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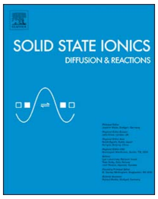

A novel solid-liquid route for synthesizing cubic garnet Al-substituted $Li_7La_3Zr_2O_{12}$

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ABSTRACT

A solid-liquid composite method (SLM) of Al-substituted cubic lithium lanthanum zirconium garnet (c-LLZO) was developed. Cubic LLZO powders whose composition was $Li_{6.23}Al_{0.26}La_3Zr_{1.88}O_{11.76}$ were prepared from the stoichiometric mixtures of lithium acetate, lanthanum oxide, zirconia and alumina, followed by an annealing of the dried precursor at 750 °C for 12 h in an air atmosphere. The resultant powders were characterized by XRD, SEM and ICP-OES. The conventional solid-state reaction methods using carbonates and hydroxides as lithium sources are also simply introduced as a comparison. In addition, the phase formation of c-LLZO powders synthesized by the ZrO_2 powders with different specific surfaces as raw material was also investigated. The results show that the cubic garnet phase LLZO powders was obtained when the value of the specific surface area (SSA) of the material ZrO_2 powder was about 110 $m^2\ g^{-1}$. Sintering these cubic phase powders at 1150 °C for 6 h in air after uniaxial pressing obtained a dense ceramic pellet with a relative density of 91.2% and ionic conductivity of 2.54×10^{-4} S cm^{-1} at 23 °C.

1. Introduction

Increasing use of fossil fuels caused heavy environmental problems and thus provoked the advent and popularization of new energy vehicle, especially hot concern about long life and safe secondary batteries [1–4]. Contrary to the liquid electrolytes, widely used in conventional Li-ion batteries, which are flammable and can cause a variety of electrochemical and packaging issues, solid-state electrolytes composed of inorganic compounds are more electrochemically stable and exhibit excellent mechanical properties. For example, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ has the conductivity as high as 5×10^{-3} S cm^{-1}, $Li_{4-x}Ge_{1-x}P_xS_4$ has the conductivity of 2.2×10^{-3} S cm^{-1} at room temperature and $Li_{0.34}La_{0.5}TiO_{2.98}$, whose bulk conductivity was reported to be as high as 10^{-3} S cm^{-1} at room temperature. Those three have been widely considered as qualified candidates for the next generation of electrolyte [1,2]. Moreover, the garnet structure Lithium ion conductor like cubic Li—La—M—O (M = Nb, Ta, Zr) compounds, due to their considerable conductivity, excellent stability to metallic lithium, and good chemical stability in air, has become a potential candidate for solid-state lithium ion electrolytes. Therefore, among many inorganic oxides ceramic electrolyte, it has aroused a growing concern in last few years [3–6].

Two kinds of structures have identified in this garnet-type compound, namely cubic phase belonging to the space group Ia3d (No. 230) and tetragonal phase belonging to the space group $I4_1/acd$ (No. 142), respectively [7]. A large number of studies have confirmed that cation doping in $Li_7La_3Zr_2O_{12}$ can stabilize highly conductive cubic phase [8–11]. Among them, aluminum substituted $Li_7La_3Zr_2O_{12}$ cubic lithium garnet was inadvertently synthesized from an alumina crucible contamination event [3]. Aluminum has been confirmed to have dual effects that increase lithium space and stable cubic structure by replacing lithium [7,12]. It is well known that the larger grain size and densities of polycrystalline ceramic materials are advantageous for the enhancement of electrical conductivity [13]. On the one hand, a stable and dense high-temperature cubic phase bulk material usually requires high temperature sintering for a long period of time (even at 1230 °C for 36 h) [3], on the other hand it is liable to cause excessive volatilization of lithium oxide and the occurrence of impure phase, which often require excess lithium salt as compensation. A lot of works have been done around reducing the LLZO densification temperature and holding time. High density LLZO can be obtained by hot-pressing [8], flowing oxygen sintering [14], or field assisted sintering [15], which enables a relative density of 96–98%. However, these techniques are unsuitable for mass production due to their high cost. Therefore, in order to obtain high-density sintered pellets, various additives were incorporated [16]. At the same time, in synthetic methodology, solid-state reaction method

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(SSR) and wet chemical method are the two most common methods used to synthesize aluminum-doped LLZO. The solid-state reaction method yields a micron-sized powder while the wet chemical method can obtain finer nano powders at lower synthesis temperature [3,17–20]. Finer primary particles are more likely to get dense ceramics at low temperature due to their higher specific surface area. However, these wet chemical processes are often complicated and consume a large amount of metal organic precursors, and are therefore not conducive to mass production. Hence, the exploration of new synthetic method and processing technology plays a vital role for the development of high performance lithium batteries based on garnet structured electrolyte [6]. In this paper, we report a novel method to synthesize phase pure c-LLZO submicron particles at relatively low temperature compared to the current solid-state reaction method. Better sintering activity is confirmed by subsequent sintering experiments at a relative low temperature for a short duration of time and finally presents a good ionic conductivity of the sintered pellet.

2. Experimental

2.1. Preparation for LLZO powder and pellet

A novel solid-liquid method was developed to prepare polycrystalline powders of Al-substituted $Li_7La_3Zr_2O_{12}$. The improved solid-liquid method uses ZrO_2 with large specific surface area as the solid form, whereas water as solvent to form a soluble lithium salt at the molecular level.

