Supplementary Materials

Post-lithiation: A way to control the ionic conductivity of solid-state thin film electrolyte

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Fig. S1-S4 are the GIXRD patterns of the as-deposited films.

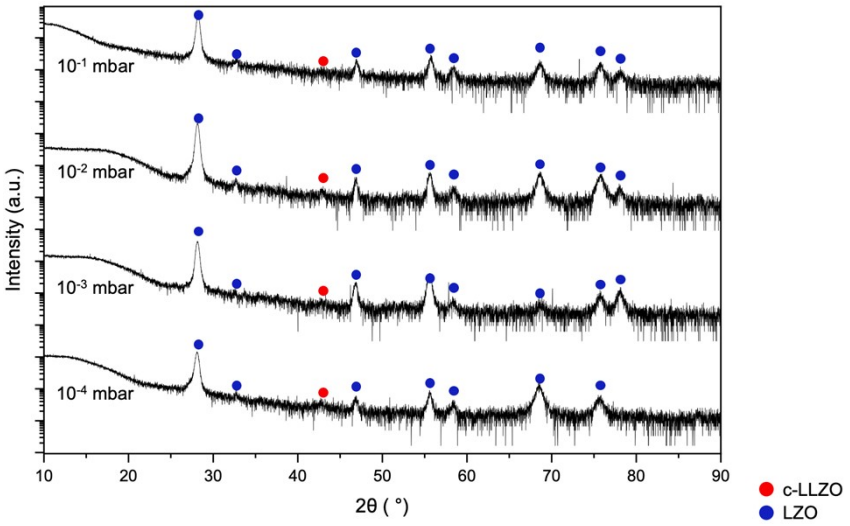

Fig. S1 GIXRD patterns of the films deposited under various oxygen pressures, the deposition temperature is kept at 700 °C and with a laser energy density of 1 J cm^{-2}. The phases of the films are almost the same while changing the oxygen pressure.

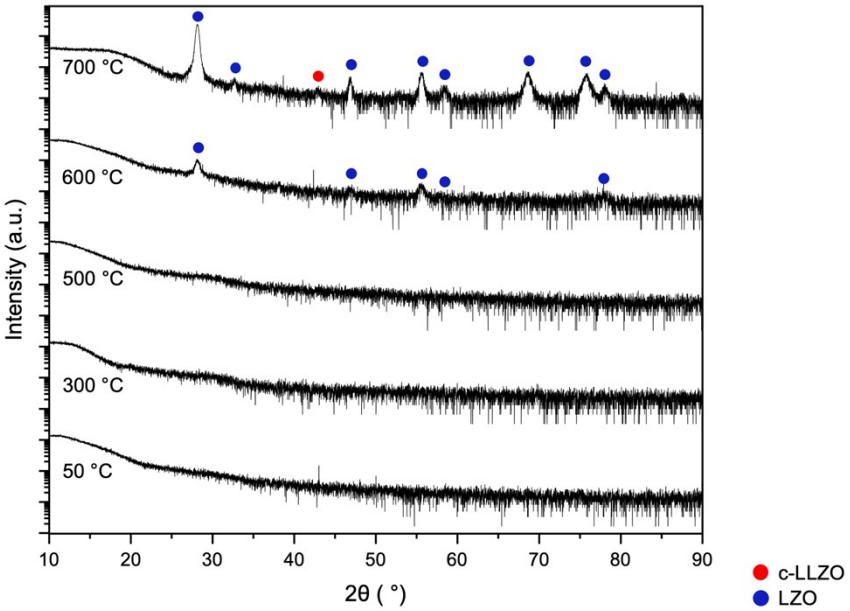

Fig. S2 GIXRD patterns of the films deposited from 50 °C to 700 °C, the oxygen pressure is kept at 1 mbar and with a laser energy density of 1 J cm^{-2}. The films are amorphous until the deposition temperature reaches 600 °C. Some LZO peaks start to show up at 600 °C, and more intense LZO peaks can be seen at 700 °C. The conclusion is that c-LLZO cannot be grown as-deposited at the specified pressure and laser fluence.

