(5)	12.83(9)
	<i>b</i> (Å)	8.508(4)	8.449(4)	8.379(3)	8.300(8)	8.2602(4)	8.30(1)
	<i>c</i> (Å)	14.5938(8)	14.5088(6)	14.4383(6)	14.3792(14)	14.2630(5)	14.22(1)
Unit cell angles	$\alpha$ (°)	90	90	90	90	90	90
	$\beta$ (°)	90	90	90	90	90	90
	$\gamma$ (°)	90	90	90	90	90	90
Volume (Å <sup>3</sup> )		1660.3(8)	1627.1(7)	1599.3(6)	1573.2(16)	1541.7(6)	1514(11)
Z/Z'		8/2	8/2	8/2	8/2	8/2	
Molecular volume (V/Z)		207.538	203.388	199.913	196.65	192.713	
Calculated density (g/cm <sup>3</sup> )		4.129	4.213	4.286	4.357	4.446	
Absorption (mm <sup>-1</sup> )		34.682	35.390	36.003	36.603	37.349	
F(000)		1792	1792	1792	1792	1792	
Crystal size (mm)		0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.20 × 0.20 × 0.04	0.30 × 0.20 × 0.04	
$\theta$ -range for data collection (°)		4.7480 to 25.3930	4.7820 to 25.5460	4.1640 to 25.6090	4.8000 to 26.0870	4.9240 to 25.6350	
Min/max indices: <i>h, k, l</i>		-16 ≤ <i>h</i> ≤ 16, -4 ≤ <i>k</i> ≤ 4, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16, -4 ≤ <i>k</i> ≤ 4, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16, -4 ≤ <i>k</i> ≤ 4, -18 ≤ <i>l</i> ≤ 18	-16 ≤ <i>h</i> ≤ 16, -3 ≤ <i>k</i> ≤ 3, -18 ≤ <i>l</i> ≤ 18	-5 ≤ <i>h</i> ≤ 5, -10 ≤ <i>k</i> ≤ 10, -18 ≤ <i>l</i> ≤ 17	
Reflect. Collected/unique		7285/1022	7077/1227	7182/1220	5843/1074	6861/1139	
Data/restraints/parameters		1239/189/148	1227/123/148	1220/118/148	1074/193/147	1139/171/148	
Goodness-of-fit on F <sup>2</sup>		1.045	1.029	1.032	1.039	1.027	
Final <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ <sub>1</sub> )		0.0443/0.0825	0.0406/0.0677	0.0412/0.0718	0.0798/0.1487	0.0368/0.0576	
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)		0.0826/0.0968	0.0685/0.0768	0.0673/0.0797	0.1503/0.1870	0.0592/0.0657	
Largest diff. peak/hole (e.Å <sup>-3</sup> )		1.02/-0.95	0.89/-0.91	0.79/-0.78	1.13/-1.31	0.81/-0.90	

$$w=1/(\sigma^2 F_o^2+w_1^2 * P^2+w_2 * P), \text{ where } P=(\text{Max}(F_o^2,0)+2 * Fc^2)$$

