Supplementary information

Pressure-Induced Unexpected -2 Oxidation States of Bromine and Superconductivity in Magnesium Bromide

Chao Wang,[a] Yunxian Liu,*[a] Xin Chen,[a] Pin Lv,[a] Hairui Sun[a] and Xiaobing Liu*[a]

[a] *Laboratory of High Pressure Physics and Material Science, School of Physics and Physical Engineering, Qufu Normal University, Qufu, 273165, P. R. China*

***E-mail:** yunxianliu1988@163.com (Y. Liu), xiaobing.phy@qfnu.edu.cn (X. Liu)

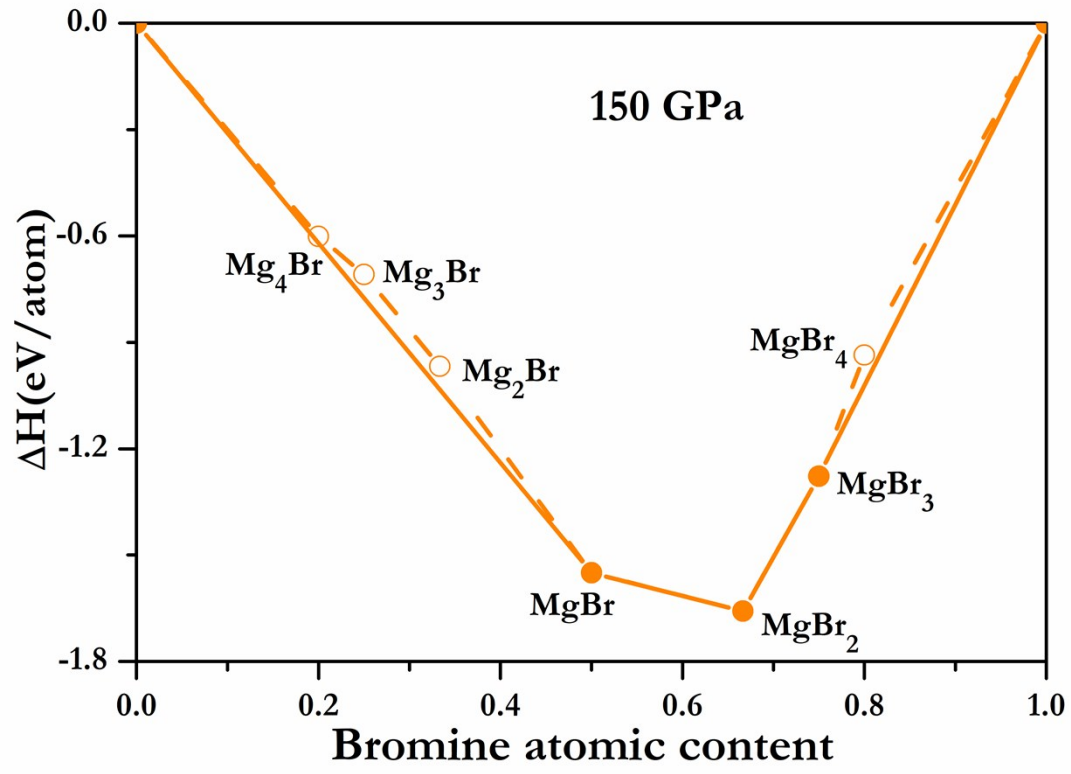

Figure S1. Calculated formation enthalpies of various Mg−Br compounds with respect to Mg and Br at 150 GPa.

