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Supporting information for

Atomistic Insight into Dopant Impacts at the Garnet $Li_7La_3Zr_2O_{12}$ Solid Electrolyte Grain Boundaries

Bo Gao[a,*], Randy Jalem[a,b,c], Yoshitaka Tateyama[a,b,*]

[a]*Center for Green Research on Energy and Environmental Materials (GREEN) and International Center for Materials Nanoarchitectonics (MANA), NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

[b]*Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan*

[c]*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 333-0012, Japan*

Email: GAO.Bo@nims.go.jp, TATEYAMA.Yoshitaka@nims.go.jp

Supplementary Methods

To understand the Li^+ diffusion at GB, the diffusion coefficient (D) was calculated based on the time average mean squared displacement (MSD) of Li^+ over a time t

$$D = \frac{1}{2Ndt}\sum_{i=1}^{N}\left\langle [r_i(t+t_0) - r_i(t_0)]^2 \right\rangle , \quad \text{(S1)}$$

where N and d refer to the total number of Li^+ and the dimensionality in the system, respectively. t_0 is the initial time, and $r_i(t)$ represents the displacement of the i-th Li^+ at time t.

Here the activation energy (E_a) is evaluated using the Arrhenius formula

$$D(T) = D_0 \times e^{-\frac{E^a}{k_B T}}. \quad \text{(S2)}$$

where D_0 is the pre-exponential factor, and k_B is the Boltzmann constant.

The Li^+ conductivity at specific temperature [$\sigma(T)$] is calculated using Nernst-Einstein equation,

$$\sigma(T) = \frac{e^2 C}{k_B T} D(T) \quad \text{(S3)}$$

where C is the Li^+ number concentration.

For the Li−Li space-time correlation, the distinct part of the van Hove space-time correlation function[1] was calculated using

$$G_d(r,t) = \frac{1}{N}\sum_i \sum_{j \neq i} \left\langle \delta(r - |r_i(t) - r_j(0)|) \right\rangle \quad \text{(S4)}$$

where N is the number of Li^+ ions, $\delta(\cdot)$ is the three- dimensional Dirac delta function, and r_j and r_i are displacements of particles j and i, respectively, at time t.

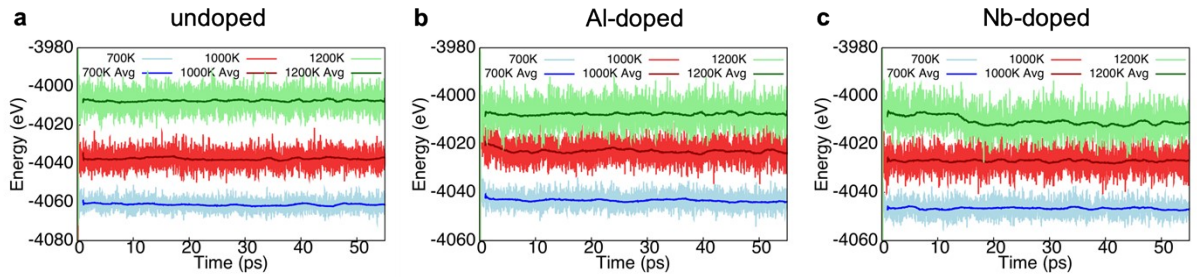

Figure S1 Energy evolutions and corresponding energies averaged over 2000 steps in the MD simulations of (a) undoped, (b) Al-doped and (c) Nb-doped Σ3(112) GB models at 700 K, 1000 K and 1200 K.

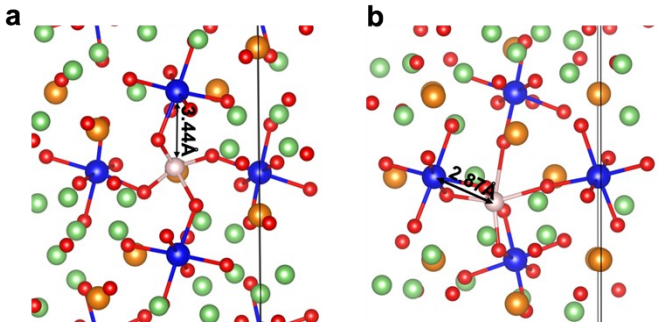

Figure S2 Local configurations of (a) Li($24d_1$) and (b) Li(96h) sites in c-LLZO bulk. The number is the nearest distance between Li and Zr ions in each figure.

