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Effect of calcining and Al doping on structure and conductivity of $Li_7La_3Zr_2O_{12}$

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ABSTRACT

$Li_7La_3Zr_2O_{12}$ (LLZ) ceramics with a garnet-type structure were prepared via the conventional solid-state reaction through different calcining processes. The calcining time and temperature were investigated. The results showed that the ionic conductivity of LLZ samples at room temperature decreased as the calcining temperature increased. The highest conductivity of 2.48×10^{-4} S cm^{-1} was obtained for the sample with the calcining process at 900 °C. The amount of doping Al was also investigated, which showed different effects depending on the calcining process.

1. Introduction

Research on all-solid-state lithium batteries is of great interest because of their high energy density, high safety and low toxicity compared with those currently using liquid electrolytes. All-solid-state lithium batteries are playing an important role in modern energy storage and conversion applications. One of the representative cells is that with $LiCoO_2$ as cathode, lithium metal or graphite as anode and LiPON as solid electrolyte [1–3]. Moreover, research in recent years has revealed more candidates as the solid electrolyte materials, such as $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ with conductivity as high as 5×10^{-3} S cm^{-1}, $Li_{4-x}Ge_{1-x}P_xS_4$ with conductivity of 2.2×10^{-3} S cm^{-1} at room temperature and $Li_{0.34}La_{0.5}TiO_{2.98}$, whose bulk lithium conductivity was reported to be as high as 10^{-3} S cm^{-1} at room temperature [4–6]. Among the many kinds of solid electrolyte materials, Li-La-M-O (M = Nb, Ta, Zr) compounds with a garnet-type structure have attracted great attention in the last few years, due to their advantages of high stability with lithium metal electrode and low resistance [7–10].

As one of the lithium garnet solid electrolytes, $Li_7La_3Zr_2O_{12}$ (LLZ), which was first reported by Murugan et al. in 2007, is more interesting than the other materials due to its superiority in ionic conductivity at room temperature and chemical/electrochemical stability [11]. LLZ was reported to have two kinds of structures, namely cubic phase belonging to the space group Ia3d (No. 230) and tetragonal phase belonging to the space group $I4_1a/cd$ (No. 142), respectively [12]. It has been revealed that the cubic phase could be stabilized at room temperature as a result of aluminum contamination from the crucibles during sintering process [13]. In the last few years, a lot of work has been done aiming at enhancing the conductivity of LLZ at room temperature. Element doping, such as Al, Ga, Ta, Nb or Ce, proves to be an effect way in stabilizing the cubic garnet structure and increasing the conductivity [13–17]. Another idea is utilizing the sol precursor method to obtain the fine powder to lower the sintering temperature [19]. Also the optimum sintering temperature has been studied to control the microstructure of LLZ [18].

With regard to the preparation of LLZ ceramics, solid-state reaction method was most frequently used because of the feature of mass production and simplicity in processing. However, much attention was paid to the sintering process which is the final step in solid-state reaction. There is little research on the calcining process which determines the powder status before sintering and possibly affects the property of final sintered products. Li evaporation is a key factor affecting the conductivity of LLZ. Sintering LLZ ceramics with the coverage of mother powder has been the common method to protect Li. Unlike the sintering step, no mother powder was used when calcining the raw materials, which will lead to the easier loss of Li in the product even at a relatively lower temperature. It is believed that the Li evaporation during the

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calcining step is also significant in affecting the Li content of the sintered LLZ sample. Thus, systematic studies on the calcining process have been performed in this contribution with an aim of evaluating its effect on structure and conductivity of the LLZ through conventional solid-state reaction method.

2. Experimental

2.1. Preparation of LLZ

$Li_7La_3Zr_2O_{12}$ was prepared by the conventional solid-state reaction. The raw materials of Li_2CO_3 (Aladdin reagent), La_2O_3 (Sinopharm Chemical Reagent Co., Ltd), ZrO_2 (Sinopharm Chemical Reagent Co., Ltd) and Al_2O_3 (Sinopharm Chemical Reagent Co., Ltd) were weighted according to the stoichiometric ratio. The molar ratio between Li, La, Zr and Al was 7.7:3:2:0.3. Excess Li (10%) was added to compensate for expected Li loss during high temperature heat treatment. The mixture of the raw materials was ball-milled with ethanol for 12 h and dried at 70 °C to obtain the homogeneous powder. Five different calcining processes were used and the details of the temperature and time are listed in Table 1. The calcined LLZ powers with different calcining processes are denoted as "#X-Y" where X indicates the first calcining temperature and Y indicates the second calcining temperature. The ball-milling was repeated after each calcining process to obtain homogeneous fine powder. Finally, the powder was pressed into a pellet followed by sintering at 1200 °C for 24 h during which each pellet was covered by the mother powder. All the calcining and sintering processes were completed in the alumina crucibles. Accordingly, the sintered pellets are denoted by adding P after the powder name. For example, the pellet sintered with powder #900 is denoted as #900P.

