Supporting Information

Atomic-Scale Study of the Influence of Grain Boundary Defects in Polycrystalline Oxide Solid-State Electrolytes on Li-Ion Conductivity

Han Li[a], Zhonglin Zhang[a], Longfei Li[a], Tao Wang[a], Feng Zhang[c], Rui Cai[d], Bingbing Chen[b,*], Jianqiu Zhou[a,b,*]

[a] Department of Mechanical and Power Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu Province, China

[b] Department of Energy Science and Engineering, Nanjing Tech University, Nanjing, 211816, Jiangsu Province, China

[c] School of Mechanical Engineering, Nanjing Institute of Technology, Nanjing, 211167, Jiangsu Province, China

[d] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing, 211816, China

*Corresponding Author: Jianqiu Zhou, E-mail: zhou@njtect.edu.cn and Bingbing Chen, E-mail: chenbb@njtech.edu.cn

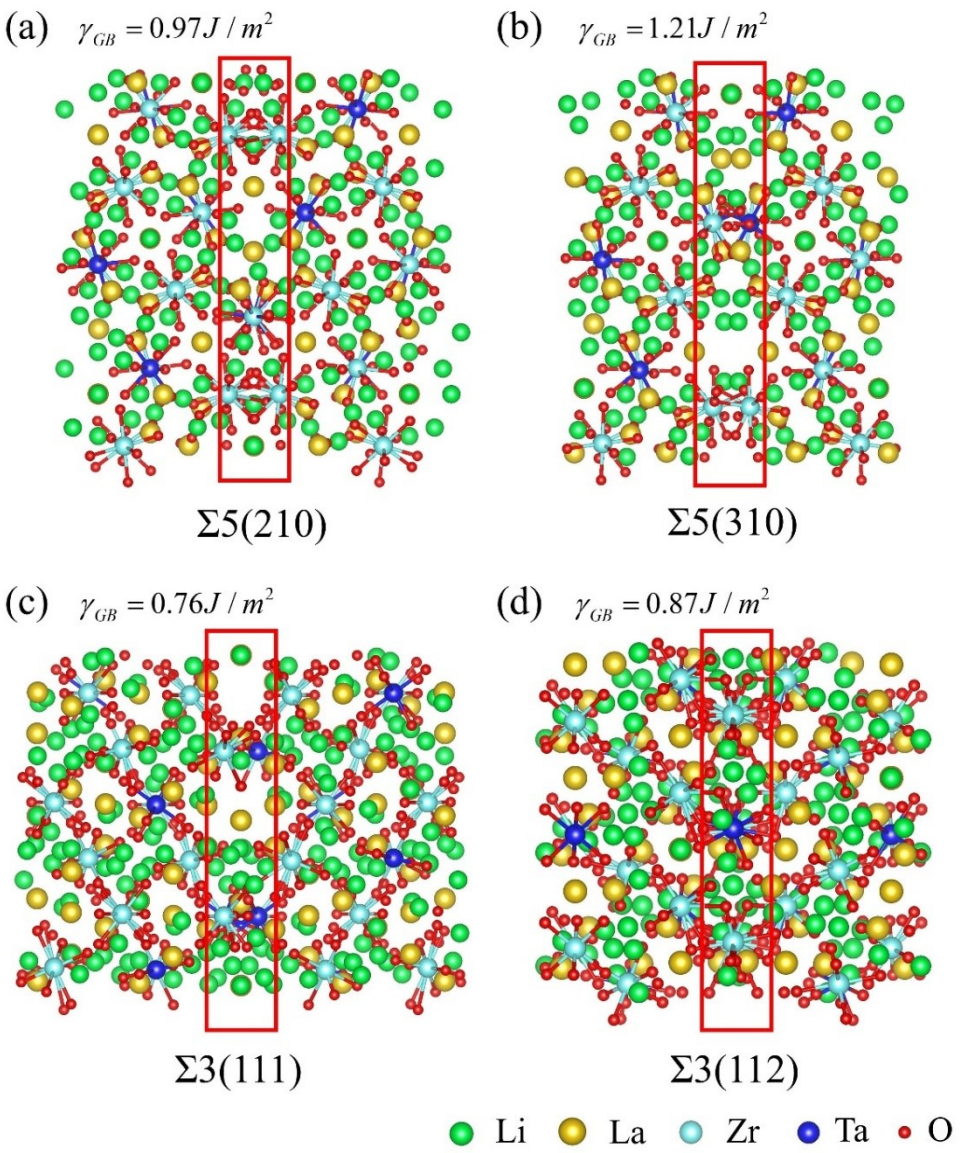

Fig. S1 Initial GB structure of LLZTO and GB formation energy at 298 K: (a) Σ5(210), (b) Σ5(310), (c) Σ3(111), and (d) Σ3(112). Where blue is Li atoms, yellow is La atoms, light blue is Zr atoms, dark blue is Ta atoms, and red is O atoms.

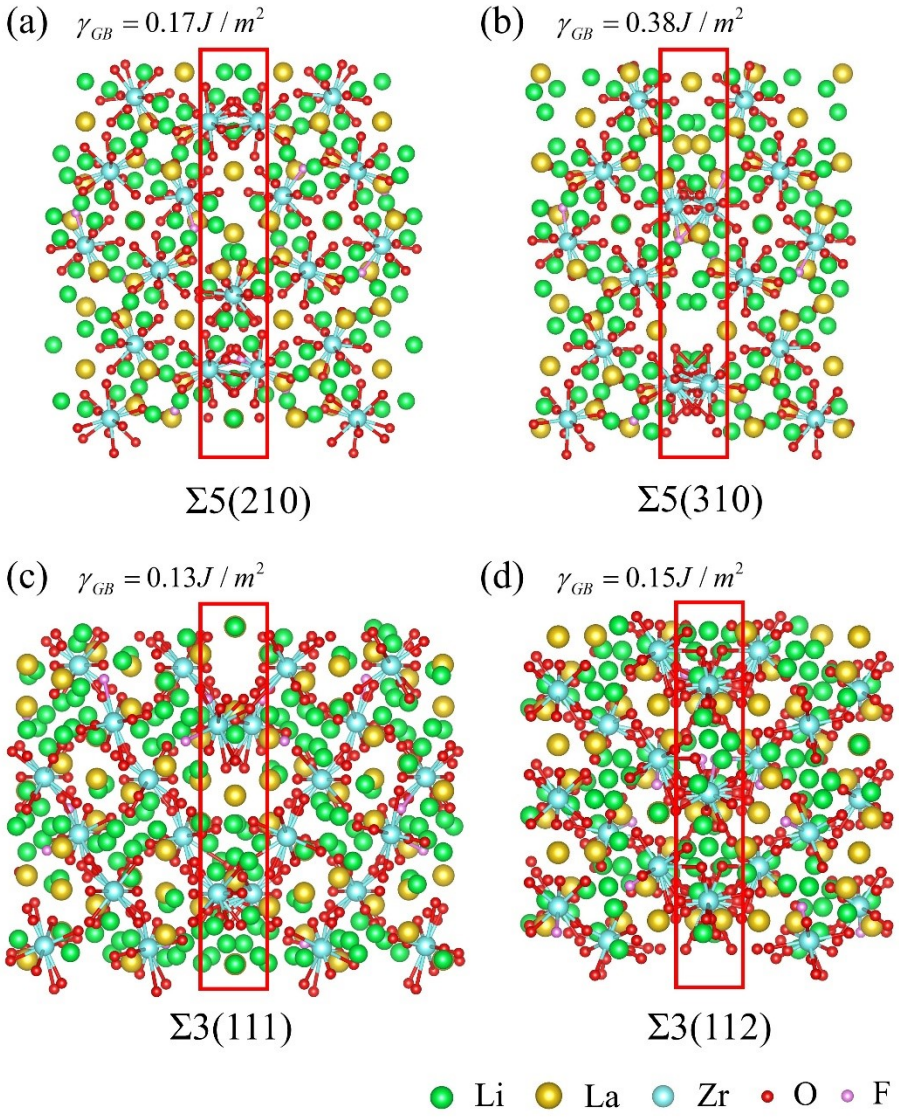

Fig. S2 Initial GB structure of LLZOF and GB formation energy at 298 K: (a) Σ5(210), (b) Σ5(310), (c) Σ3(111), and (d) Σ3(112). Where blue is Li atoms, yellow is La atoms, light blue is Zr atoms, red is O atoms, and pink is F atoms.

