**Electronic supplementary information (ESI)** 

## Epitaxial growth and lithium ion conductivity of lithium-oxide garnet for all solid-state battery electrolyte

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## Samples for AC impedance measurements:

Schematic drawings of the samples used for the impedance measurements are shown in **Fig. S1**.  $4 \times 10 \text{ mm}^2$  sized LLZO thin films were deposited on (100)- and (111)-oriented GGG substrates ( $10 \times 10 \text{ mm}^2$ ). Prior to the impedance measurement, comb-type Au electrodes were mounted on the thin films by DC sputtering (Quick Coater SC-701, Sanyu Electron Co., Ltd.). The width and length of the Au electrodes were 1 mm and 4 mm, respectively. A needle probe was used to measure AC impedance in the in-plane direction. Lithium ionic conductivities were investigated along the in-plane [110] and [11-2] directions for the LLZO(001) and LLZO(111) thin films. The measurements were carried out in an Ar-filled glove box (DBO-1, Miwa) to prevent interfacial reactions of the thin film electrolyte with the moisture and carbon dioxide in air.



Fig. S1 Schematic drawings of samples used for the impedance measurements.

## PLD synthesis conditions for epitaxial growth of LLZO:

**Fig. S2** shows out-of-plane XRD patterns for the LLZO thin films grown on the GGG(001) substrate under various conditions. No diffraction peaks of LLZO were observed for the film grown at 600 °C. The film grown at 700 °C had 004 and 008 diffraction peaks of LLZO with a cubic lattice. The 004 peak was observed for the film grown at 800 °C; however, not only was the intensity of the 004 peak significantly decreased compared to that of the film grown at 700 °C, but also, the 008 peak was not observed. No diffraction peaks of LLZO were observed for energy fluences of 1.5 and 2.0 J cm<sup>-2</sup>, and a laser frequency of 5 Hz. Epitaxial growth was confirmed at 2.5 J

 $cm^{-2}$  and 10 Hz. Similarly to the substrate temperature, the crystallinity of the epitaxial LLZO films declined at the higher energy fluence and higher laser frequency.



Fig. S2 Out-of-plane XRD patterns of LLZO thin films on GGG(001) substrate synthesized at various (a) substrate temperatures, (b) energy fluences, and (c) laser frequencies.