**Table S3.** Detailed crystallographic data for IM<sub>2</sub>PbBr<sub>4</sub> at high-pressure.

Pressure		0.41 GPa	0.65 GPa	1.12 GPa	1.80 GPa	2.22 GPa
CCDC numbers		2473968	2473969	2473970	2473971	2473972
Crystal system		triclinic	triclinic	triclinic	triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a$ (Å)	6.0172(15)	6.0024(9)	5.9525(5)	5.9111(6)	5.8790(10)
	$b$ (Å)	9.261(4)	9.245(3)	9.1849(15)	9.1347(17)	9.118(3)
	$c$ (Å)	13.551(12)	13.363(8)	13.074(5)	12.854(5)	12.730(7)
Unit cell angles	$\alpha$ (°)	74.19(6)	74.11(4)	73.89(2)	73.64(3)	73.36(4)
	$\beta$ (°)	86.64(7)	85.77(4)	85.092(17)	84.56(2)	84.27(3)
	$\gamma$ (°)	88.31(3)	87.953(19)	87.626(10)	87.363(13)	87.12(2)
Volume (Å <sup>3</sup> )		725.3(8)	711.2(5)	684.1(3)	662.8(3)	650.4(4)
Z/Z'		2/1	2/1	2/1	2/1	2/1
Molecular volume (V/Z)		362.65	355.6	342.05	331.4	325.2
Calculated density (g/cm <sup>3</sup> )		3.045	3.105	3.228	3.332	3.396
Absorption (mm <sup>-1</sup> )		22.626	23.075	23.989	24.759	25.232
F(000)		592	592	592	592	592
Crystal size (mm)		0.23 × 0.09 × 0.05	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06
$\theta$ -range for data collection (°)		2.2040 to 25.1820	2.2120 to 22.6070	3.4020 to 23.3450	3.4010 to 22.7600	3.4240 to 23.0440
Min/max indices: $h, k, l$		$-6 \leq h \leq 7, -10 \leq k \leq 10, -4 \leq l \leq 5$	$-7 \leq h \leq 7, -10 \leq k \leq 10, -5 \leq l \leq 5$	$-8 \leq h \leq 7, -10 \leq k \leq 11, -5 \leq l \leq 5$	$-8 \leq h \leq 7, -11 \leq k \leq 11, -4 \leq l \leq 4$	$-7 \leq h \leq 7, -10 \leq k \leq 10, -4 \leq l \leq 4$
Reflect. Collected/unique		1344/480	3136/613	6736/655	6104/634	6784/566
Data/restraints/parameters		480/154/121	613/152/121	655/141/120	634/124/120	566/147/120
Goodness-of-fit on F <sup>2</sup>		1.003	0.995	1.063	1.035	1.007
Final $R_1/wR_2$ ( $l > 2\sigma_1$ )		0.0808/0.1482	0.0656/0.1365	0.0595/0.1067	0.0575/0.1109	0.0615/0.1168
$R_1/wR_2$ (all data)		0.1778/0.1949	0.1350/0.1657	0.1367/0.1608	0.1253/0.1501	0.1293/0.1543
Largest diff. peak/hole (e.Å <sup>-3</sup> )		0.63/-0.72	0.82/-0.87	0.92/-0.71	0.94/-0.81	0.89/-0.64

$$w=1/(\sigma^2 F_o^2 + w_1^2 * P^2 + w_2 * P), \text{ where } P=(\text{Max}(F_o^2, 0) + 2 * Fc^2)$$

