

## Supporting Information

### **Lithium-Ion Diffusion in Grain Boundary of Polycrystalline Solid Electrolyte $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO): A Computer Simulation and Theoretical Study**

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# Contents

Methods .....	3
Sample Preparation.....	3
Scanning Electron Microscopy.....	3
Density functional theory (DFT) calculations .....	3
Ab initio molecular dynamics (AIMD) diffusivity calculations .....	4
Results .....	5
Constructs of five polycrystalline LLZTO .....	5
Arrhenius plots of lithium-ion diffusion.....	6
Mean square displacement of lithium-ion diffusion.....	7
Potential energy diagrams for lithium-ion migration .....	14
References .....	16

## Methods

### Sample Preparation

A mixture of 28.4 g LiOH·H<sub>2</sub>O, 48.9 g La<sub>2</sub>O<sub>3</sub>, 18.5 g ZrO<sub>2</sub> and 11.0 g Ta<sub>2</sub>O<sub>5</sub> was ball-milled for 4 ~ 6 h in a ball miller (FP2000H), then calcined at 950 °C for 4~6 h. and pressed into pillars at 50 MPa. Calcination was carried out in a muffle furnace at 1200 °C for 12 h in lithium atmosphere. The resulting sample is designated as Li<sub>6.75</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZTO).

### Scanning Electron Microscopy

SEM measurements were carried out with a Carl Zeiss EVO18 SEM operating at 5 kV. The samples were cut with a sharp razor and coated with platinum to increase electrical conductivity.

### Density functional theory (DFT) calculations

All DFT calculations were performed using Vienna ab initio simulation package (VASP)<sup>1</sup> within the projector augmented-wave (PAW)<sup>2, 3</sup> approach and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)<sup>4</sup> functional. The kinetic energy cut-off was set to 400 eV for the plane wave basis set, and the Brillouin zone was sampled using the gamma point only. The atomic positions were fully optimized until all the residual forces on the atoms were less than 0.05 eV/Å, and the convergence threshold for self-consistent-field (SCF) iteration was set at 10<sup>-6</sup> eV. The migration energy barriers were calculated via the nudged elastic band method (NEB) as implemented in the VTST tools for the VASP code<sup>5, 6</sup>.

The formation energy per atom of material is defined as:

$$E = \frac{E_{A_n B_m \dots C_l} - (nE_A + mE_B \dots + lE_C)}{n + m + \dots + l} \quad (1)$$

where  $E_{A_n B_m \dots C_l}$  is the total energy of unit cell  $A_n B_m \dots C_l$ ,  $E_A$ ,  $E_B$ ,  $E_C$  are the energy of A, B, and C, respectively.  $n$ ,  $m$ , and  $l$  are the stoichiometric number of A, B, and C, respectively.

## Ab initio molecular dynamics (AIMD) diffusivity calculations

The lithium-ion diffusivity and conductivity were evaluated via Ab initio molecular dynamics (AIMD) method (implemented in VASP) performed in the canonical (NVT) ensemble<sup>7</sup> through Verlet algorithm with a time step of 2 fs. The computational cost was kept to a reasonable level by using a minimal  $\Gamma$ -centered  $1 \times 1 \times 1$  k-point grid, a plane wave energy cutoff of 400 eV. The overall procedure of the AIMD simulations for solid electrolytes is as follows:

1. Acquisition of crystal structure: a. The microscopic spatial crystal structure is determined by X-ray diffraction (XRD); b. The initial crystal structure is obtained from the Inorganic Crystal Structure Database (ICSD)<sup>8</sup>.

2. Optimization: The atomic positions were fully optimized until all the residual forces on the atoms were less than 0.05 eV/Å since the crystal structure in ICSD or from XRD is not entirely in agreement with a real crystal structure.

3. Heating: The structure was allowed to equilibrate over the constant volume and temperature (NVT) ensemble by heating the system from 2273K to 4273K.

4. Annealing: The structure was allowed to equilibrate over the constant volume and energy (NVE) ensemble<sup>9</sup> after heating to target temperature.

5. Simulation: The amorphous structure was allowed to equilibrate over the NVT ensemble at 573K, 973K, 1373K and 1773K, respectively.

6. Diffusion coefficient: The diffusion coefficient is determined as the mean square displacement (MSD), as follows<sup>10</sup>:

$$MSD(t) = \langle [r(t) - r(0)]^2 \rangle \quad (2)$$

The diffusion coefficient is calculated by Einstein formula<sup>11,12</sup>:

