Supplementary information

High-pressure stabilization of open-shell bromine fluorides

Madhavi H. Dalsaniya,[a,b] Deepak Upadhyay,[b] Krzysztof Jan Kurzydłowski[a] and Dominik Kurzydłowski*[b]*

[a] *Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska 141, 02-507, Warsaw, Poland*

madhavi.dalsaniya.dokt@pw.edu.pl, krzysztof.kurzydlowski@pw.edu.pl

[b] *Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw, 01-038 Warsaw, Poland*

d.upadhyay@uksw.edu.pl, d.kurzydlowski@uksw.edu.pl

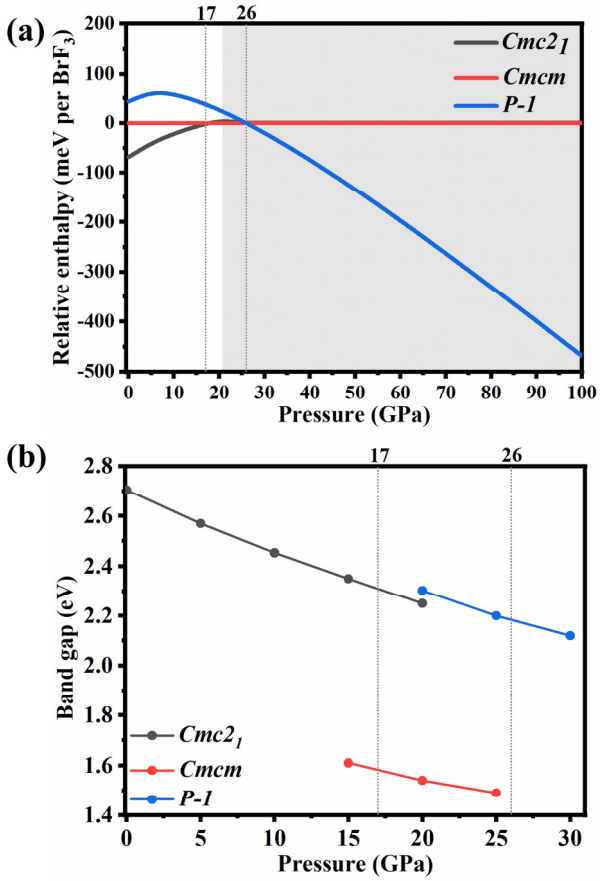

Fig. S1 (a) Pressure dependence of the relative enthalpies of BrF_3 phases (relative to the *Cmcm* structure); grey area denotes the pressure region in which BrF_3 becomes unstable with respect to decomposition into BrF_2 and BrF_5; and (b) Calculated electronic band gap as a function of pressure for *Cmc2$_1$*, *Cmcm*, and $P\bar{1}$ phases (r^{2}SCAN calculations).