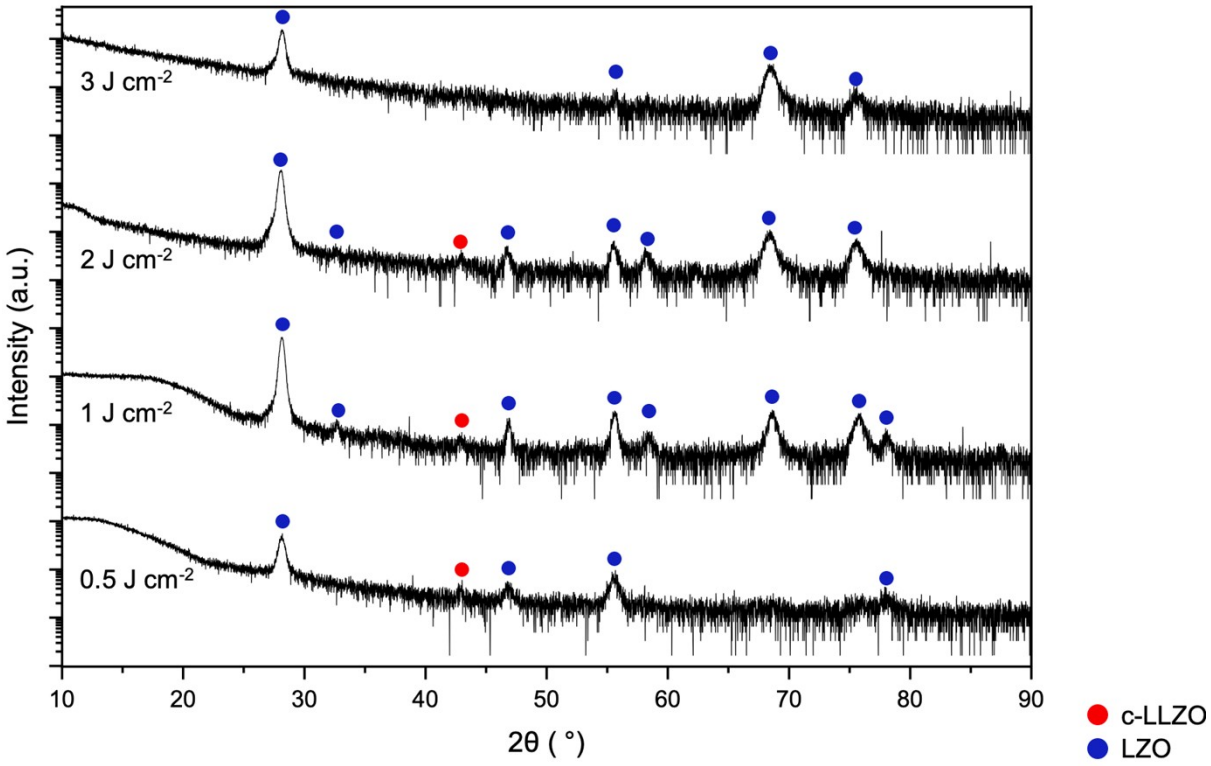

Fig. S3 GIXRD patterns of the films were deposited with a laser energy density of 1 J cm^{-2}, and the deposition temperature was kept at 700 °C with an oxygen pressure of 1 mbar. The phase of the films did not change too much when changing the laser fluence from 0.5 to 3 J cm^{-2}.