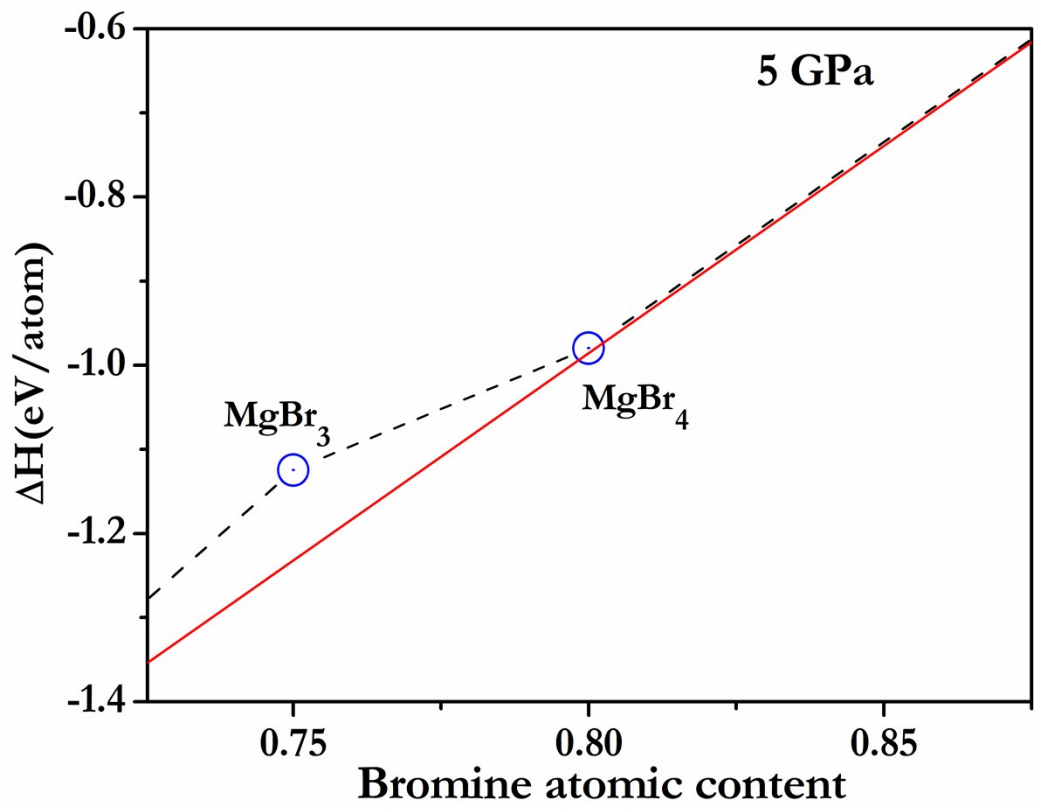

Figure S2. (a) Magnification of convex hull at 5GPa.