$$D = \frac{1}{6} \frac{dMSD(t)}{dt} \quad (3)$$

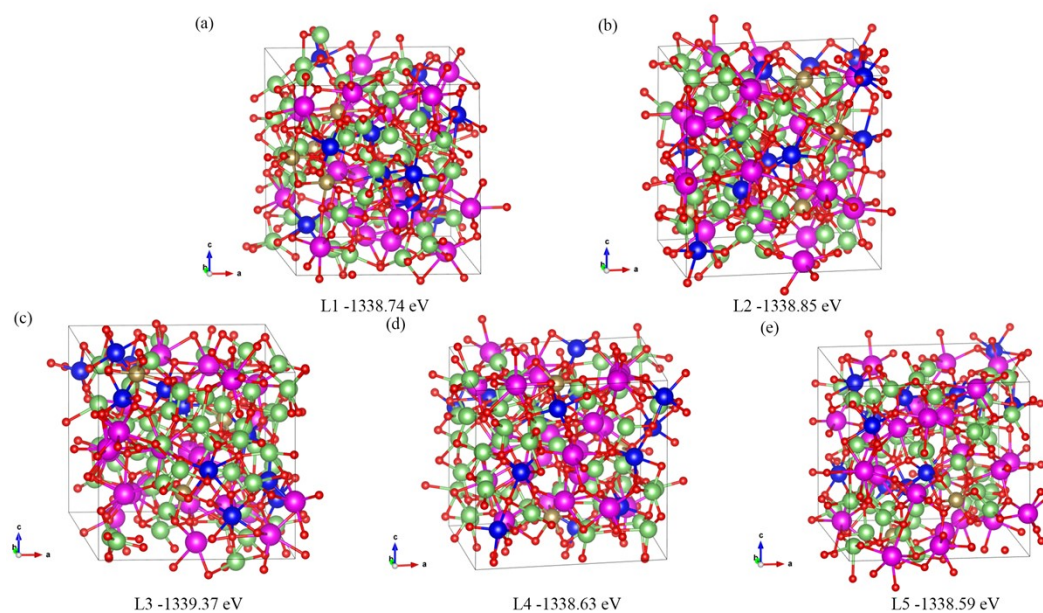
The equations are approximate single particle diffusion equations rather than cooperative multi-ion diffusion equations. In addition, NVT ensemble usually gives predictions within 10% of NVE ensemble for diffusion constants since nose thermostat frequency in NVT ensemble would interfere with atomic vibration. And NVE is the only fool-proof "Newton's second law" propagation ensemble and the rigorous ensemble to calculate dynamical properties<sup>10</sup>.

The bond breaking and rearrangement were distinguished by calculating the atom-atom distance in every step of the AIMD simulation and the sum of atom-atom covalent radii from Cambridge Structural Database. If the the atom-atom distance was greater than 1.15 times the sum of atom-atom covalent radii from Cambridge Structural Database, the bond between atoms was considered as broken. Similarly, if the the atom-atom distance was less than or equal to 1.15 times the sum of atom-atom

covalent radii, the approaching atoms were considered as bonded and a new bond has been formed. Specifically, the approaching atoms were considered as bonded in polycrystalline LLZTO when the atom-atom distances between O and Li, Ta, Zr, La were less than or equal to 2.25 Å, 2.40 Å, 2.50 Å, 2.79 Å, respectively.

