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——Supporting Information——

Elucidating the Nature of Grain Boundary Resistance in Lithium Lanthanum Titanate

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S1 Simulation Cells

Table S1 Total number of atoms in each simulation cell.

Grain boundary	Ti	O	La	Li
Σ2(110)	1920	5760	1200	240
Σ3(111)	1920	5760	1200	240
Σ5(210)	1920	5760	1200	240
Σ3(211)	1920	5760	1200	240
Σ5(310)	2176	6528	1360	272

S2 Potential Model and Additional Computational Details

The short-range forces are accounted for by Morse and Lennard-Jones type potentials and the long-range ionic interactions are treated using Coulomb terms according to **Equation 1**.

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}\left[\left(1 - e^{-a_{ij}(r-r_0)}\right)^2 - 1\right] + \frac{C_{ij}}{r^{12}} \quad (1)$$

where $z_i z_j$ are the charges on atoms i and j, D_{ij} is the depth of the potential energy well (or dissociation energy of the bond), a_{ij} is a function of the slope of the potential energy well, r is seperation, r_0 is the equilibrium distance between species i and j. C_{ij} relates to the potretnial energy well and describes the repulsion at very short distances between species i and j. The parameters for each interaction are listed in **Table S2**.

Table S2 Potential parameters.

Ion Pair	D_{ij} (eV)	A_{ij} (Å^{-2})	R_0 (Å)	C_{ij} (eV Å^{12})
$Li^{0.6}$ – $O^{-1.2}$	0.00111400	3.429506	2.681360	1.0
$La^{1.8}$ – $O^{-1.2}$	0.00016219	2.023100	4.400680	3.0
$Ti^{2.4}$ – $O^{-1.2}$	0.02423500	2.254703	2.708943	1.0
$O^{-1.2}$ – $O^{-1.2}$	0.04239500	1.379316	3.618701	22.0

The energies of bulk and grain boundaries are calculated using our in-house code METADISE,[1] and the potential parameters of **Table S2**. We first generate the GB models using METADISE, which implements classical energy minimization schemes. This procedure is well established. A surface with specific Miller index is generated from the minimized bulk structure. The surface is then mirrored to create a starting model of the grain boundary. The mirrored surface is then moved along an imaginary grid parallel to the grain boundary plane. At each point of the grid an energy minimization takes place. This allows us to generate a topological map Energy vs. coordinate of the grain boundary.

The energies in the **Equation 1** (in the main manuscript) are obtained directly from the energy minimizations, where E_{gb} is the energy of the grain-boundary unit cell and E_b is the energy of the bulk that contains the same number of species as the GB model. A is the area of the GB plane. We then take the GB configuration with the lowest energy and produce a model for classical molecular dynamics (MD) simulations. The DL_POLY code is then used to perform the classical MD simulations together with the potential parameters of **Table S2**.

We use DL_POLY[2] to perform the production MD simulations. Using an NPT ensemble with a time step of 1fs, we first anneal the GB structures at relatively high temperatures. This step ensures that the structure of the GB is stable over the entire temperature range considered. At each temperature, we then minimize the volume of our GB model using an NPT ensemble with 1fs timestep for a total of 5ns production run. This ensures the equilibration of the structure in terms of volume at a specific temperature. Thus, we perform the MD simulation at fixed volume and temperature (i.e., NVT ensemble). The MSDs are then computed, from which we extract the diffusion coefficients, as well as the electrostatic potentials.

