Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supporting Information for: Pyramidal Inversion in the Solid State

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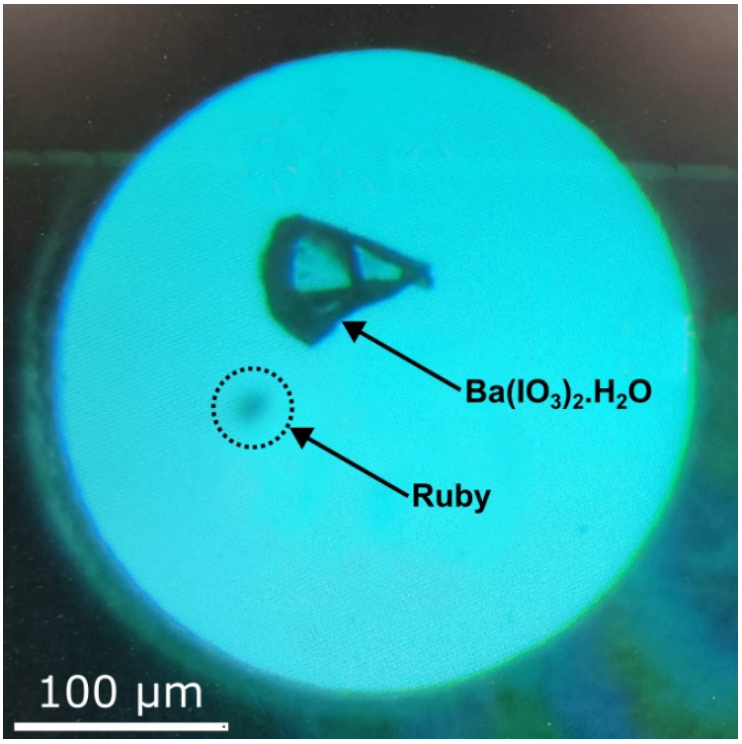

Figure S1. A single crystal of $Ba(IO_3)_2 \cdot H_2O$ loaded in the helium filled sample chamber of a membrane-driven diamond anvil cell. The chamber includes a ruby sphere for pressure measurement. The diameter of the sample chamber is 300 µm; the gasket thickness is 90 µm; the crystal size is approximately 50 µm, and the beamsize (at beamline ID15B at the ESRF, where this photograph was taken) is 1 × 1 µm, as indicated by the black dot on the right-hand side of the white scale bar.

