



Structure and ionic conductivity of cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte prepared by chemical co-precipitation method



Chongyang Shao, Hanxing Liu ^{*}, Zhiyong Yu, Zhenning Zheng, Nian Sun, Chunli Diao

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

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ABSTRACT

Solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) powder was successfully synthesized by co-precipitation method. The LLZO powder calcined at 850 °C with a tetragonal phase was confirmed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) showed that the particles sizes of LLZO precursor powder were in the range of 0.5–1 μm. LLZO pellets were sintered at different temperatures from 1150 to 1200 °C in air atmosphere. When the temperature was above 1150 °C, tetragonal LLZO would completely transform into cubic phase. The total ionic conductivity of LLZO pellet sintered at 1180 °C was $2.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C, and the activation energy was 0.25 eV. This result indicates that high quality LLZO solid electrolytes can be obtained by chemical co-precipitation method.

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1. Introduction

All-solid-state lithium batteries have attracted a lot of attention since they reduce the safety risks of electrolytic solution leakage and the flammability of organic liquid electrolytes [1–3]. Solid electrolytes require high lithium ionic conductivity, good chemical stability and compatibility with electrode materials [2]. Among current solid electrolyte materials, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) reported by Weppner et al. [4] in 2007 is considered to be one of the most promising materials for application of all-solid-state lithium batteries [5]. It was reported that LLZO has three phases: a fast lithium-conduction cubic phase prepared at high temperature (H.T.)-cubic phase, a tetragonal phase, and a low temperature (L.T.)-cubic phase formed by reaction with moisture and CO_2 [4,6–10]. Recently, a series of studies showed the existence of cubic structure at room temperature is attributed to the doping, such as aluminum [11], gallium [12] tantalum [10] and niobium [13], which induce the formation of the cubic phase LLZO at around 1000 °C.

In previous studies, solid-state reaction methods were usually used to synthesize the solid electrolyte LLZO [4,14–17]. Huang et al. [15] synthesized cubic LLZO by sintering at a high temperature of 1230 °C for 35 h resulting in LLZO with an ionic conductivity of about $3.6 \times 10^{-4} \text{ S cm}^{-1}$. In the conventional solid-state reaction method, the precursor powder had relatively large particle size and poor sintering activity, which caused the long sintering time and high sintering temperature, and it was also easy to produce a complex phase such as LaAlO_3 . In addition, the sol-gel methods were also utilized to synthesize LLZO powder [18,19].

As one method for preparing the precursor powder, chemical co-precipitation method has many advantages, such as being a simple process, molecular level mixed and creating fine precursor powder. Therefore, outstanding sintering activity (low sintering temperature and short sintering time) can be realized with chemical co-precipitation. However, there have been no reports on the preparation of LLZO electrolyte using chemical co-precipitation method. In this work, the structure, ionic conductivity and activation energy of LLZO prepared by chemical co-precipitation method were investigated.

2. Experimental

LLZO electrolyte was prepared by chemical co-precipitation method. Li_2CO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and NH_4HCO_3 were used as raw materials and all reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were dissolved in deionized water, and the concentrations of solutions were 0.3 mol/L and 0.2 mol/L respectively. The obtained solution was stirred vigorously and heated at 50 °C for 3 h, then the solution was added at the speed of 3 mL/min into NH_4HCO_3 solution (concentration was 1 mol/L) for co-precipitation. The obtained co-precipitate precursor was filtered and dried at 100 °C for 10 h in air. Stoichiometric ratio of Li_2CO_3 and the precursor power were ball-milled for 8 h. To compensate the lithium loss at elevated temperatures, an excess amount of 10% lithium was added. The mixed power was calcined at 850 °C for 10 h, and then pressed into pellets with 12 mm diameter. The green pellets were surrounded by matching LLZO composite powder to reduce lithium volatilization and sintered at 1150–1200 °C for 20 h.

^{*} Corresponding author.
E-mail address: lhxhp@whut.edu.cn (H. Liu).