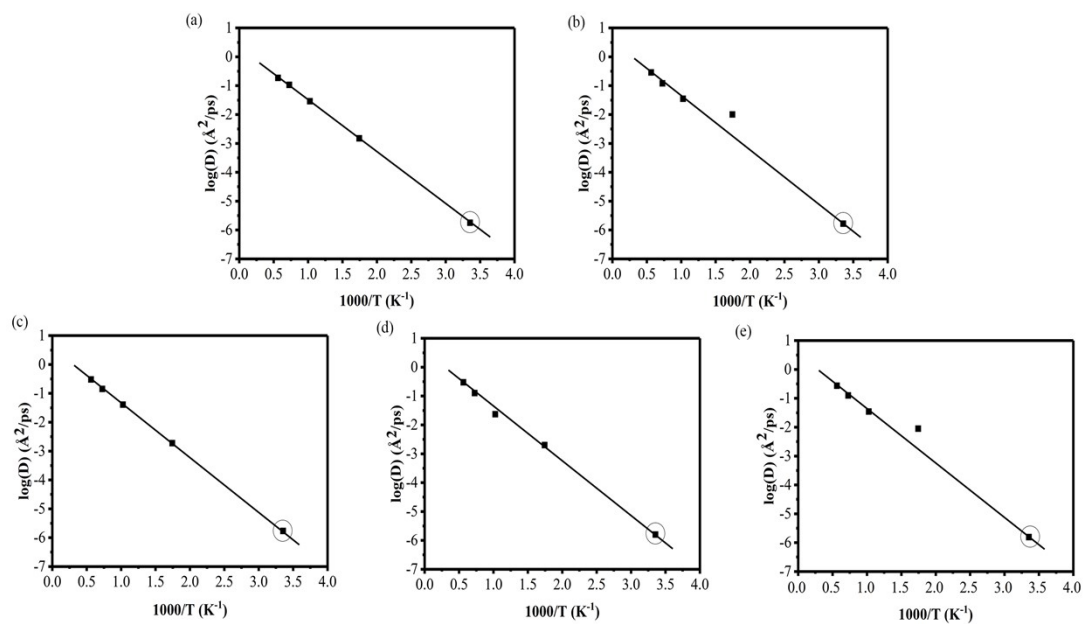
## Results

### Constructs of five polycrystalline LLZTO



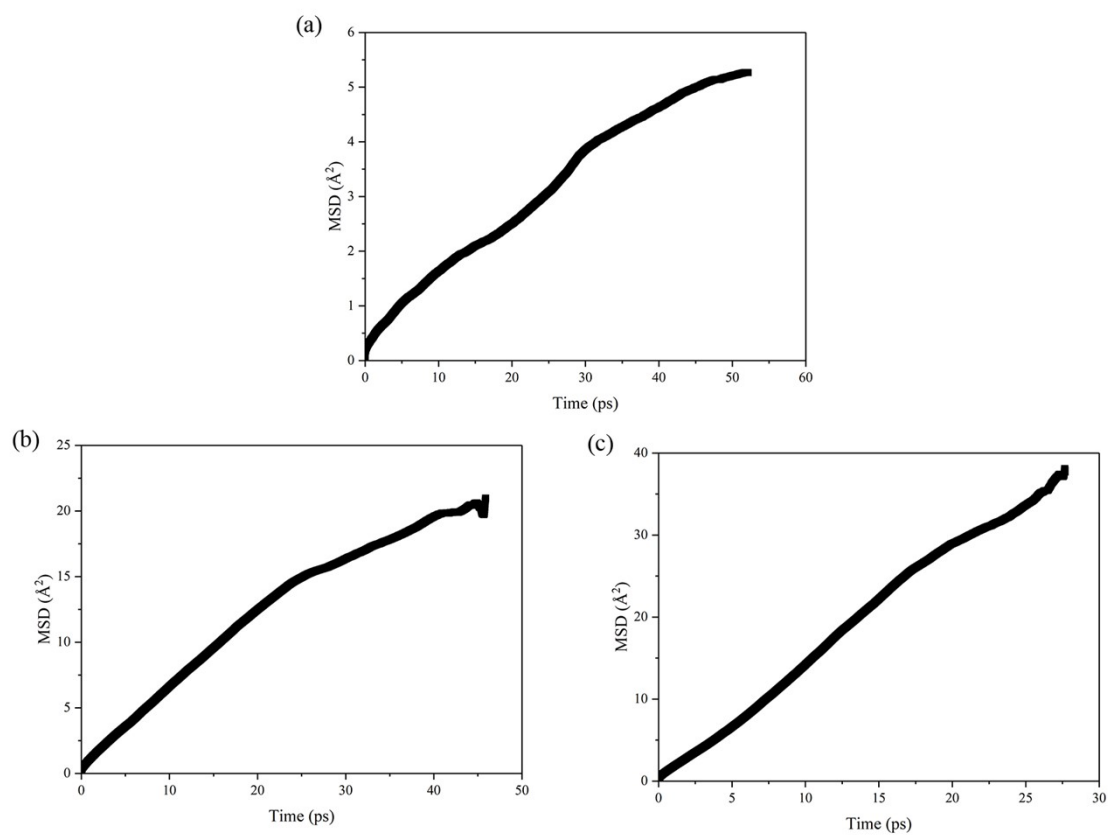
**Figure S1** Five amorphous structures of polycrystalline LLZTO. Each form is energy-minimized, and the sample numbers are L1 (a), L2 (b), L3 (c), L4 (d) and L5 (e).