**Table S4.** Detailed crystallographic data for IM<sub>2</sub>PbBr<sub>4</sub> at high-pressure.

Pressure		2.84 GPa	3.26 GPa	3.71 GPa	4.13 GPa	5.26 GPa
CCDC numbers		2473973	2473974	2473975	2473976	2473977
Crystal system		triclinic	triclinic	triclinic	triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a$ (Å)	5.8316(13)	5.808(4)	5.7758(5)	5.749(4)	5.732(4)
	$b$ (Å)	9.108(3)	9.096(6)	9.0820(16)	9.075(7)	9.062(8)
	$c$ (Å)	12.603(8)	12.435(15)	12.395(6)	12.356(16)	12.225(19)
Unit cell angles	$\alpha$ (°)	72.46(5)	72.49(10)	71.96(3)	71.40(12)	71.26(13)
	$\beta$ (°)	83.89(5)	83.38(10)	82.46(2)	81.78(12)	81.11(13)
	$\gamma$ (°)	86.50(2)	86.07(5)	85.392(10)	85.02(6)	84.70(7)
Volume (Å <sup>3</sup> )		634.3(5)	621.9(10)	612.3(4)	604.1(11)	593.5(12)
$Z/Z'$		2/1	2/1	2/1	2/1	2/1
Molecular volume (V/Z)		317.15	310.95	306.15	302.05	296.75
Calculated density (g/cm <sup>3</sup> )		3.482	3.551	3.607	3.656	3.721
Absorption (mm <sup>-1</sup> )		25.870	26.387	26.801	27.165	27.653
F(000)		592	592	592	592	592
Crystal size (mm)		0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06	0.23 × 0.10 × 0.06
$\theta$ -range for data collection (°)		3.4440 to 18.8000	3.4030 to 17.1220	3.5380 to 24.3890	3.4760 to 23.2970	3.5020 to 23.3330
Min/max indices: $h, k, l$		-6 ≤ $h$ ≤ 6, -9 ≤ $k$ ≤ 9, -4 ≤ $l$ ≤ 4	-7 ≤ $h$ ≤ 7, -10 ≤ $k$ ≤ 10, -3 ≤ $l$ ≤ 3	-6 ≤ $h$ ≤ 7, -10 ≤ $k$ ≤ 11, -3 ≤ $l$ ≤ 3	-7 ≤ $h$ ≤ 7, -11 ≤ $k$ ≤ 11, -4 ≤ $l$ ≤ 4	-7 ≤ $h$ ≤ 7, -11 ≤ $k$ ≤ 11, -4 ≤ $l$ ≤ 4
Reflect. Collected/unique		4017/424	4438/540	2353/428	2353/517	5514/537
Data/restraints/parameters		424/181/120	540/185/120	428/200/120	517/267/120	537/211/120
Goodness-of-fit on $F^2$		1.063	1.010	1.111	1.023	0.979
Final $R_1/wR_2$ ( $l > 2\sigma_1$ )		0.0748/0.1215	0.0640/0.1199	0.0482/0.1023	0.0778/0.1573	0.0732/0.1562
$R_1/wR_2$ (all data)		0.1811/0.2142	0.1649/0.1616	0.0695/0.1116	0.1795/0.1981	0.1508/0.1948
Largest diff. peak/hole (e.Å <sup>-3</sup> )		1.56/-0.90	0.85/-0.69	0.67/-0.60	0.80/-0.61	0.97/-0.65

$$w=1/(\sigma^2 F_o^2+w_1^2 * P^2+w_2 * P), \text{ where } P=(\text{Max}(F_o^2,0)+2 * Fc^2)$$

**Table S5.** Detailed crystallographic data for IM<sub>3</sub>PbBr<sub>5</sub> at high-pressure.

Pressure		<b>0.33 Pa</b>	<b>0.60 GPa</b>	<b>1.07 GPa</b>	<b>1.55 GPa</b>	<b>2.04 GPa</b>
CCDC numbers		2473978	2473979	2473980	2473981	2473982
Crystal system		triclinic	triclinic	triclinic	triclinic	triclinic
Space group		<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
Unit cell dimensions	<i>a</i> (Å)	6.0296(6)	6.0080(7)	5.9703(6)	5.9377(5)	5.9165(5)
	<i>b</i> (Å)	9.308(2)	9.260(2)	9.196(3)	9.139(2)	9.1040(18)
	<i>c</i> (Å)	9.546(4)	9.437(4)	9.275(4)	9.150(3)	9.066(3)
Unit cell angles	$\alpha$ (°)	66.89(3)	66.76(3)	66.43(3)	66.16(3)	65.96(3)
	$\beta$ (°)	85.91(2)	85.41(2)	84.81(2)	84.388(17)	84.090(16)
	$\gamma$ (°)	88.10(2)	87.83(2)	87.456(17)	87.214(15)	86.978(14)
Volume (Å <sup>3</sup> )		491.4(2)	480.9(3)	464.8(3)	452.0(2)	443.6(2)
<i>Z</i> / <i>Z'</i>		1/1	1/1	1/1	1/1	1/1
Molecular volume (V/ <i>Z</i> )		491.4	480.9	464.8	452.0	443.6
Calculated density (g/cm <sup>3</sup> )		2.750	2.811	2.908	2.991	3.047
Absorption (mm <sup>-1</sup> )		18.747	19.160	19.822	20.383	20.771
F(000)		368	368	368	368	368
Crystal size (mm)		0.25 × 0.15 × 0.05	0.25 × 0.15 × 0.05	0.25 × 0.15 × 0.05	0.25 × 0.20 × 0.05	0.25 × 0.15 × 0.05
$\theta$ -range for data collection (°)		5.1710 to 24.2380	5.2200 to 24.6900	5.2740 to 25.1390	5.3270 to 25.2100	4.5770 to 25.2810
Min/max indices: <i>h</i> , <i>k</i> , <i>l</i>		-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -7 ≤ <i>l</i> ≤ 7	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6
Reflect. Collected/unique		2413/850	2469/866	2303/817	2645/1030	2214/785
Data/restraints/parameters		850/238/166	866/237/167	817/249/166	1030/264/167	785/225/165
Goodness-of-fit on <i>F</i> <sup>2</sup>		1.032	1.036	1.077	1.045	1.045
Final <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>l</i> >2 $\sigma$ 1)		0.0396/0.0790	0.0441/0.0948	0.0542/0.1287	0.0879/0.2244	0.0369/0.0760
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)		0.0563/0.0848	0.0667/0.1030	0.0694/0.1398	0.1100/0.2536	0.0509/0.0811
Largest diff. peak/hole (e.Å <sup>-3</sup> )		0.41/-0.35	0.43/-0.38	0.55/-0.61	1.17/-0.83	0.38/-0.36

