

Supplementary material for

Not all H atoms contribute to low activation barrier diffusion in $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$

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Supplementary discussion: First principles calculations of $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$

The neural network potential (NNP) energies of some $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$ supercells were compared with VASP results that are based on the PBE approximation to density functional theory (DFT). What matters is evaluation of energies at finite temperatures, namely in the simulated temperature range of 455-741 K, and in supercells with a high density of defects.

The PBE (DFT) energies were calculated for 42 supercells. The final positions after 2,100,000 MD steps at $1/T = 0.0014$ to 0.0020 K^{-1} at 0.0001 K^{-1} intervals (seven temperatures) were used. The initial atom positions were one of the two supercells in the β , γ , or δ -phase, denoted as β -set1, β -set2, γ -set1, γ -set2, δ -set1, and δ -set1. Atom positions and lattice parameters were not relaxed in PBE calculations.

Fig. S1 plots PBE versus NNP energies of the MD snapshots. The green line is a linear regression of all points. The slope is 0.90, which means that a 1 eV energy difference in PBE is a 0.9 eV difference in NNP. To attain the same Boltzmann factor of $\exp(-\Delta E/k_B T)$, where ΔE , k_B , and T are the energy difference, Boltzmann constant, and temperature, respectively, the NNP temperature should be reduced by a factor of 0.9 compared to the PBE temperature, or in other words, the NNP temperatures are overestimated by 10%.

The NNP energies of the β -set2 supercells are underestimated by about 5 eV/supercell compared to the others with the same $1/T$, but still the change in energy with respect to the change in simulation temperature is almost the same for each of the initial atom positions. The R^2 of all points other than β -set2 supercells and β -set2 supercells only, which correspond to purple and black regression lines, respectively, are very large at 0.98 and 1.00, respectively.

Fig. S2 is the electronic density of states (DOS), based on PBE, of the final snapshot of the $1/T = 0.0014 \text{ K}^{-1}$ simulation starting from the β -set1 supercell. The majority and minority spin DOS are shown in the positive and negative directions, respectively. The thick black lines and thin red lines show the DOS for all atoms and all H atoms, respectively. The H DOS are found below the Fermi energy, thus the charge of H is -1 . One H in the supercell has a very short O-H bond length of $0.9735 \text{ \AA}$. The DOS of this H (magnified by $\times 50$) is shown with blue lines. Although the DOS peaks are below the Fermi level, the actual charge of this H should be $+1$ (see main text for details).