## Arrhenius plots of lithium-ion diffusion

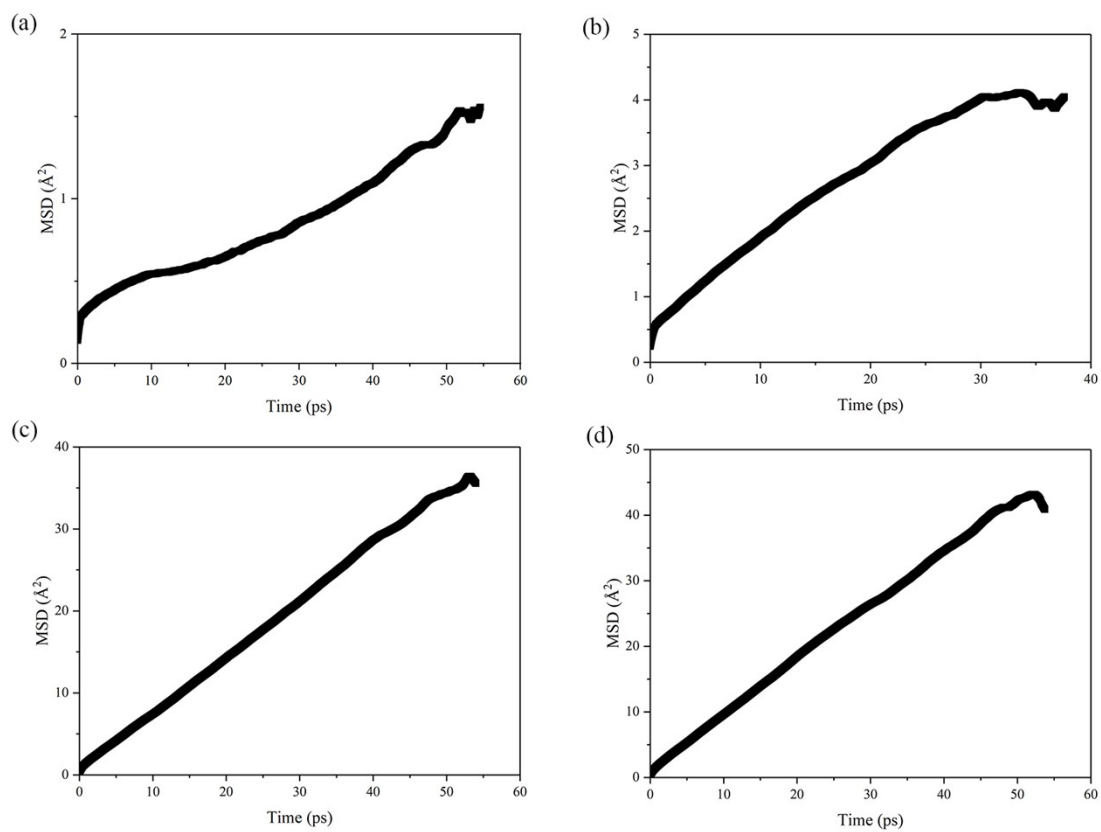


**Figure S2** Plots of diffusion coefficient vs. temperature for L1 (a), L2 (b), L3 (c), L4 (d) and L5 (e) (Scattered points are the simulated values, straight line is the fitting result, and points within circle are the predicted values at 300K).