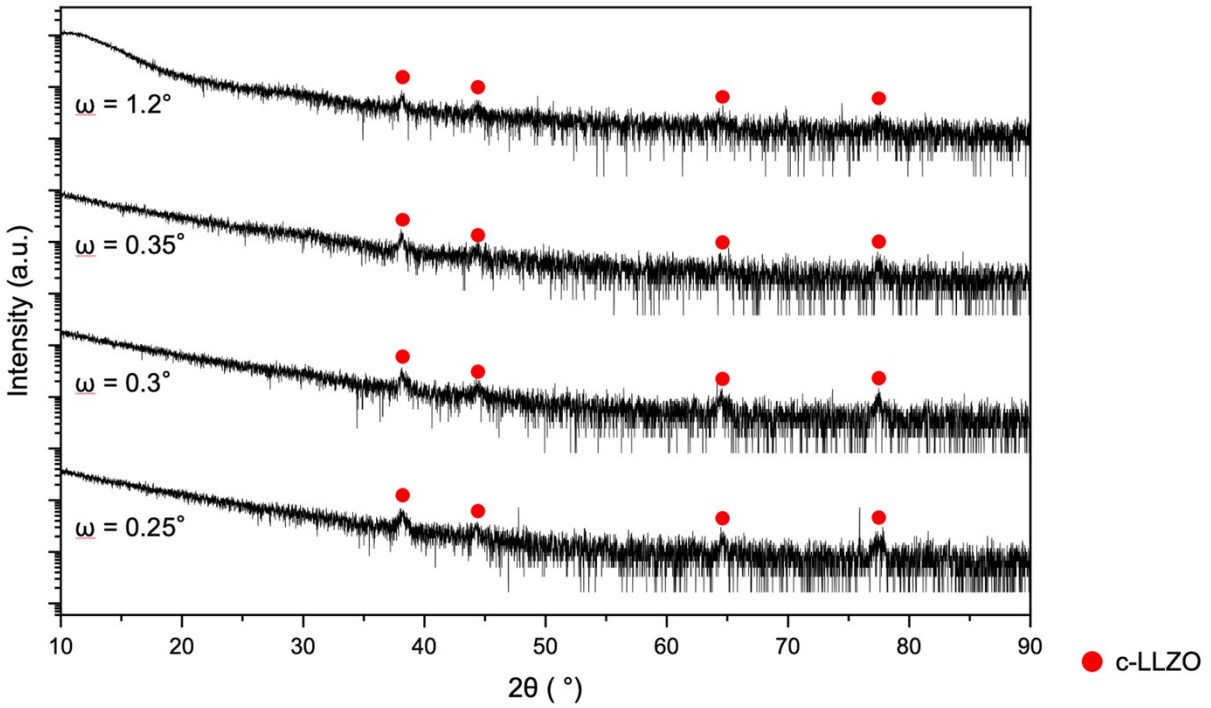

Fig. S4 GIXRD patterns of the films deposited at 50 °C, with a laser energy density of 1 J cm^{-2} and an oxygen pressure of 1 mbar. The intensity of the peaks started to decrease when the incident angle reached 0.3°, thus the thickness of the c-LLZO film is equivalent to the penetration depth of the X-ray with an incident angle of 0.3° applied on LLZO.

Fig. S5-S8 are the GIXRD patterns of the post-lithiated films.

