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Structural and Electronic Properties of Alkali Metal Peroxides at High Pressures

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Computational details

Our structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations through CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in its same-name CALYPSO code.[1,2] The high structures of studied compounds were searched with simulation cell sizes of 1−4 formula units (f.u.) at 0, 20, 40, 60, 80, and 100GPa, respectively. In the first step, random structures with certain symmetry are constructed in which the atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using VASP code,[3] were done with the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1×10^{-5} eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for the efficiency of the global search of structures. For most of the cases, the structure searching simulation for each calculation was stopped after we generated 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

To further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform structural optimization using density functional theory within the generalized gradient approximation[4] as implemented in the VASP code. The cut-off energy for the expansion of wavefunctions into plane waves is set to 600 eV in all calculations, and the Monkhorst–Pack *k*-mesh with a maximum spacing of $2\pi \times 0.015$ Å^{-1} was individually adjusted in reciprocal space with respect to the size of each computational cell. This gives total energy well converged within ~ 1 meV/atom. The force converge was set to 0.01 eV/ Å. The electron-ion interaction was described by projected-augmented-wave potentials with $2s^1p^0$, $3s^1p^0$, $4s^1p^0$, $5s^1p^0$ and $2s^22p^4$and as valence electrons for Li, Na, K, Rb and O, respectively. To ensure that the obtained structures are dynamically stable, we calculated phonon frequencies throughout the Brillouin zone using the finite-dis-placement approach as implemented in the Phonopy code.[5] Computational details about the phonon were given in the following. The supercell sizes for Li_2O_2, Na_2O_2, K_2O_2, and Rb_2O_2 are 6×6×2, 5×4×2, 4×4×2, and 2×3×3, respectively. The Monkhorst–Pack *k*-mesh with a maximum spacing of $2\pi \times 0.04$ Å^{-1} was individually adjusted in reciprocal space with respect to the size of each computational cell.

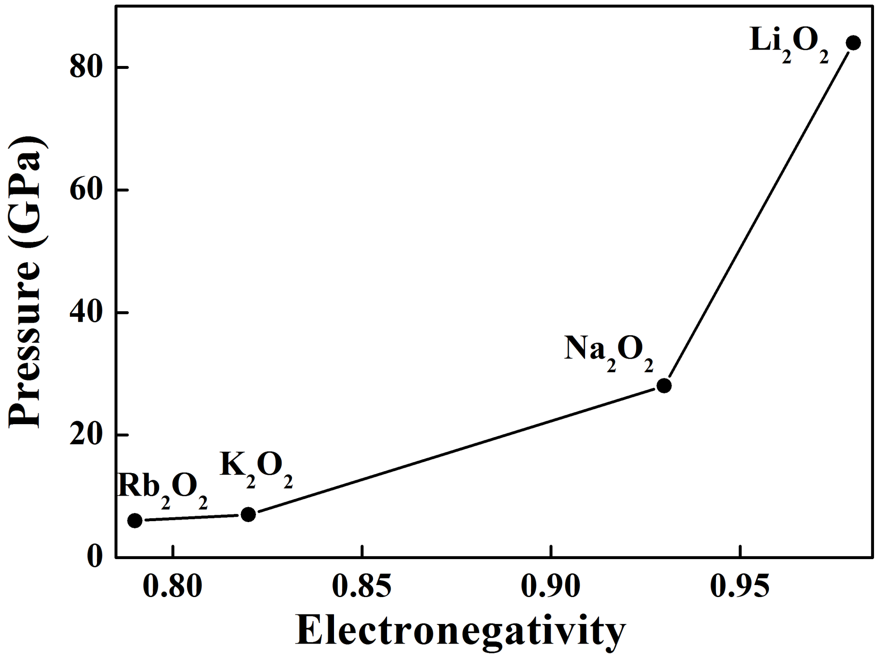


Fig. S1 The dependence of phase pressures and electronegativity for the considered alkali metal peroxides compounds.