S3 Grain Boundary Potential Energy Surfaces

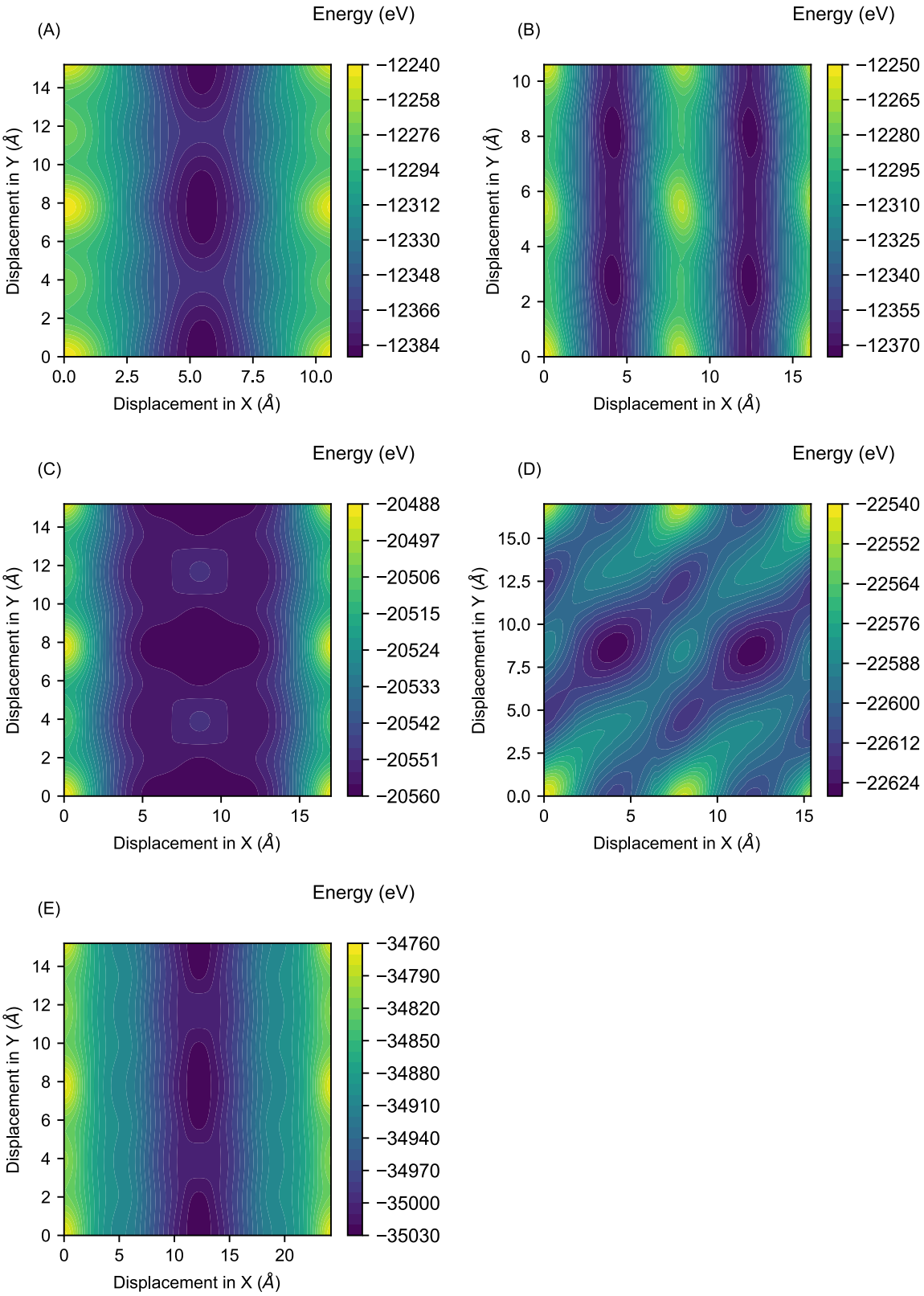

Figure S1 Panels (A) to (E) show the potential energy surfaces of the Σ2(110), Σ3(111), Σ5(210), Σ3(211) and Σ5(310) grain boundaries, respectively. Violet regions identify energetically stable regions.