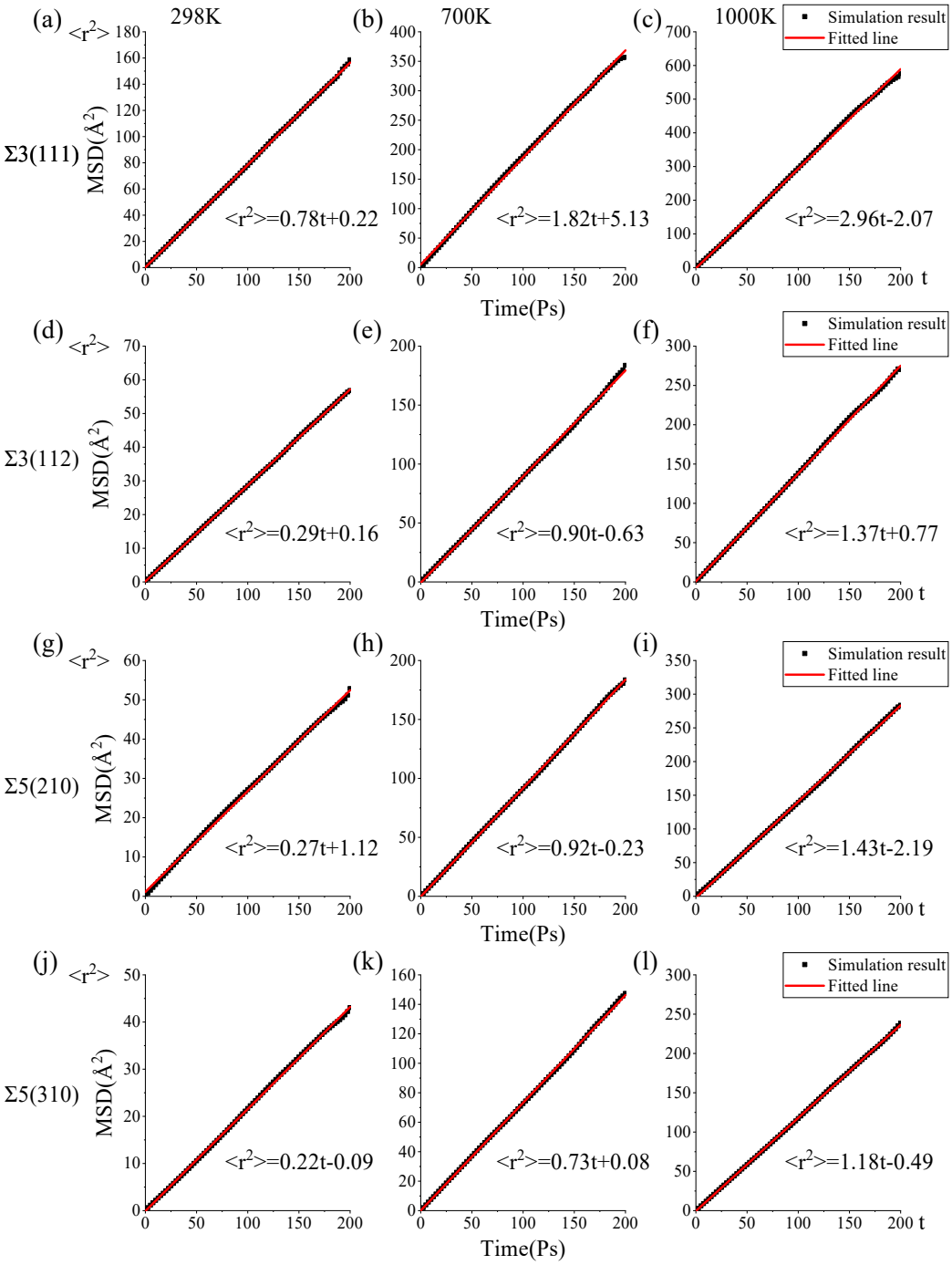

Fig. S3 MSD of Σ3(111), Σ3(112), Σ5(210), and Σ5(310) GB in LLZO at different temperatures (T=298K, 700K, 1000K).