2.2. Characterization of LLZ

The phase composition of the sintered LLZ sample was characterized with X-ray diffraction (XRD, RigakuDmax 2500). The contents of lithium and aluminum were determined by induced coupled plasma optical emission spectrometer (ICP-OES, VARIN VISTA-MPX). The morphology of the sintered sample was characterized with scanning electron microscopy (SEM, Shimadzu SSX-550). The ionic conductivity was measured with an impedance analyzer (Agilent 4294A) in the frequency range from 40 Hz to 110 MHz at the voltage amplitude of 50 mV. A thin film of Au was sputtered on each surface of the sintered pellet as ion blocking electrode. In order to obtain the activation energy, the temperature-dependant measurement was performed with an electrochemical workstation (Chenhua 760B) in the frequency range from 1 Hz to 100 kHz from −10 °C to 50 °C. The density was measured with the Archimedes method, in which the porosity and the relative density were calculated by the dry weight, wet weight and buoyant weight.

3. Results and discussions

3.1. Structure evolution

Fig. 1 shows the X-ray diffraction patterns of the powders after different calcining processes and the corresponding LLZ pellets after sintering. It can be seen that $La_2Zr_2O_7$ is identified as a major phase in #900 and #800–900 powders, indicating the raw materials did not react completely with each other at these calcination temperatures. Actually, $La_2Zr_2O_7$ is also discovered as principal phase by other researchers after low-temperature heat treatment [20], which is in agreement with our results here. When the calcination temperature was increased from 950 °C to 1125 °C, the powders underwent a phase transition from cubic to tetragonal then to cubic again. As we can see from Fig. 1, #800–950 and #900–1125 show cubic phase but #900–1050 shows a combination of cubic and tetragonal phases, indicating the existence of tetragonal phase between two cubic phases. The existence of the cubic phase at lower temperature agrees with the results reported by H. T. Hintzen [20], who prepared the LLZ powder via sol–gel method and discovered the existence of a low-temperature cubic phase. Here, we prove that a similar phase transition may also exist in the conventional solid state reaction though the reason behind the phenomenon was unclear. The transition from tetragonal phase when sintered at 1050 °C then to cubic phase when sintered at 1125 °C was also observed in our previous work [18]. However, the appearance of a cubic phase when sintered at 950 °C is very interesting. This might be a meta-stable cubic phase since increasing calcining temperature would lead to a phase transition.

Table 1
Different calcining processes used in the preparation of LLZ and their denotations.

Denotation	1st calcining Tem	1st calcining time	2nd calcining Tem	2nd calcining time
#900	900 °C	10 h	None	None
#800–900	800 °C	10 h	900 °C	10 h
#800–950	800 °C	10 h	950 °C	10 h
#900–1050	900 °C	10 h	1050 °C	10 h
#900–1125	900 °C	10 h	1125 °C	10 h

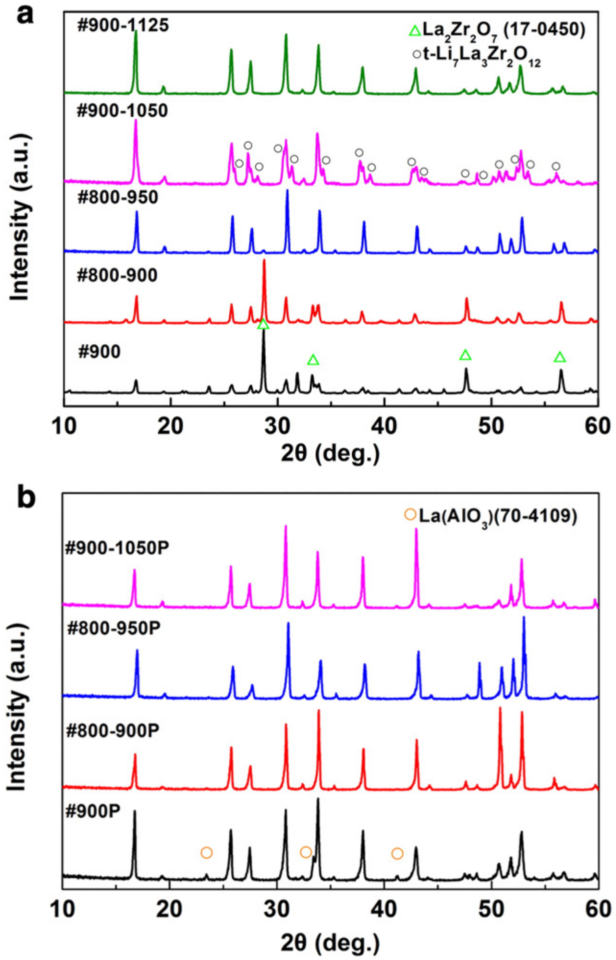

Fig. 1. (a) X-ray diffraction patterns of the LLZ powders after different calcining processes. (b) X-ray diffraction patterns of the sintered pellets.

As it was reported by previous works that the phase transition is associated with Al and Li concentration in the samples [21,22], element analysis of the powders was provided in Table 2. As the mass percentage concentration was provided when the ICP test was conducted, the La was set to be 3 per unit formula unit to get the Li and Al molar