

High Li-ion conductivity of Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ synthesized by solid-state reaction

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ABSTRACT

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has cubic garnet type structure and is a promising solid electrolyte for next-generation Li-ion batteries. In this work, Al-doped LLZO was prepared via conventional solid-state reaction. The effects of sintering temperature and Al doping content on the structure and Li-ion conductivity of LLZO were investigated. The phase composition of the products was confirmed to be cubic LLZO via XRD. The morphology and chemical composition of calcined powders were investigated with SEM, EDS, and TEM. The Li-ion conductivity was measured by AC impedance. The results indicated the optimum sintering temperature range is 800–950 °C, the appropriate molar ratio of $\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{La}(\text{OH})_3$, ZrO_2 and Al_2O_3 is 7.7:3:2:(0.2–0.4), and the Li-ion conductivity of LLZO sintered at 900 °C with 0.3 mol of Al-doped was $2.11 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C.

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1. Introduction

Rechargeable secondary Li-ion batteries are key power and energy sources for electrical vehicles, hybrid vehicles, cellular phones, laptop computers, IC cards, and other portable electronic devices, due to their high energy density, long cycle lifetime, and environmentally friendliness [1–3]. However, large-scale applications of Li-ion batteries have been hindered by safety issues posed by the organic liquid electrolyte, including flammability, leakage, and low toxicity [4,5]. Therefore, it is urgent to develop new alternative materials for use as electrolytes with improved safety as replacements for organic liquid electrolytes such as NASICON [6], perovskite [7], LiPON [8], and garnet [9] Li-ion conductors.

Of these alternatives, the garnet structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is a promising Li-ion conductor owing to its high ionic conductivity, low grain boundary resistance, and good chemical stability with lithium metal [10,11]. Two polymorphs of LLZO have been reported [12–14], cubic polymorph and tetragonal polymorph. The ionic conductivity of cubic polymorph is almost three orders of magnitude higher than that of the tetragonal polymorph at room temperature. Currently, the sol–gel process and the solid-state method are the main methods for fabricating cubic LLZO. Deubener et al. [15] studied Al-substituted LLZO using sol-gel synthesis and concluded that optimal sintering temperature is 1000 °C and ionic conductivity is $1.5 \times 10^{-5} \text{ S cm}^{-1}$. Recently,

Doeff et al. [16] reported the synthesis of cubic LLZO with doping of 0.2 g of Al_2O_3 at 1100 °C via the solid-state method. The order of magnitude of ionic conductivity was $10^{-4} \text{ S cm}^{-1}$. According to previous reports [13,17–20], cubic LLZO displays higher ionic conductivity when prepared by the solid-state method relative to that prepared by sol-gel synthesis. To obtain stable cubic LLZO, long sintering time and high sintering temperature are required [21]. However, high temperature may promote the loss of lithium and decrease the stability of LLZO. Several studies [18,22,23] demonstrated that doping with element Al and Ga allows formation of stable cubic LLZO at lower temperature, and improves the ionic conductivity. Kanamura et al. [24] reported an decrease in the required sintering temperature by the addition of Al in LLZO, from 1230 °C reported previously [10] to 1000 °C. The sintering temperature was also very high and the samples exhibited a low ionic conductivity of $1.4 \times 10^{-4} \text{ S cm}^{-1}$. Thus, the development of a strategy to produce LLZO with higher ionic conductivity and sintered at lower temperature would be very useful.

In our study, Al-doped LLZO was prepared by the traditional solid-state method. The effects of sintering temperature and Al doping contents on the structure and Li-ion conductivity of LLZO were also studied. The pure cubic LLZO phase could be obtained at a sintering temperature range of 800–950 °C and an Al-doped content range of 0.2–0.4 mol. The LLZO sintered at 900 °C with Al doping at 0.3 mol exhibited the highest Li-ion conductivity at $2.11 \times 10^{-4} \text{ S cm}^{-1}$.

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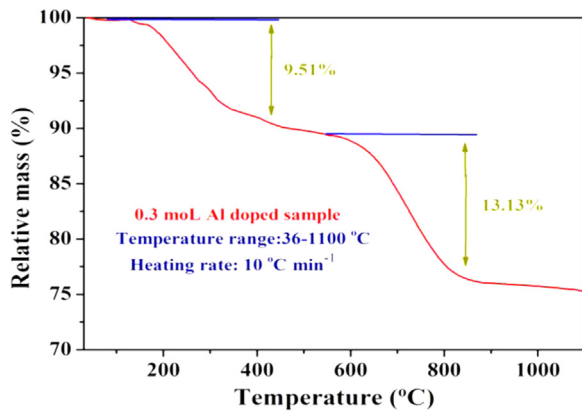


Fig. 1. TGA curve of the 0.3 mol of Al-doped precursor.

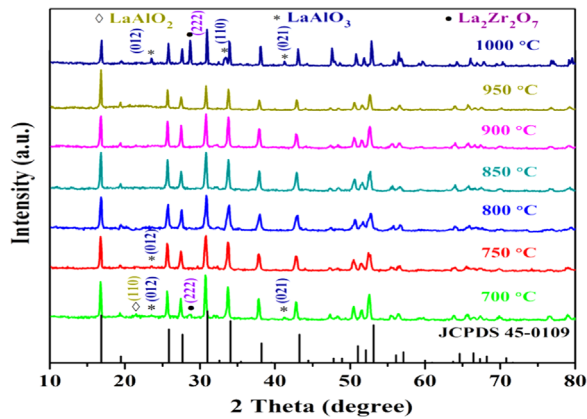


Fig. 2. XRD patterns of LLZO samples sintered at different temperatures for 12 h. The standard pattern of cubic LLZO (JCPDS 45-0109) is shown for comparison (\diamond LaAlO₂, \ast LaAlO₃, \bullet La₂Zr₂O₇).