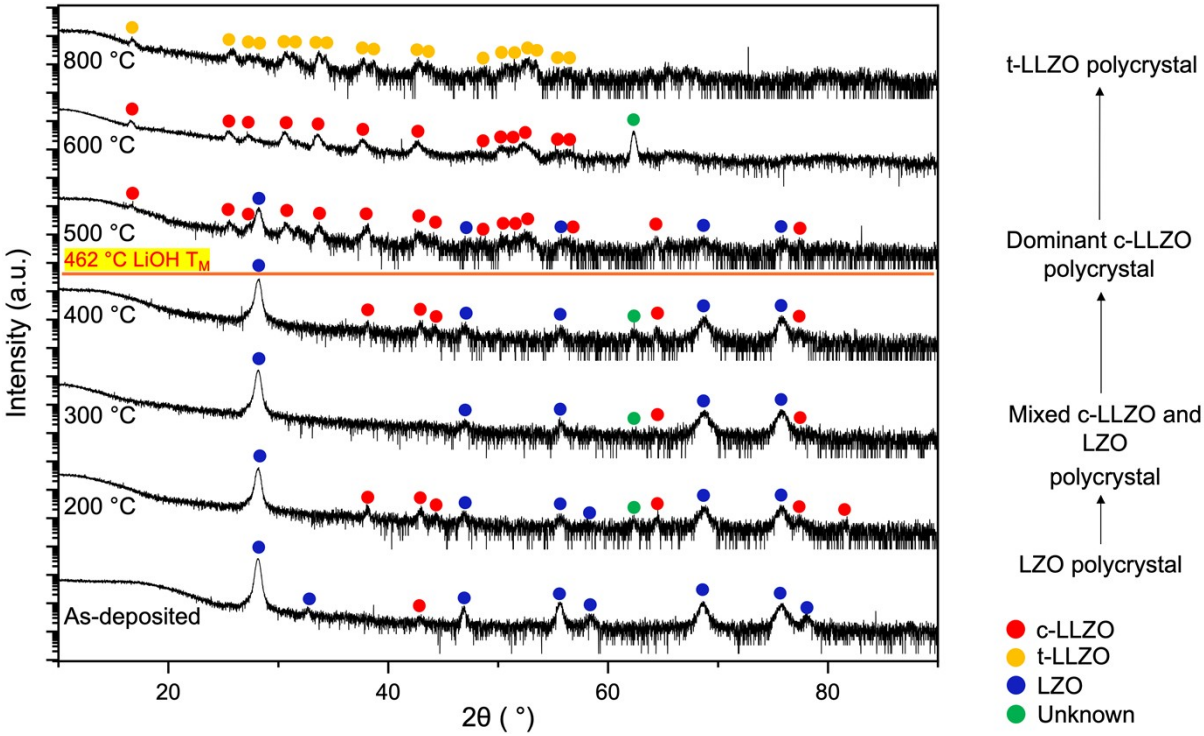

Fig. S5 GIXRD patterns of the films deposited at 700 °C then annealed with LiOH at various temperatures. The main phase of the film started from LZO polycrystal as-deposited to a mixed phase of LZO and c-LLZO at 500 °C (when the temperature reaches above the melting point of LiOH), then chan\ged to a c-LLZO dominant phase at 600 °C. t-LLZO is the main phase at 800 °C.

