

Supplementary material for “First-principles investigation of the elastic and Li⁺ transport properties of lithium superoxides under high pressure and temperature”

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DETAILS ON COMPUTATIONAL METHODS

The elastic constants calculation

The elastic constants of the crystal are expressed as the relationship between stress σ and strain ε :

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \#(1)$$

where σ_{ij} is the stress tensor, ε_{kl} refers to the strain tensor, and C_{ijkl} is the elastic modulus which is a fourth-order tensor. Furthermore, we determined the independent elastic constants according to different crystal systems, which contributes to reducing the computation. Considering the symmetry of C_{ijkl} , the equation can be simplified as follows:

$$\sigma_i = C_{ij} \varepsilon_j \#(2)$$

The equation could be expanded as follow:

$$\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{pmatrix} \times \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} \#(3)$$

where ε_j ($j = 1, \dots, 6$) corresponds to the following equation:

$$\varepsilon = \begin{pmatrix} \varepsilon_1 & \varepsilon_6 & \varepsilon_5 \\ \varepsilon_6 & \varepsilon_2 & \varepsilon_4 \\ \varepsilon_5 & \varepsilon_4 & \varepsilon_3 \end{pmatrix} \#(4)$$

For a cubic crystal system (Li_2O_3 , $I m\bar{3}m$) with only 3 independent constants, C_{11} , C_{12} , and C_{44} , we can calculate C_{11} , C_{12} by a strain tensor:

$$\varepsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \#(5)$$

and we obtained C_{44} using a strain tensor as below:

$$\varepsilon = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta/2 \\ 0 & \delta/2 & 0 \end{pmatrix} \#(6)$$

where δ is the magnitude of deformation. To reduce the error and obtain more accurate results, we exerted the strain symmetrically for ε_4 , ε_5 and ε_6 .

For tetragonal classes ($4/mmm$) (LiO_2 , $P 4/mbm$) with 6 independent elastic constants, $C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, C_{13}$, we can calculate C_{11}, C_{12}, C_{13} by a strain tensor as Eq. (5) and calculate C_{33} by a strain tensor as follows:

$$\varepsilon = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \delta \end{pmatrix} \#(7)$$

Moreover, we obtained C_{44} using a strain tensor:

$$\varepsilon = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \delta/2 \\ 0 & \delta/2 & 0 \end{pmatrix} \#(8)$$

and obtained C_{66} using a strain tensor:

$$\varepsilon = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \#(9)$$

For orthorhombic systems (LiO_4 , $I bam$) with 9 constants and no relationships between them, $C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, C_{23}$, we can calculate C_{11}, C_{12}, C_{13} by a strain tensor as Eq.(5) and calculate C_{22}, C_{23} using a strain tensor:

$$\varepsilon = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & 0 \end{pmatrix} \#(10)$$

We can also calculate C_{33}, C_{44}, C_{66} by a strain tensor as Eq. (7), (8) and (9), respectively. In addition, we calculated C_{55} by a strain tensor as follows:

$$\varepsilon = \begin{pmatrix} 0 & 0 & \delta/2 \\ 0 & 0 & 0 \\ \delta/2 & 0 & 0 \end{pmatrix} \#(11)$$

With those structures at different pressures, we exerted positive and negative strains $\Delta\varepsilon$ in $\pm 0.01, \pm 0.005, 0$ on them in each direction to accurately determine the stresses in the appropriate limit of zero strain. The relation between the strained lattice matrix a' and the unstrained lattice matrix a is defined by:

$$a' = a(I + \varepsilon) \#(12)$$

where I represents third-order identity matrix. The elastic constants are determined by the stress - strain:

$$\Delta\sigma = C_{ij} \cdot \Delta\varepsilon \#(13)$$

where C_{ij} is the elastic constant, $\Delta\varepsilon$ is the exerted strain and $\Delta\sigma$ is the stress caused by $\Delta\varepsilon$.

The elastic anisotropy

In high-symmetry directions, when polarization directions are parallel or vertical with the propagation directions of velocities, the modes are called pure longitudinal or transverse,

respectively. In general directions, the velocities are divided into quasi-longitudinal V_p (closest to propagation directions) and two splitting shear-wave velocities (V_{S1} and V_{S2}). The seismic anisotropy of the P wave and S wave are defined as:

$$AV = \frac{(V^{MAX} - V^{MIN})}{(V^{MAX} + V^{MIN})} \times 200\% \quad (14)$$

where V^{MAX} and V^{MIN} are the maximum and minimum velocities, respectively. The velocities along lattice directions are exhibited by circular patterns (Fig. 3).