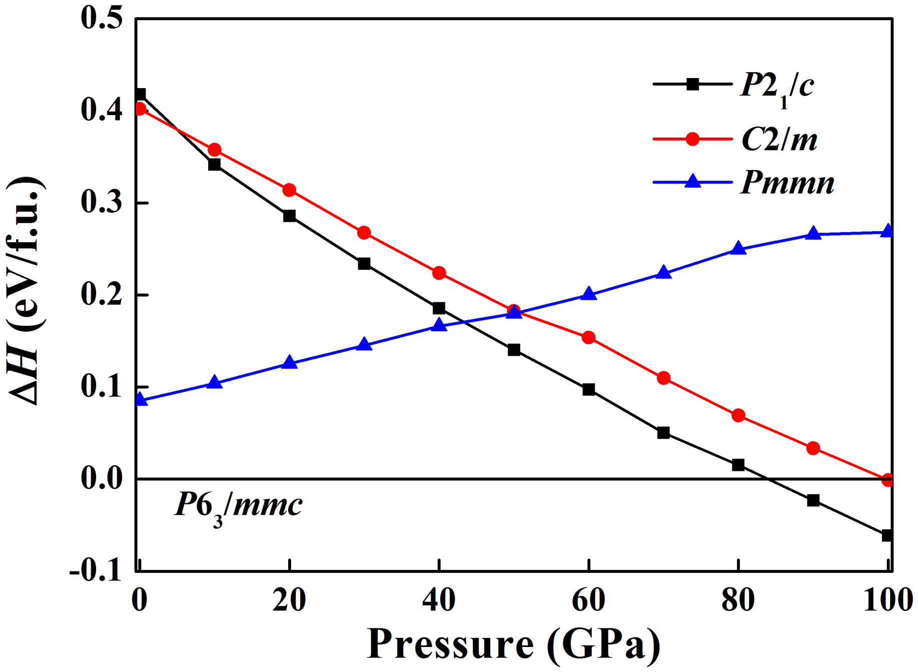


Fig. S2 Calculated enthalpies per formula unit of various structures for Li_2O_2in the pressure range of 0–100 GPa with respect to $P6_3/mmc$ structure.

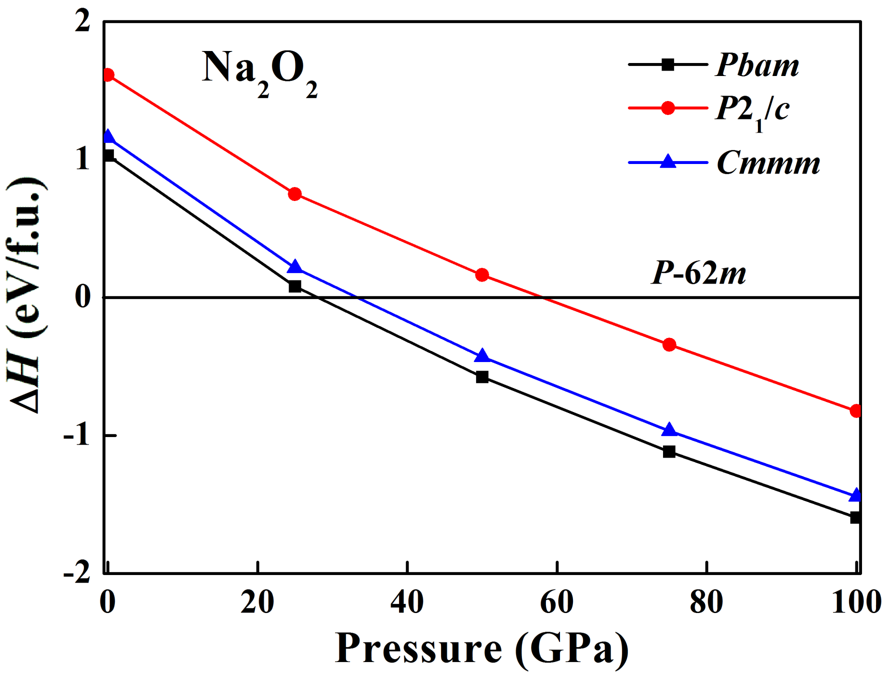


Fig. S3 Calculated enthalpies per formula unit of various structures for Na_2O_2 in the pressure range of 0–100 GPa with respect to *P*-62*M* structure.