$$w=1/(\sigma^2 F_o^2 + w_1^2 * P^2 + w_2 * P), \text{ where } P=(\text{Max}(F_o^2, 0) + 2 * Fc^2)$$

**Table S6.** Detailed crystallographic data for IM<sub>3</sub>PbBr<sub>5</sub> at high-pressure

Pressure		2.43 Pa	2.97 GPa	3.45 GPa	3.92 GPa	4.35 GPa
CCDC numbers		2473983	2473984	2473985	2473986	2473987
Crystal system		triclinic	triclinic	triclinic	triclinic	triclinic
Space group		<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
Unit cell dimensions	<i>a</i> (Å)	5.8912(5)	5.8382(4)	5.8206(4)	5.8103(6)	5.8034(10)
	<i>b</i> (Å)	9.0889(19)	9.0575(19)	9.0421(18)	9.030(2)	9.018(4)
	<i>c</i> (Å)	8.999(3)	8.999(3)	8.859(3)	8.837(3)	8.829(6)
Unit cell angles	$\alpha$ (°)	65.73(3)	65.44(3)	65.34(2)	65.33(3)	65.20(5)
	$\beta$ (°)	83.808(16)	83.329(15)	83.175(14)	83.145(19)	82.86(3)
	$\gamma$ (°)	86.707(14)	86.199(13)	86.025(12)	85.946(17)	85.75(3)
Volume (Å <sup>3</sup> )		436.6(2)	429.8(2)	420.62(17)	418.21(19)	416.1(4)
<i>Z</i> / <i>Z'</i>		1/1	1/1	1/1	1/1	1/1
Molecular volume (V/ <i>Z</i> )		436.6	429.8	420.62	418.21	416.1
Calculated density (g/cm <sup>3</sup> )		3.096	3.145	3.214	3.232	3.249
Absorption (mm <sup>-1</sup> )		21.100	21.437	21.904	22.030	22.142
F(000)		368	368	368	368	368
Crystal size (mm)		0.25 × 0.15 × 0.05	0.25 × 0.15 × 0.05	0.25 × 0.15 × 0.05	0.25 × 0.15 × 0.05	0.25 × 0.20 × 0.05
$\theta$ -range for data collection (°)		4.6120 to 25.3030	4.6820 to 25.5930	5.4310 to 25.6550	4.3570 to 25.3680	4.3850 to 23.7140
Min/max indices: <i>h</i> , <i>k</i> , <i>l</i>		-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6	-7 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -6 ≤ <i>l</i> ≤ 6
Reflect. Collected/unique		2206/777	2167/759	2147/752	2091/737	1983/716
Data/restraints/parameters		777/247/167	759/245/167	752/245/167	737/245/166	716/252/166
Goodness-of-fit on F <sup>2</sup>		1.132	1.049	1.064	1.024	1.052
Final <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>l</i> >2 $\sigma$ 1)		0.0438/0.0954	0.0393/0.0916	0.0364/0.0778	0.0389/0.0776	0.0728/0.1698
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)		0.0549/0.0995	0.0449/0.0944	0.0410/0.0795	0.0458/0.0805	0.0917/0.1830
Largest diff. peak/hole (e.Å <sup>-3</sup> )		0.46/-0.40	0.69/-0.38	0.46/-0.38	0.46/-0.40	1.24/-0.85

