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Supplementary Information

Atomic-scale origin of the large grain-boundary resistance in perovskite Li-ion-conducting solid electrolytes

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Experimental Details

Bulk ceramic samples of ($Li_{3x}La_{2/3-x}$)TiO_3 were prepared via a sol-gel approach. Appropriate amount of $LiNO_3$, $La(NO_3)_3\cdot 6H_2O$, tetrabutyl titanate, and acetylacetone (the complexing agent) were used as the starting materials. $LiNO_3$ and $La(NO_3)_3\cdot 6H_2O$ were dissolved in ethylene glycol monomenthyl ether, and then mixed with the solution of tetrabutyl titante and acetylacetone to form the sol. The gel was obtained by drying the sol at 70 °C. Calcination was performed at 900 °C for 6 hours. As-calcined ($Li_{3x}La_{2/3-x}$)TiO_3 powder was ball milled for 12 hours in isopropanol, dried, pressed into pellets with 12 mm diameter, and then sintered at 1350 °C for 6 hours. In order to minimize the loss of Li, the pellets were buried in the protective powders with the same composition during sintering. The inductively coupled plasma spectroscopy indicated $x = 0.108$ for the sintered ceramics, which was close to the nominal composition $x = 0.11$. The x-ray diffraction pattern suggested a pure perovskite phase.

In order to prepare the specimens for STEM/EELS study, a piece of ceramic with approximately 2×2 mm^2 was cut from the bulk sample, followed by mechanical grinding, polishing, and dimpling to around 20 μm thick. This procedure was performed with oil, and the direct exposure to water was strictly prevented. The dimpled ceramic was attached to a 3mm Mo aperture grid with G1 epoxy, and then Ar-ion-milled to electron transparency within the Fischione 1010 Ion Mill below -100 °C. The ion-mill was performed with 4 kV and 4 mA until perforation, and finished up with 0.5 kV and 3 mA to remove the residual amorphous layer at the surface. The specimen was stored under 10^{-6} Torr vacuum immediately after the ion mill. STEM-HAADF imaging and EELS measurements were performed on an aberration-corrected FEI Titan S 80-300 TEM/STEM equipped with a Gatan Image Filter Quantum-865 operated at 300 kV. Z-contrast HAADF imaging was performed with a probe convergence angle of 30 mrad and a large inner collection angle of 65 mrad. EELS spectra were collected in STEM mode using a dispersion of 0.25 eV per channel and a 5 mm aperture.

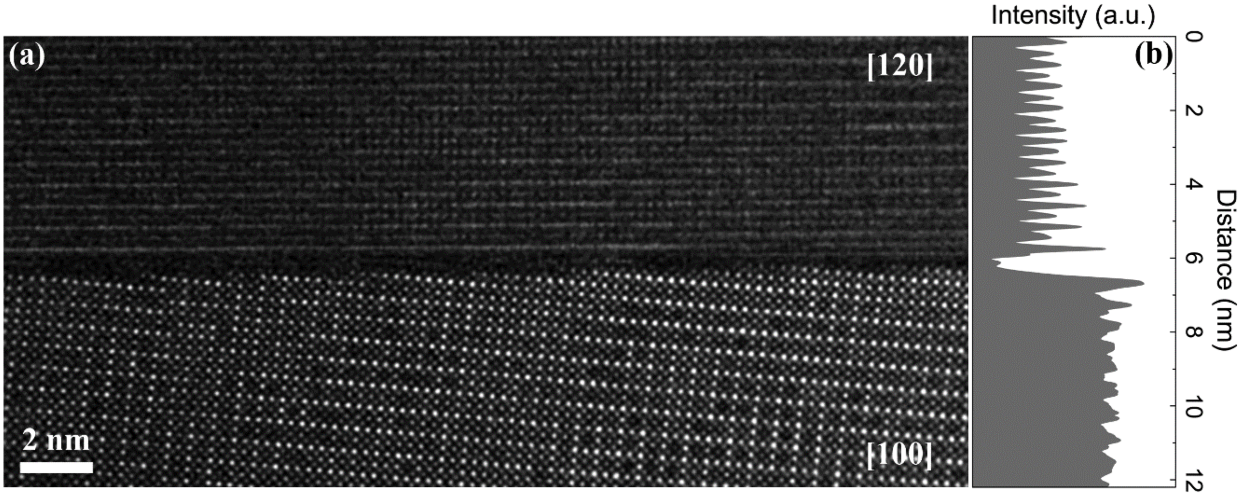

Fig. S1 (a) Z-contrast HAADF image of a grain boundary showing darker contrast. (b) Accumulated intensity profile across the grain boundary shown in (a).