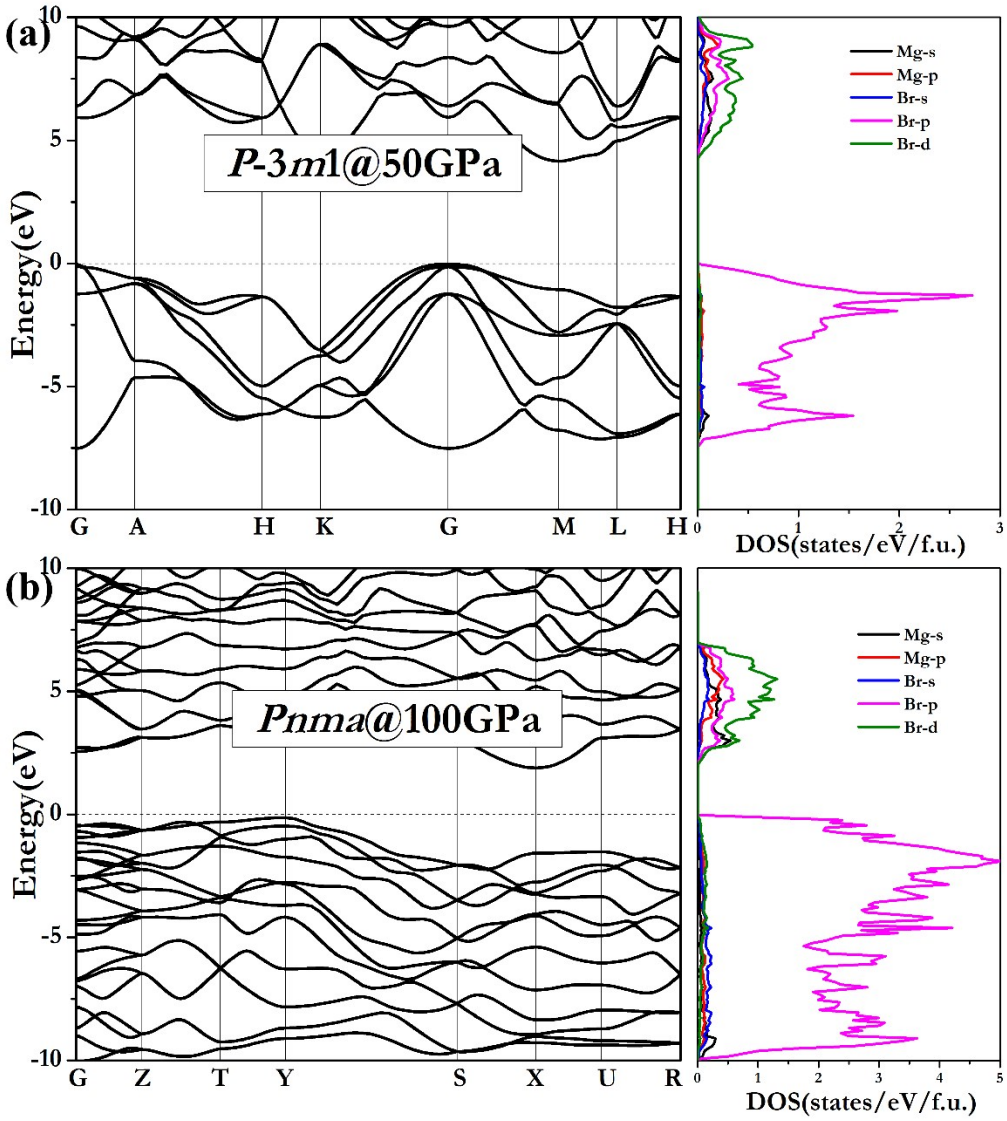

Figure S3. The electronic band structure and corresponding projected density of states (PDOS) for (a) *P*-3*m*1 $MgBr_2$ at 50 GPa and (b) *Pnma* $MgBr_2$ at 100 GPa.

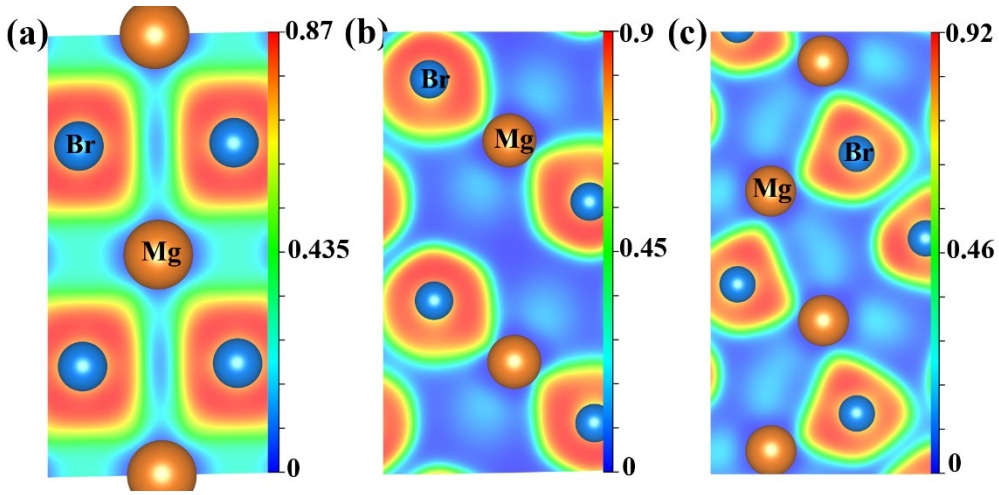

Figure S4. The calculated electron localization function (ELF). (a) *Pm*-3*m* MgBr, (b) *P*-3*m*1 $MgBr_2$, and (c) *Pnma* $MgBr_2$.