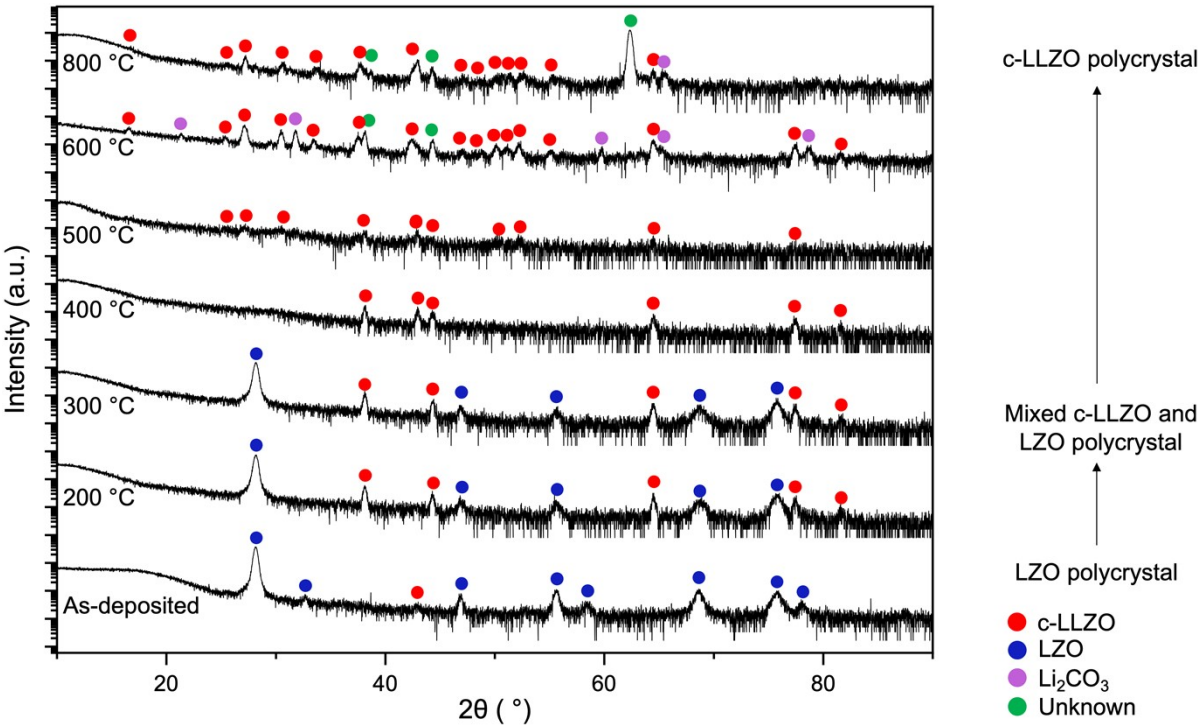

Fig. S6 GIXRD patterns of the films deposited at 700 °C then annealed with Li_2O at various temperatures. The dominant phase was LZO polycrystal as-deposited, at 200 °C, the film has a mixed phase of c-LLZO and LZO. A c-LLZO dominant phase can be seen from 500 °C.

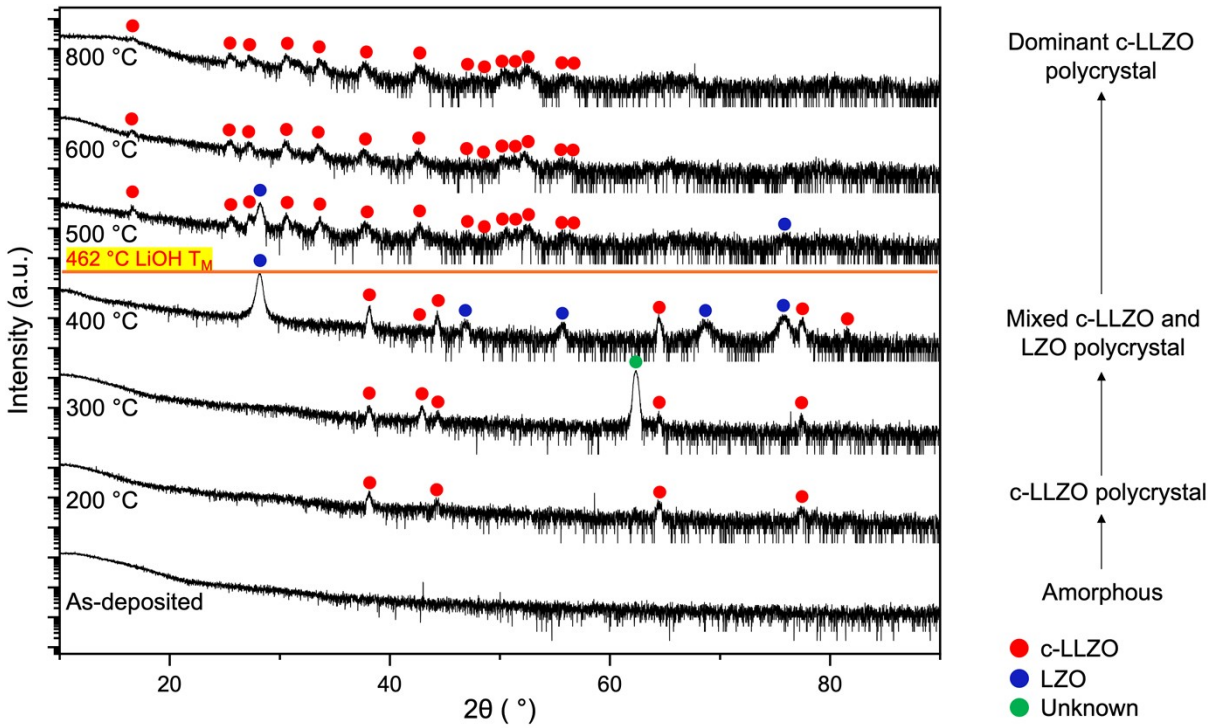

Fig. S7 GIXRD patterns of the films deposited at 50 °C then annealed with LiOH at various temperatures. The film started to be amorphous as-deposited, and then some c-LLZO peaks started to appear from 200 °C. At 400 °C, LZO starts to show up which is an indicator of lithium loss. However, when the temperature reaches above the melting point of LiOH (462 °C), the tendency of Li-loss is reversed, and c-LLZO dominates the film again.