$$w=1/(\sigma^2 F_o^2 + w_1^2 * P^2 + w_2 * P), \text{ where } P=(\text{Max}(F_o^2, 0) + 2 * Fc^2)$$

**Table S7.** Linear fitting results of pressure-dependencies of Raman bands of IMPbBr<sub>3</sub>.

III		IV		Assignment
$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	
3350.3	-2.95	3346.4	-6.40	$\nu_{\text{NH}} + \nu_{\text{NH}^+}$
3190.8	4.15	3187.5	5.02	$\nu_{\text{CH}}$
3175.2	5.76	3183.5	2.85	
3148.8	4.86	3148.7	4.78	
1440.4	1.25	1440.3	2.79	$\nu_{\phi} + \delta_{\text{NH}} + \delta_{\text{NH}^+}$
		1427.0	2.41	
		1416.7	0.74	
1189.0	1.72	1186.0	2.30	$\nu_{\phi}$
1162.5	-0.45	1156.5	1.12	$\delta_{\text{CH}} + \nu_{\phi}$
1159.5	-0.34	1160.4	-0.48	
1107.8	1.62	1094.4	5.42	
1042.3	1.33	1043.4	0.95	
918.0	0.12	912.8	0.70	$\delta_{\phi}$
615.0	0.45	609.1	2.06	$\gamma_{\theta}$
		606.5	1.23	
139.4	3.69	104.6	16.8	$\nu_{\text{PbBr}}$
		83.3	15.9	
		124.1	6.45	
		127.6	5.00	
95.1	7.46	106.3	3.22	$\nu_{\text{PbBr}}$
		93.1	8.74	
57.5	2.06	60.3	2.53	$\delta_{\text{PbBr}}$
		55.4	2.39	

Key:  $\delta$ , bending (scissoring);  $\delta_{\phi}$ , in-plane ring bending;  $d\omega/dp$ , slope;  $\gamma_{\phi}$ , out-of-plane ring bending,  $\nu$ , stretching;  $\nu_{\phi}$ , ring stretching,  $\omega_0$ , intercept