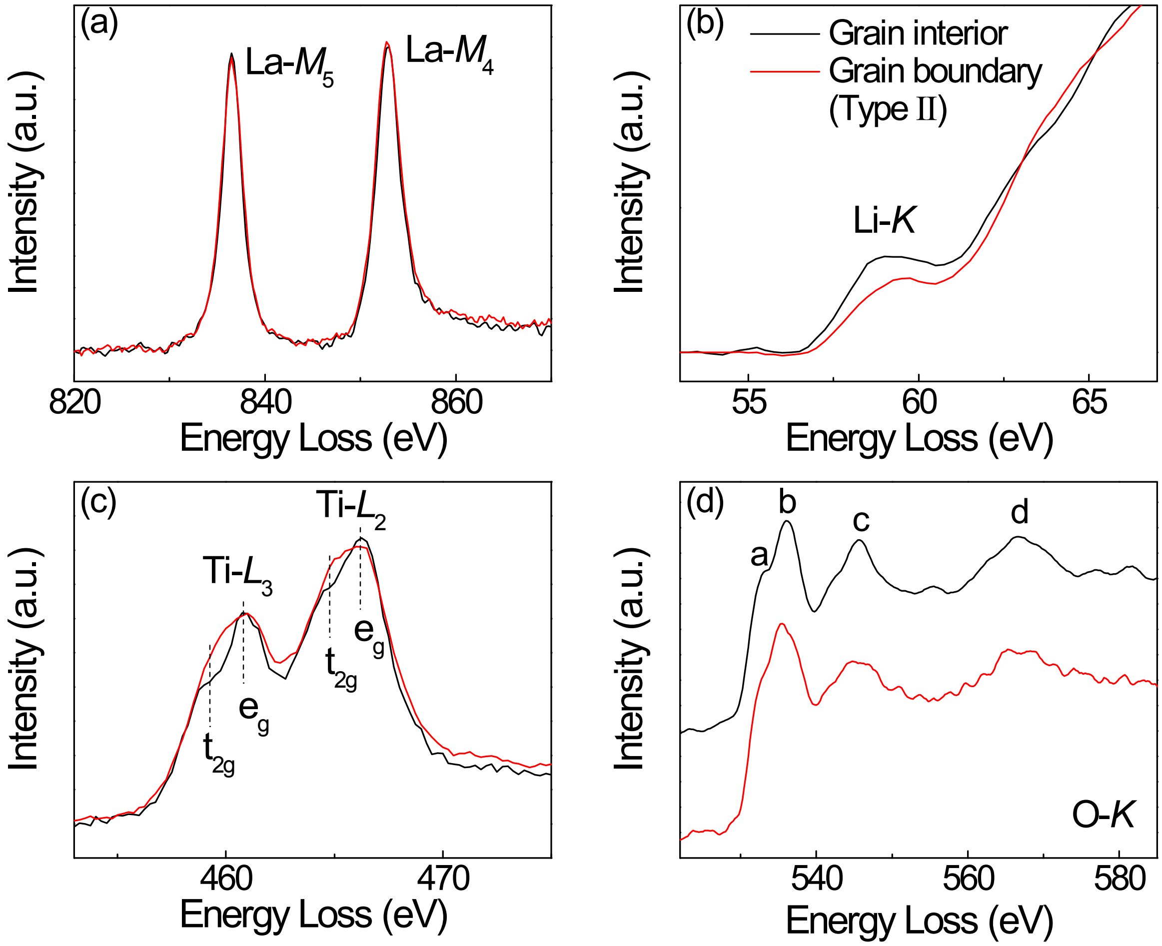

Fig. S2 EELS data of (a) La-$M_{4,5}$, (b) Li-K, (c) Ti-$L_{2,3}$, and (d) O-K edges for the Type II grain boundary and the bulk. The Ti-$L_{2,3}$ spectrum was normalized to the maximum of the Ti-L_3 edge for a straightforward comparison of the L_3/L_2 ratio. All the other spectra were normalized to the integrated intensity of the Ti-$L_{2,3}$ edge, and the normalized O-K edge of the grain interior was shifted vertically for clarification.