

## In Situ Phase Transformation during Sol-Gel Synthesis of Garnet Solid Electrolytes

Hongkui Zheng<sup>1</sup>, Kai He<sup>1,2\*</sup>

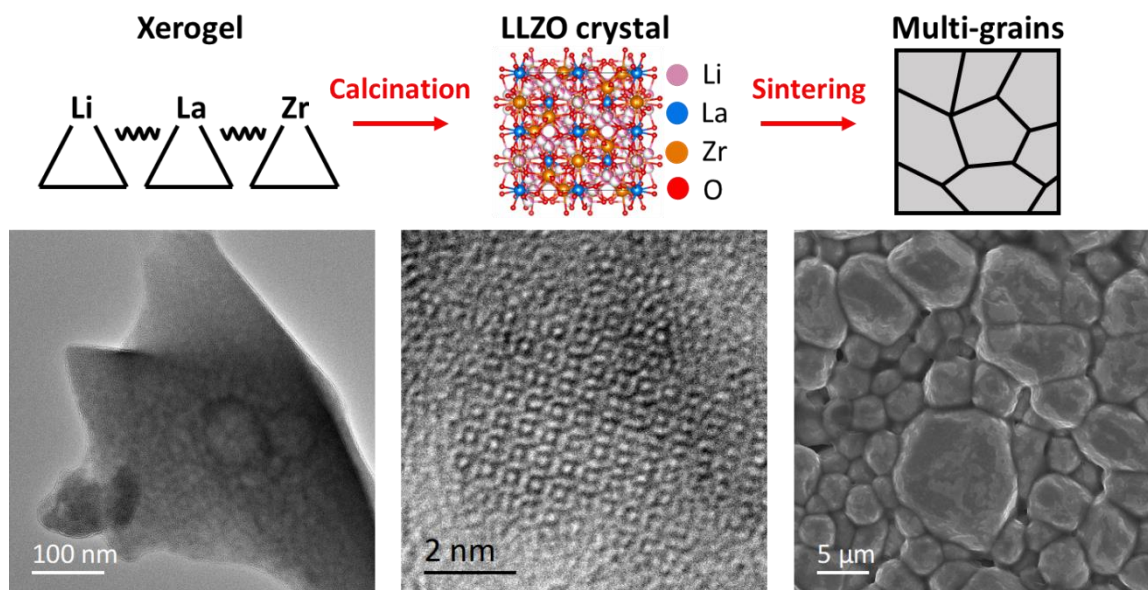
<sup>1</sup>. Department of Materials Science and Engineering, Clemson University, Clemson, SC, United States.

<sup>2</sup>. Department of Materials Science and Engineering, University of California, Irvine, CA, United States.