S4 Σ2(110) Li/La-ion Density Maps

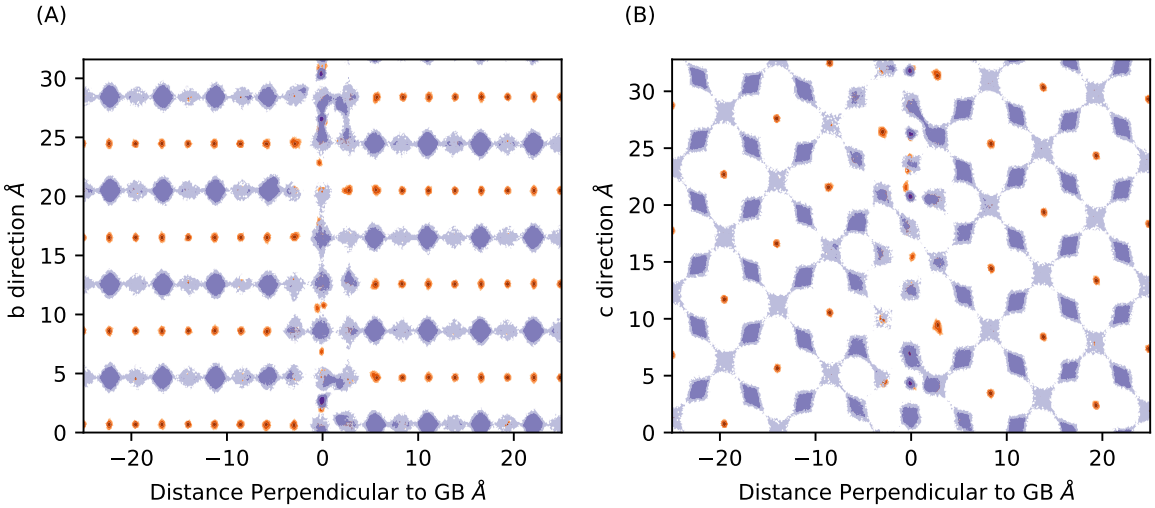

Figure S2 Panels (A) and (B) show the Li-ion density maps in the Σ2(110) grain boundary. The centre of mass of all Li and La atoms has been displayed in purple and orange. The GB is located at 0 Å in these plots.

S5 Σ3(111) Li/La-ion Density Maps

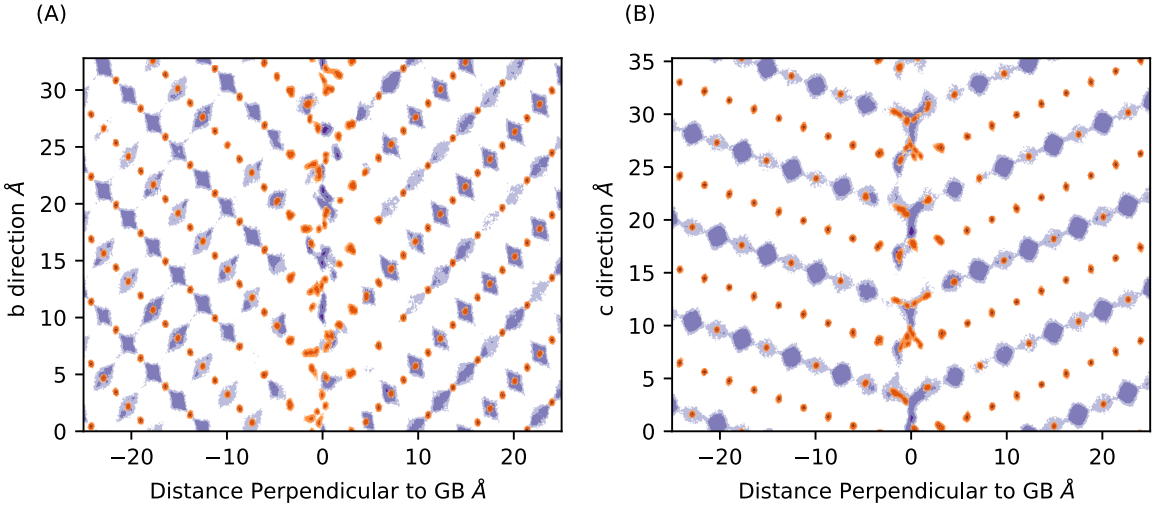

Figure S3 Panels (A) and (B) show the Li-ion density maps in the Σ3(111) grain boundary. The centre of mass of all Li and La atoms has been displayed in purple and orange. The GB is located at 0 Å in these plots.