## Mean square displacement of lithium-ion diffusion

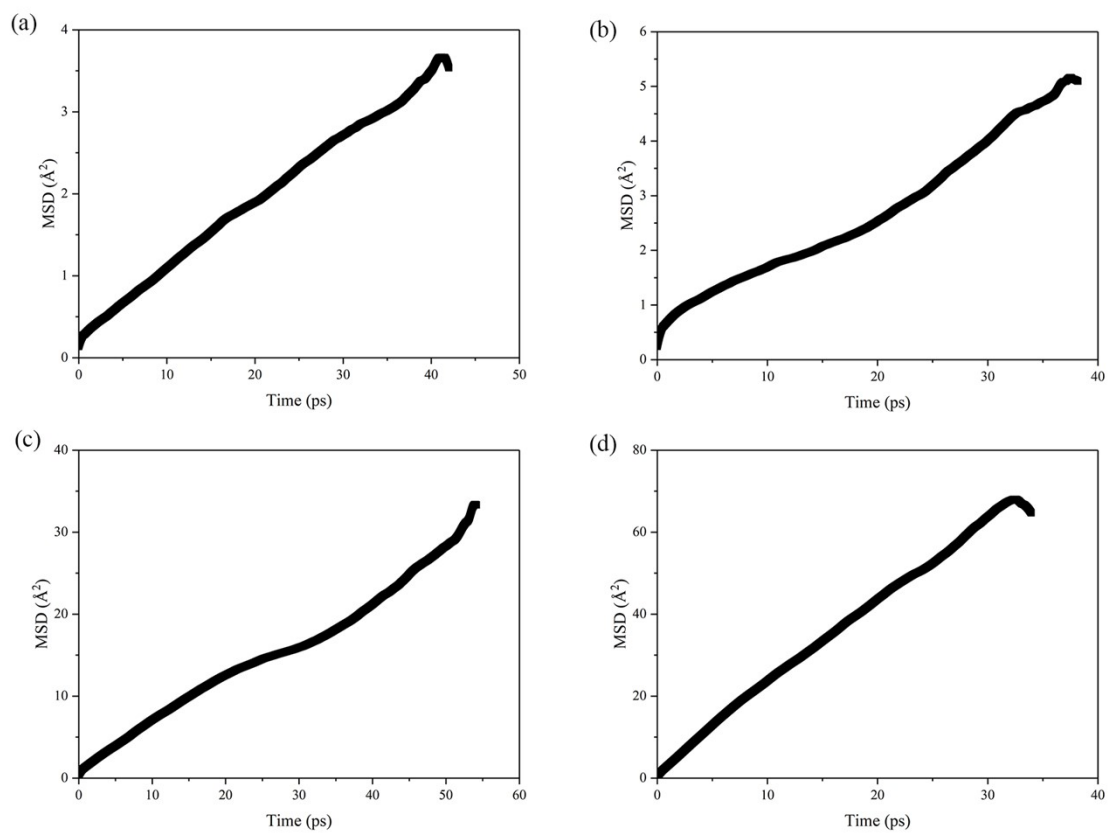


**Figure S3** The MSD curves of lithium ions in single-crystal LLZTO at 573K (a), 973K (b) and 1773K (c), respectively.

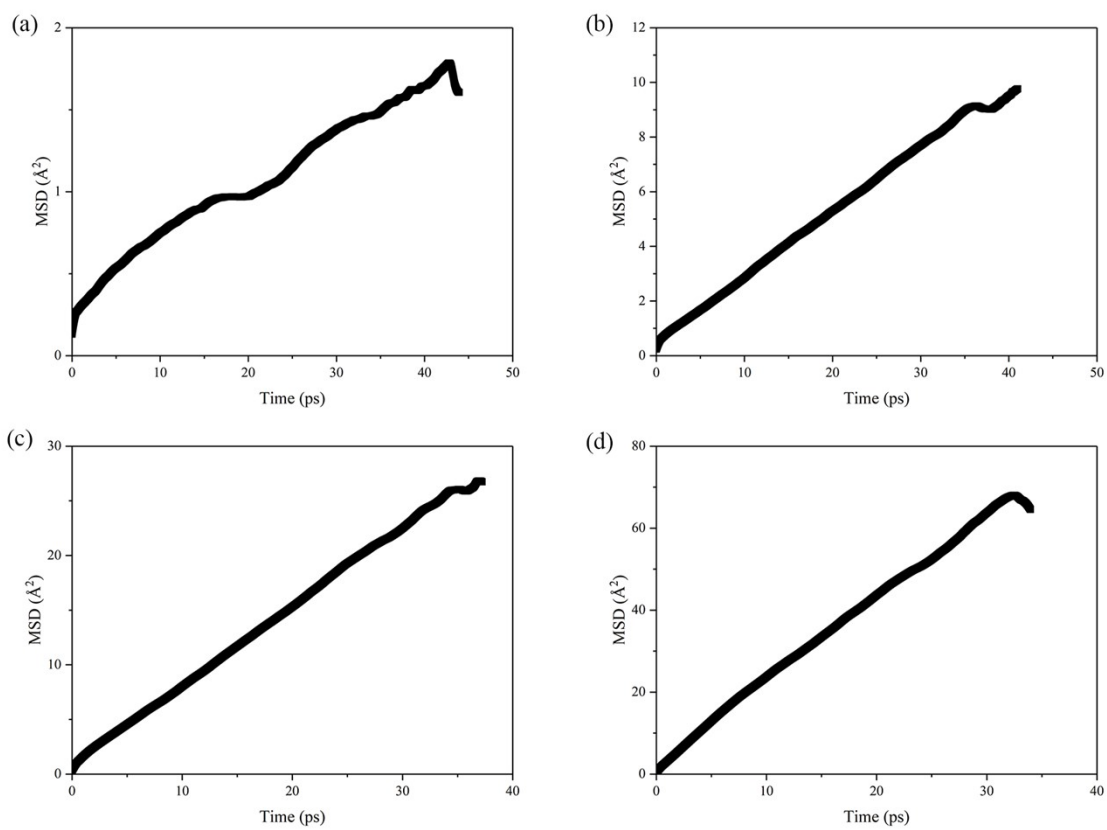