Supplementary figures

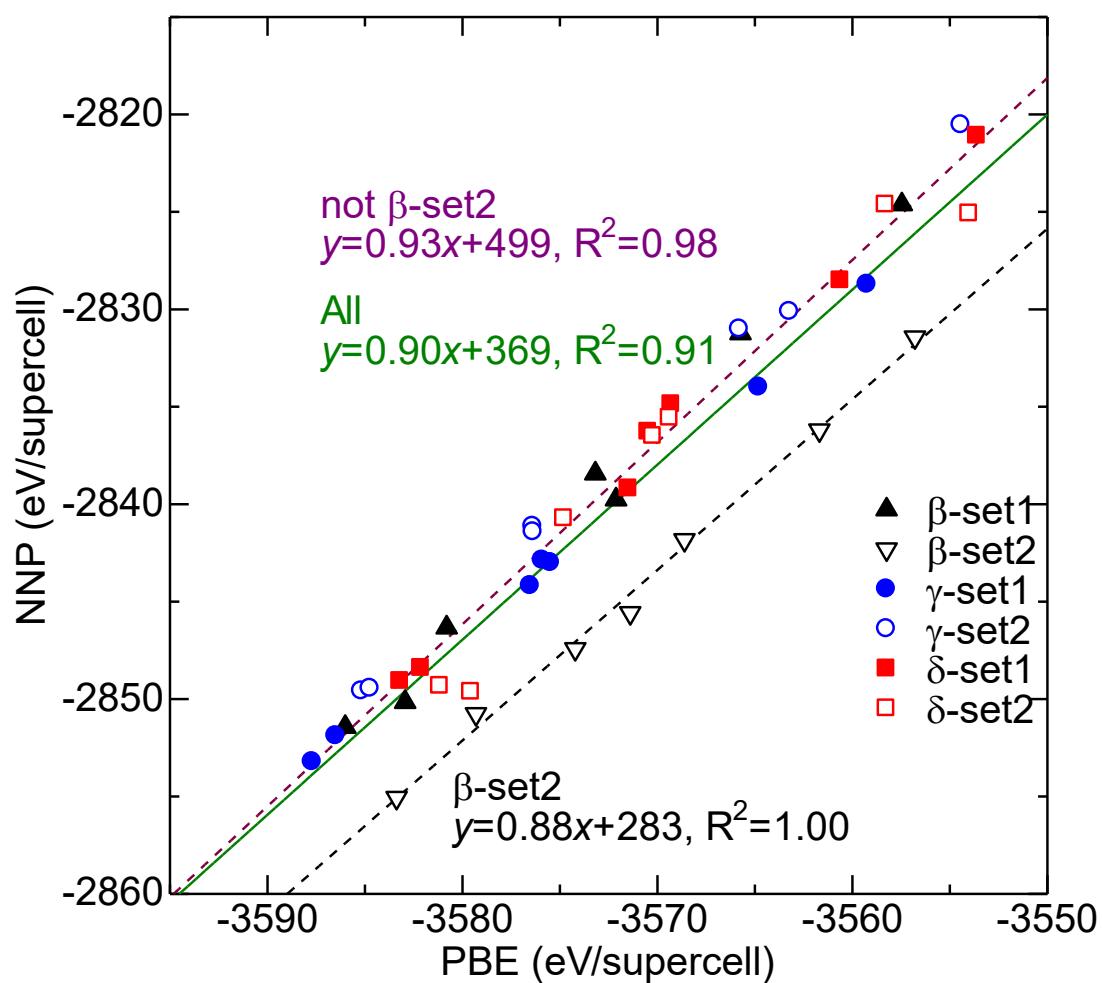


Fig. S1. Comparison of NNP and PBE (DFT) energies of MD snapshots at different temperatures starting from different phases (β , γ , or δ) and initial positions (set1 or set2).

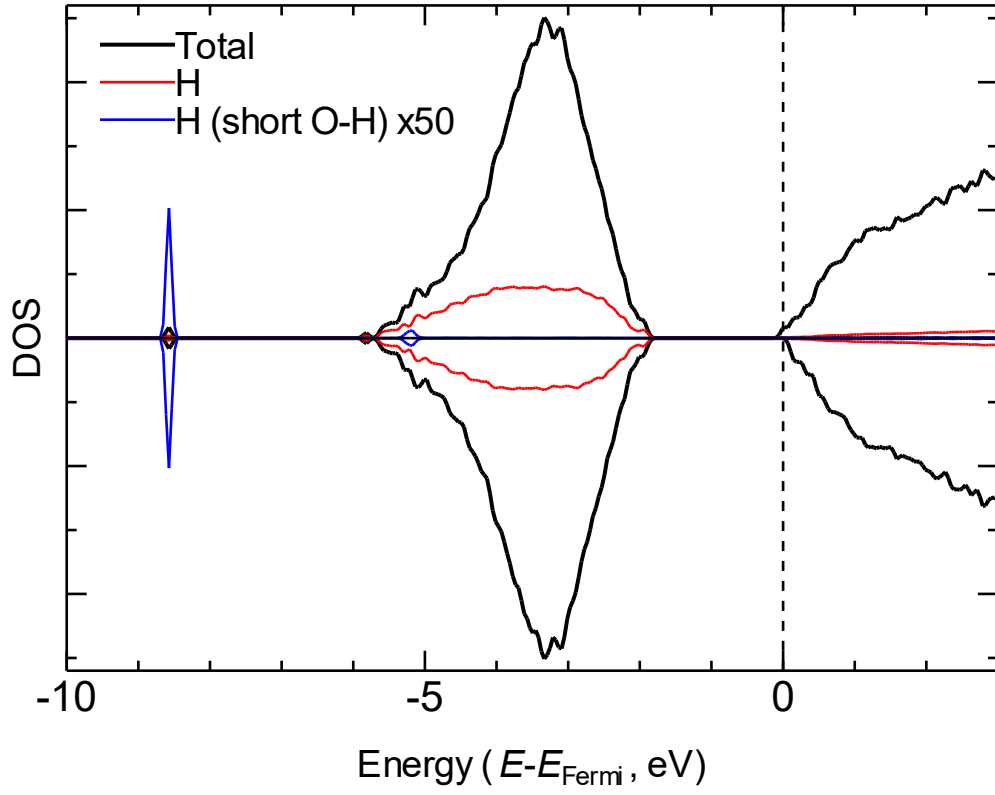


Fig. S2. Electronic DOS of the final snapshot of the $1/T = 0.0014 \text{ K}^{-1}$ simulation starting from the β -set1 supercell. The H DOS with the short O-H bond is magnified by 50 times.

