

Low-temperature and short-time synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ powder

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$\text{La}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) is a lithium-ion conductive oxide with a high ionic conductivity ($\sim 10^4$ S/cm) at room temperature [1]. LLZ has a chemical stability against Li metal and is expected to be an electrolyte material for all-solid-state Li-ion secondary batteries and also a protective layer material for Li metal anode in Li-air batteries. However, in a conventional solid-state process, long-time heat-treatments, typically for several days, are required to obtain LLZ powders in a single phase. In this study, we have revealed formation mechanisms of LLZ in a conventional process where Li_2CO_3 , $\text{La}(\text{OH})_3$ and ZrO_2 are used as starting powder materials, and a new low-temperature and short-time solid-state process is proposed based on the mechanisms.

Figure 1 shows x-ray diffraction (XRD) patterns of the stoichiometric mixture (Li:La:Zr=7:3:2) of Li_2CO_3 , $\text{La}(\text{OH})_3$ and ZrO_2 after heated at 650-1000°C for 12 h in air. Three crystalline phases (LLZ, $\text{La}_2\text{Zr}_2\text{O}_7$ and LiZrO_3) were appeared and their contents/proportions were changed complicatedly by temperature. $\text{La}_2\text{Zr}_2\text{O}_7$ is formed at 650°C and disappeared at 700°C, and appeared again above 900°C. LiZrO_3 is formed at 650-700°C and the content is almost constant at higher temperature upto 1000°C. LLZ is formed at 700°C, and decreased above 900°C.

These results indicate that there are two routes to form LLZ in this system. One is a low-temperature route, where LLZ is formed from $\text{La}_2\text{Zr}_2\text{O}_7$ intermediate product at 700°C, and another is a high-temperature route, where LLZ is formed after decomposition of LiZrO_3 above 1000°C. Decrease of LLZ content and increase of $\text{La}_2\text{Zr}_2\text{O}_7$ above 900°C suggests a decomposition of LLZ caused by volatilization of Li at high temperature. Thus, in order to obtain pure LLZ powders at a lower temperature, the formation of LiZrO_3 should be suppressed.

Synthesis of LLZ from the stoichiometric mixture of Li_2CO_3 , $\text{La}(\text{OH})_3$ and $\text{La}_2\text{Zr}_2\text{O}_7$ has been examined. This system contains no ZrO_2 , and the formation of LiZrO_3 could be evaded. Figure 2 shows XRD patterns of the resulting specimens after heated at 650-800°C for 1 h. LLZ was formed at 700°C, and at 750°C, diffraction peaks from unreacted sources were disappeared. Formation of LiZrO_3 or other intermediate/byproduct was not observed.

A SEM image of LLZ powder obtained by our new process is demonstrated in Figure 3 together with source $\text{La}_2\text{Zr}_2\text{O}_7$ powder (Fig.3(b)). The average size of LLZ was about 3 μm , and crystalline facets are observed at the surface suggesting a high degree of crystallinity. The size of LLZ is much larger than that of source $\text{La}_2\text{Zr}_2\text{O}_7$ powder although the heating condition was mild (800°C, 1 h), and this would indicates a formation of liquid phase at low temperature in this system.

References

- [1] R. Murugan et al., *Angew. Chem. Int. Ed.*, **46**, 7778(2007) .