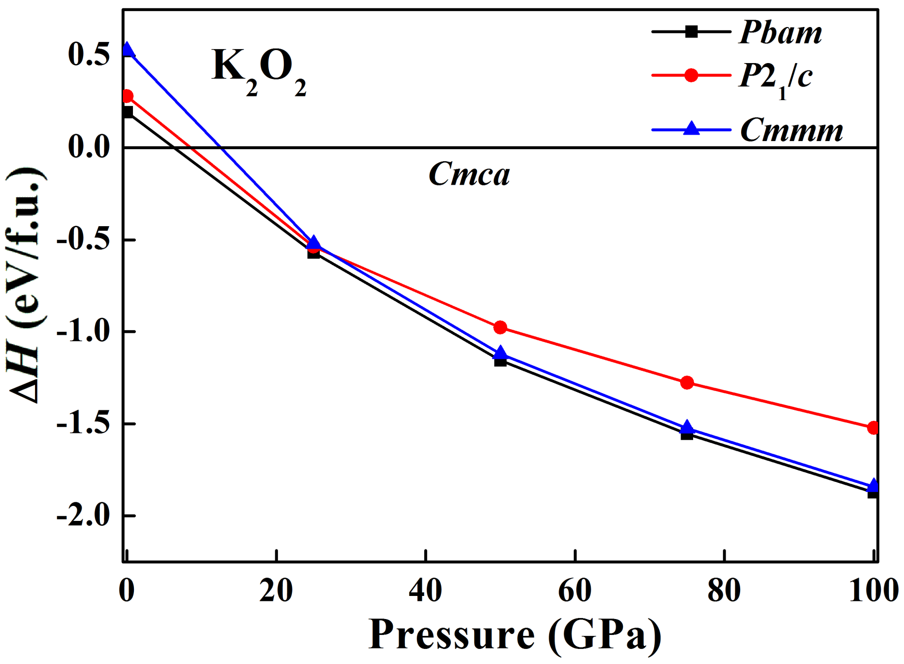


Fig. S4 Calculated enthalpies per formula unit of various structures for K_2O_2 in the pressure range of 0–100 GPa with respect to *Cmca* structure.

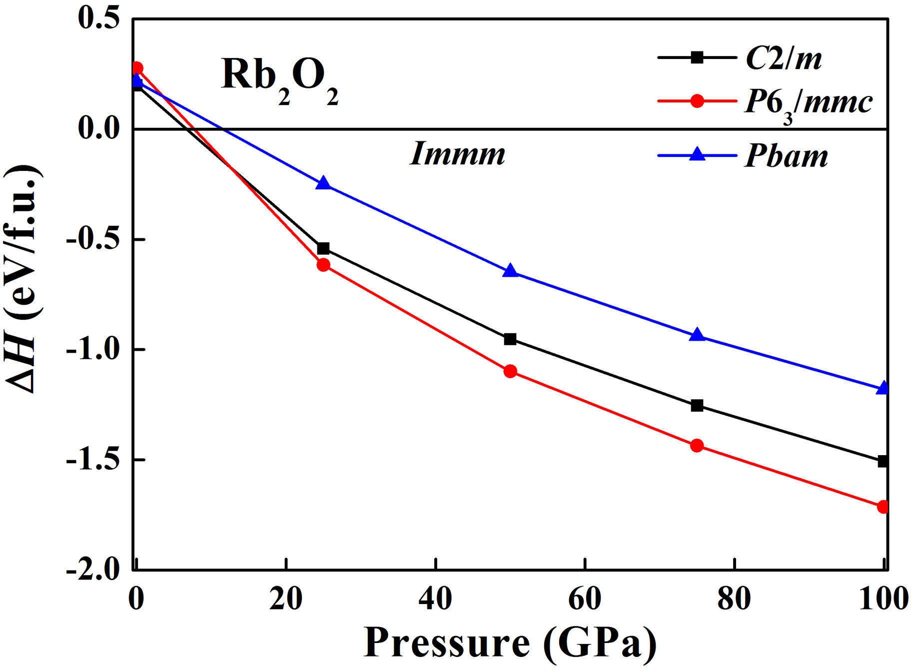


Fig. S5 Calculated enthalpies per formula unit of various structures for Rb_2O_2 in the pressure range of 0–100 GPa with respect to *Immm* structure. It is noted that Rb_2O_2 are transformed to $P6_3/mmc$ structure at 18 GPa.