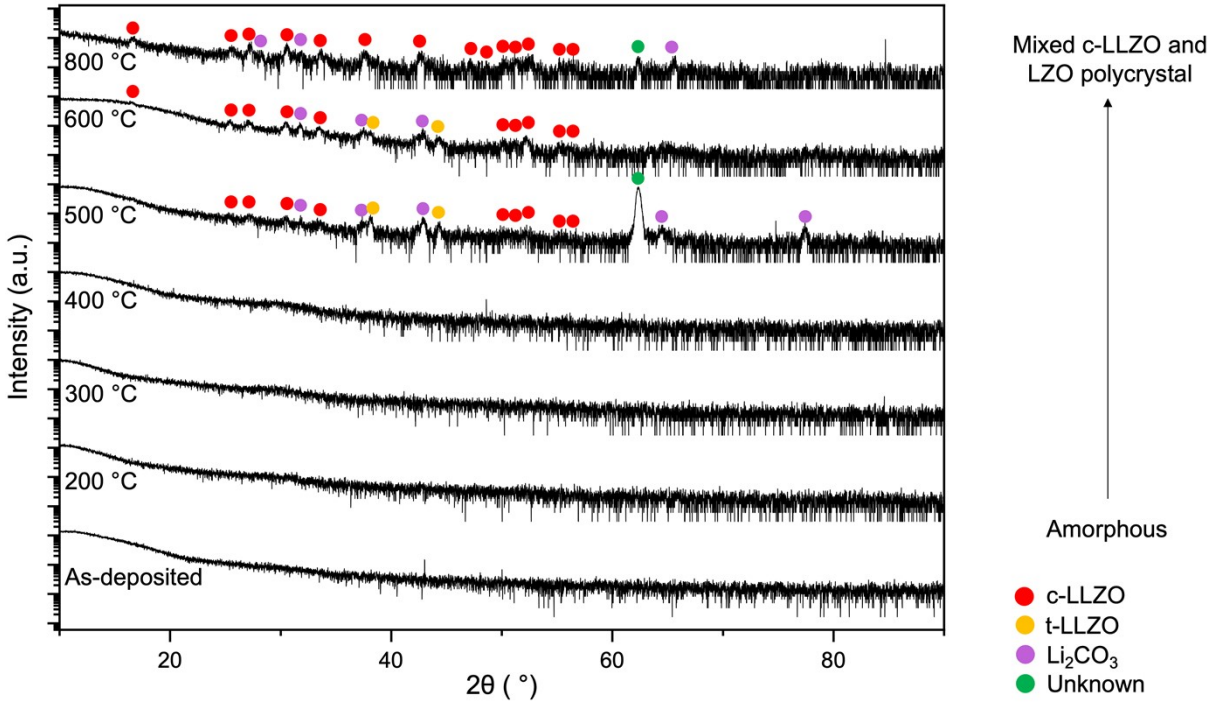

Fig. S8 GIXRD patterns of the films deposited at 50 °C then annealed with Li_2O at various temperatures. The film appeared to be amorphous until the temperature reached 500 °C. c-LLZO phase started to appear from 500 °C.