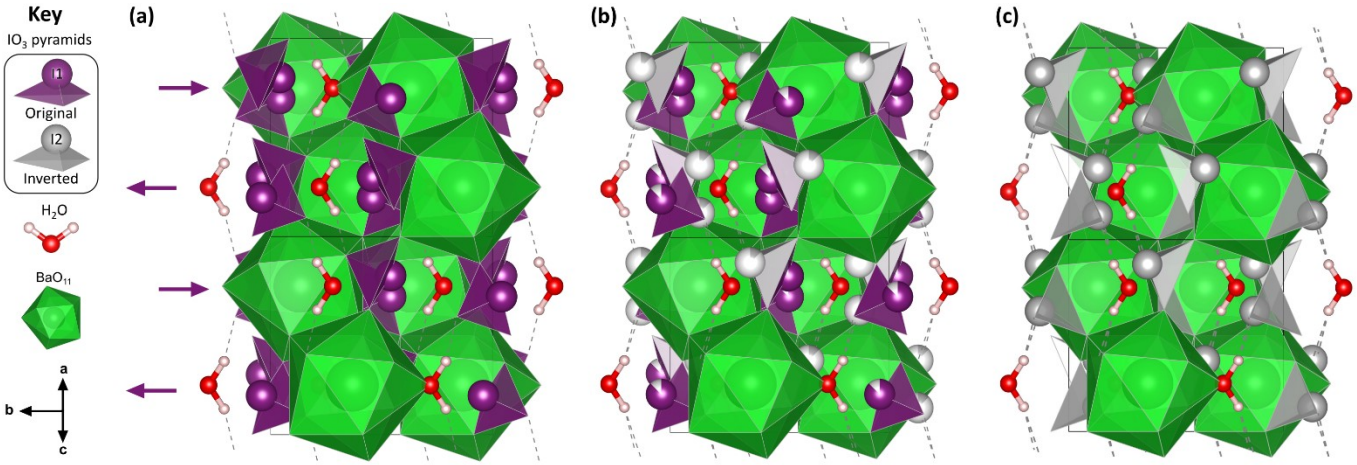

Figure S2 | The crystal structure of $Ba(IO_3)_2 \cdot H_2O$ showing all atoms, to compliment Fig. 1. (a) The structure at ambient pressure. **(b)** The structure at 9.6 GPa where the occupation of the I2 site is 12.5 %. **(c)** The hypothetical fully inverted structure. The crystal structure is viewed along the *ac* body diagonal, perpendicular to the *b* axis: *uvw* projection vector (101), *hkl* upwards vector (100). Hydrogen bonds are shown as dashed lines. The key shows the essential molecular units of the structure. The black arrows below the key indicate the crystal axes.

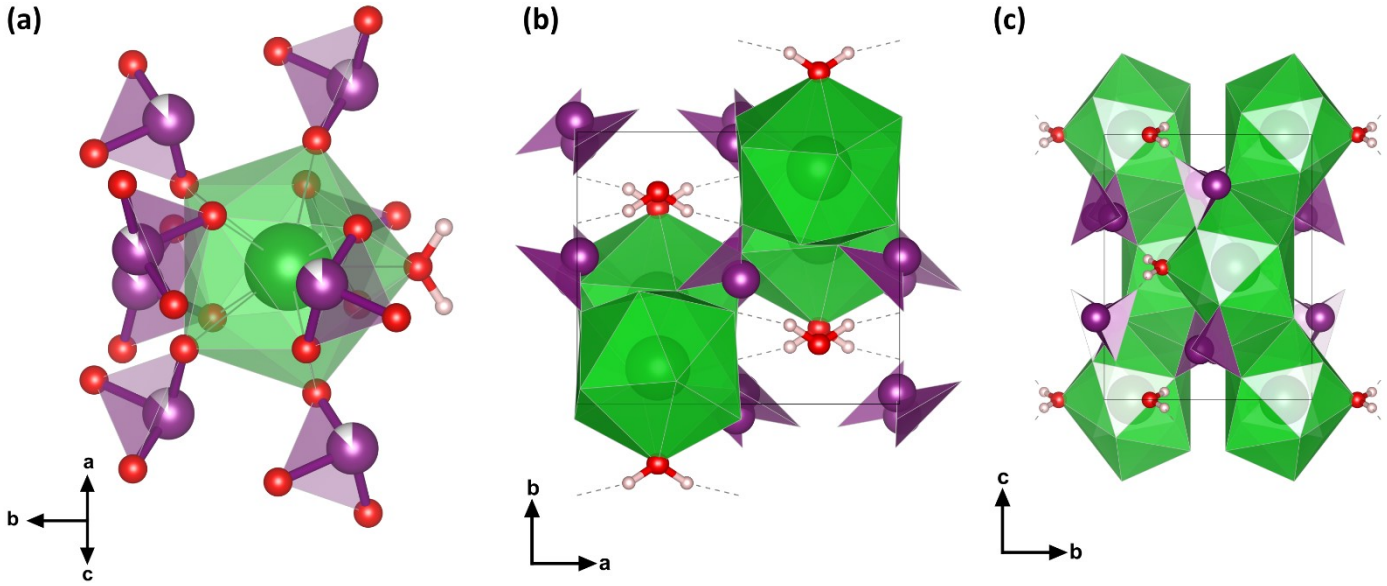

Figure S3 | The BaO_{11} unit and BaO_{11} chains in the $Ba(IO_3)_2 \cdot H_2O$ crystal structure. (a) The BaO_{11} unit showing the coordinating IO_3^- pyramids. The eleven Ba-O distances range between 2.686(8) Å and 3.173(4) Å at ambient pressure. **(b)** The projection along the *c* axis to show the chains of edge-sharing BaO_{11} octadecahdra which run parallel to the *c*-axis. **(c)** The projection along the *a*-axis to show the chains running from top to bottom of the figure.