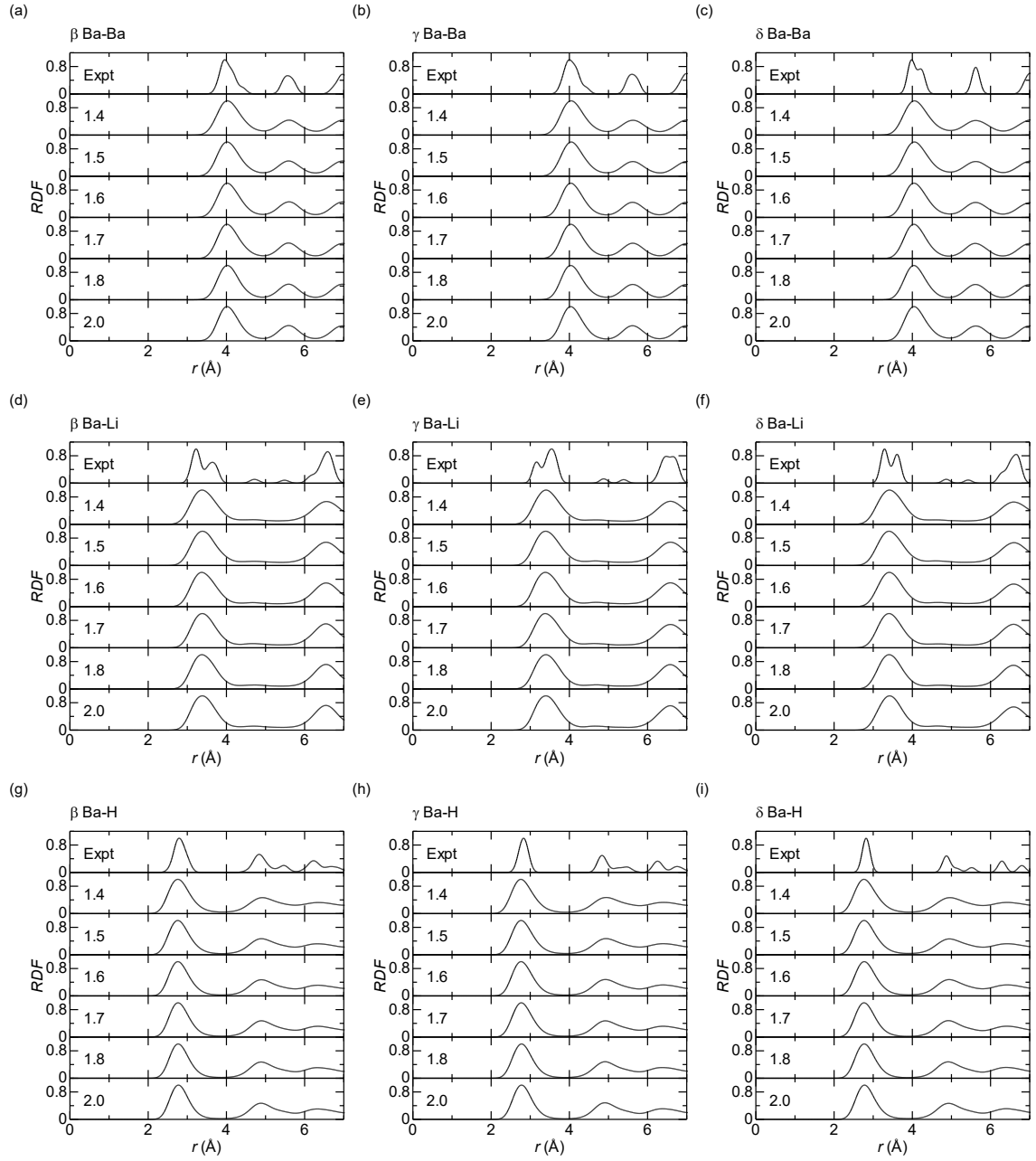


Fig. S3. (a-i) RDFs of BLHO. “Expt” is the RDFs of supercell models derived from refinements of experimental synchrotron X-ray diffraction results (ref. 15 in the main text). Numbers from 1.4 to 2.0 are the reciprocal temperature in units of 10^{-3} K^{-1} .