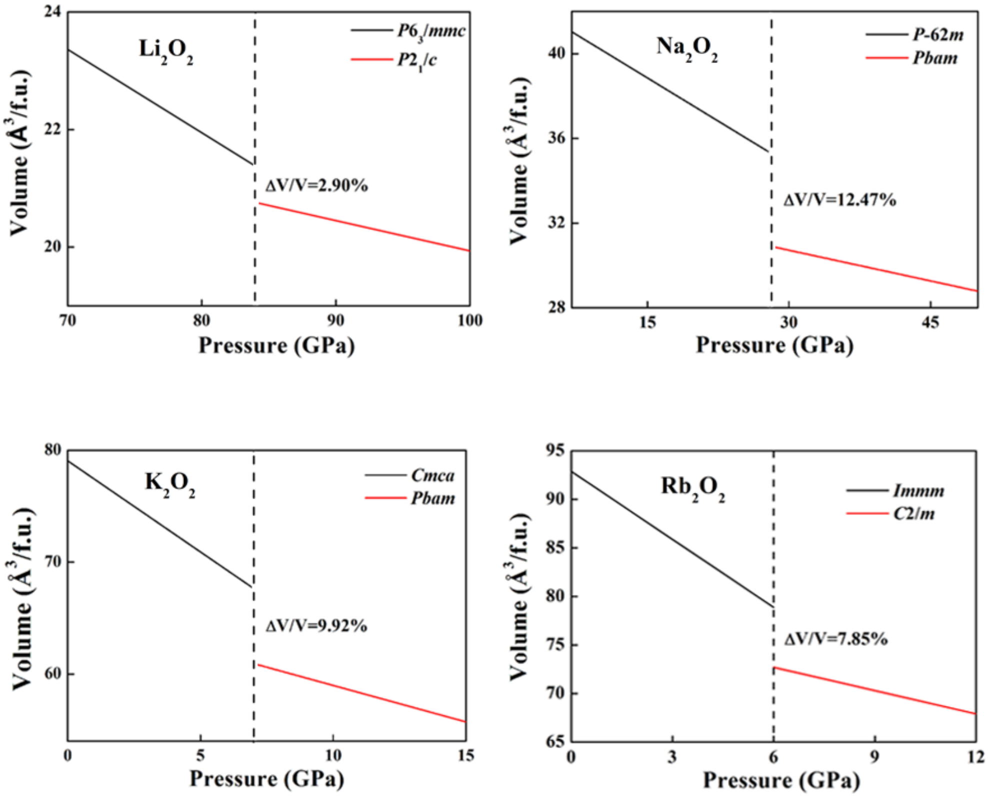
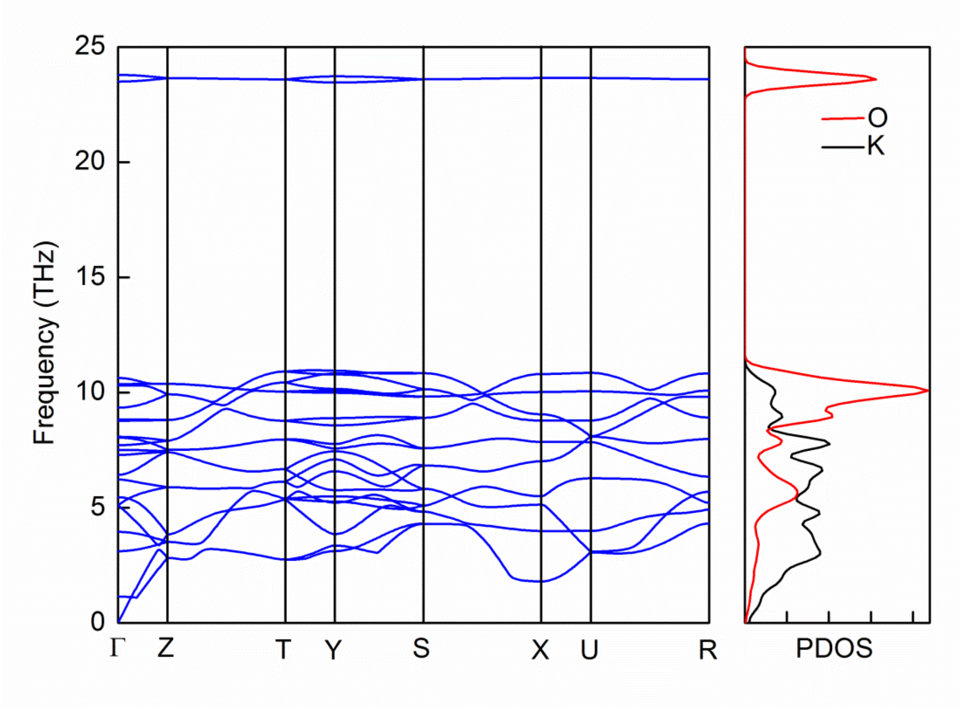