Table S1 | The SCXDR refinement data for selected pressures.

Pressure (GPa)	**0.0 (air)**	**4.77(5)**	**11.59(5)**	**14.84(5)**
Formula	$BaH_2I_2O_7$	$BaH_2I_2O_7$	$BaH_2I_2O_7$	$BaH_2I_2O_7$
$D_{calc.}$/ g cm^{-3}	4.687	5.252	5.773	5.773
μ/mm^{-1}	14.158	15.866	17.437	17.437
Formula Weight	505.16	505.16	505.16	505.16
Colour	colourless	colourless	colourless	colourless
Shape	plate	plate	plate	plate
Size/mm^3	0.15×0.10×0.06	0.15×0.10×0.06	0.08×0.05×0.04	0.08×0.05×0.04
T/K	298(2)	298(2)	298(2)	298(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$I2/a$	$I2/a$	$I2/a$	$I2/a$
a/Å	9.0494(2)	8.9191(6)	8.7759(4)	8.7461(14)
b/Å	7.9814(2)	7.4877(6)	7.1478(11)	6.9730(13)
c/Å	9.9187(3)	9.578(8)	9.2808(11)	9.136(3)
α/°	90	90	90	90
β/°	92.147(2)	92.91(3)	93.209(6)	93.19(2)
γ/°	90	90	90	90
V/Å^3	715.89(3)	638.8(6)	581.26(12)	556.3(3)
Z	4	4	4	4
Z'	0.5	0.5	0.5	0.5
Wavelength/Å	0.71073	0.71073	0.71073	0.410
Radiation type	Mo K_α	Mo K_α	Mo K_α	Synchrotron
Θ_{min}/°	3.28	3.48	3.60	2.69
Θ_{max}/°	28.33	26.35	26.34	17.02
Measured Refl.	1287	547	1287	513
Independent Refl.	782	257	861	317
Reflections with I > 2(I)	746	257	346	317
R_{int}	0.0190	0.0378	0.0184	0.0219
Parameters	52	33	34	35
Restraints	0	0	3	3
Largest Peak	0.931	0.94	2.13	2.23
Deepest Hole	-1.234	-1.10	-1.52	-1.97
GooF	1.099	1.227	1.080	1.082
wR_2 (all data)	0.0499	0.1186	0.0753	0.1762
wR_2	0.0487	0.1167	0.0742	0.1721
R_1 (all data)	0.0235	0.0407	0.0358	0.0798
R_1	0.0223	0.0378	0.0338	0.0755

