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Effect of Al_2O_3 on the sintering of garnet-type $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$

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ABSTRACT

It is widely recognized that Al plays a dual role in the fabrication of garnet-type solid electrolytes, i.e., as a dopant that stabilizes the cubic structure and a sintering aid that facilitates the densification. However, the sintering effect of Al_2O_3 has not been well understood so far because Al is typically "unintentionally" introduced into the sample from the crucible during the fabrication process. In this study, we have investigated the sintering effect of Al on the phase composition, microstructure, and ionic conductivity of $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ by using an Al-free crucible and intentionally adding various amounts of γ-Al_2O_3. It was found that the densification of $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ occurred via liquid-phase sintering, with evidence of morphology change among different compositions. Among all of the compositions, samples with 0.05 mol Al per unit formula of garnet oxide (i.e., 0.3 wt% Al_2O_3) exhibited the optimal microstructure and the highest total ionic conductivity of 5×10^{-4} S cm^{-1} at room temperature.

1. Introduction

While increasing energy and power density is the primary goal of Li-ion battery research, improving cell safety is also a crucial consideration, especially in transportation-related applications [1–5]. Liquid electrolytes, which are flammable and cause a variety of electrochemical and packaging issues, are still the choice for conventional Li-ion batteries. Solid-state electrolytes composed of inorganic compounds are non-flammable and generally more electrochemically stable [6–9]. Therefore, they are considered promising candidates in next-generation all-solid-state batteries. Inorganic systems that have been extensively investigated include sulfide- and oxide-based Li-ion conductors [10–12]. Despite their high ionic conductivity and ductile nature, many sulfide-based compounds are electrochemically unstable against Li metal and cathode materials [6,13–15]. Their high air sensitivity also imposes a cost barrier for practical production. A number of oxide systems show good ionic conductivity (>1 mS cm^{-1}) [16–19]. More importantly, the chemical and electrochemical stabilities of oxide-based conductors are generally very good. Recently, garnet-type Li-ion conductors have become one of the most popular ionic conductors with a total conductivity as high as 1.6 mS cm^{-1} [20–22]. Also, it has been shown that garnet-type conductors are stable with Li metal [23]. Although Li dendrites have been observed in the garnet oxides, this is likely related to defects (e.g., grain boundaries) rather than intrinsic mechanical problems in the samples [24,25].

Recent progress has shown that cation substitution in $Li_7La_3Zr_2O_{12}$ is required to stabilize its highly conductive cubic phase [26–28]. One of the most effective dopants is Ta, and the optimized composition is $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZT0.5) [19,29]. The dopant Al plays a duel role in the garnet system. Al ions can create vacancies and stabilize the cubic structure by replacing Li ions, which is similar to the effect of Ta ions [30,31]. In addition, Al ions can react with other ions in the system and form liquid phases that facilitate densification during the sintering process [19,32–35]. In fact, unless the expensive hot-press or spark-plasma sintering techniques are used [22,30,36], most of the approaches to fabricate Li garnet oxides in the literature take advantage of the sintering effect of Al. It should be noted that, as a dopant, Al ions typically reside along the conduction path of Li ions, which blocks Li-ion transport [27,37,38], so the Al-stabilized garnet-type oxides in general show lower conductivity compared to those with Ta [30,32]. It is preferred that Al ions do not enter the garnet framework but only act as a sintering aid while the Li content, phase composition, and conductivity are tuned by other dopants such as Ta.

So far, Al has been introduced into garnet oxides mainly by 1) "unintentional" transfer from an Al_2O_3 crucible during high-temperature sintering and 2) addition in the starting materials. In the first method, the content of Al contaminant is uncontrollable, so the results are typically unrepeatable. For the second method, Ta-doped and Al/Ta co-doped samples have been prepared through an Al-free calcination/sintering process [26]. However, Al is likely to be introduced into the garnet framework with this method. In our current study, we chose γ-Al_2O_3 as a sintering aid for the densification of LLZT0.5 in an Al-free crucible. Compared to α-Al_2O_3, γ-Al_2O_3 has a lower melting point and is thermodynamically less stable, so the eutectic mixing between γ-Al_2O_3 and Li_2O is expected to occur more readily during the sintering process. The sintering aid was added to the samples after the garnet phase was formed, and the final sintering step for densification was carried out thereafter. The purpose of such a process is to prevent Al from entering the garnet framework so that the effect of γ-Al_2O_3

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on the sintering process of $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ can be exclusively investigated and understood.

2. Experimental

All samples were prepared by a conventional solid-state reaction technique. Stoichiometric amounts of $LiOH\cdot H_2O$ (>98%, Sigma-Aldrich), La_2O_3 (>99.9%, Sigma-Aldrich), ZrO_2 (>99.5%, Alfa Aesar), and Ta_2O_5 (>99.85%, Alfa Aesar) were ball-milled using a roller mixer in a polyethylene jar filled with 2-propanol. LiOH was obtained by drying $LiOH\cdot H_2O$ at 200 °C for 12 h. An extra 10 wt% $LiOH\cdot H_2O$ was added into the starting powders to compensate for the loss of Li during high-temperature sintering. La_2O_3 powders were dried at 900 °C in a MgO crucible (Aremco Products, Inc.). The weight ratio between powder and solvent during the ball-milling was 1:1. Yttrium stabilized ZrO_2 balls with diameter of 5 mm (Inframat Advanced Materials) were used as the grinding medium, and the weight ratio between powder and grinding media was 1:16.