S6 Σ5(210) Li/La-ion Density Maps

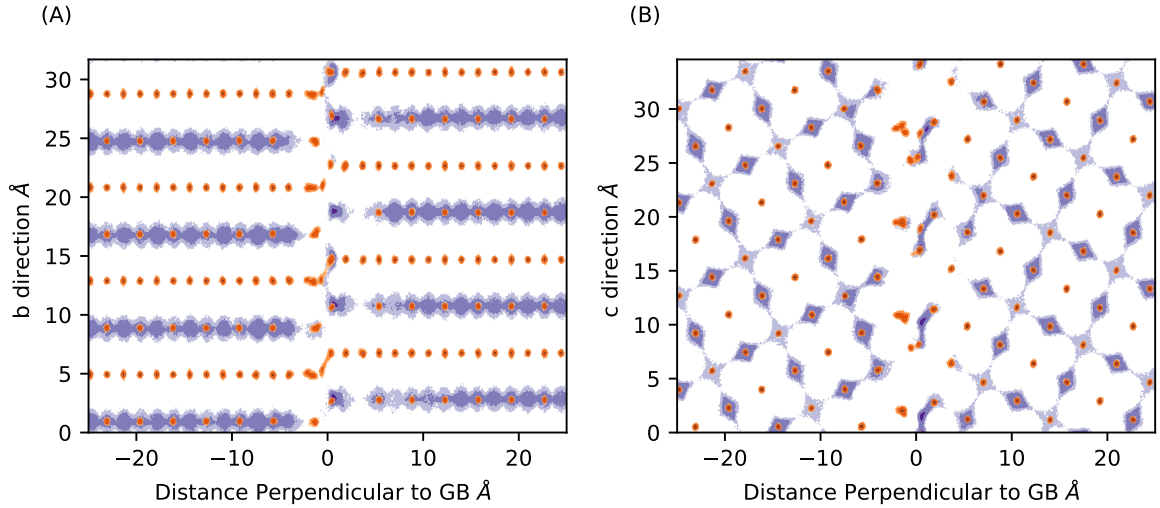

Figure S4 Panels (A) and (B) show the Li-ion density maps in the Σ5(210) grain boundary. The centre of mass of all Li and La atoms has been displayed in purple and orange. The GB is located at 0 Å in these plots.

S7 Σ3(211) Li/La-ion Density Maps

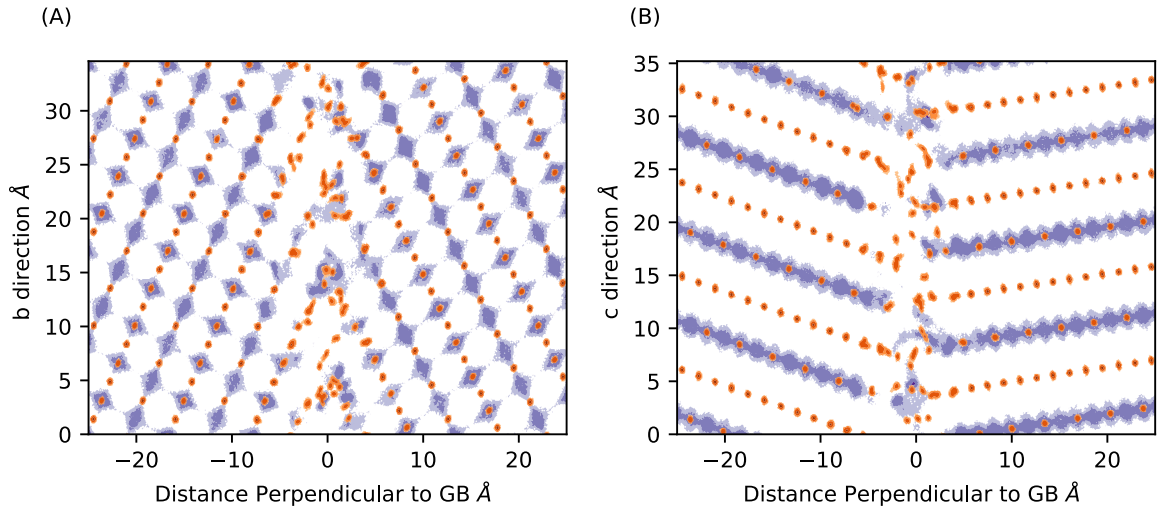

Figure S5 Panels (A) and (B) show the Li-ion density maps in the Σ3(211) grain boundary. The centre of mass of all Li and La atoms has been displayed in purple and orange. The GB is located at 0 Å in these plots.