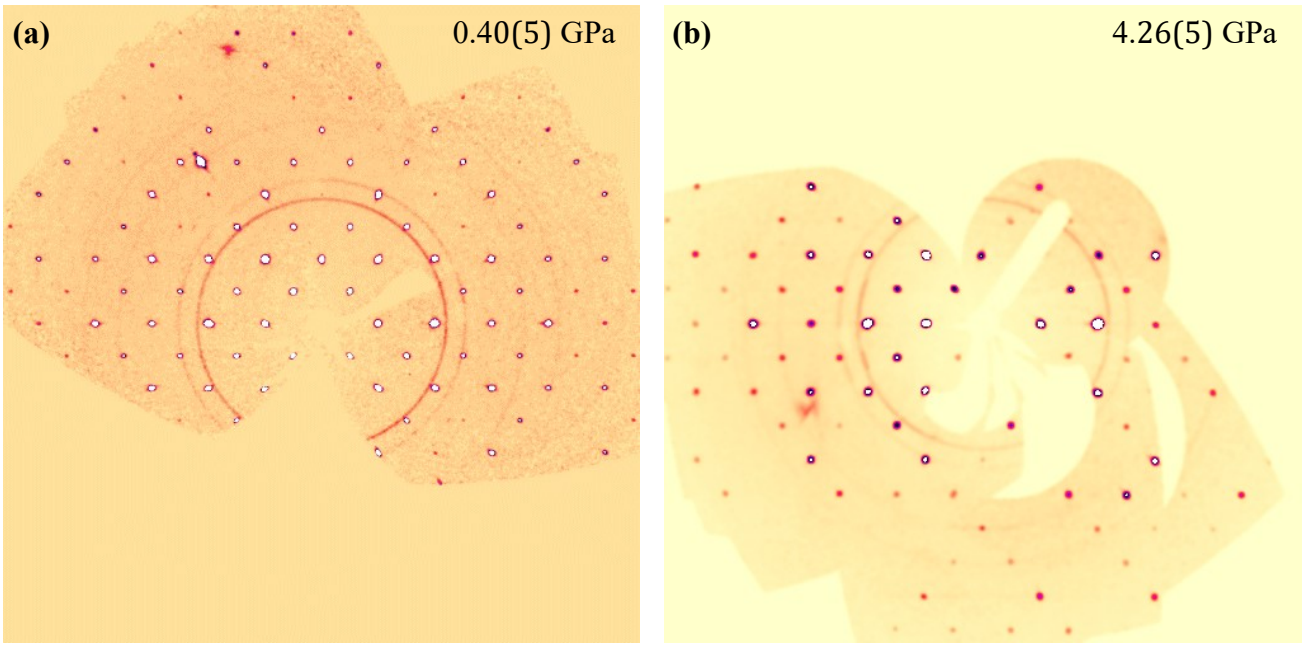

Figure S4. Single crystal X-ray diffraction patterns of $Ba(IO_3)_2.H_2O$ at **(a)** 0.40(5) and **(b)** 4.26(5) GPa respectively.

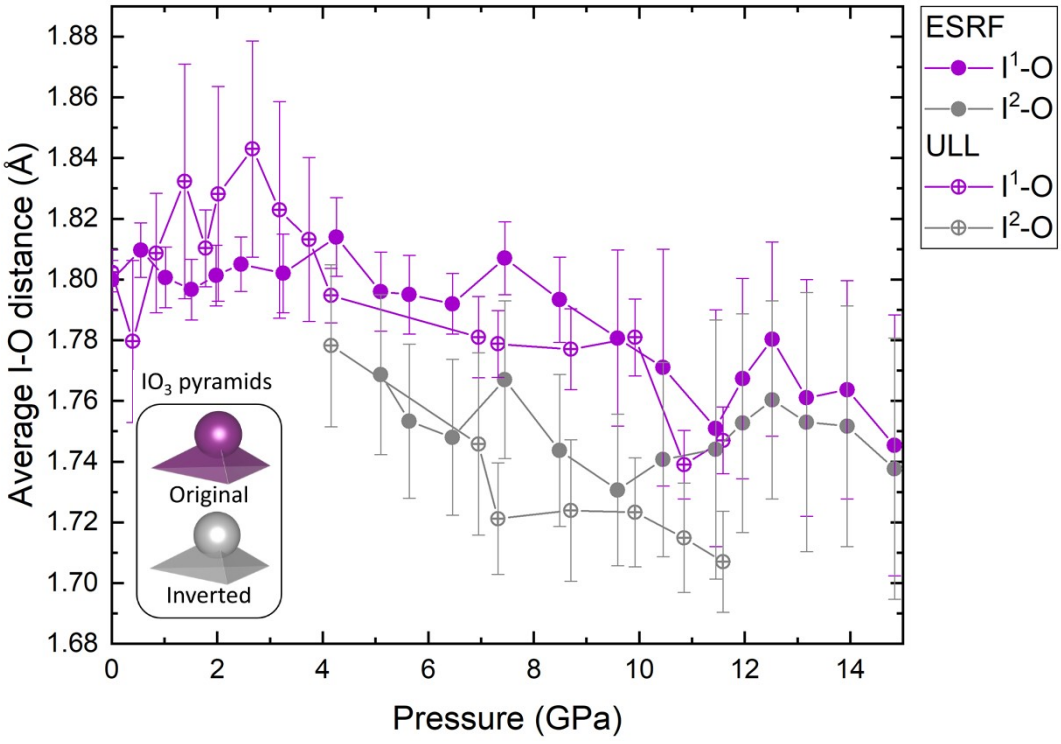

Figure S5 | The average I-O bond distance as a function of pressure.