Fig. S6 Variation of the unit cell volume as a function of pressure for the ambient pressure structures and first-ordered phase transtition structures. Vertical dotted line indicates the transition pressure.



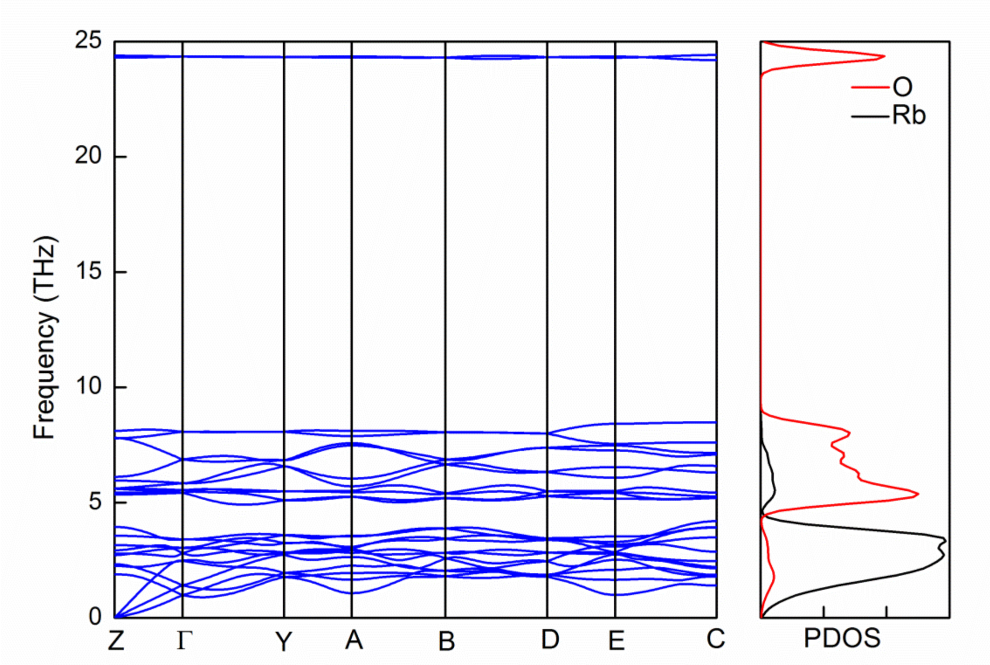


Fig. S7 Phonon dispersion curve (blue) and partial phonon density ofstates (PDOS) for K_2O_2 in the *pbam* structure and Rb_2O_2 in the *C2/m*structure, respectively.