A flow chart of the SLM method used to prepare LLZO powders is shown in Fig. 1. The stoichiometric amount of $LiCH_3COO$ (99%, Aladdin Reagent Co., Ltd.) was dissolved in deionized water (the mass ratio of water to reactants is 1.8 to 1) by magnetic stirring and then citric acid monohydrate (99.5%, Sinopharm Chemical Reagent Co., Ltd.; 15 wt% of total mass of reactants) as powder leavening agent was added to obtain a clear solution. Then, γ-Al_2O_3 (20 nm, 99.99%, Aladdin Reagent Co., Ltd.) and stoichiometric amount of La_2O_3 (99.99%, Sinopharm Chemical Reagent Co., Ltd.; 900 °C preheated for at least 12 h) was added to the above clear solution and mixed using a planetary mill in a zirconia vial with zirconia balls for 3 h at a rotation speed of 300 rpm. After that, the above suspension and stoichiometric amount of ZrO_2 (97.7%; $Zr(OH)_4$ was previously heated at 400, 500, and 800 °C for 5 h, respectively) were mixed by continuing ball milling for 12 h. The molar ratio between Li, La, Zr and Al was 7:3:2:0.24. The mixed slurry dried carefully through a three-step heating process in air, which was heated at 80 °C for 1 h, 120 °C for 2 h and 250 °C for 6 h, respectively. Then, a brown precursor was obtained. The precursor was calcined in MgO crucible at 700 °C, 750 °C and 800 °C for 12 h, respectively. Subsequently, the obtained powders were milled again in a zirconia vial with zirconia balls in 2-propanol at a rotation speed of 400 rpm for 12 h and dried at 60 °C. About 0.35 g of powders were uniaxially pressed into pellets in a 10 mm green body with a pressure of 200 MPa; the green pellets were covered with the powders (prepared at the same steps, but with excess 10% of the mass of lithium salt was added) to inhibit the volatilization of lithium oxide and were sintered in a MgO crucible at 1150 °C for 6 h for avoiding the excessive aluminum pollution from commonly-used alumina crucible during high temperature [8]. As a comparison, we also used other common lithium sources such as lithium hydroxide and lithium carbonate to synthesize cubic Al-LLZO powders according to the existing work using solid-state reaction method [21,22].

2.2. Characterization of Al-LLZO

The density of samples was measured by the Archimedes method in water and the theoretical density of 5.11 g cm^{-3} was used to calculate their relative density [7]. The phase composition of the calcined powders and sintered sample were characterized with X-ray diffraction (XRD, Bruker D8 Advance, Bruker AXS, Germany) with Cu Kα radiation at a step of 0.02° s^{-1} in the range of 2θ from 10° to 80°. The contents of lithium and aluminum were determined by induced coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 2100 DV). Thermogravimetric analysis/differential thermal analysis (TG-DTA) was employed to narrow the proper temperature range for

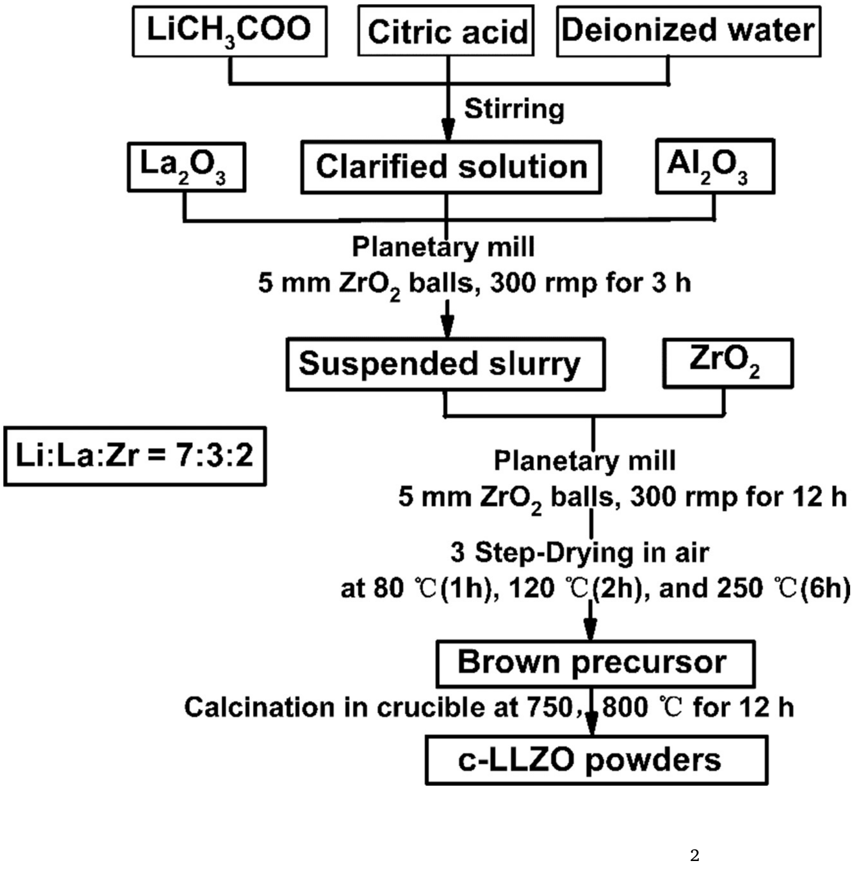

Fig. 1. Flow chart of the c-LLZO synthesis by SLM.