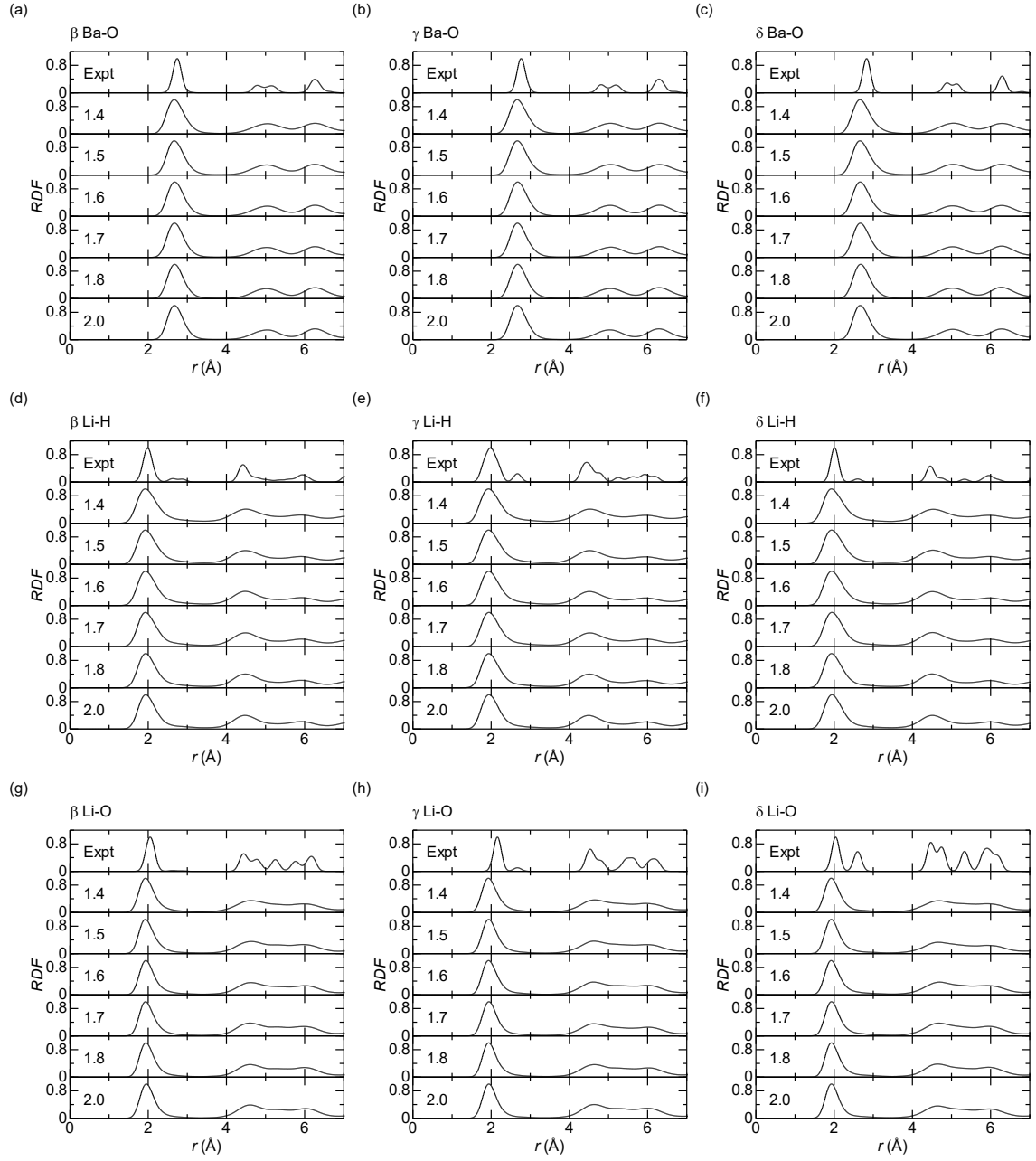


Fig. S4. (a-i) RDFs of BLHO. “Expt” is the RDFs of supercell models derived from refinements of experimental synchrotron X-ray diffraction results (ref. 15 in the main text). Numbers from 1.4 to 2.0 are the reciprocal temperature in units of 10^{-3} K^{-1} .