**Table S8.** Linear fitting results of pressure-dependencies of Raman bands of IM<sub>2</sub>PbBr<sub>4</sub>.

$\omega_0$ (cm <sup>-1</sup> )	II		III		IV		Assignment	
	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )		
3167.9	6.51	3171.2	9.31	3146.9	13.85	vCH		
		3174.1	3.94	3160.1	6.64			
				3172.8	2.40			
3134.9	7.35	3141.2	1.37	3101.0	9.23	vCH		
		3155.8	-4.60	3128.8	0.49			
1440.8	0.75	1439.9	1.65	1417.3	5.79	v <sub>φ</sub> + δNH + δNH <sup>+</sup>		
		1440.6	0.84	1416.6	3.93			
		1418.0	0.37	1390.3	5.29			
1190.2	1.92	1190.1	3.61	1183.1	5.04	v <sub>φ</sub>		
		1189.1	2.19	1176.1	4.48			
		1184.8	1.04	1172.0	3.23			
1154.3	2.94	1165.5	0.41	1187.3	-3.25	δCH + v <sub>φ</sub>		
		1159.2	0.22	1183.8	-3.94			
1106.8	-1.63	1104.6	0.88	1101.3	1.39	δCH + v <sub>φ</sub>		
1044.8	-0.13	1044.1	1.59	1037.4	2.92	v <sub>φ</sub> + δCH		
		1041.6	-0.13	1023.3	3.00			
919.7	0.45	918.8	0.42			δ <sub>φ</sub>		
904.5	1.88	905.7	1.36	903.2	1.94			
874.6	-2.13	868.8	0.92	856.0	4.53	γCH		
				891.1	-3.04			
767.1	3.17	763.7	4.80	761.2	3.94	γNH + γNH <sup>+</sup>		
		751.5	2.86					
622.5	1.67	621.2	1.52	615.4	2.57	v <sub>φ</sub>		
620.9	-0.31	616.7	1.41	617.3	1.50			
		614.4	0.59	618.4	-0.15			
108.5	3.35	163.5	14.74	207.2	9.12	vPbBr		
		131.5	13.59	145.1	11.86			
		97.6	8.11	99.7	8.21			
69.1	10.73	74.5	7.11	132.4	3.13	vPbBr		
60.1	2.52	54.8	1.37	48.9	7.21	δPbBr		
				55.2	6.43		85.8	1.66
				52.1	5.29		102.7	-2.83
							26.7	6.02
							50.0	2.63
							69.1	-0.52

Key: δ, bending (scissoring); δ<sub>φ</sub>, in-plane ring bending; dω/dp, slope; γ<sub>φ</sub>, out-of-plane ring bending, v, stretching; v<sub>φ</sub>, ring stretching, ω<sub>0</sub>, intercept

**Table S9.** Factor group analysis for IM<sub>3</sub>PbBr<sub>5</sub>.

Ion	Free ion sym. $C_{2v}$ ( <i>mm2</i> )	Site symmetry			Factor group symmetry			
		III $C_1$ (1)	II <sup>a</sup> $C_1$ (1)	I $C_{2v}$ ( <i>mm2</i> )	III $C_1$ (1)	II <sup>a</sup> $C_i$ ( $\bar{1}$ )	I $D_{2h}$ ( <i>mmm</i> )	
IM <sup>+</sup>	vNH <sup>+</sup>	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	vNH	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	3×vCH	3A	3A		9A	3A <sub>g</sub> +3A <sub>u</sub>		
	5×v <sub>φ</sub>	5A	5A		15A	5A <sub>g</sub> +5A <sub>u</sub>		
	δNH <sup>+</sup>	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	δNH	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	3×δCH	3A	3A	Structural disorder	9A	3A <sub>g</sub> +3A <sub>u</sub>	Structural disorder (90) <sup>b</sup>	
	2×δ <sub>φ</sub>	2A	2A		6A	2A <sub>g</sub> +2A <sub>u</sub>		
	γNH <sup>+</sup>	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	γNH	A	A		3A	A <sub>g</sub> +A <sub>u</sub>		
	3×γCH	3A	3A		9A	3A <sub>g</sub> +3A <sub>u</sub>		
	2×γ <sub>φ</sub>	2A	2A		6A	2A <sub>g</sub> +2A <sub>u</sub>		
	T'	3A	3A		9A	3A <sub>g</sub> +3A <sub>u</sub>		
L	3A	3A		9A	3A <sub>g</sub> +3A <sub>u</sub>			
		$C_1$ (1)	$C_1$ (1)	$D_{2h}$ ( <i>mmm</i> )	$C_1$ (1)	$C_i$ ( $\bar{1}$ )	$D_{2h}$ ( <i>mmm</i> )	
Br <sup>-</sup>	T'	15A	12A	2A <sub>g</sub> +A <sub>u</sub> +2B <sub>1g</sub> +B <sub>1u</sub>	15A	6A <sub>g</sub> +6A <sub>u</sub>	2A <sub>g</sub> +A <sub>u</sub> +2B <sub>1g</sub> +B <sub>1u</sub>	
			$C_i$ ( $\bar{1}$ )	+B <sub>2g</sub> +2B <sub>2u</sub> +B <sub>3g</sub> +2B <sub>3u</sub>		$C_s$ ( <i>m</i> )	$C_i$ ( $\bar{1}$ )	+B <sub>2g</sub> +2B <sub>2u</sub> +B <sub>3g</sub> +2B <sub>3u</sub>
			3A <sub>u</sub>	B <sub>1u</sub> +B <sub>2u</sub> +B <sub>3u</sub>		3A <sub>u</sub>	B <sub>1u</sub> +B <sub>2u</sub> +B <sub>3u</sub>	
		$C_1$ (1)	$C_i$ ( $\bar{1}$ )	$D_{2h}$ ( <i>mmm</i> )	$C_1$ (1)	$C_i$ ( $\bar{1}$ )	$D_{2h}$ ( <i>mmm</i> )	
Pb <sup>2+</sup>	T'	3A	3A <sub>u</sub>	B <sub>1u</sub> +B <sub>2u</sub> +B <sub>3u</sub>	3A	3A <sub>u</sub>	B <sub>1u</sub> +B <sub>2u</sub> +B <sub>3u</sub>	