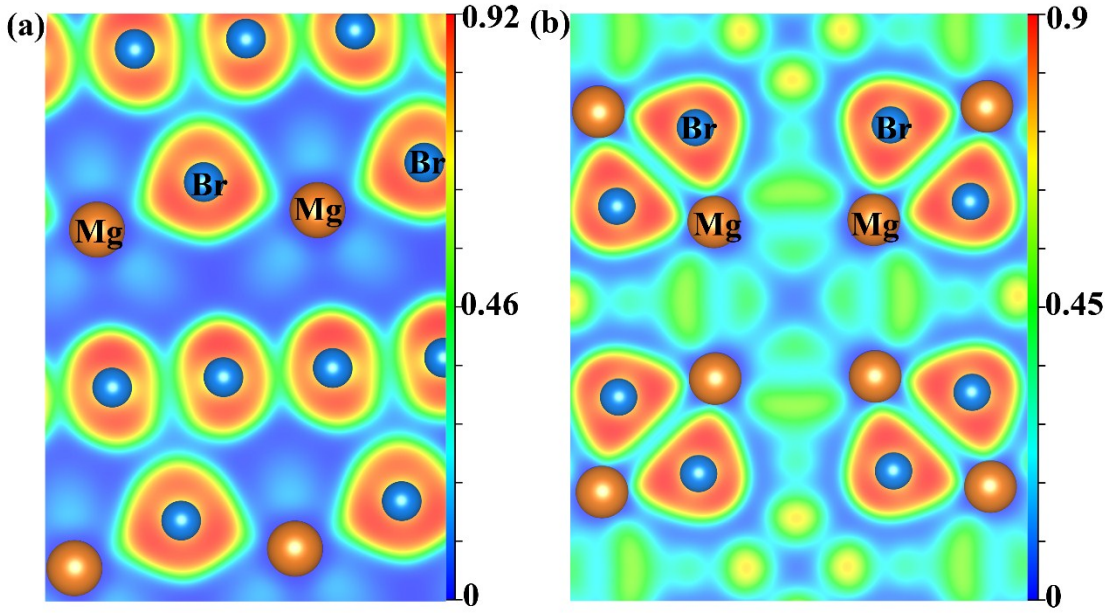

Figure S5. The calculated electron localization function (ELF). (a) $P2_1/m$ $MgBr_3$, and (b) I-$42m$ $MgBr_3$.

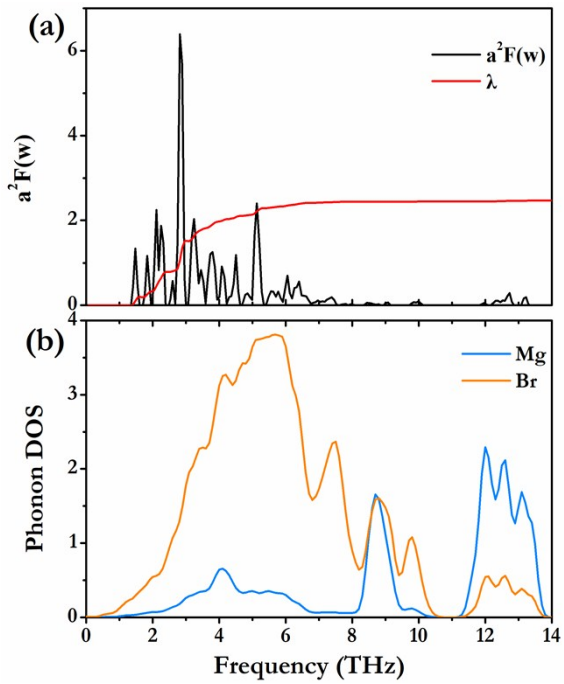

Figure S6. The Eliashberg phonon spectral function $\alpha^2F(\omega)$ and the partial electron–phonon integration $\lambda(\omega)$ for $P2_1/m$ $MgBr_3$.

Table S1 Structural parameters of Mg-Br system at selected pressure.

Space group pressure	Lattice parameters (Å, °)	Atomic coordinates (fractional)	Sites
Mg_4Br (*I*4/*mmm*)	a=b=2.7399 c=12.2715	Mg1 1.50000 1.50000 0.10146	4e
200GPa	α=β=γ=90	Mg3 0.50000 0.50000 -0.29774	4e
		Br1 1.00000 2.00000 0.00000	2a
MgBr (*Pm*-3*m*)	a=b= c=2.8596	Mg1 0.00000 -1.00000 -2.00000	1a
100GPa	α=β=γ=90	Br1 0.50000 -1.50000 -1.50000	1b
$MgBr_2$ (*P*-3*m*1)	a=b=3.2294	Mg1 0.00000 0.00000 0.50000	1b
50GPa	c=5.2451	Br1 -0.33333 0.33333 1.21638	2d
	α=β= 90 γ=120		
$MgBr_2$ (*Pnma*)	a=6.4963	Mg1 0.69416 0.75000 -0.16620	4c
100GPa	b=2.9981	Br1 0.16414 0.25000 -0.56029	4c
	c=7.8923	Br5 0.00873 0.75000 -0.83983	4c
	α=β=γ=90		
$MgBr_3$ ($P2_1/m$)	a=7.7779	Mg1 0.67188 1.25000 -0.70795	2e
50GPa	b=3.2222	Br1 0.85497 0.75000 -0.40949	2e
	c=5.0965	Br3 0.85649 0.75000 0.08601	2e
	α=γ= 90	Br9 0.44152 1.75000 0.23528	2e
	β=99.509		
$MgBr_3$ (*I*-42*m*)	a=b=9.4055	Mg1 -0.00000 0.70822 0.00000	8f
100GPa	c=4.6925	Br1 -0.40870 0.40870 0.23434	8i
	α=β=γ=90	Br5 -0.29527 0.29527 -0.26885	8i
		Br6 0.14448 0.50000 -0.00000	8g