2. Experimental

A series of Al-doped LLZO powders were prepared using a conventional solid-state method with LiOH·H₂O, La(OH)₃, ZrO₂ and Al₂O₃ as starting materials. All the chemical reagents were of analytical grade and used as purchased from Aladdin reagent (China) without further purification. The molar ratio of the starting materials was 7.7:3:2:(0–0.8), and excess LiOH·H₂O (10%) was added to compensate for the loss of lithium during the high temperature annealing. The starting materials were mixed by planetary ball-milling in 2-Propanol with zirconia balls for 24 h at milling speed constants of 400 rpm min⁻¹ and then dried at 60 °C. Next, the mixed powders were pressed into a pellet 20 mm in

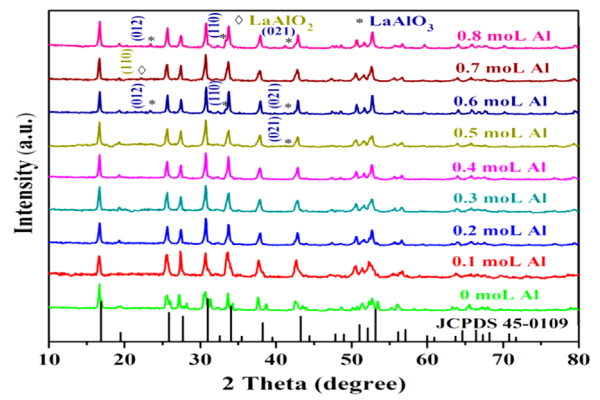


Fig. 4. XRD patterns of LLZO with different Al-doped content after sintering at 900 °C for 12 h.

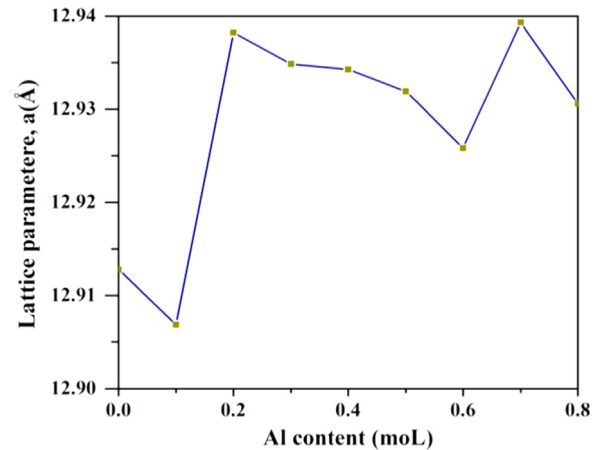


Fig. 5. The lattice parameters of the LLZO samples with different Al-doped content.

diameter under an isostatic pressure of 40 MPa and then sintered at 700–1000 °C for 12 h using a zirconia crucible to obtain cubic LLZO.

Thermo-gravimetric analysis (TGA) was performed on a STA 449F3 thermal analyzer in the temperature range of 36–1100 °C under air condition at a heating rate of 10 °C min⁻¹. The phase purity and lattice parameters of the as-prepared powders were characterized by X-ray powder diffraction (XRD, TD-3500X) with Cu/K α radiation at room temperature in the 2 θ range of 10–80°. The surface morphology and microstructure of the obtained LLZO samples were performed by scanning electron microscopy (SEM, FEI Quanta 250) and transmission electron microscopy (TEM, FEI Tecnai G2F20). The elemental distribution of the samples was investigated by energy-dispersive X-ray (EDS) with SEM.

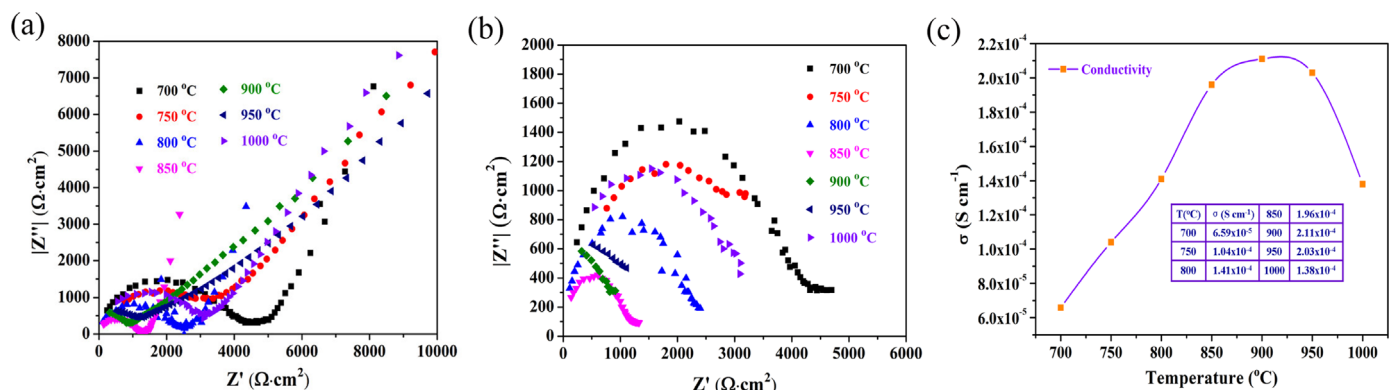


Fig. 3. (a)–(b) The typical impedance plots and (c) the corresponding Li-ion conductivity of LLZO sintered at different temperatures.

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