**Figure S4** The MSD curves of lithium ions in L1 at 573K (a), 973K (b), 1373K (c) and 1773K (d), respectively.

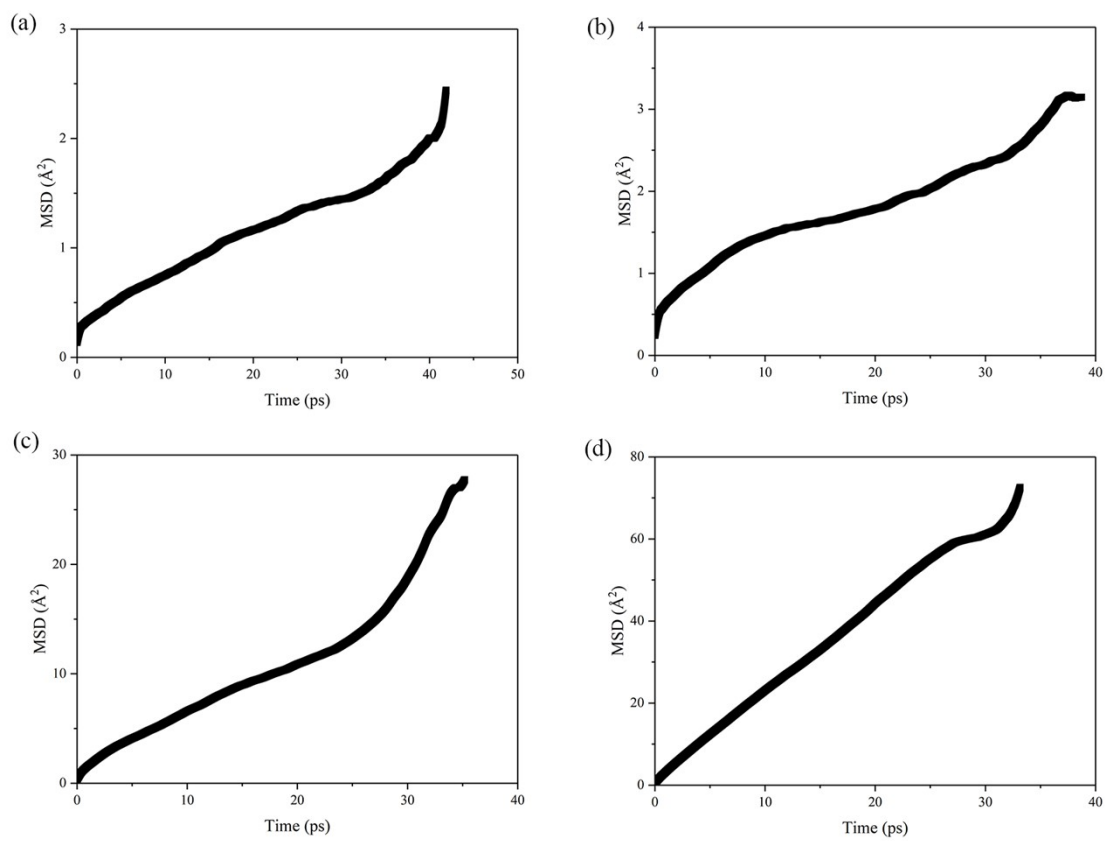




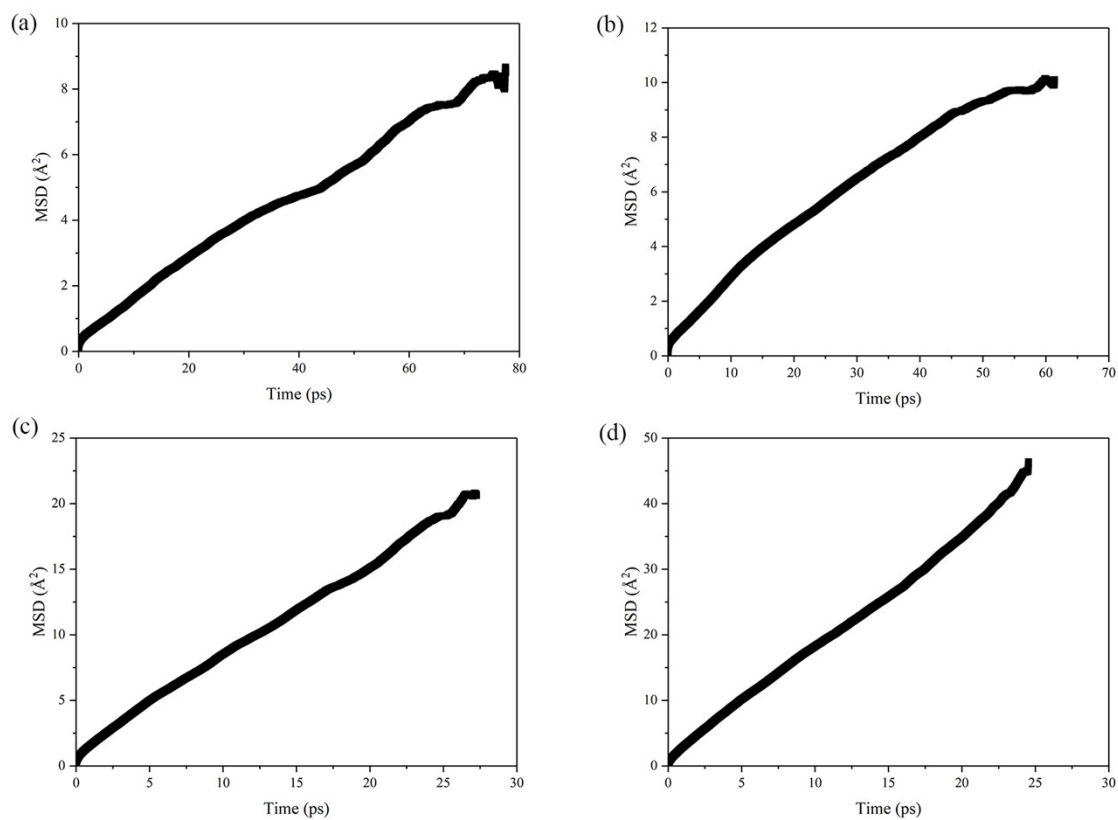
**Figure S5** The MSD curves of lithium ions in L2 at 573K (a), 973K (b), 1373K (c) and 1773K (d), respectively.