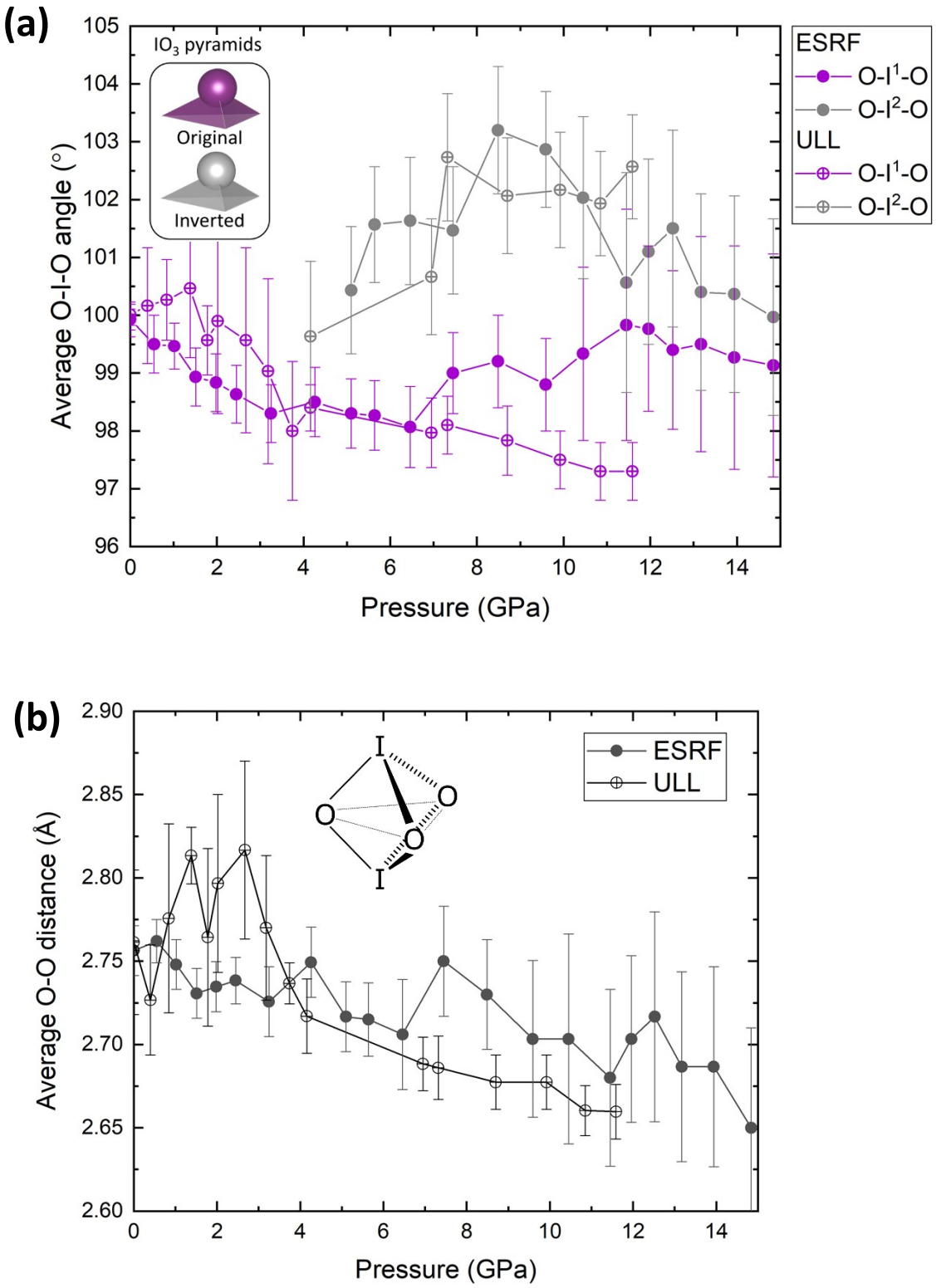

Figure S6 | (a) The average O-I-O angle as a function of pressure. **(b)** The average O-O distance (i.e., triangular base edge length) as a function of pressure.

