Supplementary Information

Thermal Properties and Lattice Anharmonicity of Li-ion Conducting Garnet Solid Electrolyte $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$

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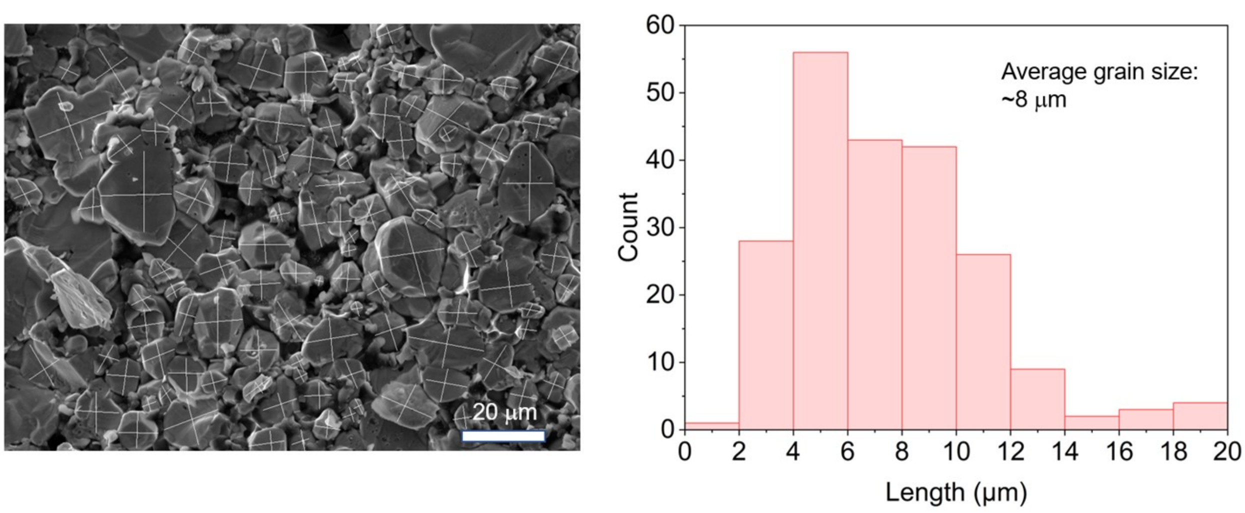

Figure S1. The analysis on SEM image to determine the average grain size of cold-pressed LLZTO sample.

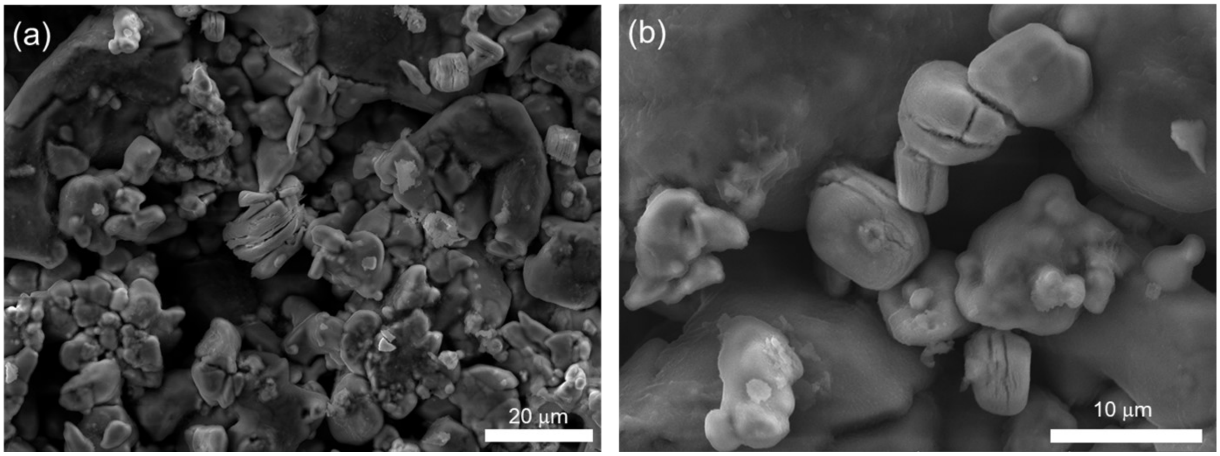

Figure S2. Additional SEM images of aged LLZTO sample showing cracked grains.

