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Supporting Information of "Superhalogen-based Lithium Superionic Conductors"

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Fig.S1The planar configuration of the superalkali Li_3O^+ in its gas phase.

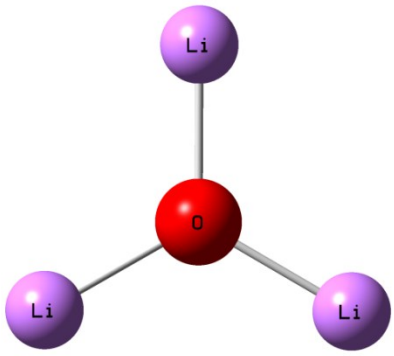


Fig.S2 Interaction between the superalkali Li_3O^+ and the superhalogen BH_4^- in a cluster model. Li_3O^+ becomes a pyramidal configuration due to the repulsion between the lone pair on the oxygen (in red) and the negative BH_4^- (boron in pink and hydrogen in grey) as well as the attraction between lithium (in violet) and the negative BH_4^-.

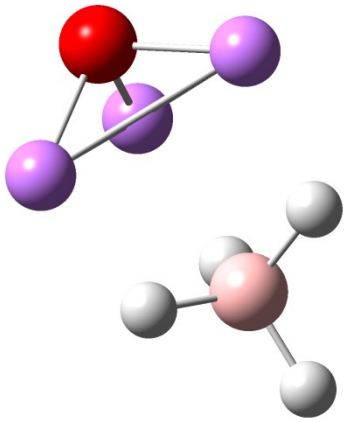


Fig. S3Given the similar ionic radius of BH_4^- compared to that of Br^-, we expected that $Li_3O(BH_4)$could be stabilized in the same cubic phase as Li_3OBr where BH_4would occupy the Br sites. However, unlike Br atom which is spherical, BH_4 cluster has tetrahedral symmetry. Thus, one has to determine the precise orientation of the BH_4 tetrahedron. We have carried out an extensive testing with different starting orientation of BH_4, among which the three high-symmetry configurations are listed below: (i) an H atom of BH_4 pointing to the lattice center, (ii) two opposite edges of BH_4 tetrahedron pointing along the diagonals of the corresponding faces, and (iii) two opposite edges of BH_4 tetrahedron parallel to the corresponding planes of the lattice. The first configuration is the ground-state structure which lies 0.3 eV and 0.48 eV lower in energy than the other two. These are shown in the figurewhere the white, purple, green and red balls represent H, Li, B, O respectively. For each case, the corresponding total energy is given.

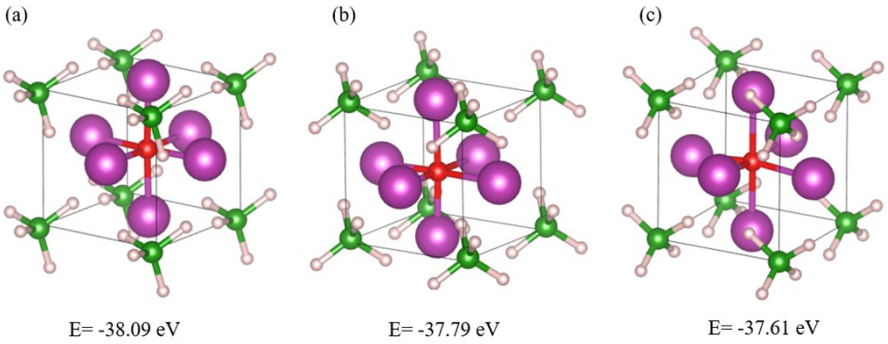


Fig. S4 (a) Low-barrier migration for aninterstitial Li in $Li_3O(BH_4)$: left and right are the initial and final configurations, respectively. The Li atoms involved in the migration are in red and migration direction isindicated by green arrows. Insets are the enlarged views of rotation of BH_4 cluster as the Li^+ ion migrates. (b) The calculated migration energy barrier as a function of distance travelledby the Li^+-ion.

