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High lithium ionic conductivity of garnet-type oxide $Li_{7+x}La_3Zr_{2-x}Sm_xO_{12}$ (x = 0–0.1) ceramics

Xishu Wang, Jie Liu *, Rui Yin, Yichen Xu, Yonghua Cui, Liang Zhao, Xibin Yu *

Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry, Shanghai Normal University, Shanghai 200234, China

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$Li_7La_3Zr_2O_{12}$ (LLZO) garnet is one of the most promising Lithium-ion solid electrolytes in all-solid-state Lithium-ion batteries, due to its higher chemical stability to Li metal and relatively higher lithium-ion conductivity. To further increase the electrical conductivity of LLZO, Sm^{3+} is doped into the Zr^{4+} site of LLZO so that excess Li occupies the position of the octahedral. Thereby lithium ion transport and increasing ionic conductivity are promoted. The optimal addition of Sm^{3+} is 0.06. $Li_{7+x}La_3Zr_{2-x}Sm_xO_{12}$ (LLZSO, x = 0.06) electrolyte with cubic phase is obtained with sintering at 1200 °C for only 3 h. It has higher relative density and better ionic conductivity than the pristine LLZO. Its bulk and total ionic conductivity are $\sim 6.4 \times 10^{-4}$ S·cm^{-1} and 2.46×10^{-4} S·cm^{-1} at 20 °C, respectively.

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1. Introduction

Lithium-ion secondary batteries have been widely used in the fields of consumer electronics and communications. However, the organic electrolyte has flammable, easily corrodible, and poor thermal stability safety issues. The development of conventional lithium-ion batteries is limited, and all-solid-state lithium batteries (ASSLB) are considered to be able to completely solve the above problems [1–3]. As a core component of ASSLB, solid electrolyte is a key material for achieving high energy density, high cycle stability and high safety performance of ASSLB [4]. Garnet-type solid electrolytes exhibit better overall performance, in contrast to some other inorganic solid state electrolytes such as NASICON [5], nitrides [6], sulfides [7], perovskite oxides [8] and antiperovskite [9].

Typical Li-stuffed garnets are $Li_xA_3B_2O_{12}$ type oxides, in which A sites are generally occupied by La cations in 8-fold coordination, and B sites are occupied by pentavalent Nd or Ta cations, or by tetravalent Zr cations in 6-fold coordination. $Li_5La_3M_2O_{12}$ (M = Nb, Ta) [10] and $Li_7La_3Zr_2O_{12}$ (LLZO) [11] are promising compositions among garnet-type solid electrolytes, and they attracted significant attention from academic and industrial communities. LLZO garnet oxide is regarded as an ideal solid electrolyte material for ASSLB. In this work, we increased the total conductivity of LLZO through partial substitution of Zr^{4+} with Sm^{3+}.

2. Experimental

2.1. Materials and methods

Cubic phase $Li_{7+x}La_3Zr_{2-x}Sm_xO_{12}$ (LLZSO, x = 0, 0.06, 0.1) samples were prepared by high temperature solid-state reactions. Zirconium and lanthanum oxides were pre-dried at 900 °C for 10 h. The starting powders of Li_2CO_3 (AR), La_2O_3 (99.99%), ZrO_2 (AR), Sm_2O_3 (99.99%) were mixed with an isopropyl alcohol by stoichiometry ratio and moistly ball-milled for 8 h. 10 wt% excess of Li_2CO_3 was added to compensate lithium loss during the calcination process. Firstly the mixture was calcined at 950 °C for 6 h, then the calcined powders were pressed into green pellets of 15 mm in diameter under 300 MPa. Subsequently these green pellets were covered with the as-calcined LLZSO powder and calcined at 1200 °C for 3 h.

2.2. Material characterizations

The phase purity and crystal structure of the calcined samples were examined by X-ray diffraction (Bruker, D8 Advance, Karlsruhe, Germany 40 kV, 30 mA). The microstructure and the elemental mapping images of the calcined pellets were characterized by scanning electron microscopy (SEM, Hitach S-4800 Field

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* Corresponding authors.
E-mail addresses: liujie@shnu.edu.cn (J. Liu), xibinyu@shnu.edu.cn (X. Yu).

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Emission). The relative density values were obtained through the Archimedes method. Ionic conductivities of samples were measured in the temperature range (20–150 °C) using an electrochemistry impedance spectrometer (ZAHNER Xpot, Germany) from 1 Hz to 1 MHz with a 10 mV perturbation amplitude and sputtered Ag blocking electrodes.

3. Results and discussion

3.1. Structure and morphology of LLZO-based electrolytes

Fig. 1 shows the XRD patterns of LLZO-based pellets. Apparently, the diffraction peaks are assigned to a crystalline garnet-type structure (JCPDS 45-0109), so all the electrolyte samples are essentially cubic garnet-type oxides. For the undoped LLZO sample, there is no significant diffraction peak associated with the impurity, indicating that the applied sintering schedule at 1200 °C for 3 h is effective for obtaining a relatively pure cubic LLZO. All the XRD peaks of LLZSO (x = 0.06, 0.1) show left migration. This is because the doped Sm ions is larger than Zr ions, resulting in the lattice constant enlargement. In Fig. 1(A), a small amount of second phases corresponding to Li_2ZrO_3 and $La_2Zr_2O_7$ are observed, resulted from the addition of excess Li_2CO_3 in the starting materials for preparing LLZSO [12].