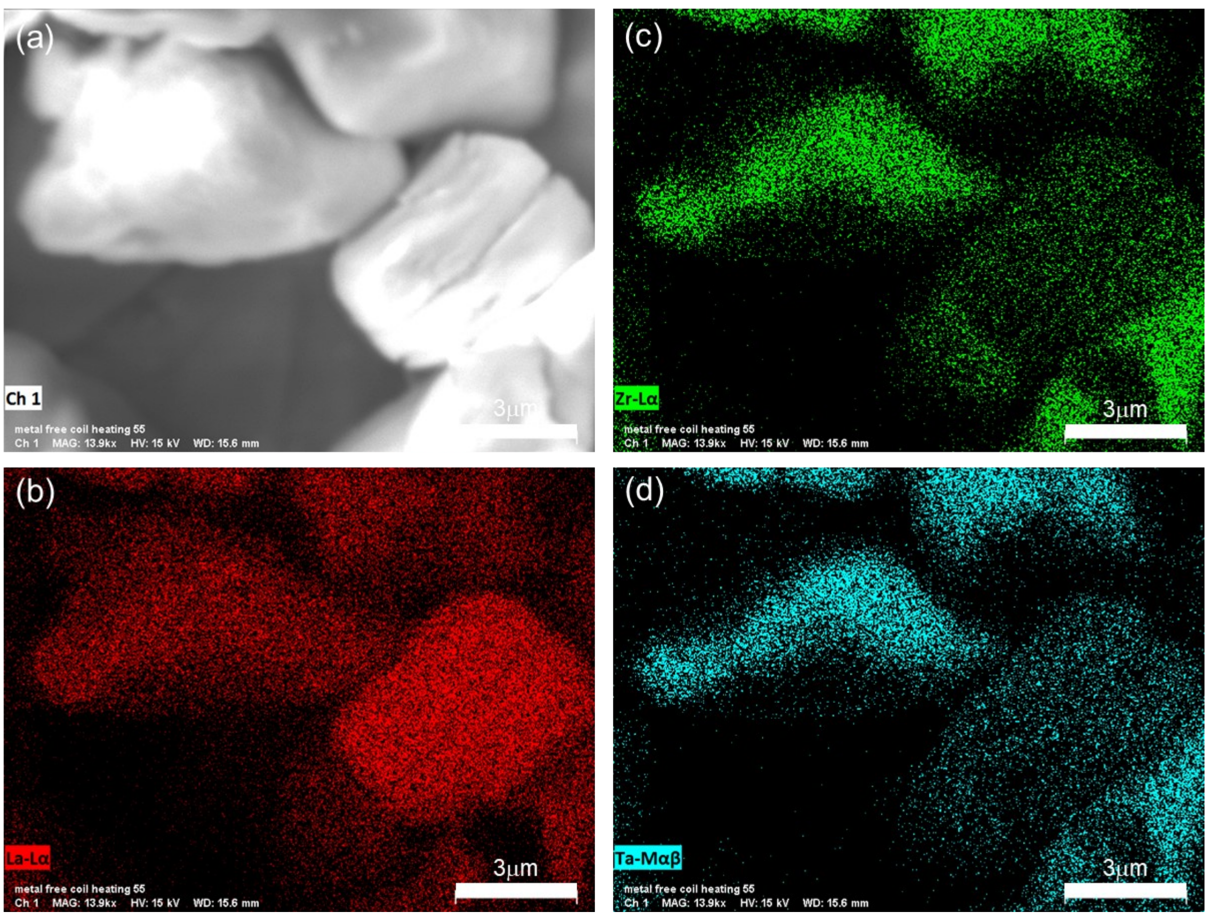

Figure S3. (a) Selected region for EDS mapping of aged LLZTO sample. (b-d) EDS mapping results of the selected region for La, Zr, and Ta elements.

Calculation of thermal boundary resistance

The thermal boundary resistance (TBR), or Kapitza resistance, arising from the grain boundaries in LLZTO was calculated for the unaged and aged samples using an effective medium approach for polycrystals.[1] The grains were treated as randomly oriented ellipsoidal crystallites with isotropic TBR and grain thermal conductivity (κ^0), which is taken as the value for single crystal LLZTO, as 1.58 W m^{-1} K^{-1} at 290 K. The TBR was calculated using an expression for measured thermal conductivity (κ) of polycrystals given by

$$\kappa/\kappa^o = \left[\sqrt{g^2 + 2f(L_{11} + 2L_{33})} + g\right]/f$$

where $L_{ii,\, i=1,\, 3}$ is the Kapitza length given by $L_{K_{ii}} = R_{K_{ii}}\kappa^0_{ii}$ with $R_{K_{ii}}$being the Kaptiza resistance along the crystallite's $X_i$axes. Additionally, g and *f* are given by

$$g = 2 - 3L_{33} + \gamma L_{11}(2 - 3L_{11})$$

$$f = 2(1 + 3L_{11})(1 + \gamma L_{11})(1 + \gamma L_{33})$$

$$\gamma = 4p^{1/3}(1 + 1/2p)L_K/d$$

where *d* is the equivalent spherical diameter synonymous with the grain size given by $d = 2(a_1^2 a_3)^{1/3}$, and *p* is the aspect ratio given by $p = \frac{a_3}{a_1}$, with a_i being the radii of the crystallite along its X_i axes. a_1 and a_3 were chosen to give a value for *d* which equates to the average grain size of 8 µm. $R_{K_{ii}}$ was then numerically solved using a nonlinear least-squares solver. It was assumed that the axes $X_{11}$and X_{33} are equivalent. The obtained TBR values for the aged and pristine samples are 5.5×10^{-4} and 9.2×10^{-4} $\frac{m^2\,K}{W}$ respectively at 290 K.

References

1. Nan, C. W., & Birringer, R. *Physical review B*, 1998, **57**, 8264-8268.