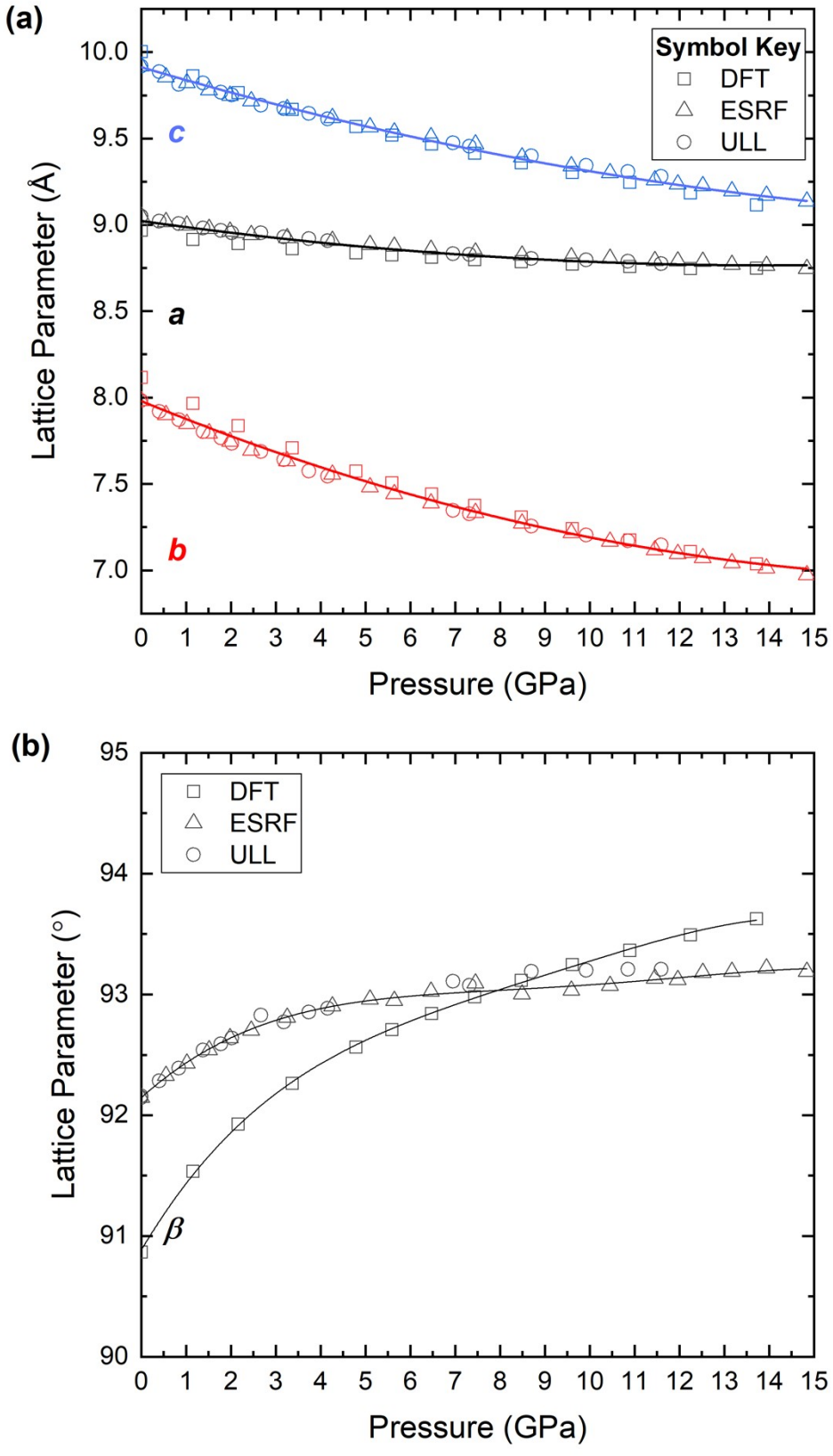

Figure S7 | The pressure-evolution of the lattice parameters of the monoclinic (*C*2/*c*) unit cell of $Ba(IO_3)_2 \cdot H_2O$ according to DFT (squares) and SCXRD (triangles and circles).