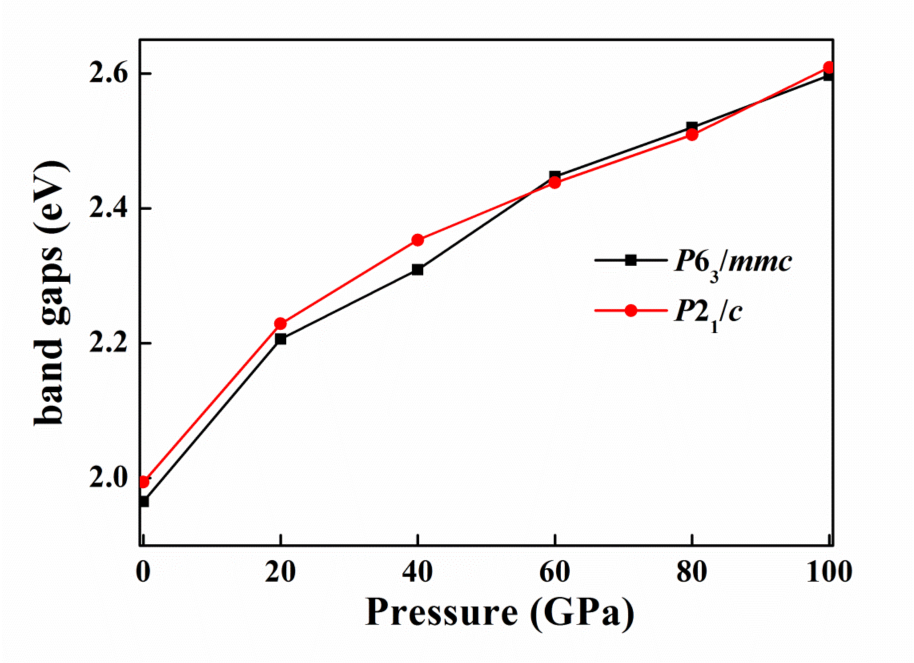


Fig. S8 Pressure dependence of band gaps for the *P*6₃*mmc* and *P*2₁/*c* structures in Li_2O_2.

Table S1. The Bader or Mulliken charge for the $P6_3mmc$ and $P2_1/c$ structures of Li_2O_2.

Li_2O_2	$P6_3mmc$		$P2_1/c$	
Atom	Bader	Mulliken	Bader	Mulliken
Li	0.90	0.99	0.85	0.90
Li	0.90	0.99	0.85	0.90
Li	0.86	0.77	0.85	0.90
Li	0.86	0.77	0.85	0.90
O	-0.90	-0.88	-0.85	-0.90
O	-0.90	-0.88	-0.85	-0.90
O	-0.86	-0.88	-0.85	-0.90
O	-0.86	-0.88	-0.85	-0.90

Table S2. Detailed structural information of the predicted first-order phase transition structures at selected pressures.

Phases	Pressure (GPa)	Lattice parameters (Å, °)	Atomic coordinates (fractional)			
Li_2O_2-$P2_1/c$	84	*a* = 6.393	Li(2a)	0.270	0.392	-0.095
		b = 2.561	O(2a)	-0.192	0.899	-0.594
		c = 6.801				
		a = *γ* = 90.000				
		β = 158.107				
Na_2O_2-*Pbam*	28	*a* = 3.424	Na(4g)	-0.852	0.358	0
		b = 6.579	O(4h)	-0.370	0.407	-0.5
		c = 2.745				
		α = *β* = *γ*= 90.000				
K_2O_2-*Pbam*	7	*a* = 4.668	K(4g)	-0.804	0.358	0
		b = 7.738	O(4h)	-0.399	0.422	-0.5
		c = 3.375				
		α = *β* = *γ*= 90.000				
Rb_2O_2-*C2/m*	6	*a* = 9.254	Rb(4i)	0.860	0	0.221
		b = 3.70	O(4i)	0.938	0.5	0.631
		c = 4.270				
		α = *γ* =90.000				
		β = 83.927				

Reference:

(1) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. Crystal Structure Prediction via Particle-Swarm Optimization. *Phys. Rev. B* **2010**, *82*, 094116.

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