The migration barrier energy calculations

The Li^+ migration barrier energy was calculated by the climbing-image nudged elastic band (CINEB) method. Larger supercells adopted for the calculations were made up of $2 \times 2 \times 2$, $3 \times 3 \times 4$ and $2 \times 2 \times 2$ containing 160, 96 and 160 atoms for Li_2O_3 , LiO_2 and LiO_4 , respectively. Five images were duplicated in our simulations between the starting point and the end point of migration ions to simulate the intermediate states. For the large supercell adopted in the CINEB calculations, only the gamma point was adopted for k-point sampling to reduce the computational cost. The convergence check indicated that a denser k mesh did not affect our conclusion.

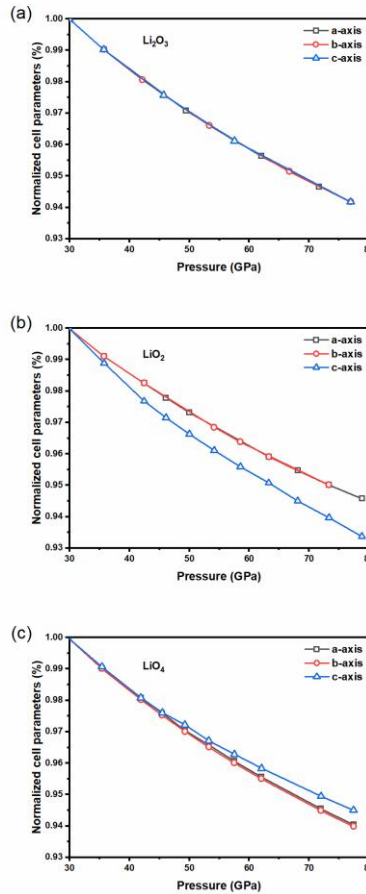


Fig. S1 The pressure dependence of normalized cell parameters to the values at 30 GPa. (a) Li_2O_3 , (b) LiO_2 , (c) LiO_4 .

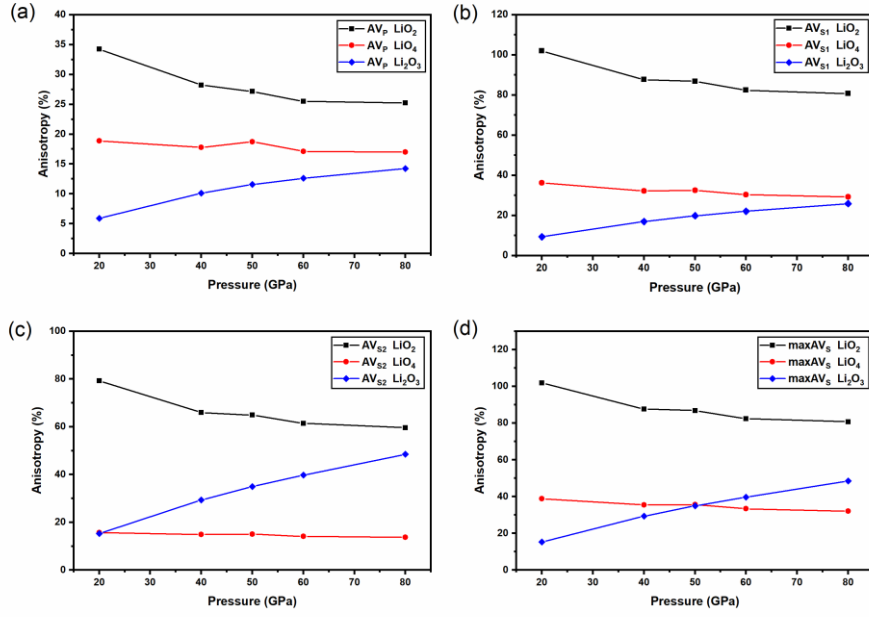


Fig. S2 The evolution of seismic velocity anisotropies with pressure. (a) P-wave anisotropy. (b) Anisotropy of fast S-wave velocities. (c) Anisotropy of slow S-wave velocities. (d) The max AV_S .