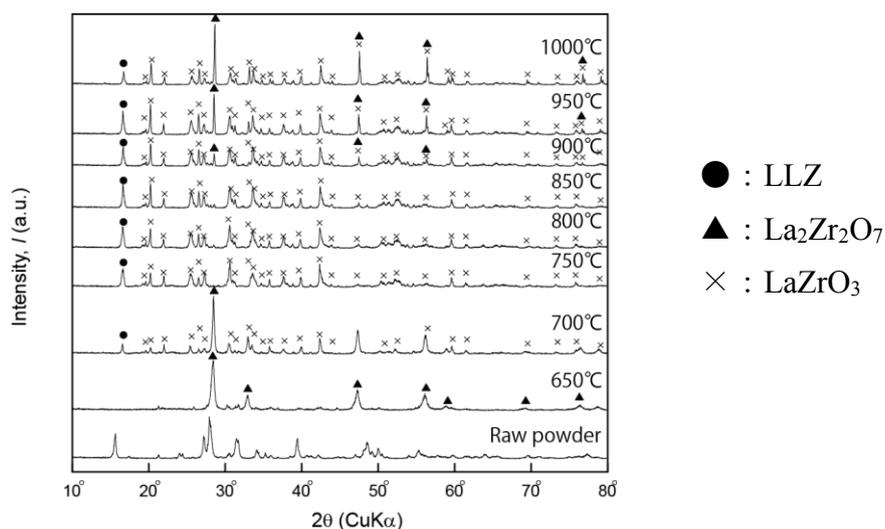


Figure 1 XRD patterns of stoichiometric mixture (Li:La:Zr=7:3:2) of Li_2CO_3 , $\text{La}(\text{OH})_3$ and ZrO_2 after heated at 650-1000°C for 12 h in air.

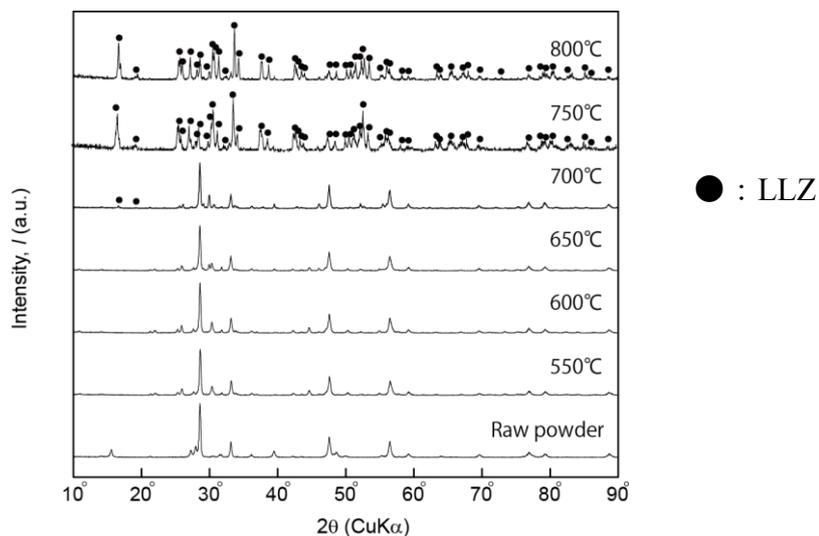


Figure 2 XRD patterns of stoichiometric mixture (Li:La:Zr=7:3:2) of Li_2CO_3 , $\text{La}(\text{OH})_3$ and $\text{La}_2\text{Zr}_2\text{O}_7$ after heated at 650-1000°C for 12 h in air.

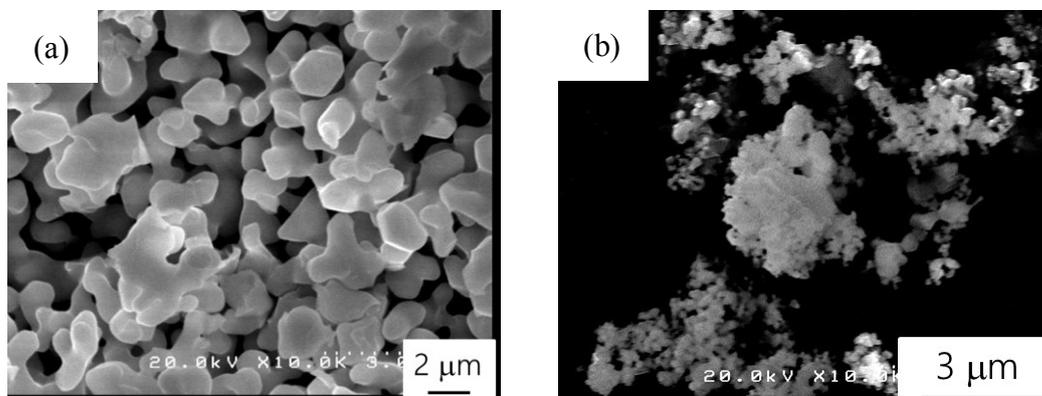


Figure 3 SEM images of (a) LLZ synthesized at 800°C for 1 h in air and (b) raw $\text{La}_2\text{Zr}_2\text{O}_7$ powder.