Supplementary Information

A Study of Suppressed Formation of Low-Conductive Phases in Doped Li$_7$La$_3$Zr$_2$O$_{12}$ Garnets by *in-situ* Neutron Diffraction

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I. Phase stability of $Li_{5.4}Zn_{0.8}La_3Zr_2O_{12}$ (LLZO-Zn80) in the temperature range of -267.5 °C ~ 25 °C

The cubic LLZO-Zn80 garnet phase and a small amount of tetragonal phase coexist in the as-synthesized sample at RT. As the sample was cooled down to -267.5 °C, neither a structural transition nor a reaction was observed, as indicated by the neutron diffraction patterns compared in Fig. S1. The lower temperature does not move forward the cubic-to-tetrahedral phase transition, and the relative cubic phase fraction in the garnet almost maintains constant within the full temperature range (Fig. S2). The lattice parameter of cubic phase exhibits normally (Fig. S2): nearly linear expansion at -153 ~ 25 °C, and the less expansion at the temperatures approaching the absolute zero degree.

The observation supports the hypothesis that the cubic-to-tetrahedral phase transition in doped garnet is probably diffusion-controlled. The low temperature is not able to activate the diffusion process or the phase transition.
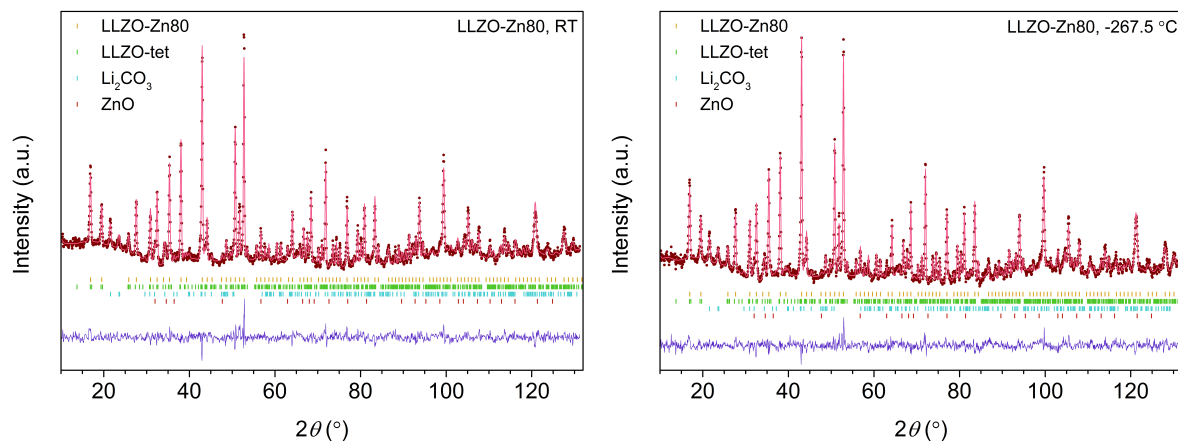
Fig. S1. Neutron diffraction patterns (wavelength = 1.54 Å) and the Rietveld refinement of the phases in LLZO-Zn80 as-synthesized samples at RT (left) and -267.5 °C (right).
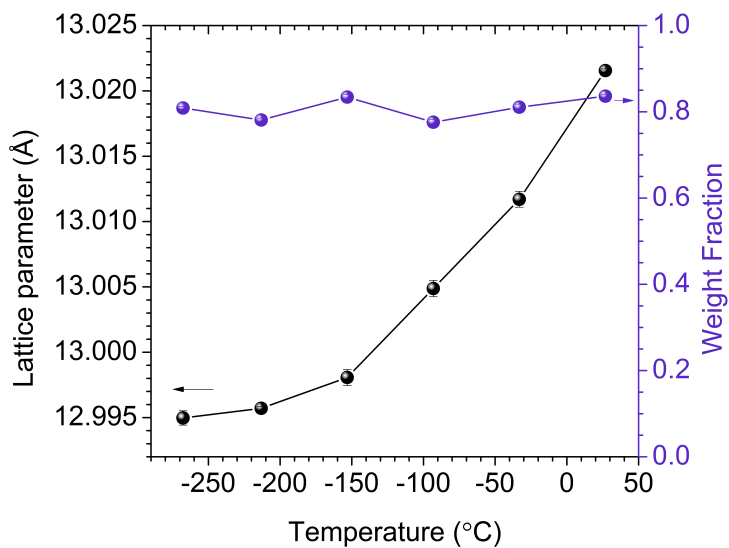

Fig. S2. The lattice parameter of the cubic LLZO-Zn80 garnet phase, and the relative cubic phase fraction in the mixture of the cubic and tetragonal phases, as extracted from the neutron diffraction and Rietveld refinement.

II. Comparison of the crystallite sizes of cubic phase and tetragonal phase in the garnets

The average crystallite size is clued by the profile broadening of neutron diffraction, as the relation below

$$\text{Crystallite size} \propto \frac{1}{\sqrt{\sigma_2^2}}$$

where $\sigma_2{}^2$ is one of the profile coefficients used in Rietveld refinement with GSAS software (See the manual for details: A. C. Larson and R. B. von Dreele, General structure analysis system (GSAS). Los Alamos National Laboratory Report LAUR 86–748 (2004)). The value of $\frac{1}{\sqrt{\sigma_2^2}}$ of each phase is listed in the Table S1.

In LLZO-Al24, the crystallite of tetragonal phase (t-phase) is much smaller than that of cubic phase (c-phase), which supports the hypothesis that the t-phase having fine crystallites can be coherently adapted (with strains) within the c-phase matrix. In contrast, in LLZO-Zn60, the crystallite size in the t-phase is as large as that in the c-phase, and it does not seem to raise such connection as in LLZO-Al24 whilst accommodating the large mismatch from the tetragonal distortion. The small quantity of t-phase in LLZO-Zn60 is probably precipitated from c-phase and grows without strong constraints from surrounding c-phase.

For the majority, the c-phase crystallites of LLZO-Al24 and LLZO-Zn60 both have comparable dimension with the t-phase in LLZO. However, the c-phase crystallite is slightly smaller in LLZO-Zn60 than in LLZO-Al24. It supports the hypothesis that the precipitation of t-phase breaks up the c-phase crystallites in LLZO-Zn60, resulting in a decrease of c-phase crystallite size in average. Differently, the coexisting fine t-phase crystallites in the c-phase matrix do not significantly decrease the c-phase crystallite size in LLZO-Al24.

Table S1 The fitting parameters of $\dfrac{1}{\sqrt{\sigma_2^2}}$ in the cubic and tetragonal garnet phases in the three samples, which is contributed by the crystallite size broadening, as extracted from Rietveld refinement. Those values are used to qualitatively compare the average crystallite sizes of the phases. The data of LLZO-Al24 and LLZO-Zn60 are measured at ~180 °C, and the data of LLZO are averaged in the temperature range of 600 – 180 °C.

Sample	$\dfrac{1}{\sqrt{\sigma_2^2}}$ of cubic phase	$\dfrac{1}{\sqrt{\sigma_2^2}}$ of tetragonal phase
LLZO	-	0.072(3)
LLZO-Al24	0.072(3)	0.038(4)
LLZO-Zn60	0.065(2)	0.067(14)