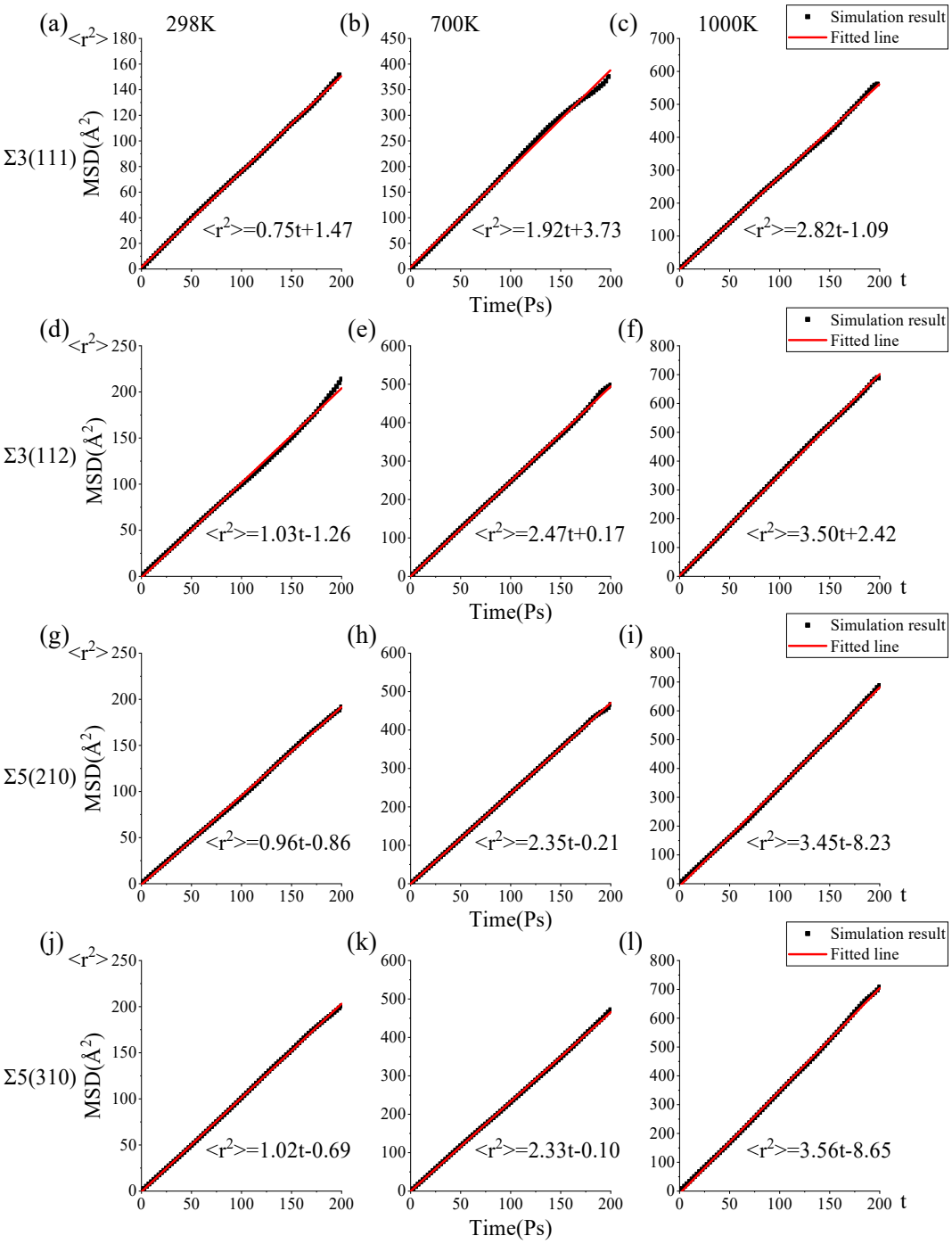

Fig. S4 MSD of Σ3(111), Σ3(112), Σ5(210), and Σ5(310) GB in LLZTO at different temperatures (T=298K, 700K, 1000K)