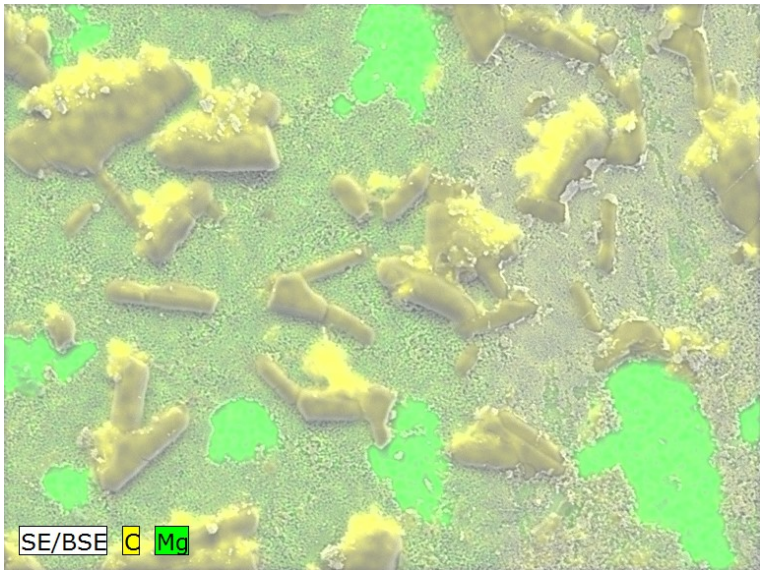

Fig. S9 EDX image of the film deposited at 50 °C with a laser energy density of 1 J cm^{-2} and an oxygen pressure of 1 mbar, then annealed at 600 °C with Li_2O powder. The carbon-rich particles are presumably Li_2CO_3, and the Mg-rich parts are the films exfoliated by exposing the MgO substrate. Lithium cannot be detected directly with EDX, so carbon was used as an indicator for the presence of lithium.

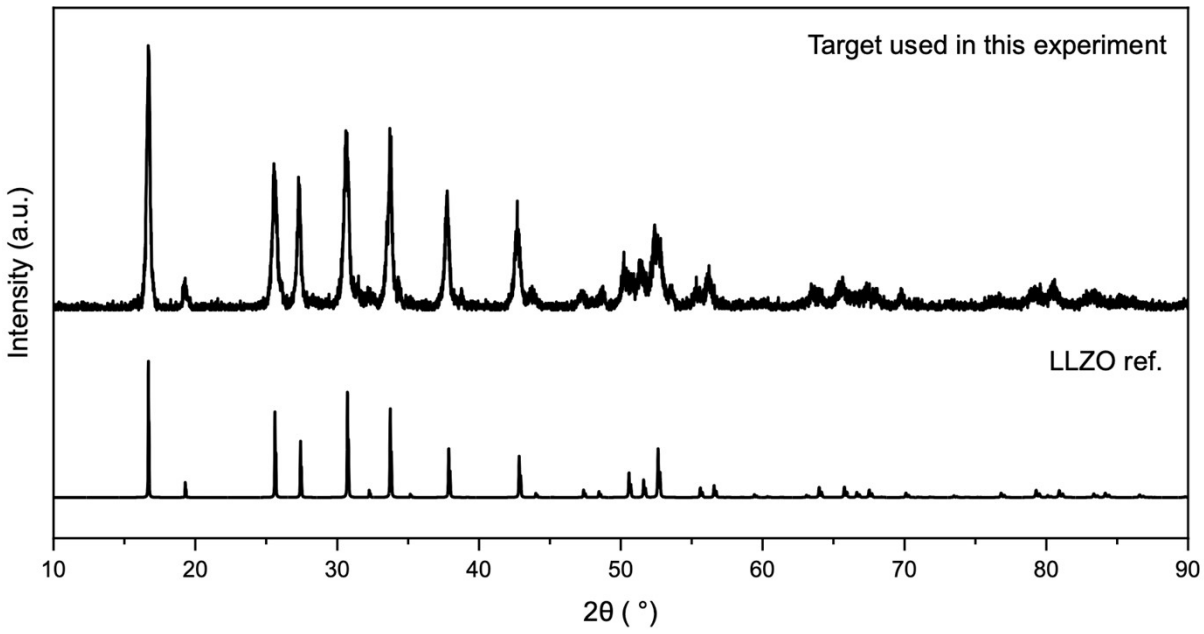

Fig. S10 XRD pattern of the LLZO target used in this study, along with the LLZO reference pattern (PDF Card No: **00-063-0174**).

Fig. S11-S12 are pictures of the crucible used for the annealing process.

Fig. S11 A picture showing how the powder was dispersed for the post-annealing process. The Li_2O powder is on the left (upstream of the O_2 gas flow) and the film/substrate is on the right.

Fig. S12 A picture of the crucible and the lid which covers the powder and the film.