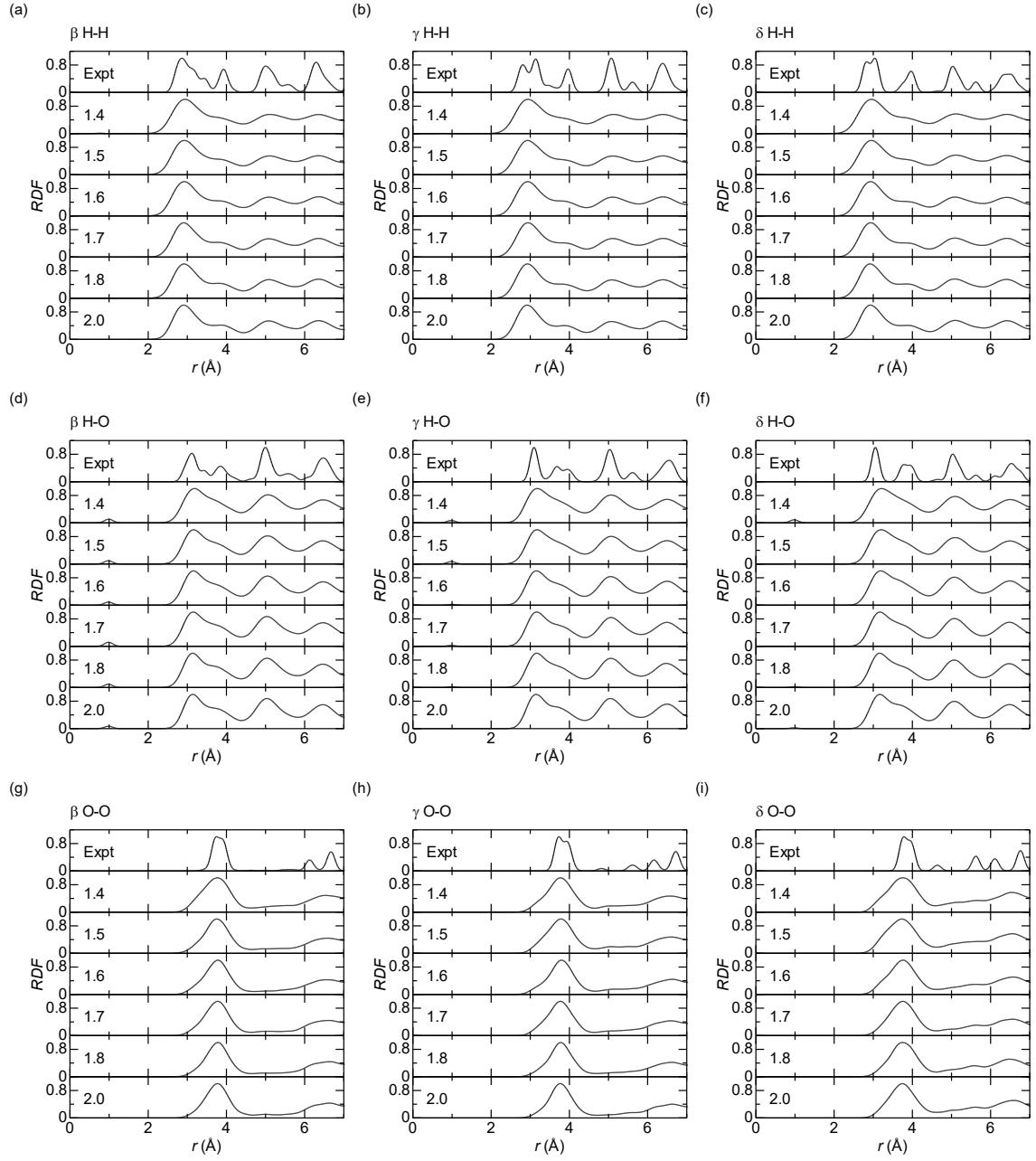


Fig. S5. (a-i) RDFs of BLHO. “Expt” is the RDFs of supercell models derived from refinements of experimental synchrotron X-ray diffraction results (ref. 15 in the main text). Numbers from 1.4 to 2.0 are the reciprocal temperature in units of 10^{-3} K^{-1} .