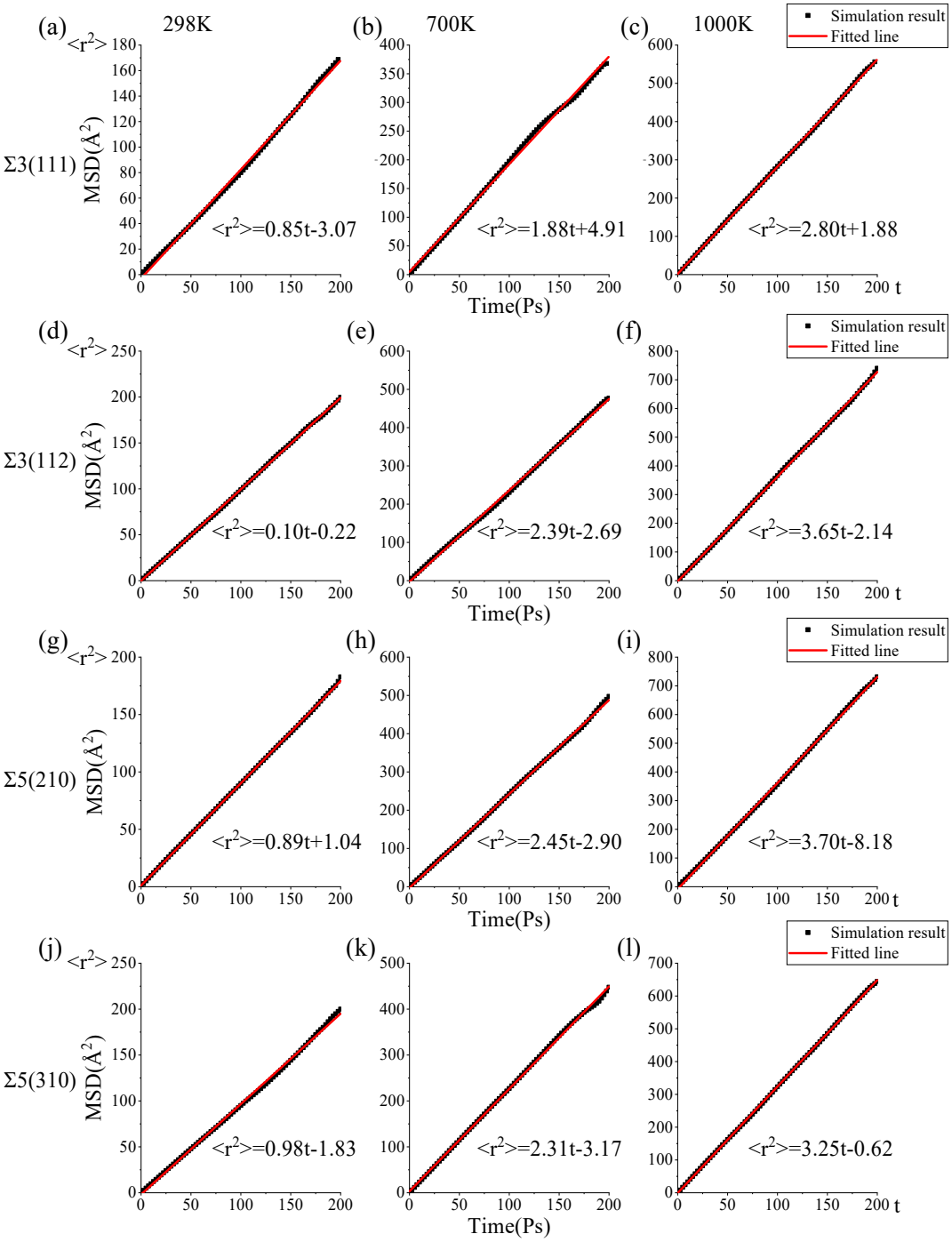

Fig. S5 MSD of Σ3(111), Σ3(112), Σ5(210), and Σ5(310) GB in LLZOF at different temperatures (T=298K, 700K, 1000K)

Total conductivity model

Resistance (R) is the inverse ratio of geometric parameter length (l) and conductivity (σ)[1]:

$$R = \frac{l}{\sigma A} \tag{S1}$$

The calculation of total conductivity is derived from the two Li-ion conduction paths shown in Figure 8. The circuit model of the two conduction modes is shown in Figure S6: Li-ion conduction cross the GB and conduction along the GB respectively.

