Electronic Supplementary Material (ESI) for RSC Advances.

Structural transitions and electronic properties of sodium superoxide at high pressures

Naihang Deng[a], *Guochun Yang*[a,b,*], *Wenyong Wang*[a], *and YongqingQiu*[a*]

[a] Faculty of Chemistry, Northeast Normal University, Changchun 130024

[b] Center for Advanced Optoelectronic Functional Materials Research and Key Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China

Computational details

Our structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations with CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in the CALYPSO code.[1,2] The high structures of NaO_2 were searched with simulation cell sizes of 1−4 formula units (f.u.) at 0, 5, 15, 20 and 25 GPa, 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 construct the next generation structures by PSO (Particle Swarm Optimization) 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 structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating 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 usually gives total energies well converged within ~ 1 meV/atom. The force converge was set to 0.01 eV/ Å. Electron-ion interactions were described within the projector augmented wave method with $3s^1$ and $2s^22p^4$ orbitals as valence states for Na and O atoms, 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 NaO_2 in *Pnnm*, *Immm* and *P*4/*mbm* are 2×2×3, 1×3×3, and 2×2×3, respectively. The Monkhorst–Pack k-mesh with a maximum spacing of $2\pi \times 0.03$ $Å^{-1}$ was individually adjusted in reciprocal space with respect to the size of each computational cell.

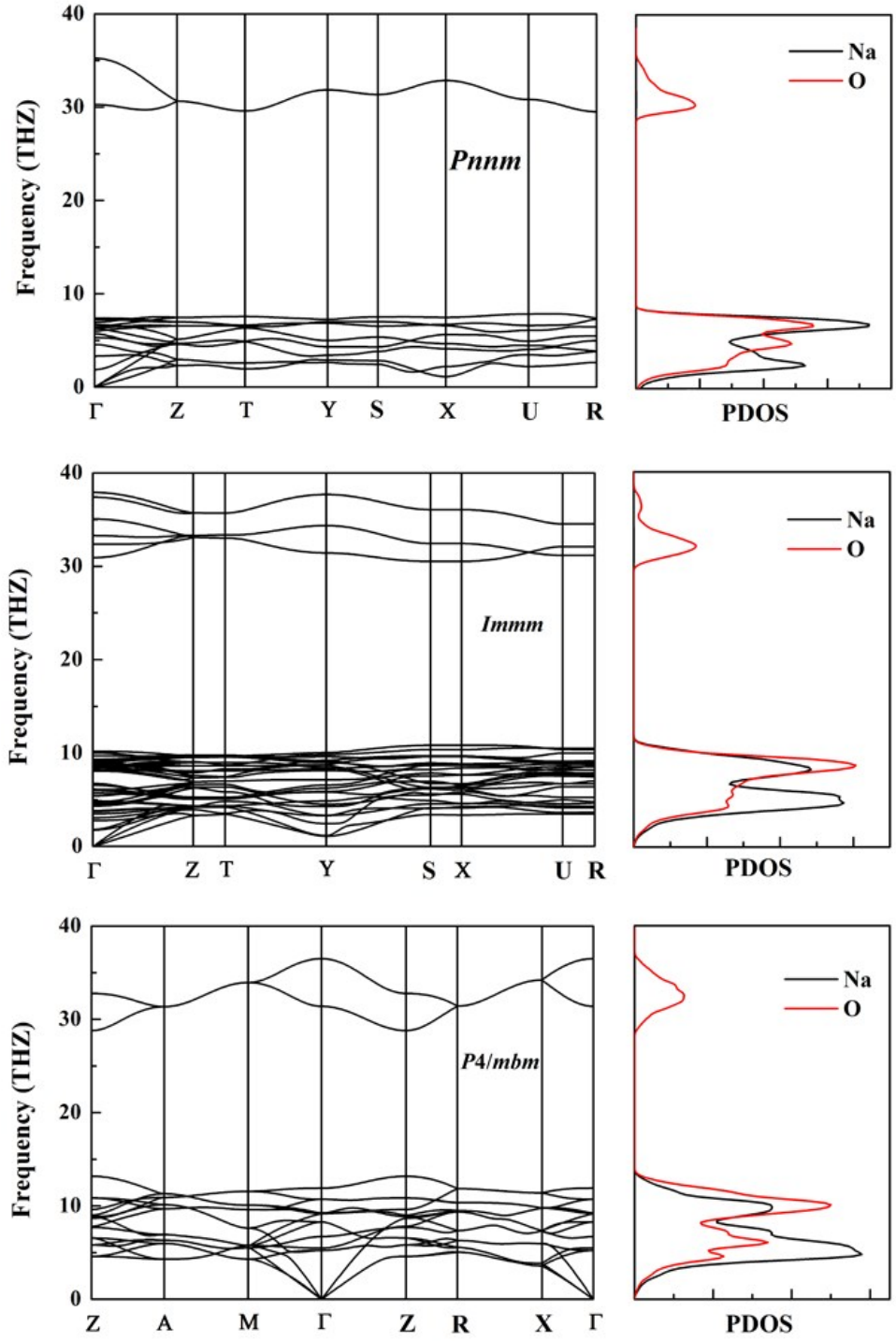

Fig. S1 Phonon dispersion curve for NaO_2 in the *Pnnm*, *Immm* and *P4/mbm* structures, respectively.

Table S1. Detailed calculated structural information of the predicted NaO_2 structures at selected pressures and the experimental data from[6] are also listed for comparison.

Phases	Pressure (GPa or ℃)	Lattice parameters (Å, °)	Atomic coordinates (fractional)			
Pnnm	0 GPa	a = 4.169 b = 5.613 c = 3.432 a =β = γ = 90.000	Na(2a) O(4g)	0 0.116	0 0.416	0 0
Immm	4.6 GPa	a = 12.702 b = 3.806 c = 3.940 α = β = γ = 90.000	Na1(4f) Na2(2a) O1(8n) O2(4h)	0.832 0 0.156 0	0 0 0.677 0.673	0.5 0 0 0.5
P4/mbm	6.7 GPa	a = b = 4.577 c = 2.802 α = β = γ= 90.000	Na(2b) O(4g)	0 0.603	0 0.103	0.5 0
Pnnm[a]	-77 ℃	a=4.260 b=5.540 c=3.440 α = β = γ= 90.000	Na(2a) O(4g)	0 0.120	0 0.430	0 0

[a] Experimental structural information of NaO_2.

Reference:

(1) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. *Phys. Rev. B* **2010**, *82*, 094116.

(2) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. *Comput. Phys. Commun.* **2012**, *183*, 2063.

(3) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

(4) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(5) Togo, A.; Oba, F.; Tanaka, I. *Phys. Rev. B* **2008**, *78*, 134106.

(6) Carter, G. F.; Templeton, D. H. *J. Am. Chem. Soc.* **1953**, *75*, 5247.