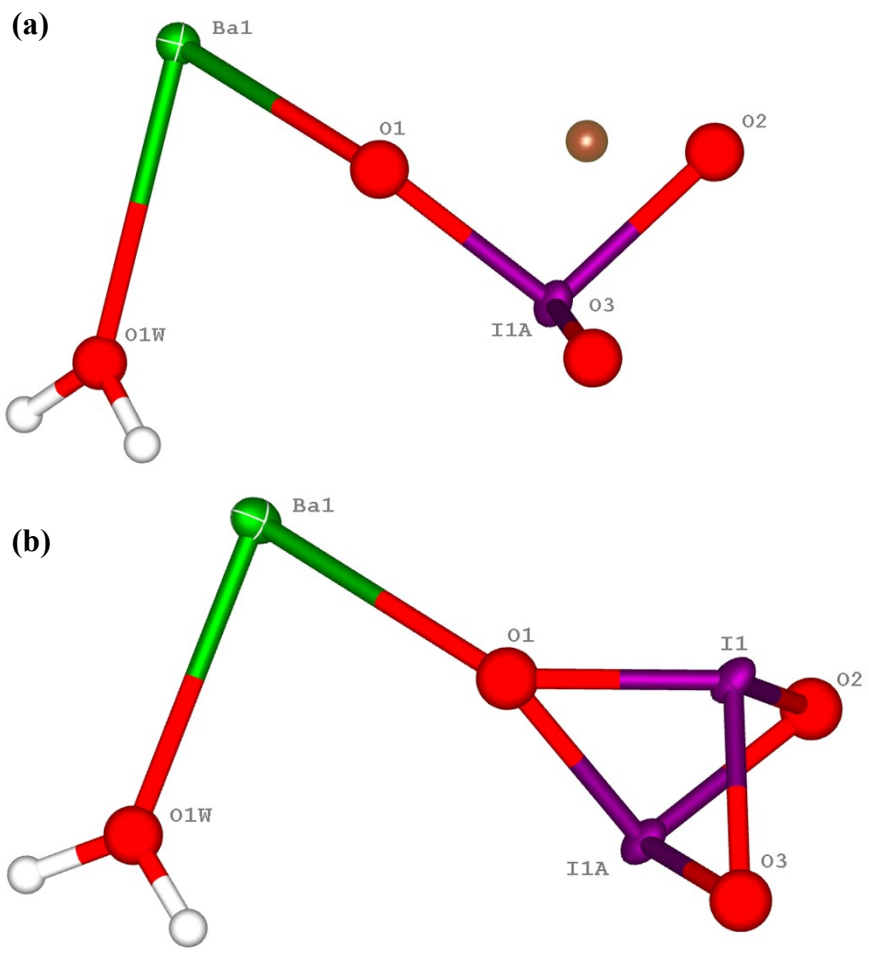

Figure S8. The $Ba(IO_3)_2 \cdot H_2O$ structure at 4.26(5) GPa. **(a)** The residual charge density peak is shown in brown. **(b)** The I2 atom is placed at the location of the residual peak.

