## Electronic Supplementary Information for:

## Defect Chemistry and Electrical Properties of

## Garnet-Type Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>

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S1. Full-pattern fitting for synchrotron XRD of powder crushed from (a) cubic 15LLZO pellets prepared with 15% Li excess and (b) cubic 20LLZO pellets prepared with 20% Li excess.



S2. SEM micrographs of the fracture surface of sintered pellets. From left to right: 10LLZO, 15LLZO, and 20LLZO pellet.





S3. Arrhenius plots for the sintered cubic (a) 15LLZO, and (b) 20LLZO pellet.

S4. <sup>27</sup>Al MQMAS NMR spectrum of the 10LLZO sample.



S5. (a) Polarization and depolarization results obtained for the 15LLZO sample by using electron-blocking LiI electrode. (b) Polarization results obtained for the 15LLZO sample by using ion-blocking Au electrode.



S6. (a) Polarization and depolarization results obtained for the 20LLZO sample by using electron-blocking LiI electrode. (b) Polarization results obtained for the 20LLZO sample by using ion-blocking Au electrode.