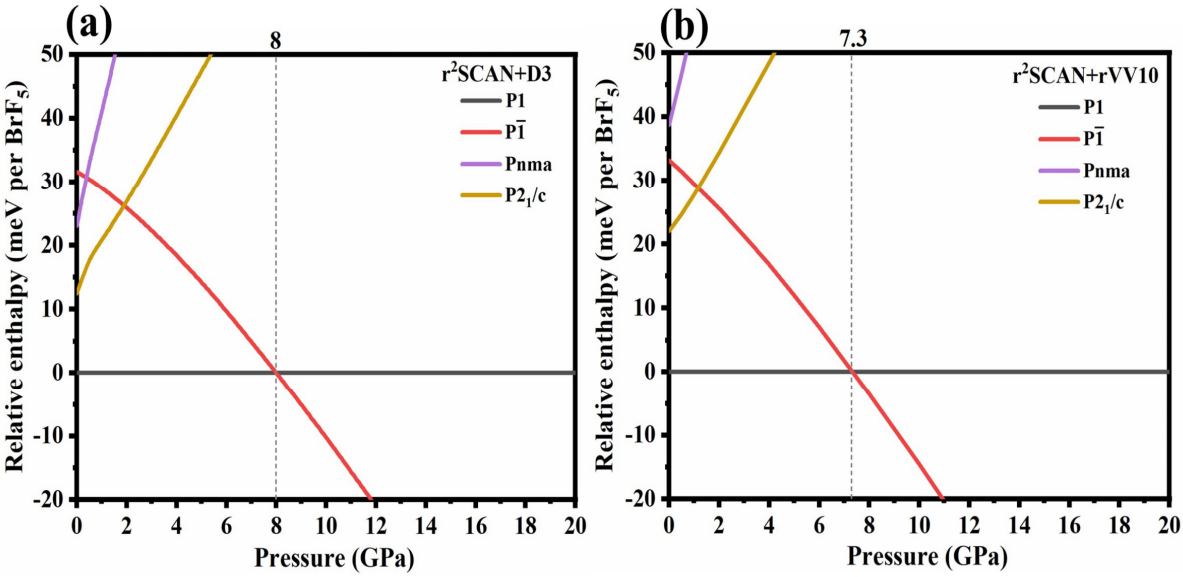

Fig. S2 Pressure-dependent relative enthalpies of BrF_5 phases relative to the P1 structure calculated using (a) r^{2}SCAN +D3 and (b) r^{2}SCAN+rVV10

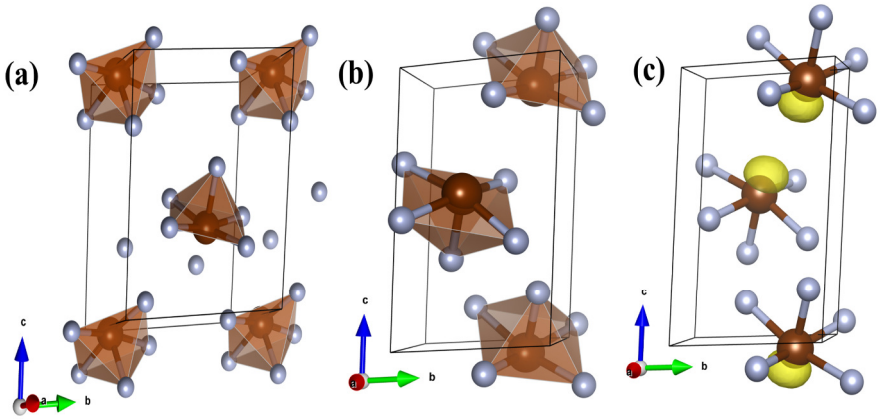

Fig. S3 Crystal structures of BrF_5: (a) $P1$ at 0 GPa; (b) $P\bar{1}$ at 100 GPa; and the (c) Isosurface of the ELF function (at a value of 0.9) for $P\bar{1}$ at 100 GPa.

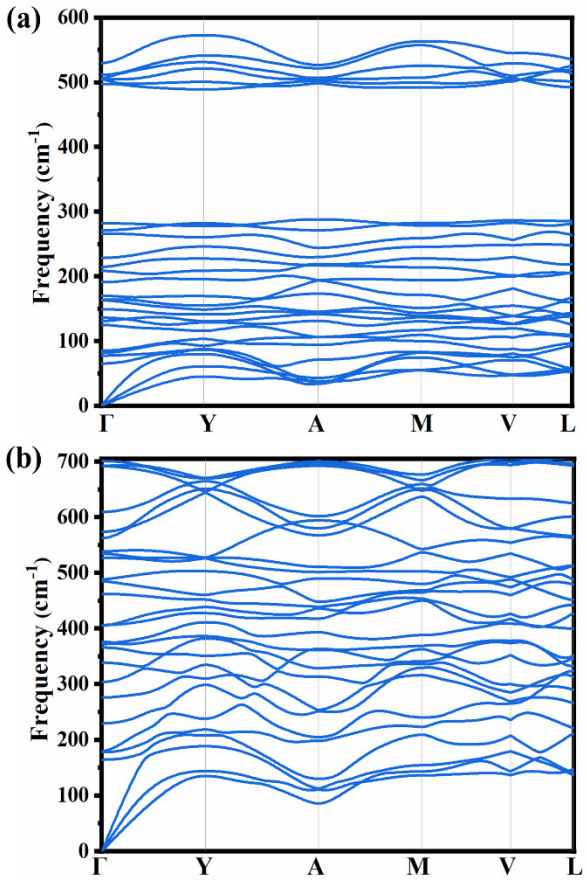

Fig. S4 Phonon dispersion curves of BrF_2; (a) *C2/m* at 0 GPa and (b) *C2/m* at 100 GPa.

