

Formation Mechanism of Garnet-Like $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Powder Prepared by Solid State Reaction



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Abstract: The formation mechanism of garnet-like $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) phase was investigated using $\text{LiOH}\cdot\text{H}_2\text{O}$ as raw materials by XRD and DTA/TG measurements. It is found that the reaction mechanism of the LLZO formation is as follows: $7\text{Li}_2\text{O}+3\text{La}_2\text{O}_3+4\text{ZrO}_2=2\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. The LLZO phase forms at about 680 °C according to the XRD patterns, which is in agreement with the thermic peak at 700 °C in DTA/TG curves, and the peak arises from the formation of LLZO phase. The temperature range of stable LLZO phase is wider, from 720 to 1000 °C. However, LLZO is thermally unstable at the high temperatures (>1000 °C) due to a serious loss of lithium element, and it decomposes into pyrochlore phase $\text{La}_2\text{Zr}_2\text{O}_7$. And the amount of the decomposed products increases, and LLZO decreases gradually with the increase of the calcination temperature. When the reactant mixture is calcined at low temperature, the produced phases are identified to be lanthanum compounds because La_2O_3 absorbs moisture and CO_2 very easily. The chemical reactions at lower temperature are mainly related with the reactions among lanthanum compounds. LLZO powder could be synthesized by solid state reaction at 800 °C. It is found that the LLZO crystal belongs to the tetragonal symmetry. SEM observation shows that the obtained LLZO powder is nano-sized.

Key words: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO); calcination temperature; phase transition; DTA/TG

In recent years, lithium ion secondary all-solid-state battery finds remarkable applications in a great number of energy conversion and storage devices owing to its good thermal and chemical stability, high power and energy densities, and especially good safety^[1-7]. As an important component in the chargeable all-solid-state lithium ion battery, inorganic solid state electrolytes play a crucial impact on the performance of the battery, for they can effectively prevent explosive accidents which often happen in lithium ion batteries with organic electrolytes. Many solid state lithium ion conductors with different types of crystal structures have been extensively studied, including perovskite structure ABO_3 -type fast ion conductors^[8-10], SINACON fast ion conductors^[11-16] and so on, due to their excellent ionic conduction behavior at room temperature. More recently, a new kind of lithium ion

conductor with garnet-related structure attracts a great deal of attention owing to its high lithium ion conductivity at room temperature and good electrochemical stability^[17-25]. Among the garnet-like conductors, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) ceramics possess much higher ionic conductivity, about 10^{-4} S/cm in the cubic LLZO phase synthesized at higher sintering temperature^[24,26]. The relative density of this cubic LLZO phase with 92% is high. However, the tetragonal LLZO phase with lower relative density of 60% was obtained by sintering at lower temperature^[25], whose ionic conductivity is three orders of magnitude lower than that of cubic phase. In the former lattice structure, lithium ion arrangement is complicatedly disordering on these tetrahedral and octahedral sites, which is beneficial for the lithium ion motion. For the later, e. g. the tetragonal LLZO, the tetrahedral and octa-

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hedral sites in conduction pathway are completely ordered by lithium atoms and vacancies, which is adverse for the lithium ion movement. Hence, its ionic conductivities are much more different, and it is believed that the ionic conduction behavior is dependent on the lithium ion arrangement in the lattice structure of LLZO phase which is dominated by the sintering temperature. Therefore, it is very necessary to make an attempt to reveal the formation mechanisms of LLZO phase with the calcination temperature. But few efforts have been made to investigate the LLZO phase formation. In the present work, the mixed raw materials LiOH·H₂O, La₂O₃ and ZrO₂ were calcined at different temperatures and quenched in air. The phase transition with different calcination temperatures was identified and investigated by XRD and DSC/TG measurements. Furthermore, tetragonal structure LLZO powder was obtained at 800 °C using a solid state reaction method. The LLZO powder was characterized using XRD and SEM measurements.