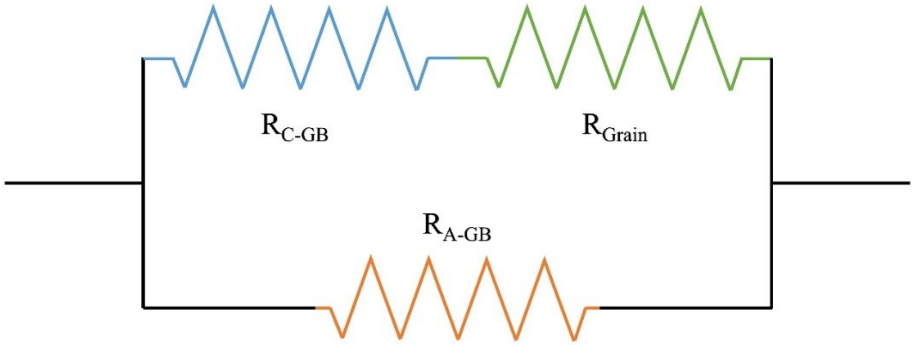

Fig. S6 DC circuit model of two Li-ion conduction paths (where the resistances of Cross-grain conduction are $R_{C\text{-}GB}$ and R_{Grain}, and the resistance of along-grain conduction is $R_{A\text{-}GB}$).

The total resistance R_{Total} associated with ionic conductivity is

$$R_{Total} = \left(\frac{1}{R_{C-GB} + R_{Grain}} + \frac{1}{R_{A-GB}}\right)^{-1} \tag{S2}$$

$$\frac{l_{Total}}{\sigma_{Total} A_{Total}} = \left(\frac{1}{\frac{l_{C-GB}}{\sigma_{C-GB} A_{C-GB}} + \frac{l_{Grain}}{\sigma_{Grain} A_{Grain}}} + \frac{1}{\frac{l_{A-GB}}{\sigma_{A-GB} A_{A-GB}}}\right)^{-1} \tag{S3}$$

Assuming that bending effects are not taken into account, ions migrate in a direction parallel to the applied current. Regardless of the method of ion conduction employed, the length l that ions must traverse within the electrolyte material remains

constant. Therefore $l_{Total} = l_{C-GB} + l_{Grain} = l_{A-GB}$ .When ions conduct across GBs, they must traverse the GB (with a thickness of δ) each time they reach the end of a grain, so $l_{C-GB} = \frac{l_{Total}}{\delta + d} \cdot \delta$, where d is grain size.

Under these assumptions, ionic conductivity is independent of the macroscopic sample length:

$$\sigma_{Total} A_{Total} = \frac{1}{\frac{\delta}{\delta + d} \frac{1}{\sigma_{C-GB} A_{C-GB}} + \frac{1}{\sigma_{Bulk} A_{Bulk}}} + \frac{1}{\frac{1}{\sigma_{A-GB} A_{A-GB}}} \tag{S4}$$

A parameter λ_{Grain} is introduced to express the volume fraction of grain structure of ion across conduction mechanism, λ_{GB}=1-λ_{Grain} is used to indicate the volume fraction of GB structure of Li-ion intergranular conduction mechanism, these parameters can reflect the contribution of two ionic conduction modes to the total ionic conductivity in polycrystalline samples. Assuming that the microstructure is isotropic, the conduction region of each conduction mode depends on the volume fraction of grains and GBs, then $A_{C-GB} = A_{Grain} = \lambda_{Grain} A_{Total}$ and $A_{A-GB} = \lambda_{GB} A_{Total}$, finally give the total ionic conductivity of polycrystalline samples independent of geometry:

$$\sigma_{Total} = \lambda_{Grain} \left(\frac{\delta}{\delta + d} \frac{1}{\sigma_{C-GB}} + \frac{1}{\sigma_{Grain}} \right)^{-1} + \lambda_{GB} \sigma_{A-GB} \tag{S5}$$

where σ_{Grain} is the electrical conductivity of the grain structure, σ_{C-GB} and σ_{A-GB} is the components of conductivity of ions cross GBs and conducting along GBs respectively, and $\sigma_{C-GB} = \sigma_{A-GB} = \sigma_{GB}$, thus equation (S5) simplifies to

$$\sigma_{Total} = \lambda_{Grain} \left(\frac{\delta}{\delta + d} \frac{1}{\sigma_{GB}} + \frac{1}{\sigma_{Grain}} \right)^{-1} + \lambda_{GB} \sigma_{GB} \tag{S6}$$