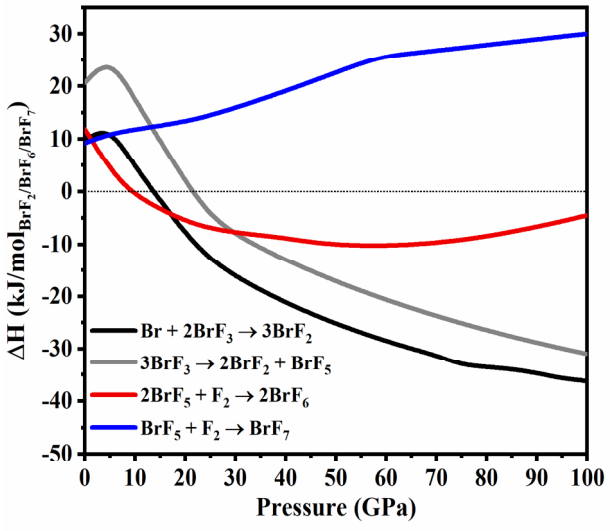

Fig. S5 Enthalpy of reactions leading to the formation of BrF_2, BrF_6, and BrF_7, as a function of pressure.

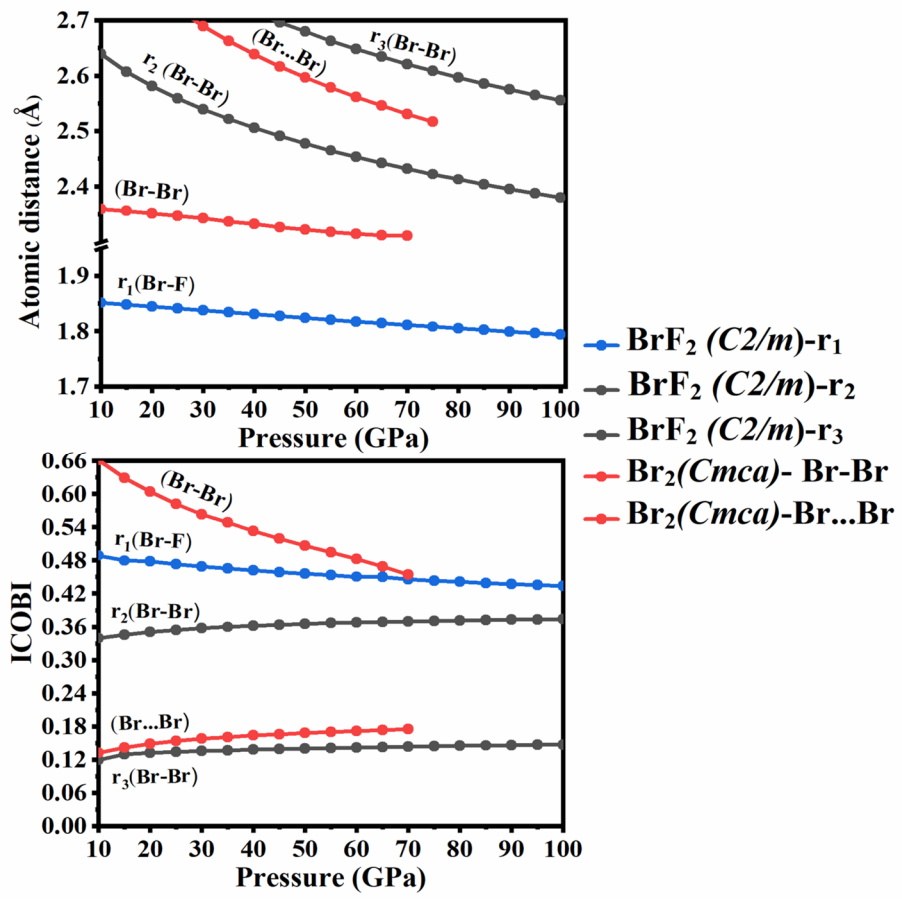

Fig. S6 (a) Calculated interatomic distances as a function of pressure for *C2/m* phase of BrF_2 with comparison of *Cmca* phase of Br_2; and (b) Pressure dependence of the integrated crystal orbital bond index (ICOBI) for Br-F distances.