After ball-milling, the slurry was dried and calcined at 900 °C for 10 h in the MgO crucible. Various amounts of γ-Al_2O_3 (>99%, Alfa Aesar, 20 nm, measured in mol per mol of LLZT0.5) were then added to the calcined powders, and the mixture was ball-milled again. The second ball-milling was similar to the first one except the polyethylene jar was filled in an argon-filled glove box (moisture and oxygen level <0.1 ppm) and the solvent was tetrahydrofuran (anhydrous, 99.9%, Sigma-Aldrich). The jar was sealed before being removed from the glove box.

The slurry was dried again after the second ball-milling. 1 g of the powders was pelletized using cold-pressing in a 13-mm die with a pressure of 350 MPa. Then the pellet was sandwiched between two layers of the mother powders (2 g in each layer) in a small MgO crucible. The powders at the bottom could prevent possible reaction with the MgO crucible and the covering powders could suppress Li evaporation. The pellet was finally sintered at 1100 °C in air. The sintering conditions are summarized in Table 1. The heating and cooling rates were 3 and 2 °C min^{-1}, respectively.

The morphology of the sintered samples was characterized using scanning electron microscopy (SEM, JEOL 5900, 15 kV for low-resolution images and FEI Quanta 3D focused ion beam/SEM, 20 kV for high-resolution images) on fracture surfaces. Energy-dispersive X-ray spectroscopy (EDS) was employed for elemental analysis. The density and porosity were measured by Archimedes' method. A theoretical density of 5.406 g cm^{-3}, based on the lattice parameters derived from the Rietveld refinement, was used to calculate relative density of the samples. The phase composition of the samples was characterized by X-ray diffraction (XRD, Rigaku MiniFlex II) with a scan speed of 1° min^{-1} and a step size of 0.05°.

To test the ionic conductivity, the samples were polished on both sides. Gold paste (PELCO) was applied to both sides and the samples were then cured at 700 °C for 1 h. The samples then were loaded into a spring-loaded Swagelok cell with stainless steel electrodes. Impedance spectra were collected with an electrochemical interface (Solartron 1287, Solartron Analytical) and a frequency response analyzer (Solartron 1260, Solartron Analytical) under open-circuit voltage (OCV). The frequency range was from 1 MHz to 1 Hz and the ac amplitude was 10 mV. Temperature-dependent ionic conductivities were measured from the range of 25 to 150 °C in a tube furnace.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows XRD patterns of selected samples. The experimental conditions of the samples are summarized in Table 1. All of the samples showed a cubic garnet structure, which was in agreement with literature reports that the critical doping level of Ta for the cubic-tetragonal phase transition is around 0.5 mol [39,40]. Note that the absence of impurities in the XRD patterns does not necessarily suggest that the Al_2O_3 sintering aid was fully incorporated into the garnet lattice; instead, it may suggest that the amount of secondary phases was below the detection limit of the X-ray diffractometer. Indeed, even for the sample with 0.3 mol Al, the weight fraction of Al_2O_3 was only ~1.7 wt% (refer to Table 1). Another possibility is that the secondary phases may appear as an amorphous phase, as suggested by several reports [33,41].

A quick Rietveld refinement was performed to obtain the lattice parameters using PowderCell. According to Duvel et al. [42], a small amount of Al ions can act as an aliovalent dopant by replacing three Li ions in the garnet structure, which results in significant change of the lattice parameters because of the difference in size of Al ions from that of Li ions. In our current study, it was found that the standard deviation of lattice parameters for the samples sintered at 1100 °C for 12 h was <0.003 Å with the addition of 0–0.3 mol Al. In comparison, replacing 0.1 mol Zr with Ta in the garnet structure resulted in an average change of 0.01 Å in the lattice parameters [29,43]. Thus, the negligible change in the lattice parameters with different amounts of Al_2O_3 addition suggested that the substitution of Al for Li in the garnet structure in the current study was minimal.

3.2. Morphology and elemental analysis

The morphology of the sintered samples was characterized using SEM. As shown in Fig. 2a, the sample without addition of Al_2O_3 had a large amount of pores and an average grain size of around 10 μm. The volume of the open pores and the relative density were around 11% and 80%, respectively. The lower relative density indicated that the sample was not well-sintered without addition of sintering aid. In comparison, the sample with 0.02 mol Al (~0.1 wt% Al_2O_3, sample #2, Fig. 2b) showed a density of 91% under similar sintering conditions. The density further increased to 94% with addition of 0.05 mol Al (~0.3 wt% Al_2O_3), as shown in Fig. 2c. Meanwhile, the morphology of the samples with the addition of Al_2O_3 was significantly different from that of the Al-free sample (compare Fig. 2b and c with a). For the sample

Table 1
Summary of experimental conditions, room-temperature transport properties and relative densities.

Sample ID	Al content (mol)	Al_2O_3 content (wt%)	Sintering time (h)	σ_b r.t. (mS cm^{-1})	σ_t r.t. (mS cm^{-1})	$E_a(b)$ (eV)	$E_a(t)$ (eV)	Relative density
#1	0	0	12	0.1	0.022	0.41	0.51	0.798
#2	0.02	0.1	12	0.26	0.17	0.39	0.43	0.910
#3	0.05	0.3	12	0.53	0.49	0.37	0.38	0.942
#4	0.1	0.6	12	0.43	0.33	0.42	0.45	0.934
#5	0.1	0.6	18	0.37	0.32	0.42	0.43	0.938
#6	0.1	0.6	24	0.33	0.32	0.32	0.32	0.944
#7	0.2	1.2	12	0.58	0.47	0.40	0.42	0.921
#8	0.2	1.2	18	0.51	0.47	0.38	0.39	0.927
#9	0.2	1.2	24	0.16	0.11	0.36/0.64	0.39/0.69	0.927
#10	0.3	1.7	12	0.46	0.33	0.36	0.39	0.886