1 Experiment

In the experiment the raw materials included LiOH·H₂O, La₂O₃ and ZrO₂. 10 wt% excess of LiOH·H₂O (purity of 99.8%) was used as the lithium source to compensate the lithium loss, La₂O₃ (purity of 99.99%) was heat treated at 1000 °C for 10 h to remove the water and CO₂ absorbed in air, and ZrO₂ (purity of 99%) was also dried at 120 °C in order to keep the chemical stoichiometric ratio. The raw materials were weighed according to the chemical stoichiometric ratio and mixed by ball-milling with isopropyl alcohol for 12 h. Then the mixed powder was dried at 75 °C and pressed into several pellets with 12 mm in diameter and weight of 0.5 g for suppressing the lithium evaporation. Finally, these pellets were put on the Al₂O₃ crucible lid, placed into a furnace, and calcined from room temperature to given temperatures at the heating rate of 3 °C/min, held for 30 min at set temperatures, and quenched in air to maintain the phase at set temperatures. The calcined pellets were crushed into powder in order to characterize the powder. The LLZO powder was prepared at 800 °C by mixing the raw materials adopting the solid state reaction. Differential thermal analysis and thermo-gravimetric (DTA/TG) analysis of the mixed reactant were carried out on a METTLER TOLEDO (TGA/DSC1, Switzerland) thermal analyzer. Mixed powder of about 15 mg was placed into Al₂O₃ crucibles and then heated up to 1400 °C at a scanning rate of 10°/min.

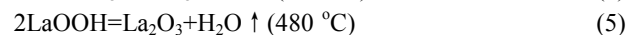
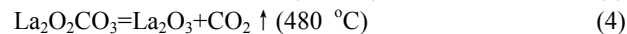
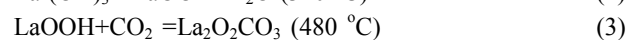
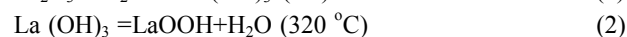
Crystalline phase of the LLZO powder was identified by powder X-ray diffraction (XRD, Rigaku D/max 2500 diffraction meter with CuK α radiation source) in the 2 θ range from 10° to 90° with the scan speed of 6°/min. The patterns were indexed and the lattice parameters were determined by means of PowderX program. The microstructure in LLZO powder calcined at 800 °C was observed using scanning

electron micrographs (JSM-6460LV scanning electron microscope).

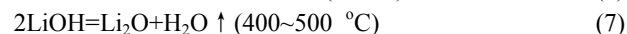
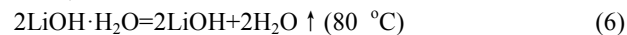
2 Results and Discussion

2.1 DTA/TG results

DTA/TG measurements were necessary to select the proper calcination temperature to analyze the phase transition in the calcination process of the mixed reactants, as shown in Fig.1. As seen, four thermic peaks appear in the DTA curve, according to four mass loss steps in the TG curve. From the comparison among these raw materials of LiOH·H₂O, La₂O₃ and ZrO₂, it is observed that ZrO₂ is stable without thermic peaks and mass loss during the heating process until 1300 °C (see Fig.2), and thus ZrO₂ can not account for the appearance of these peaks. As to the DTA/TG curves of La₂O₃, it can be seen that the endothermic peak at about 320 °C could be related with the loss of water in La(OH)₃ (La₂O₃ exists in the state of La(OH)₃ phase at room temperature) and the presence of LaOOH compound, and the one at about 480 °C could be ascribed to the formation of La₂O₂CO₃ due to the absorption of CO₂ and then the presence of La₂O₃ because of the loss of water and CO₂. At this temperature, the chemical reactions are very complicated. The chemical reactions are as follows:



There are three thermic peaks from 400 to 500 °C for the DTA/TG curves in LiOH·H₂O as indicated Fig.1, which result from the decomposition of LiOH into Li₂O corresponding to the mass loss of about 21% in this temperature range. A peak at 80 °C can be observed because LiOH·H₂O loses crystal water to become LiOH through the calculation of mass loss of about 41%. Furthermore, a peak appearing at about 1060 °C could be attributed to the evaporation of lithium element, corresponding to the calculation of mass loss of lithium element, about 8%. These reactions are described as follows:



Thus through the comparison and analysis, the peaks appearing at 340 and 420 °C in the mixed raw materials could originate from the chemical reactions among these lanthanum compounds and also from the decomposition of LiOH phase. With regard to the thermic peak at 700 °C in the mixed raw materials, it is believed that LLZO phase could form at this temperature. When the temperature increases to 1340 °C, there is a big endothermic peak, which is in consistence with the decomposition of LLZO phase. Actually, LLZO phase already begins to decompose at 1100 °C. Consequently, the mixed reactants are calcined at 16 temperature points selected in the light of the analysis of DTA/TG results.

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