Typical SEM images of $Li_{7.06}La_3Zr_{1.94}Sm_{0.06}O_{12}$ pellet are shown in Fig. 2(A) and (B). The surface and the cross-section of the electrolyte ceramic are dense without pinholes, and the grain boundaries are quite small. To confirm of elements distribution in the $Li_{7.06}La_3Zr_{1.94}Sm_{0.06}O_{12}$ grains, Energy-dispersive X-ray spectroscopy (EDS) was conducted. In Fig. 2(C–G), EDS element mapping images indicate La, O, Sm and Zr are uniformly distributed in this bulk [13].

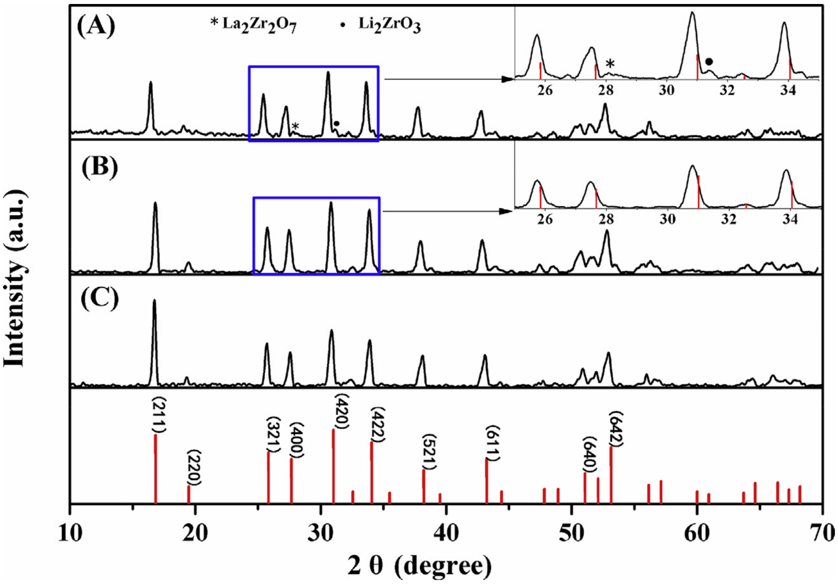

Fig. 1. XRD patterns of (A) $Li_{7.1}La_3Zr_{1.9}Sm_{0.1}O_{12}$; (B) $Li_{7.06}La_3Zr_{1.94}Sm_{0.06}O_{12}$; (C) $Li_7La_3Zr_2O_{12}$. Inset: enlarged patterns from 25 to 35°.

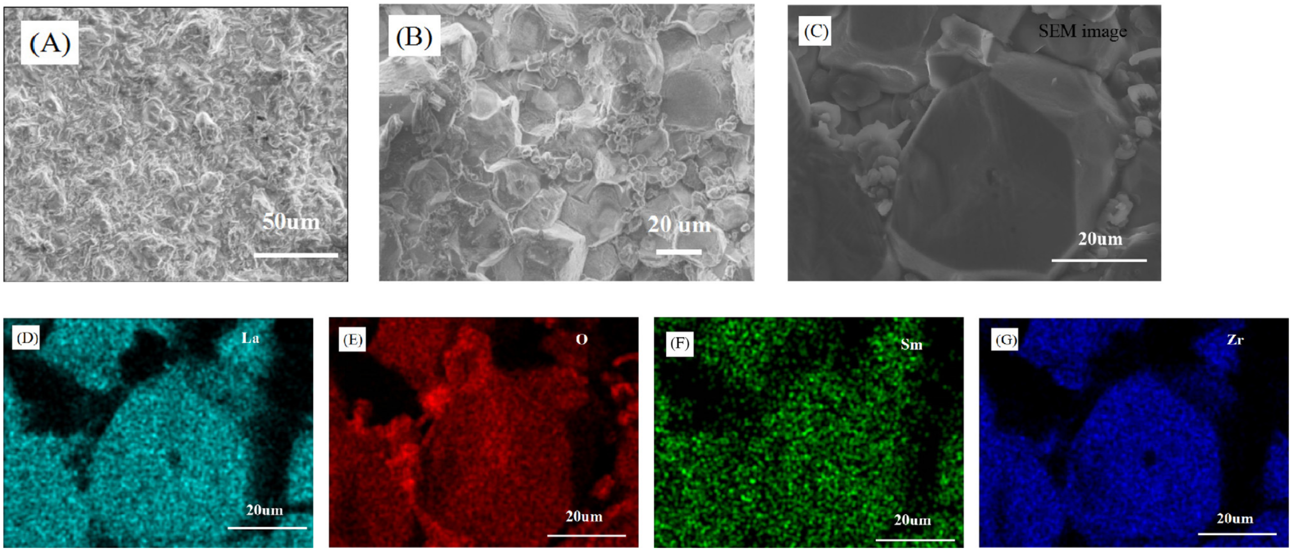

Fig. 2. Typical SEM images of the $Li_{7.06}La_3Zr_{1.94}Sm_{0.06}O_{12}$. (A) surface; (B) cross-section. And (C–G) EDS elemental mapping images of $Li_{7.06}La_3Zr_{1.94}Sm_{0.06}O_{12}$.

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