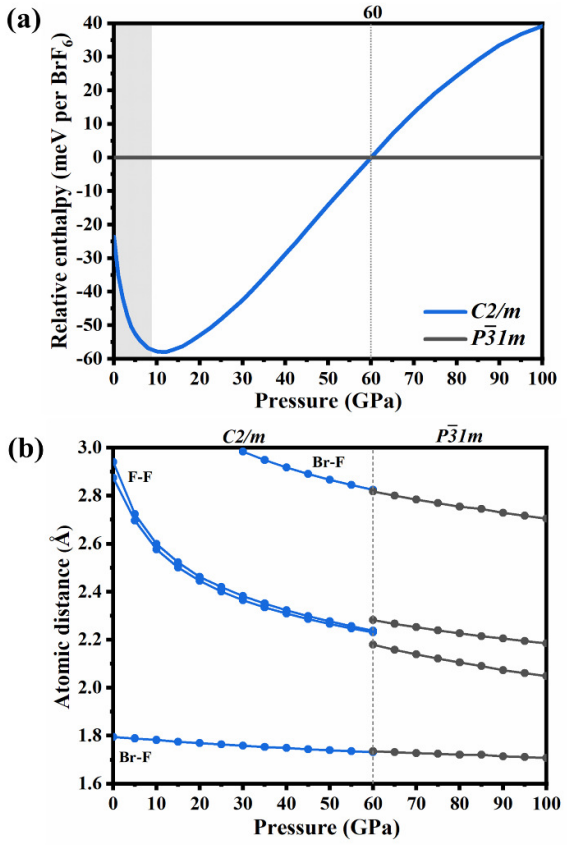

Fig. S7 (a) Pressure-dependent relative enthalpy of the *C2/m* structure of BrF_6 phases relative to the $P\bar{3}1m$ polymorph, grey area denotes the pressure region in which BrF_6 is thermodynamically unstable; (b) Calculated interatomic distances as a function of pressure for both phases in their region of stability.