S8 Σ5(310) Li/La-ion Density Maps

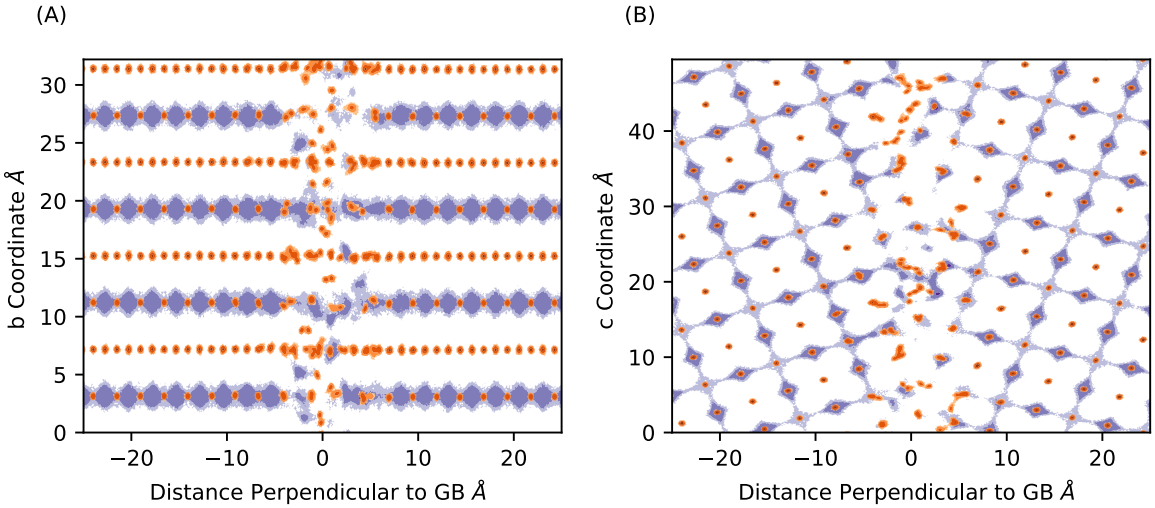

Figure S6 Panels (A) and (B) show the Li-ion density maps in the Σ5(310) grain boundary. The centre of mass of all Li and La atoms has been displayed in purple and orange. The GB is located at 0 Å in these plots.