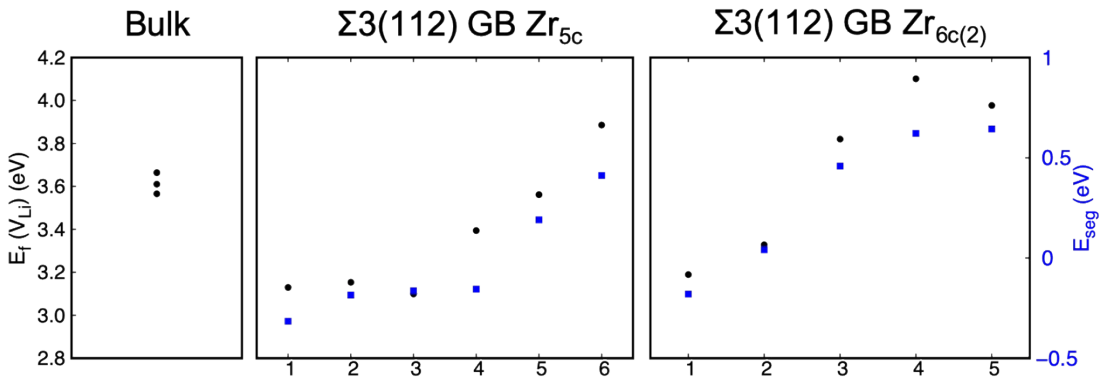

Figure S3 Calculated Li vacancy formation energies [$E_f(V_{Li})$] for the selected sites in bulk and Σ3(112) GB, and corresponding segregation energies of Nb dopant located at the Zr_{5c} and $Zr_{6c(2)}$ at the Σ3(112) GB.

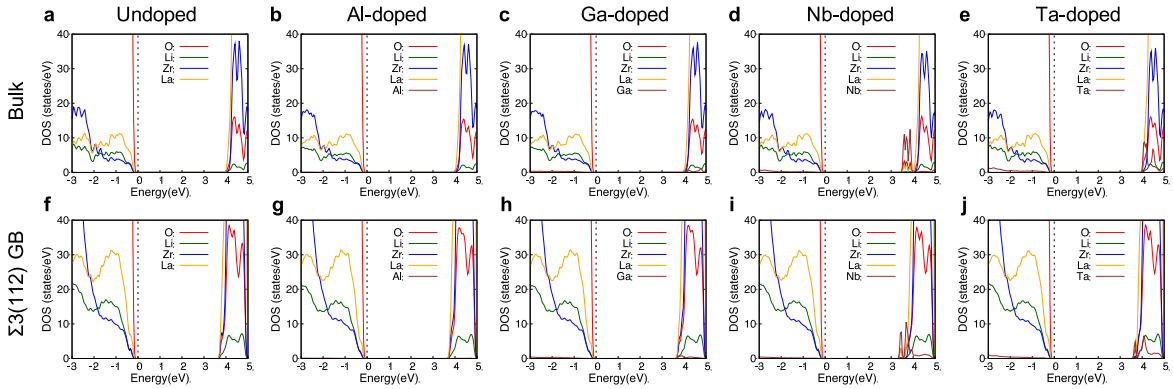

Figure S4 Partial densities of states of (a) undoped and (b-e) doped LLZO bulks, and (f) pristine and doped (g-j) Σ3(112) GB models. Here the dashed lines indicate the Fermi levels. Here the energetically most stable structures are selected for doped bulks and GB models.

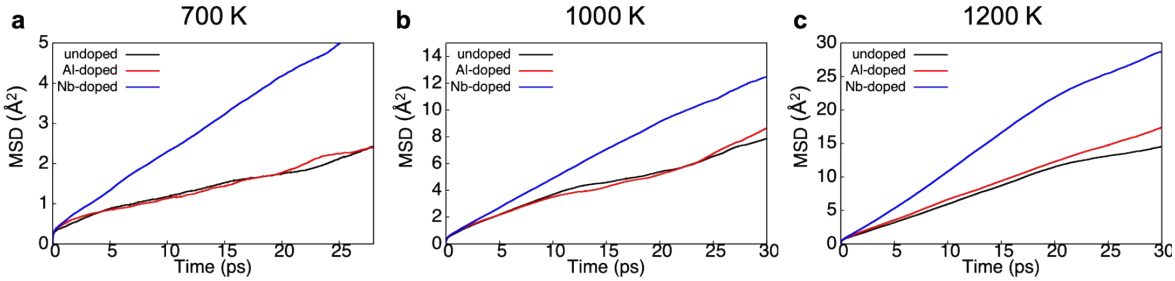

Figure S5 Time average MSD profiles of Li for undoped, and Al and Nb-doped Σ3(112) GB models at temperatures of (a) 700, (b) 1000 and (c) 1200 K.

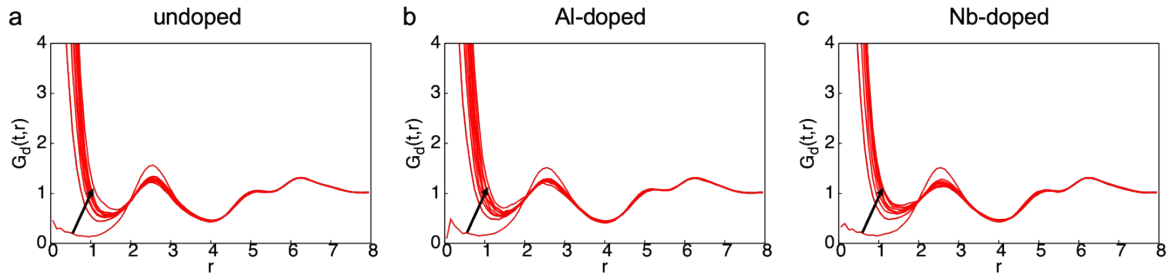

Figure S6 Distinct part $G_d(t,r)$ of van Hove correlation function for the Li diffusion in the range of 20-55 ps in (a) undoped, (b) Al-doped and (c) Nb-doped Σ3(112) GB models. Arrows indicate the direction of change with respect to time.

