



Short communication

Densification and ionic-conduction improvement of lithium garnet solid electrolytes by flowing oxygen sintering

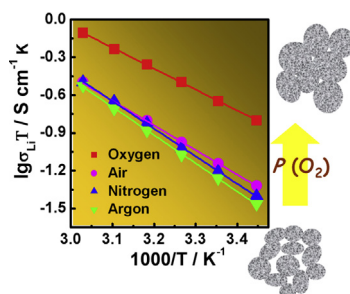
Yiqiu Li¹, Zheng Wang¹, Chilin Li^{*}, Yang Cao, Xiangxin Guo^{*}

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, China

HIGHLIGHTS

- Flowing oxygen sintering to improve lithium garnet electrolytes is firstly studied.
- Densification is enhanced by filling pores with oxygen and its lattice diffusion.
- A high density (96%) and overall conductivity ($7.4 \times 10^{-4} \text{ S cm}^{-1}$) are achievable.

GRAPHICAL ABSTRACT



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ABSTRACT

High density ($\sim 96\%$) garnet-type Al-contained $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (LLZTO-Al) solid electrolytes are prepared by conventional solid-state reaction and the following flowing oxygen sintering process. An overall ionic conductivity as high as $7.4 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C is achievable, remarkably higher than that obtained by sintering in other atmospheres. The dependence of density and conductivity of solid electrolytes on sintering under different oxygen partial pressures is discussed. Atmosphere sintering is proved to be an effective method to improve the relative density of lithium oxide ceramics.

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1. Introduction

Solid state electrolytes have attracted much attention owing to their potential application in all-solid-state lithium batteries, which are thought to be superior to the presently used liquid-electrolyte based ones in terms of safety and environmental issues [1,2]. So

far, a large number of solid state electrolyte prototypes have been reported, such as amorphous nitrided phosphate (LiPON) [3,4], perovskite-type titanates [5], NASICON-type phosphates [6], LISICON-type sulfides [7], and their glass-ceramic analogs [8,9]. Recently, the cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), a typical garnet framework oxide, showed a high ionic conductivity of approximately $2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, as well as good thermal and chemical stabilities [10–12]. Stabilization of cubic garnet LLZO may need introduction of e.g. Al, Nb or Ta [13–15], since formation of tetragonal LLZO is also possible while causing a poor ionic conductivity [16]. Besides the crystalline structure, the microstructure related to grains and grain boundaries is also a critical issue. For

^{*} Corresponding authors. Tel.: +86 21 52411030, +86 21 52411032; fax: +86 21 52411802.

E-mail addresses: chilinli@mail.sic.ac.cn (C. Li), XXGuo@mail.sic.ac.cn (X. Guo).

¹ The authors have the equal contribution to this work.

polycrystalline ceramic electrolytes, a dense material with large grain size is highly desired. High porosity in solid electrolytes may cause a high grain boundary resistance as well as mechanical failure. Owing to the volatilization of Li components or inert gas filling in pores during sintering, the LLZO solid electrolytes obtained via conventional solid state method usually show a limited density as well as ionic conductivity. High density LLZO can be obtained by hot-pressing, which enables a relative density of 96–98% [16–18]. However, this technique is unsuitable for continuous mass production, and its production cost is high.

Flowing oxygen sintering is a powerful and economical alternative method, which had been used to prepare high density Pb-based piezoelectric ceramics [19–21]. Flowing oxygen during sintering can facilitate sintering by filling pores with pure oxygen, aiding densification compared with other molecules in air or inert atmospheres. To the best of our knowledge, this technique has not been applied in garnet-type solid electrolytes. In view of the good solubility and diffusivity of oxygen, the pores filled with oxygen could disappear easily by oxygen migration via lattice diffusion or vacancy transport. Therefore, we expect that the pure oxygen sintering can significantly enhance both the density and ionic conductivity of solid electrolytes. In this work, we compare the Al-contained $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (LLZTO-Al) solid electrolytes which undergo the sintering processes with different oxygen partial pressures, respectively using oxygen, air, nitrogen and argon atmospheres. Their relative densities, microstructures and ionic conductivities are discussed, highlighting oxygen-sintering driven densification mechanism and conduction performance.

2. Experimental

LLZTO-Al ceramics were prepared via conventional solid state reaction, from stoichiometric LiOH (Alfa Aesar, 99.995%), $\text{La}(\text{OH})_3$ (Alfa Aesar, 99.95%), ZrO_2 (Aladdin Reagent, 99.99%), Ta_2O_5 (Aladdin Reagent, 99.99%) and a 15 wt.% excess of LiOH for compensating volatile Li components during synthesis. The powders were ball-milled for 12 h, and then were heated in air at 900 °C for 12 h to ensure the formation of cubic LLZTO phase, and then were ball-milled for 12 h again. After that, the powders were pressed into pellets with a diameter of 12 mm at 100 MPa, and sintered at 1140 °C for 9 h in different atmospheres, i.e. oxygen, air, nitrogen and argon, respectively. During sintering the pellets were covered with their respective mother powders and put in covered alumina crucibles in a tube furnace.