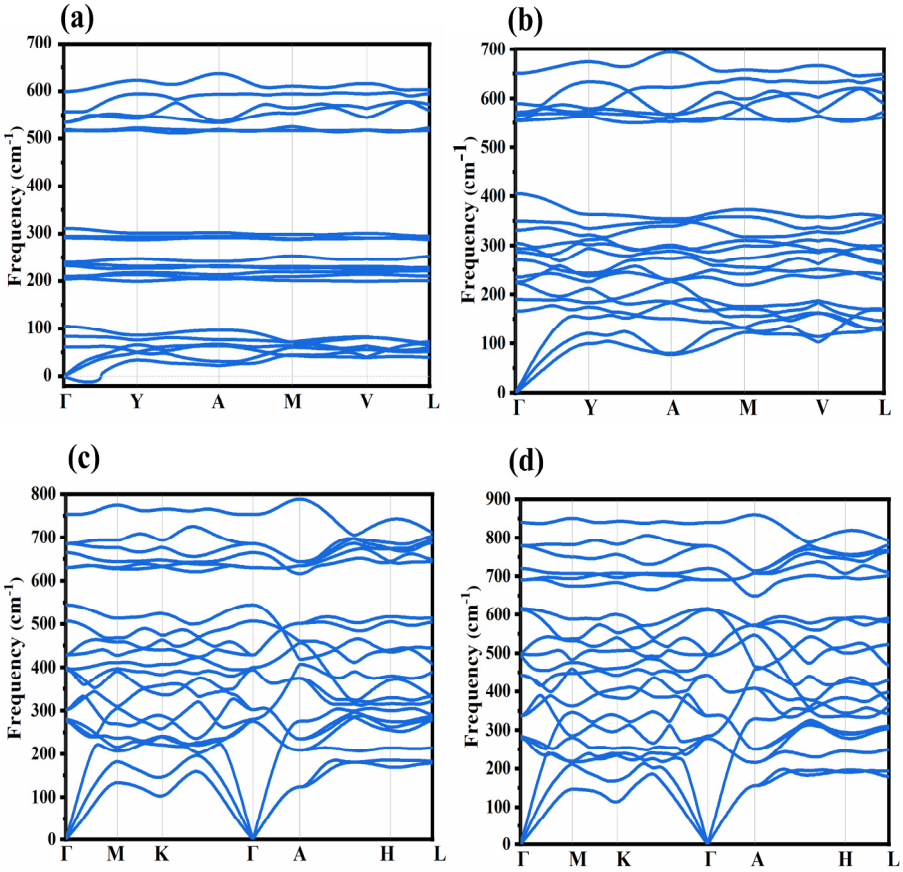

Fig. S8 Phonon dispersion curves calculated for BrF_6 in the *C2/m* at (a) 0 GPa and (b) 15 GPa, and in the $P\bar{3}1m$ structure at (c) 60 GPa and (d) 100 GPa. Small imaginary frequencies around Γ-point in panel (a) are an artefact of the computational method.

Table S1. Comparison of Br-F distances (R_{Br-F}) in Å and heats of formation (ΔH_f at 0K) in kJ/mol calculated for isolated BrF, BrF_3, and BrF_5 molecules.

Molecule	R_{Br-F}			ΔH_f		
	r²SCAN [this work]	CCSD(T) [1]	Exp. [2–5]	r²SCAN [this work]	CCSD(T) [1]	Exp. [2–5]
BrF	1.771	1.771	1.759	–72	–56	–59 ± 2
BrF_3	1.749 1.830	1.730 1.817	1.721 1.810	–319	–253	–256 ± 3
BrF_5	1.730 1.793	1.707 1.771	1.700 1.768	–563	–445	–429 ± 2

Table S2. Löwdin charges on bromine atoms for the most stable phases of bromine fluorides at 20 GPa.

BrF stoichiometry	Symmetry	q(Br)	q_{av}(Br)
BrF (=Br·BrF_2)	$Cmc2_1$	0.11 *e*, 1.00 *e*	0.55 *e*
BrF_2	$C2/m$	1.05 *e*, 1.04 *e*	1.04 *e*
BrF_3	$Cmcm$	1.46 *e*	1.46 *e*
BrF_4 (=BrF_3·BrF_5)	$P1$	1.45 *e*, 2.31 *e*	1.88 *e*
BrF_5	$P\bar{1}$	2.32 *e*	2.32 *e*
BrF_6	$C2/m$	2.56 *e*	2.56 *e*
BrF_7 (=BrF_6·½F_2)	$P\bar{1}$	2.56 *e*	2.56 *e*

Table S3. Structural details of bromine fluorides.