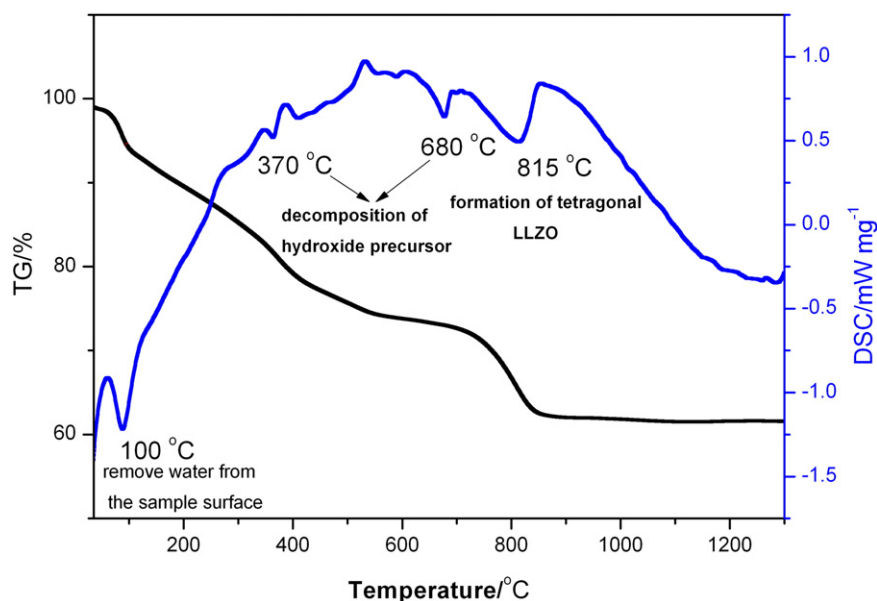


Fig. 1. TG/DSC curves of the raw materials.

Thermal analysis of the raw materials mixture was conducted with a thermal gravimetric (TG) and differential scanning calorimeter (DSC) synchronous analyzer (STA449c/3/G) at a heating rate of 10 °C/min in flowing air. The phase identifications of the products were examined by an X-ray diffraction (XRD, PANalytical X'Pert PRO). The morphology of the powder and the microstructure of the sintered pellets were characterized with a scanning electron microscopy (SEM, JSM-5610F).

The pellet samples were thoroughly polished after sintering and thin films of Ag were sputtered on both surfaces to act as the Li ion blocking electrodes. The ionic conductivity at room temperature was measured by the AC impedance method with a precision impedance analyzer (Agilent 4294 A) in the frequency range from 100 Hz to 5 MHz. The activation energy was calculated based on the complex impedance spectra measured in the temperature range from 15 °C to 90 °C with an impedance analyzer (Agilent E4980A) in the frequency range from 20 Hz to 2 MHz with an amplitude of 10 mV.

3. Results and discussion

Ball-milled raw materials were submitted to TG/DSC analysis shown in Fig. 1. The first step at room temperature to 100 °C about 4% weight

loss is assumed to remove water from the sample surface. In the second step, two endothermic peaks were observed on the DSC curve at 370 °C and 680 °C corresponding to about 13% and 3% weight loss respectively on the TG curve, which could be ascribed to decomposition of hydroxide precursor. The decomposition of hydroxide is an endothermic process. The third step, which occurred at the temperature from 700 °C to 850 °C was accompanied by a strong endothermic signal (peak at 815 °C), and the 12% weight loss also corresponded to the formation of tetragonal LLZO as confirmed by XRD. At temperatures above 850 °C no further weight loss was measured.

The XRD patterns for the samples are shown in Fig. 2. It can be seen that the XRD pattern of the powder calcined at 850 °C showed pure tetragonal phase LLZO. At the temperature of 1200 °C, some peaks ascribed to LaAlO_3 can be detected from the sample, which may be due to the reaction of sample and the alumina crucible at high temperature [11]. Accompanied with the temperature increases from 850 °C to 1200 °C, LLZO undergoes a phase change from tetragonal to cubic structure. This structure evolution could be observed in Fig. 2 (right). The one single peak is indexed as (400) for the cubic structure, which splits into (400) and (004) peaks for the tetragonal structure. At 1150 °C, there is still a small amount of residual tetragonal phase LLZO.

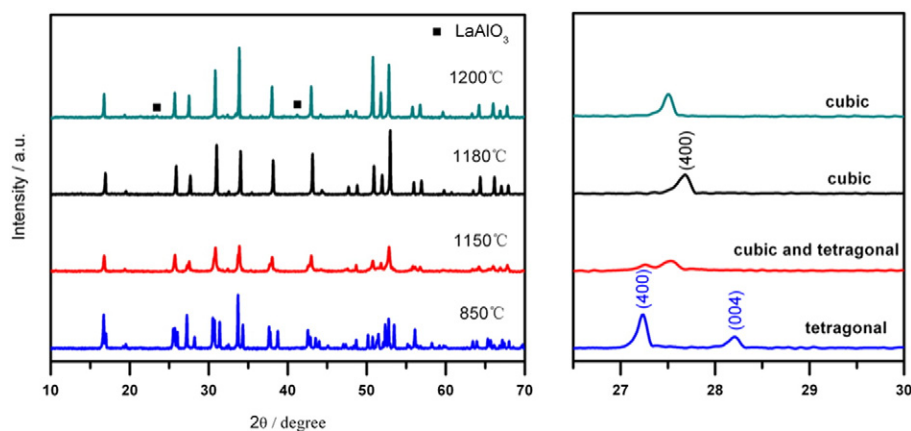


Fig. 2. (Left) XRD patterns of the ceramics samples sintered at high temperatures from 1150 °C to 1200 °C, and (right) the local XRD patterns showing evolution of the crystal structure. For comparison, the XRD pattern of the powder calcined at 850 °C is also shown.

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