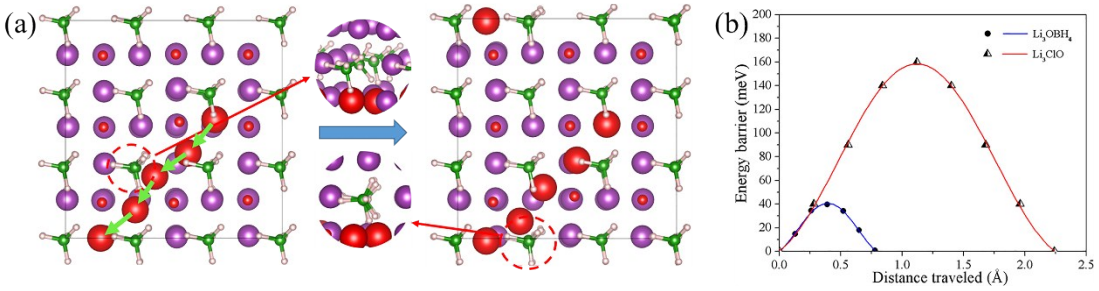
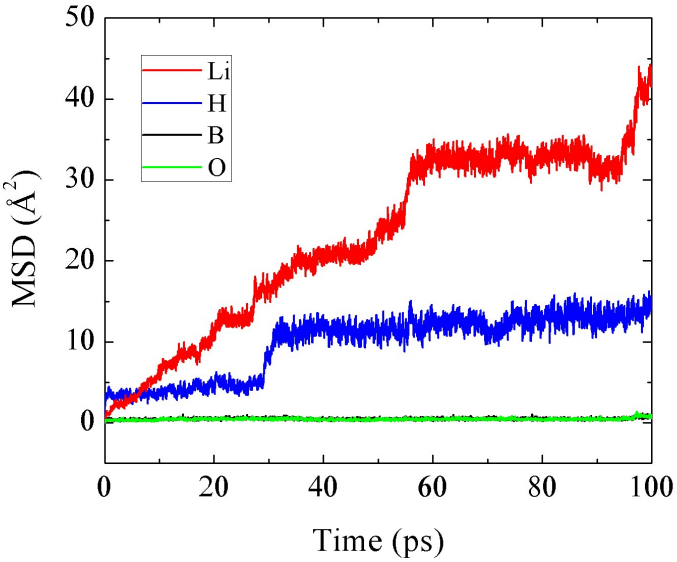


Fig. S5 The mean square displacement (MSD) of different ions of $Li_3O(BH_4)$ at 2000 K. H^+ ion also exhibits superionic conductivity at this temperature.



Symmetry operations

Following shows the operations to obtain the symmetry-related orientations in the T_d, D_{2d}, C_{2v} and C_{3v} groups. $x(\pi/2)$, $y(\pi/2)$ and $z(\pi/2)$ denotes the rotation of $\pi/2$ about the x, y and z axes, respectively. "i" is the inversion operation.

$$T_d: 1 \xrightarrow{z(\pi/2)} 2$$

$$D_{2d}: 1 \xrightarrow{z(\pi/2)} 2$$

$$1 \xrightarrow{x(\pi/2)} 3 \xrightarrow{y(\pi/2)} 4$$

$$1 \xrightarrow{y(\pi/2)} 5 \xrightarrow{x(\pi/2)} 6$$

$$C_{2v}: 1 \xrightarrow{z(\pi/2)} 2 \xrightarrow{z(\pi/2)} 3 \xrightarrow{z(\pi/2)} 4$$

$$1 \xrightarrow{x(\pi/2)} 5 \xrightarrow{y(\pi/2)} 6 \xrightarrow{y(\pi/2)} 7 \xrightarrow{y(\pi/2)} 8$$

$$C_{3v}: 1 \xrightarrow{z(\pi/2)} 2 \xrightarrow{z(\pi/2)} 3 \xrightarrow{z(\pi/2)} 4$$

$$1 \xrightarrow{i} 5 \xrightarrow{z(\pi/2)} 6 \xrightarrow{z(\pi/2)} 7 \xrightarrow{z(\pi/2)} 8$$

$$1 \xrightarrow{y(\pi/2)} 9 \xrightarrow{x(\pi/2)} 10 \xrightarrow{x(\pi/2)} 11 \xrightarrow{x(\pi/2)} 12$$

Fig.S6Reaction of Li_2O with $LiBH_4$in both cluster (upper) and crystalline forms, where B is in pink, H in grey, Li in violet and O in red.