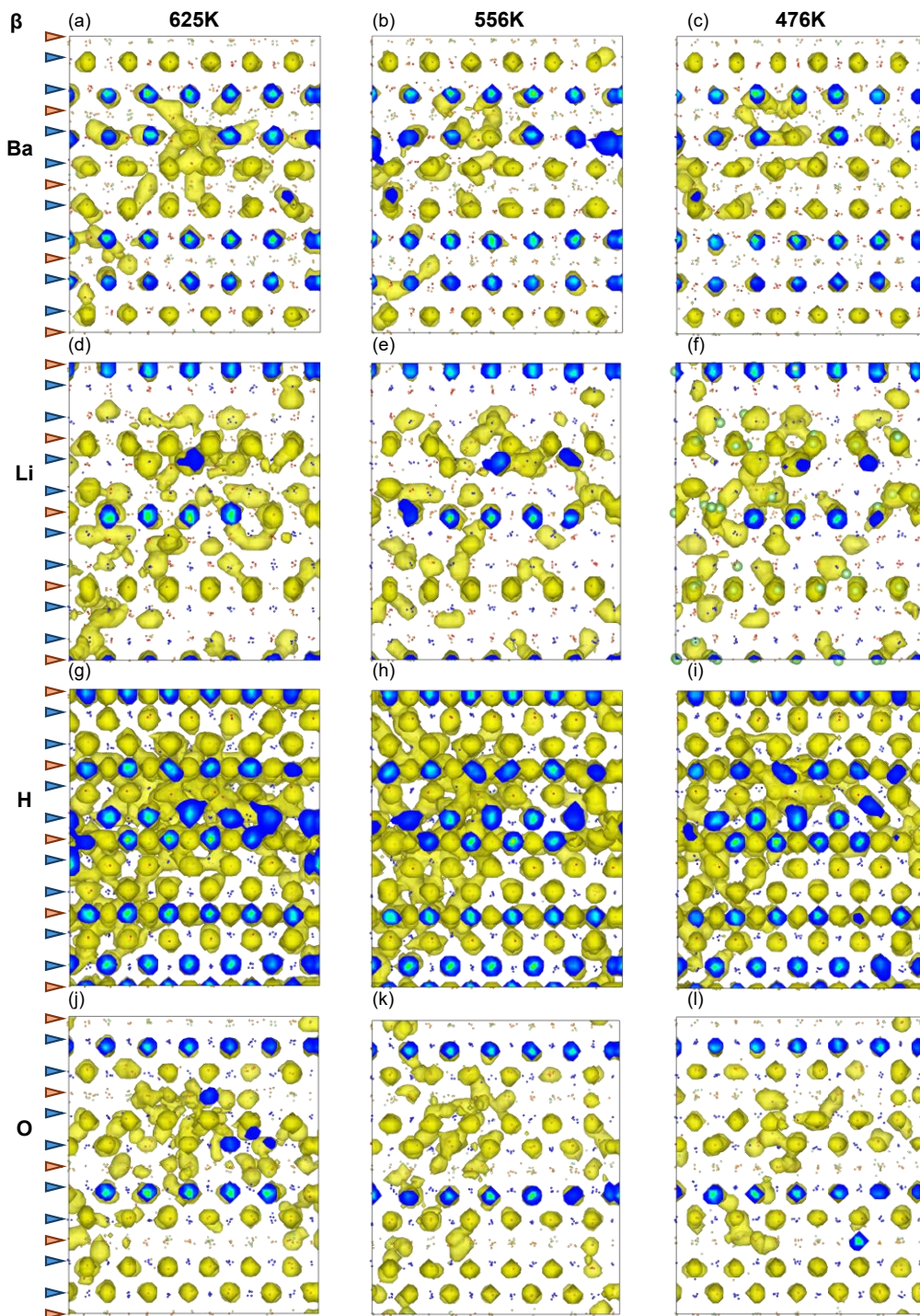


Fig. S6. (a-l) Isosurface plots showing the distribution of atom positions in β -BLHO. The plots are projected normal to the a -axis. The threshold is 0.001 based on the “isosurface” utility in the pfcc-extras package of Matlantis. Atom positions of a snapshot are given using very small blue, green, orange, and red dots for Ba, Li, H, and O, respectively. Blue wedges at the left indicate Li and equatorial H positions and the orange wedges are Ba and axial O/H positions.