The relative density values were obtained by the Archimedes method using alcohol ($\text{C}_2\text{H}_5\text{OH}$) for measurement. Crystalline structure of synthesized phases was obtained by X-ray diffraction (XRD, Bruker D2 Phaser), using $\text{Cu K}\alpha$ radiation with 2θ in range of 10–80° and step size of 0.02° and was rechecked at the beamline of BL14B1 in the Shanghai Synchrotron Radiation Facility. Their lattice parameters were estimated from Rietveld refinement by using Fullprof software. The compositions of LLZTO-Al samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 725). Microstructure and morphology were characterized by scanning electron microscope (SEM, Hitachi

S-3400N) at a 5 kV accelerating voltage, as well as transmission electron microscope (TEM, JEOL JEM-2100F) at a 200 kV accelerating voltage. Elemental distribution in grains and grain boundaries was detected by energy dispersive X-ray detector (EDX, IXRF Model 550i) equipped on SEM. Two sides of the pellet samples were polished and coated with dry Au slurry films with a diameter of 8 mm for the measurements of alternating current impedance and directing current polarization. Ionic conductivities of LLZTO-Al samples were measured in air in a temperature range from 20 to 60 °C, and in a frequency range from 0.1 Hz to 20 MHz with an amplitude of 10 mV using an impedance analyzer (Novocontrol Beta High Performance Impedance Analyzer). Electronic conductivities were examined by potentiostatic polarization experiment, using a battery test station (Arbin BT-2000) with an applied voltage of 5 V.

3. Results and discussion

The preparation of LLZTO-Al ceramics is characterized by different atmosphere sintering. The element composition of samples determined by ICP-OES is listed in Table 1. The mole ratios of La/Zr/Ta in these samples are almost the same, very close to the expected composition as shown in stoichiometric $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, e.g. Li:La:Zr:Ta:Al = 7.40:3:1.75:0.26:0.23 for oxygen-sintered sample. Note that all the samples show a bit higher lithium content than expected (e.g. 7.4 mol of Li exceeds 6.29 mol of Li required for charge balance in oxygen-sintered sample), which likely stems from Al reaction with Li to precipitate Li–Al–O phases at grain boundaries as discussed later [22]. Indeed, a certain amount of Al (~24 mol%) was detected from ICP-OES. It should come from the Al_2O_3 crucibles used for sintering, since no Al is intentionally added in the starting materials. Fortunately, Al contamination has been indicated to be beneficial to the improvement of conductivity, serving as grain boundary additive and/or lattice dopant [13,14,22]. The relative densities of the samples sintered in oxygen, air, nitrogen and argon are approximately 96%, 93%, 91% and 90%, respectively, through measuring three samples for each atmosphere by Archimedes method. It indicates that pure oxygen atmosphere can significantly increase the LLZTO-Al density, which is comparable to the value obtained by hot-press sintering [16,17].

Fig. 1 shows the X-ray diffraction (XRD) patterns for LLZTO-Al samples sintered in different atmospheres. Each of them displays a typical cubic garnet phase similar to $\text{Li}_5\text{La}_2\text{Nb}_2\text{O}_{12}$ (JCPDS 01-084-1753), and no obvious impurity phases can be detected. The lattice parameters from Rietveld refinement are ~12.96 Å for all the samples, close to the values reported in other Ta-doped LLZO with the same Ta content [17]. This result indicates that the three dimensional garnet framework is quite stable even in inert atmosphere sintering [23], and no serious oxygen evolution and structure collapse occur compared with less stable oxides of layer structures at high temperature.

In contrast to other atmospheres, sintering in pure oxygen leads to a much denser microstructure from the scanning electron microscope (SEM) images of cross sections of LLZTO-Al samples as shown in Fig. 2(a–d). Its grain size mainly lies in the range from 5 to

Table 1

Composition, relative density, lattice parameter a , total conductivity (σ_{total}), activation energy for total conductivity (E_a) and electronic conductivity (σ_e) of LLZTO-Al electrolytes depending on sintering atmospheres (oxygen, air, nitrogen and argon).

Sintering atmosphere	Atomic ratio of Li:La:Zr:Ta:Al ^a	Relative density (%)	Lattice parameter a (Å)	σ_{total} (S cm^{-1})	E_a (eV)	σ_e (S cm^{-1})
Oxygen	7.40:3:1.75:0.26:0.23	96	12.964	7.4×10^{-4}	0.33	2.1×10^{-7}
Air	7.53:3:1.75:0.26:0.24	93	12.963	2.4×10^{-4}	0.39	1.2×10^{-7}
Nitrogen	7.48:3:1.76:0.26:0.25	91	12.963	2.1×10^{-4}	0.43	9.0×10^{-8}
Argon	7.57:3:1.75:0.25:0.25	90	12.962	1.8×10^{-4}	0.44	6.2×10^{-8}

^a Atomic ratio of Li:La:Zr:Ta:Al is normalized by La content as shown in the formula $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$.

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