S9 Li-ion Mobility and Average Coordination Number

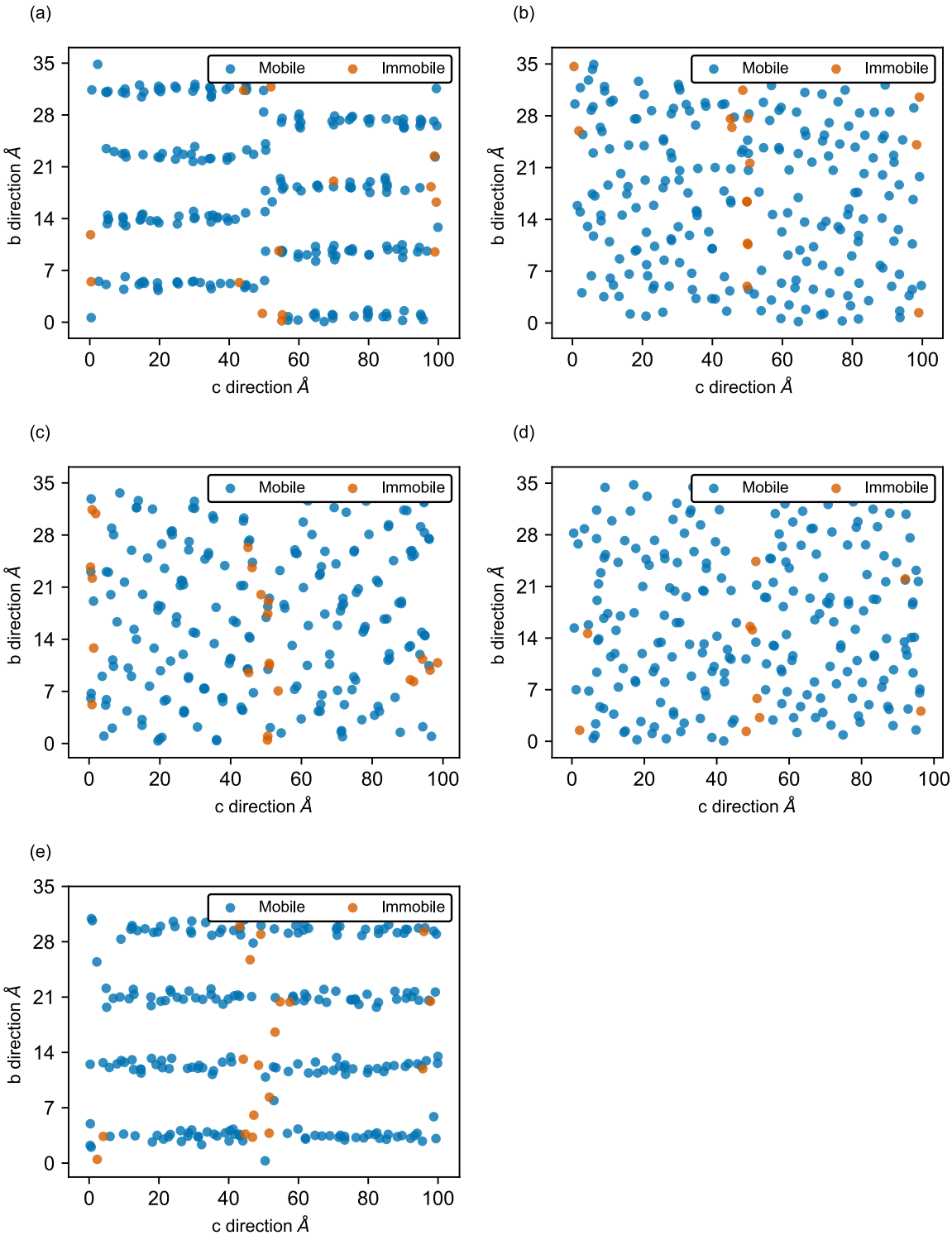

Figure S7 Mobile (blue) and immobile (red) Li ions in Σ2(110), Σ3(111), Σ5(210), Σ3(211) and Σ5(310) grain boundaries along the *b* and *c* directions of the model structures.

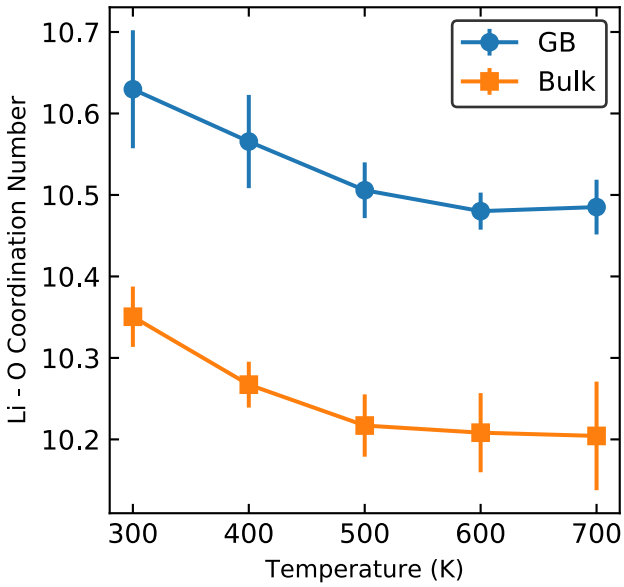

Figure S8 Average coordination number of Li-ions in the GB and the bulk as function of temperature.

References

1. Watson, G. W.; Parker, S. C.; Kresse, G., Ab initio calculation of the origin of the distortion of α-PbO. *Physical Review B* **1999,** *59* (13), 8481-8486.
2. Smith, W.; Forester, T. R., DL_POLY_2.0: A general-purpose parallel molecular dynamics simulation package. *Journal of Molecular Graphics* **1996,** *14* (3), 136-141.