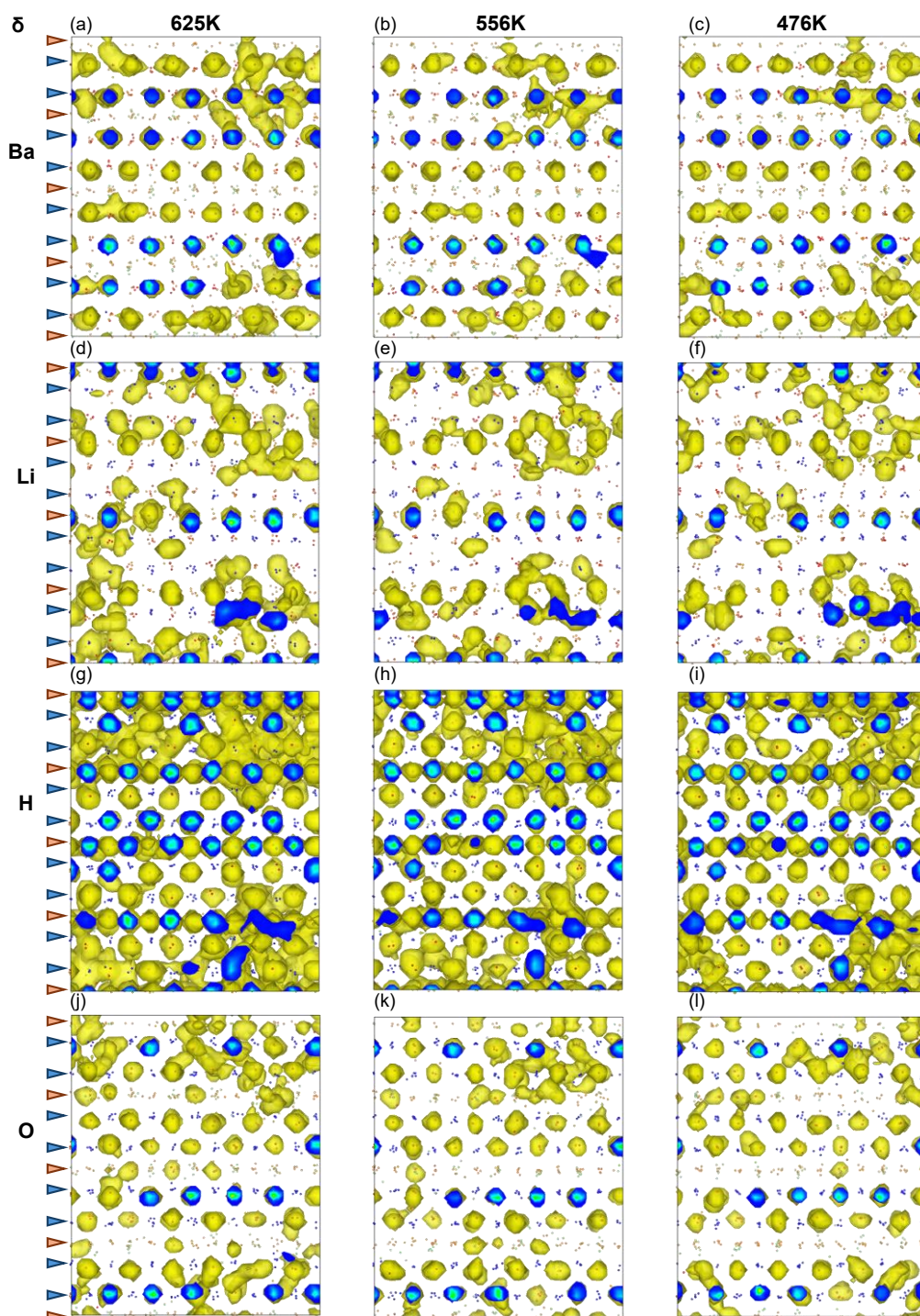


Fig. S7. (a-l) Isosurface plots showing the distribution of atom positions in δ -BLHO. The plots are projected normal to the a -axis. The threshold is 0.001 based on the “isosurface” utility in the pfcc-extras package of Matlantis. Atom positions of a snapshot are given using very small blue, green, orange, and red dots for Ba, Li, H, and O, respectively. Blue wedges at the left indicate Li and equatorial H positions and the orange wedges are Ba and axial O/H positions.