Phase	Pressure (GPa)	Lattice parameters (Å)	Atomic coordinate
BrF_2 (*C2/m*)	15	*a* = 5.205 *b* = 6.149 *c* = 6.719 $\alpha = \gamma = 90.000°$ $\beta = 99.260°$	Br 0.29642 0.00000 0.83010 Br 0.00000 0.50000 0.50000 F 0.82142 0.20021 0.83096 F 0.00000 0.19966 0.50000
BrF_2 (*C2/m*)	100	*a* = 4.472 *b* = 5.786 *c* = 5.937 $\alpha = \gamma = 90.000°$ $\beta = 100.494°$	Br 0.27447 0.00000 0.83335 Br 0.00000 0.50000 0.50000 F 0.81180 0.19129 0.83199 F 0.00000 0.18988 0.50000
BrF_3 ($Cmc2_1$)	0	*a* = 5.241 *b* = 7.449 *c* = 6.255 $\alpha = \beta = \gamma = 90.000°$	Br 0.00000 0.65976 0.56492 F 0.00000 0.76091 0.82131 F 0.00000 0.88046 0.44844 F 0.00000 0.42375 0.72732
BrF_3 (*Cmcm*)	20	*a* = 4.741 *b* = 6.108 *c* = 5.966 $\alpha = \beta = \gamma = 90.000°$	Br 0.00000 0.85135 0.2500 F 0.00000 0.1917 0.44079 F 0.00000 0.56681 0.2500
BrF_3 ($P\bar{1}$)	25	*a* = 3.957 *b* = 4.029 *c* = 5.5003 $\alpha =$ 86.6279° $\beta =$ 77.5542° $\gamma =$ 73.3234°	Br 0.6356 0.24515 0.79084 F 0.42544 0.66719 0.68602 F -0.05848 0.76736 0.39509 F 0.16409 0.21221 0.05419
BrF_5 (*P1*)	0	*a* = 4.753 *b* = 5.318 *c* = 7.149 $\alpha =$ 87.102° $\beta =$ 71.5168° $\gamma =$ 80.2046°	Br 0.53129 0.02779 -0.02889 Br 0.85342 0.52966 0.34709 F 0.62445 0.83775 0.39913 F -0.08581 0.56576 0.56886 F 0.36048 0.87922 0.82751 F 0.3477 0.33336 -0.08142 F 0.18464 0.68368 0.24432 F 0.09903 0.22412 0.33682 F 0.8047 0.06477 0.75038

			F 0.77104 0.72486 -0.01785 F 0.5414 0.3863 0.48913 F 0.7594 0.1865 0.07532
BrF_5 **($P\bar{1}$)**	8	a = 4.420 b = 4.816 c = 6.931 α = 80.278° β = 82.882° γ = 64.815°	Br 0.18878 0.7007 0.70888 F 0.21596 0.05705 0.59117 F 0.19469 0.36484 0.86083 F 0.64263 0.50507 0.65821 F 0.22326 0.07425 0.2054 F 0.69988 0.2182 0.08589
BrF_5 **($P\bar{1}$)**	100	a = 3.711 b = 3.951 c = 6.133 α = 84.4994° β = 88.2614° γ = 70.8106°	Br 0.15909 0.66974 0.70505 F 0.23646 0.07104 0.58052 F 0.1520 0.31629 0.88297 F 0.6654 0.47970 0.6509 F 0.24635 0.04187 0.20654 F 0.66549 0.23881 0.07144
BrF_6 **($C2/m$)**	15	a = 4.413 b = 7.580 c = 4.379 $\alpha = \gamma$ = 90.000° β = 109.928°	Br 0.00000 0.50000 0.50000 F 0.75539 0.33520 0.24476 F 0.25015 0.00000 0.74296
BrF_6 **($C2/m$)**	60	a = 4.049 b = 7.019 c = 4.053 $\alpha = \gamma$ = 90.000° β = 109.232°	Br 0.00000 0.50000 0.50000 F 0.74028 0.32556 0.23798 F 0.23680 0.00000 0.76224
BrF_6 **($P\bar{3}1m$)**	60	$a = b$ = 4.0469 c = 3.819 $\alpha = \beta$ = 90.000° γ = 120.000°	Br 0.00000 0.00000 0.00000 F 0.34946 0.00000 0.73659
BrF_6 **($P\bar{3}1m$)**	100	$a = b$ = 3.910 c = 3.688 $\alpha = \beta$ = 90.000° γ = 120.000°	Br 0.00000 0.00000 0.00000 F 0.35610 0.00000 0.73206

References

1 K. S. Thanthiriwatte, M. Vasiliu, D. a Dixon and K. O. Christe, *Inorg. Chem.*, 2012, **51**, 10966–10982.

2 R. E. Willis and W. W. Clark, *J. Chem. Phys.*, 1980, **72**, 4946–4950.

3 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Springer US, Boston, MA, 1979, vol. 1999.

4 D. W. Magnuson, *J. Chem. Phys.*, 1957, **27**, 223–226.

5 R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, 1957, **27**, 982–983.