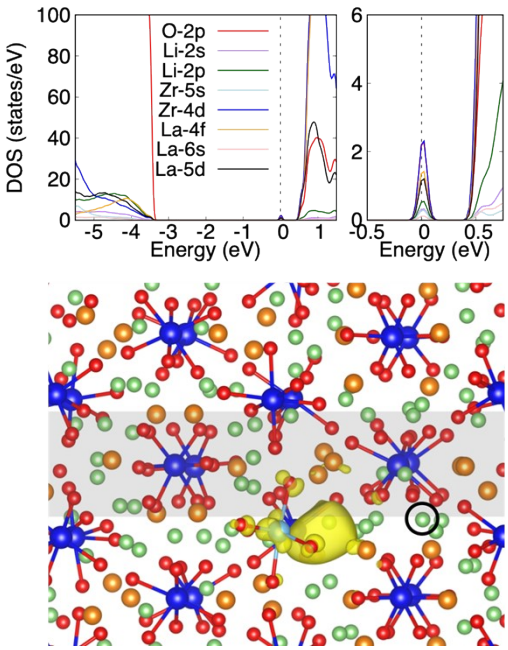

Figure S7 (upper panel) PDOSs and (lower panel) partial charge density associated with the states in the energy range from −0.1 to 0.1 eV of Σ3(112) GB model with a Li_i in the GB region.[2] In the PDOSs, the dashed lines indicate the Fermi levels. The upper right panel refers to the enlarged PDOS around the Fermi level. For the partial charge density, the isosurface is set to 0.005 e $bohr^{-3}$. The Li_i site is highlighted using the black circle. The grey area indicates the GB region.

Table S1 The reactions with relatively higher E_r for doped LLZO decomposing into the pristine LLZO and corresponding ternary oxides. For comprehensive, the datas in Table 2 in the main text are also included.

	E_r (eV)
Al-doped	
$Li_{53}AlLa_{24}Zr_{16}O_{96} + 4Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + Li_5AlO_4$	-1.12
$Li_{53}AlLa_{24}Zr_{16}O_{96} + 2Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + LiAlO_2$	-0.86
$Li_{53}AlLa_{24}Zr_{16}O_{96} + 1.5Li_2O + La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.5La_4Al_2O_9$	-0.69
$Li_{53}AlLa_{24}Zr_{16}O_{96} + 1.5Li_2O + 0.5La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + LaAlO_3$	-0.54
$Li_{53}AlLa_{24}Zr_{16}O_{96} + 1.6Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.2LiAl_5O_8$	-0.38
Ga-doped	
$Li_{53}GaLa_{24}Zr_{16}O_{96} + 4Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + Li_5GaO_4$	-1.21
$Li_{53}GaLa_{24}Zr_{16}O_{96} + 2Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + LiGaO_2$	-0.93
$Li_{53}GaLa_{24}Zr_{16}O_{96} + 1.5Li_2O + La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.5La_4Ga_2O_9$	-0.66
$Li_{53}GaLa_{24}Zr_{16}O_{96} + 1.6Li_2O \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.2LiGa_5O_8$	-0.48
$Li_{53}GaLa_{24}Zr_{16}O_{96} + 1.5Li_2O + 0.3La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.2La_3Ga_5O_{12}$	-0.47
Nb-doped	
$Li_{55}La_{24}Zr_{15}NbO_{96} + 2.5Li_2O + ZrO_2 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + 0.5Li_8Nb_2O_9$	-1.08
$Li_{55}La_{24}Zr_{15}NbO_{96} + 2Li_2O + ZrO_2 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + Li_3NbO_4$	-0.92
$Li_{55}La_{24}Zr_{15}NbO_{96} + 0.5Li_2O + ZrO_2 + 1.5La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + La_3NbO_7$	-0.39
$Li_{55}La_{24}Zr_{15}NbO_{96} + 0.5Li_2O + ZrO_2 + 0.5La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + LaNbO_4$	-0.13
Ta-doped	
$Li_{55}La_{24}Zr_{15}TaO_{96} + 3Li_2O + ZrO_2 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + Li_5TaO_5$	-1.05
$Li_{55}La_{24}Zr_{15}TaO_{96} + 2Li_2O + ZrO_2 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + Li_3TaO_4$	-0.81
$Li_{55}La_{24}Zr_{15}TaO_{96} + 0.5Li_2O + ZrO_2 + 1.5La_2O_3 \rightarrow Li_{56}La_{24}Zr_{16}O_{96} + La_3TaO_7$	-0.34

References:

1 L. Van Hove, *Phys. Rev.*, 1954, **95**, 249–262.

2 B. Gao, R. Jalem, H.-K. Tian and Y. Tateyama, *Advanced Energy Materials*, 2021, **12**, 2102151.