<sup>a</sup> for ordered molecules in the primitive cell (half); <sup>b</sup> total number of expected vibrational modes; key: IR-active; Raman-active; both IR- and Raman active; silent; v, stretching; v<sub>φ</sub>, ring stretching; δ, in-plane bending; δ<sub>φ</sub>, in-plane ring bending; γ, out-of-plane bending; γ<sub>φ</sub>, out-of-plane ring bending; T', translation; L, libration.

**Table S10.** IR and Raman bands (cm<sup>-1</sup>) of IM<sub>3</sub>PbBr<sub>5</sub> together with relative intensity and assignments.

Raman	IR	Assignment
3244 <sub>b,vw</sub>	3255 <sub>b,s</sub>	vNH + vNH <sup>+</sup>
3171 <sub>vw</sub> , 3135 <sub>vw</sub> , 3110 <sub>sh</sub>	3144 <sub>sh</sub> , 3123 <sub>m</sub> , 3099 <sub>m</sub>	vCH
3031 <sub>vw</sub> , 2996 <sub>vw</sub>	2998 <sub>sh</sub> , 2982 <sub>w</sub>	vNH + vNH <sup>+</sup>
	2875 <sub>w</sub> , 2844 <sub>w</sub> , 1747 <sub>vw</sub> , 1630 <sub>w</sub>	overtones
1580 <sub>w</sub>	1579 <sub>m</sub>	v <sub>φ</sub>
1528 <sub>vw</sub>	1526 <sub>vw</sub> , 1497 <sub>sh</sub>	δCH + v <sub>φ</sub>
1442 <sub>m</sub> , 1421 <sub>sh</sub>	1441 <sub>sh</sub> , 1417 <sub>w</sub>	v <sub>φ</sub> + δNH + δNH <sup>+</sup>
1239 <sub>vw</sub>	1307 <sub>vw</sub>	δCH
1192 <sub>m</sub> , 1173 <sub>vw</sub>	1191 <sub>vw</sub>	v <sub>φ</sub>
1158 <sub>vw</sub> , 1109 <sub>vw</sub>	1157 <sub>vw</sub> , 1114 <sub>vw</sub>	δCH + v <sub>φ</sub>
1088 <sub>sh</sub> , 1084 <sub>w</sub>	1089 <sub>w</sub> , 1084 <sub>sh</sub>	v <sub>φ</sub>
1046 <sub>w</sub>	1045 <sub>m</sub>	v <sub>φ</sub> + δCH
921 <sub>vw</sub> , 906 <sub>vw</sub>	921 <sub>vw</sub>	δ <sub>φ</sub>
874 <sub>vw</sub>	874 <sub>vw</sub>	γCH
767 <sub>vw</sub>	763 <sub>m</sub>	γNH + γNH <sup>+</sup>
623 <sub>vw</sub>	621 <sub>sh</sub> , 618 <sub>m</sub>	γ <sub>φ</sub>
138 <sub>sh</sub>	135 <sub>sh</sub>	vPbBr
110 <sub>s</sub>	111 <sub>s</sub>	vPbBr + T'
74 <sub>sh</sub>	81 <sub>vs</sub>	δPbBr + L
61 <sub>vs</sub>	69 <sub>vs</sub>	δPbBr + T' + L