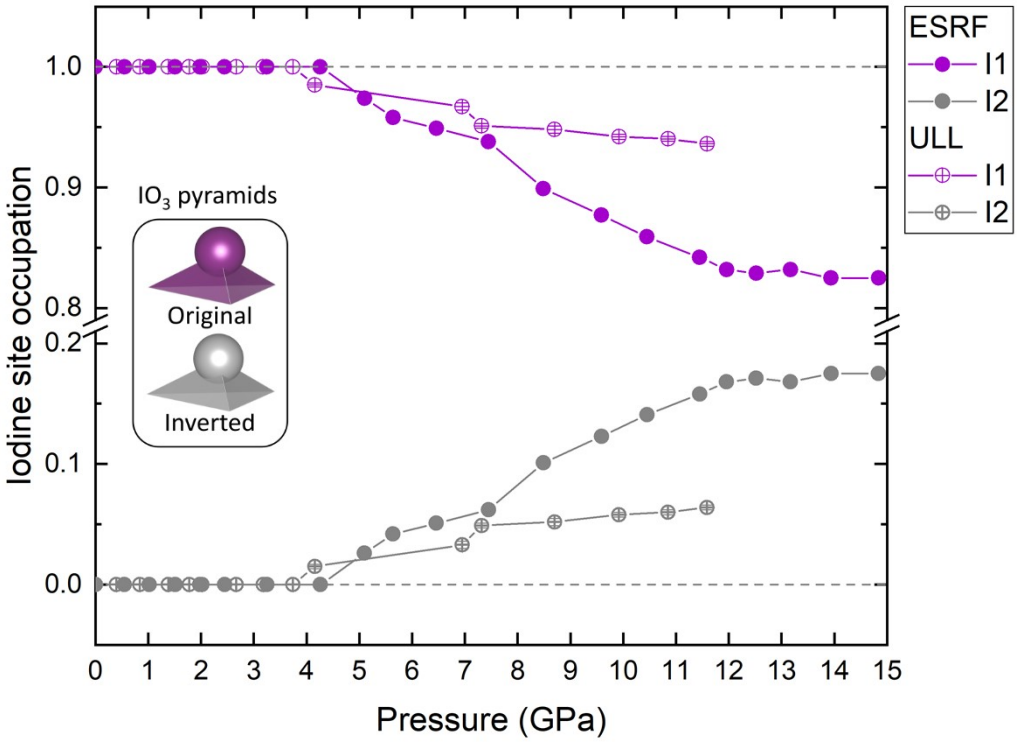

Figure S9 | The iodine site occupation as a function of pressure. Error bars are included but the errors are smaller than the symbols.

Text to create CIF file of the crystal structure of $Ba(IO_3)_2.H_2O$ at 0 GPa:

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  _atom_site_type_symbol
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  O1       1.0    0.4873(4)   0.5502(5)    0.3553(4)   Uani  0.022513 O
  O2       1.0    0.4921(4)   0.6568(5)    0.0896(4)   Uani  0.023840 O
  O3       1.0    0.6835(4)   0.4099(5)    0.1866(4)   Uani  0.020630 O
  O4       1.0    0.250000    0.3032(9)    0.500000    Uani  0.053100 O
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Text to create CIF file of the crystal structure of $Ba(IO_3)_2.H_2O$ at 11.59 GPa:

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   I2        0.0640  0.4080(13)   0.857(2)     0.2870(13)  Uani  0.016303 I
   O1        1.0     0.3028(10)   1.0780(15)   0.3114(11)  Uiso  0.019000 O
   O2        1.0     0.5046(10)   0.9372(15)   0.1408(11)  Uiso  0.020000 O
   O3        1.0     0.5192(11)   0.8476(17)   0.4205(13)  Uiso  0.029000 O
   O4        1.0     0.250000     0.758(3)     0.000000    Uiso  0.056000 O
   H1        0.5000  0.244590     0.684685     0.073469    Uiso  0.083000 H
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   I1         0.01390  0.02490  0.01000  0.00910 -0.00030 -0.00090
   I2         0.01390  0.02490  0.01000  0.00910 -0.00030 -0.00090
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Text to create CIF file of the crystal structure of $Ba(IO_3)_2.H_2O$ at 14.84 GPa:

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  I1       0.8250  0.5085(2)   0.4509(4)   0.8114(4)   Uani  0.030829 I
  I2       0.1750  0.4098(11)  0.6488(15)  0.7929(18)  Uani  0.030829 I
  O1       1.0    0.503(2)    0.568(2)    0.651(4)    Uiso  0.034000 O
  O2       1.0    0.528(4)    0.629(4)    0.943(9)    Uiso  0.102000 O
  O3       1.0    0.301(2)    0.421(2)    0.810(4)    Uiso  0.036000 O
  O4       1.0    0.750000    0.250(5)    0.500000    Uiso  0.049000 O
  H1       0.5000  0.838612    0.157349    0.469363    Uiso  0.074000 H
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  _atom_site_aniso_U_13
  _atom_site_aniso_U_23
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  I1       0.02610  0.05320  0.01300 -0.01490 -0.00060  0.00090
  I2       0.02610  0.05320  0.01300 -0.01490 -0.00060  0.00090
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