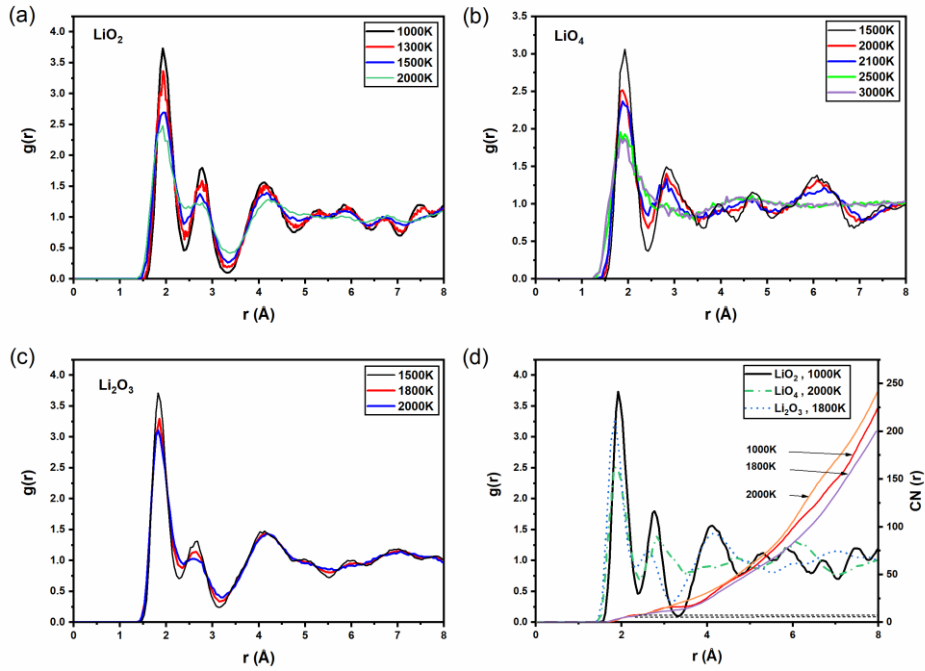


Fig. S3. The radial distribution function (RDF) and coordination number (CN) between Li atoms (central atoms) and O atoms (coordination atoms) at 1000-3000 K and 50 GPa for (a) LiO_2 , (b) LiO_4 , and (c) Li_2O_3 . (d) The RDF and CN at a stable temperature. For LiO_2 , the x-coordinate of the intersection between $g(r)$ and $\text{CN}(r)$ is 2.425 Å, and the CN is approximately 8. For LiO_4 , the x-coordinate of the intersection between $g(r)$ and $\text{CN}(r)$ is 2.45 Å, and the CN is approximately 8. For Li_2O_3 , the x-coordinate of the intersection between $g(r)$ and $\text{CN}(r)$ is 2.3 Å, and CN is approximately 6. These CNs are consistent with those in the primitive cell.

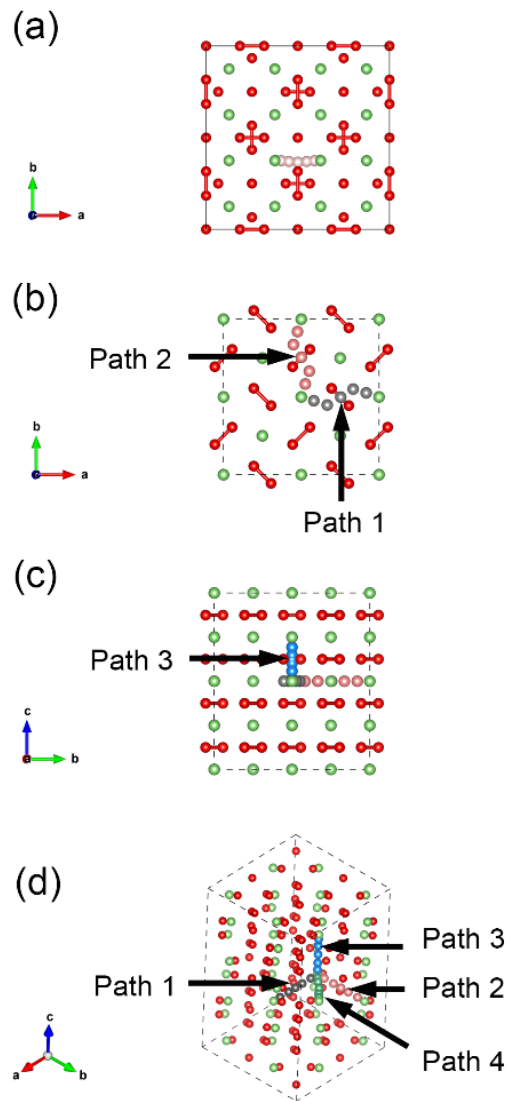


Fig. S4. The migration path of Li-O compounds. (a) Li_2O_3 along $[100]$. (b) The pink spheres represent the path of LiO_2 along $[010]$, the black spheres represent the path of LiO_2 along $[100]$. (c) The blue spheres represent the path of LiO_2 along $[001]$. (d) The black, pink, blue and green spheres represent the path of LiO_4 along $[100]$, $[010]$, $[001]$ and $[110]$, respectively. Li and O are shown with light green and red spheres.