Key: broad, b; very strong, vs; strong, s; medium, m; weak, w; very weak, vw; v, stretching; v<sub>φ</sub>, ring stretching; δ, in-plane bending; δ<sub>φ</sub>, in-plane ring bending; γ, out-of-plane bending; γ<sub>φ</sub>, out-of-plane ring bending; T', translation; L, libration.

**Table S11.** Linear fitting results of pressure-dependencies of Raman bands of IM<sub>3</sub>PbBr<sub>5</sub>.

	III		IV		V		Assignment
$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )	$\omega_0$ (cm <sup>-1</sup> )	$d\omega/dp$ (cm <sup>-1</sup> GPa <sup>-1</sup> )		
3288.5	-9.16	3293.9	-6.28				$\nu_{\text{NH}} + \nu_{\text{NH}^+}$
3169.1	8.15	3174.4	5.94	3177.4	5.46		$\nu_{\text{CH}}$
3139.5	2.87	3149.6	-1.22	3130.0	1.69		$\nu_{\text{CH}}$
3124.2	1.85						$\nu_{\text{CH}}$
1440.8	10.42	1444.6	5.87	1448.8	5.63		$\nu_{\phi} + \delta_{\text{NH}} + \delta_{\text{NH}^+}$
1440.7	0.76	1438.8	1.97				
		1186.4	4.17	1184.8	4.83		$\nu_{\phi}$
1191.3	1.61	1191.3	1.59	1191.3	2.81		
				1182.0	2.98		
		1158.5	2.33	1165.7	1.43		$\delta_{\text{CH}} + \nu_{\phi}$
1154.0	4.06	1161.5	0.55	1154.1	1.74		
		1102.4	2.73	1108.4	2.07		$\delta_{\text{CH}} + \nu_{\phi}$
1108.0	-0.99	1104.7	1.71	1091.4	3.16		
		1048.0	0.64	1019.6	5.27		$\nu_{\phi} + \delta_{\text{CH}}$
1045.8	0.41	1043.0	0.58	1034.3	2.09		
921.5	0.04	918.1	1.71	917.6	2.29		$\delta_{\phi}$
905.3	1.36	904.7	1.73	904.8	2.00		
				902.3	1.67		
875.3	4.59	873.8	4.62	864.2	4.08		$\gamma_{\text{CH}}$
867.5	-3.94	863.6	-0.73	847.6	1.26		
		765.6	4.64	753.2	7.98		$\gamma_{\text{NH}} + \gamma_{\text{NH}^+}$
770.2	2.81			750.8	5.72		
				753.8	2.15		
734.5	1.85	722.5	6.01	736.3	1.67		
624.5	2.31	624.3	2.49	612.6	3.57		$\gamma_{\phi}$
621.3	0.86	620.5	1.30	606.4	2.94		
153.5	10.39	160.1	18.23				$\nu_{\text{PbBr}}$
		119.0	6.37	110.7	8.58		$\nu_{\text{PbBr}}$
118.8	7.02	131.2	1.61				
78.2	11.36	82.9	7.46				$\delta_{\text{PbBr}}$
		58.1	7.39	57	7.75		$\delta_{\text{PbBr}}$
62.2	6.18	40.7	7.01	52.2	5.81		

Key:  $\delta$ , bending (scissoring);  $\delta_{\phi}$ , in-plane ring bending;  $d\omega/dp$ , slope;  $\gamma_{\phi}$ , out-of-plane ring bending,  $\nu$ , stretching;  $\nu_{\phi}$ , ring stretching,  $\omega_0$ , intercept.