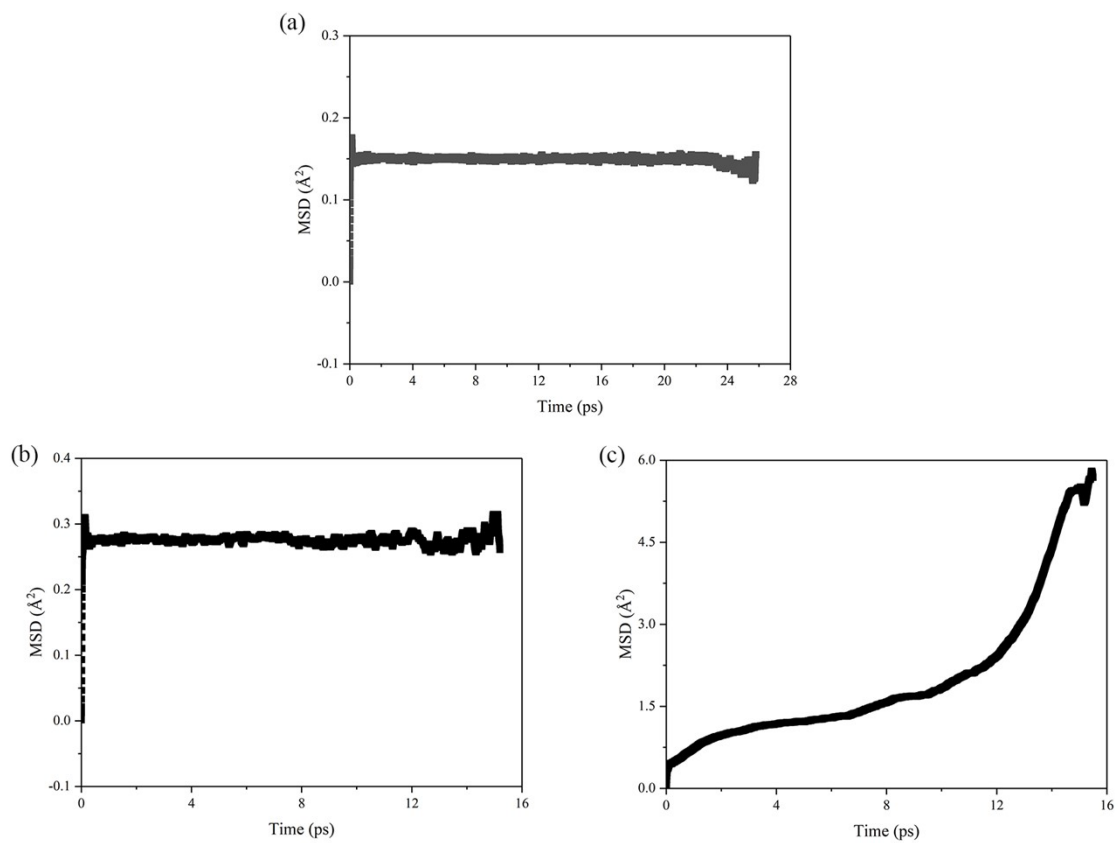
**Figure S6** The MSD curves of lithium ions in L3 at 573K (a), 973K (b), 1373K (c) and 1773K (d), respectively.