In order to consider the possibility of different densification behavior of

polycrystalline samples, the volume fraction of grain structure (i.e., densification) is expressed using the above definition $\lambda_{Grain} = D$.Density D is calculated as $D = \frac{\rho_{实际}}{\rho_{理论}} \times 100\%$ [2], where $\rho_{实际}=\rho_{Grain}$, $\rho_{理论}=\rho_{Grain} + \rho_{GB} \times P(E_i)$.The theoretical density and density of LLZO, LLZTO and LLZOF are calculated from the grain structure and density of four GB structures combined with energy-dependent Boltzmann distribution probability. The GB thickness (δ) of the three materials is calculated from the Boltzmann distribution probability of the four grain boundary structures: $\delta=\delta_i \times P(E_i)$.

Table S1 Structural parameters of cubic $Li_7La_3Zr_2O_{12}$ at room temperature[3]

Atom	Site	Occupancy	x	y	z
Li1	24d	0.658	3/8	0	1/4
Li2	96h	0.345	0.0745	0.706	0.603
La	24c	1	1/8	0	1/4
Zr	16a	1	0	0	0
O	96h	1	0.284	0.106	0.194

Table S2 Parameters for the Buckingham interatomic potential for LLZO[4]

Species	z(e)	A(eV)	ρ(Å)	C(eVÅ^6)
Li	1.00	1087.29	0.260	0.00
La	2.50	2075.26	0.326	23.25
Zr	2.65	1650.32	0.311	5.10
O	-1.65	4870.00	0.267	77.00

Table S3 Parameters used to calculate the total conductivity of polycrystalline solid electrolyte at 298K

Grain	LLZO	LLZTO	LLZOF
ρ (gcm^{-3})	5.013	5.195	5.172
σ (Scm^{-1})	2.44×10^{-4}	5.19×10^{-4}	4.81×10^{-4}

Table S4 Parameters used to calculate the total conductivity of polycrystalline LLZO samples at 298K.

GB	Σ5(310)	Σ5(210)	Σ3(112)	Σ3(111)
γ_{GB} （Jm^{-2}）	1.30	1.11	1.00	0.87
δ (Å)	12.70	13.71	21.53	18.72
ρ (gcm^{-3})	4.029	4.641	4.546	4.552
σ (Scm^{-1})	4.54×10^{-5}	4.87×10^{-5}	5.44×10^{-5}	1.04×10^{-4}

Table S5 Parameters used to calculate the total conductivity of polycrystalline LLZTO samples at 298K.

GB	Σ5(310)	Σ5(210)	Σ3(112)	Σ3(111)
γ_{GB} （Jm^{-2}）	1.21	0.97	0.87	0.76
δ (Å)	14.43	15.41	22.47	21.2
ρ (gcm^{-3})	4.673	4.362	4.213	4.645
σ (Scm^{-1})	1.26×10^{-4}	1.15×10^{-4}	1.38×10^{-4}	1.22×10^{-4}

Table S6 Parameters used to calculate the total conductivity of polycrystalline LLZOF samples at 298K.

GB	Σ5(310)	Σ5(210)	Σ3(112)	Σ3(111)
γ_{GB} （Jm^{-2}）	0.38	0.17	0.15	0.13
δ (Å)	14.45	15.45	23.25	20.97
ρ (gcm^{-3})	4.583	4.250	4.112	4.524
σ (Scm^{-1})	1.03×10^{-4}	9.68×10^{-5}	1.14×10^{-4}	1.04×10^{-4}

References

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3. T. Alam and A. Das, Crystal Research and Technology, 2024, 59.
4. M. J. Klenk and W. Lai, Solid State Ionics, 2016, 289, 143-149.