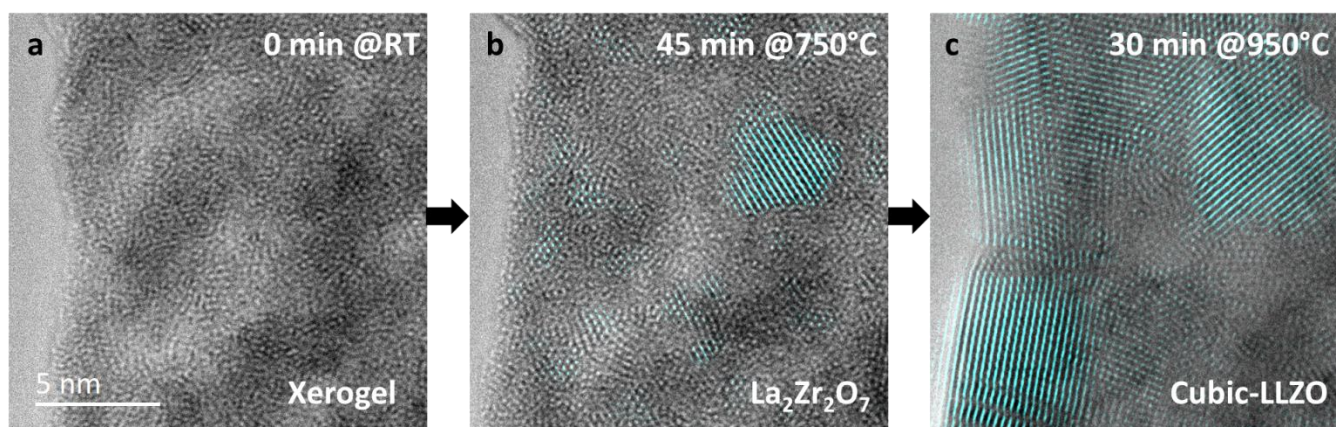
\* Corresponding author: kai.he@uci.edu

Solid-state batteries have attracted numerous interest due to the improved safety and higher energy capacity compared with traditional Li-ion batteries (LIBs). The use of solid-state electrolytes (SSEs) greatly mitigates the safety concerns arising from the flammable liquid electrolyte and allows Li metal to work as the anode to further improve the capacity of LIBs. Among various SSEs, garnet-type  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) is considered as one of promising candidates due to its relatively high Li-ion conductivity and better stability against metallic Li [1]. The cubic-LLZO phase is found to possess superior ionic conductivity one order of magnitude higher than the tetragonal polymorph [2]. Therefore, understanding and controlling the calcination process during LLZO synthesis is important to achieve high performance of electrolyte materials. Sol-gel process is a common technique used for ceramics synthesis with low calcination temperature, precise control of stoichiometry and high scalability comparing to the conventional solid-state route [3]. To better control the final products and avoid potential decomposition reactions, the phase transformation behavior during the sol-gel synthesis of LLZO requires in-depth investigation.

Transmission electron microscopy (TEM) is a powerful characterization tool that can provide high spatial and temporal resolution to retrieve the localized structure information. The recent development of in situ heating TEM technique has enabled the real-time observation of dynamic morphology and phase evolutions at elevated temperatures [4]. Herein, we report the dynamic observation of phase transformations during the in situ synthesis of LLZO SSEs. Figure 1 shows the schematics of the synthetic process of LLZO solid electrolytes. The highly porous amorphous xerogel was firstly obtained after evaporation of wet gel, which was further transformed into the crystalline garnet LLZO phase upon calcination followed by the subsequent densification via high-temperature sintering to form the multi-grain microstructure in dense LLZO pellets. Although the corresponding TEM, HRTEM, and SEM images have confirmed this entire process, detailed information about the intermediate phase transitions was still lacking. For this purpose, we conducted in situ heating experiments using a MEMS-based heating setup and acquired the time-sequenced HRTEM images at a function of temperature from the same region of interest, as shown in Figure 2. The pristine xerogel shows the amorphous nature at the room temperature. The amorphous-to-crystal transition was firstly observed after heating for 45 min at 750 °C, leading to the formation of  $\text{La}_2\text{Zr}_2\text{O}_7$  phase. The subsequent heating to 950°C for 30 min triggered the formation of cubic-LLZO phase. The intermediate phase transitions and their growth processes were highlighted by the overlaid FFT-filtered HRTEM images in Figure 2a-c. These findings of in situ phase transitions during the calcination process show direct relevance and implications to the sol-gel synthesis of garnet-LLZO and may provide useful information to guide the design of synthetic processing of ceramic SSEs for energy-related applications [5].



**Figure 1.** Schematics of the synthetic processes of LLZO solid electrolytes through sol-gel, calcination, and sintering steps, confirmed by the corresponding TEM, HRTEM, and SEM images.



**Figure 2.** HRTEM images showing the in situ phase transformations from the pristine amorphous xerogel to the intermediate crystalline  $\text{La}_2\text{Zr}_2\text{O}_7$  phase followed by the formation of cubic-LLZO phase at elevated temperatures. The overlaid FFT-filtering highlights the formation of intermediate phases and their growth processes.

#### References:

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