**Figure S7** The MSD curves of lithium ions in L4 at 573K (a), 973K (b), 1373K (c) and 1773K (d), respectively.

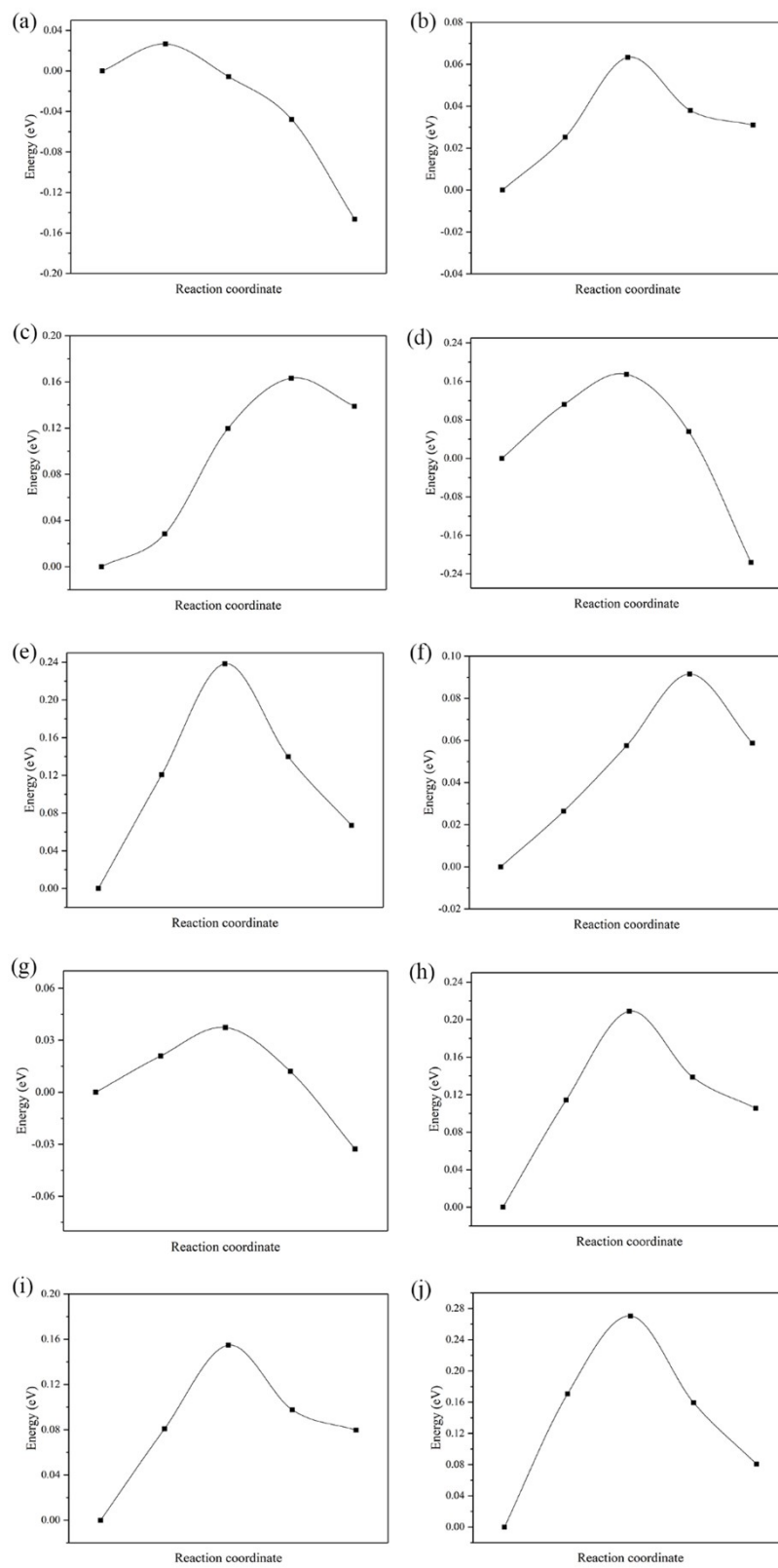


**Figure S8** The MSD curves of lithium ions in L5 at 573K (a), 973K (b), 1373K (c) and 1773K (d), respectively.

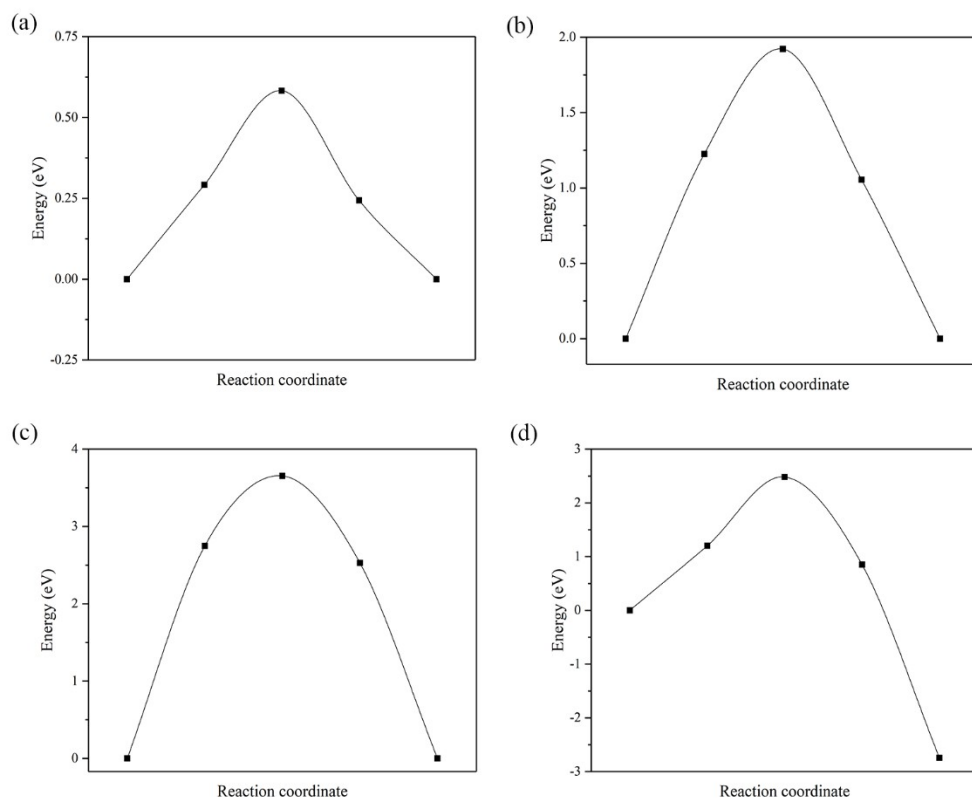


**Figure S9** The MSD curves of lithium ions in single-crystal LLZO at 573K (a), 973K (b) and 1373K (c), respectively.

## Potential energy diagrams for lithium-ion migration



**Figure S10** Potential energy diagrams of lithium-ion migration in single-crystal LLZTO (a:1-2; b:2-3; c:3-4; d:4-1#; e: 1#-2#; f: 2#-3#; g: 3#-4#; h: 4#-1##; i: 3-4'; j: 4-4').



**Figure S11** Potential energy diagrams of lithium-ion migration in  $\text{Li}_2\text{O}$  (a:5-6; b:5-7; c:5-8) and  $\text{La}_2\text{Zr}_2\text{O}_7$  (d:9-10).

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