Effect of Al₂O₃ on the Sintering of Garnet-Type Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂

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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 Al₂O₃ 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}La₃Zr_{1.5}Ta_{0.5}O₁₂ by using an Al-free crucible and intentionally adding various amounts of γ -Al₂O₃. It was found that the densification of Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂ 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% Al₂O₃) exhibited the optimal microstructure and the highest total ionic conductivity of 5×10^{-4} S cm⁻¹ at room temperature.

Key words: garnet oxide, lithium ion conductor, solid electrolyte, liquid-phase sintering, Al₂O₃.

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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 ($>1 \text{ mS cm}^{-1}$) [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 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is required to stabilize its highly conductive cubic phase [26-28]. One of the most effective dopants is Ta, and the optimized composition is $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZT0.5) [19,29]. The dopant Al plays a dual 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 $\gamma\text{-Al}_2\text{O}_3$ as a sintering aid for the densification of LLZT0.5 in an Al-free crucible. Compared to $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ has a lower melting point and is thermodynamically less stable, so the eutectic mixing between $\gamma\text{-Al}_2\text{O}_3$ 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 $\gamma\text{-Al}_2\text{O}_3$ on the sintering process of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ can be exclusively investigated and understood.

2. Experimental

All samples were prepared by a conventional solid-state reaction technique. Stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (>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 $\text{LiOH}\cdot\text{H}_2\text{O}$ at 200°C for 12 h. An extra 10 wt% $\text{LiOH}\cdot\text{H}_2\text{O}$ 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 $\gamma\text{-Al}_2\text{O}_3$ (>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 less than 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

Figure 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 less than 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 **Error! Reference source not found.**a, 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, Figure 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 **Error! Reference source not found.**b and c with a). For the sample with 0.02 mol Al, the microstructure consisted of larger grains (~20 μm) with micron-size smaller grains and pores distributed along the grain boundaries. With the addition of 0.05 mol Al (sample #3, Figure 2c), the sample was further densified and the pores almost disappeared, which clearly showed the effectiveness of the sintering aid during the densification process.

The microstructure of a sample with addition of 0.1 mol Al (sample #4) was significantly different from those with lower amounts of Al. As shown in Figure 2d, the sample exhibited a duplex microstructure consisting of larger grains and micron-size smaller grains. The smaller grains were distributed at the grain boundaries of the larger ones. The average size of the larger grains was around 50 μm . Meanwhile, a large amount of pores smaller than 5 μm was found inside the grains. This type of pore structure has been reported by German [44]. During final stage of sintering, small pores coalesce into large ones and they are distributed at grain boundaries. If the grain boundaries move too fast during sintering, the pores are trapped in the grains. The grain boundaries and pores are then separated from each other. This sintering behavior is usually detrimental to densification as it is difficult to eliminate the trapped pores, especially when the sample is sintered in air and the residual N_2 gas in the pores is not readily soluble in oxygen lattices [45].

The microstructure of a sample with 0.2 mol Al (sample #7) was very similar to that with 0.1 mol Al, except it had more micron-size smaller grains, as seen in Figure 2e. Elemental analysis using SEM/EDS was carried out for sample #8 with 0.2 mol Al. The concentration of Al

element in the larger particles was much lower than that in the smaller particles. The uneven distribution of Al is illustrated in the EDS mapping, as shown Figure 3. It can be seen that La, Zr, Ta, O, and a very small amount of Al were uniformly distributed in the larger particles, suggesting a pure garnet phase. Meanwhile, Al-concentrated regions were found at the grain boundaries and in the smaller particles. The tendency of Al to segregate at the grain boundaries has also been observed and reported in the literature [19,33]. According to our study, these areas were also oxygen-rich regions. As seen in Figure 4a and b, EDS maps at a higher resolution showed that the compounds at the grain boundary and in the smaller particles mainly contained Al and O. Considering that Li signals cannot be detected by EDS, we postulate that the phase may actually be compounds of Li-Al-O, which have been widely reported as secondary phases during garnet oxide sintering [32-35]. The formation of such types of secondary phases may be responsible for the different morphology of the smaller particles compared to the larger ones in the samples with 0.1 and 0.2 mol Al. In contrast, no visible Al enrichment was detected at the grain boundaries for the sample with 0.05 mol Al. The microstructure of the sample with 0.3 mol Al (sample #10) is shown in Figure 2f. An even great amount of small-size particles was observed in the sample compared to that with 0.2 mol Al, which was probably due to the formation of more secondary phases of Li-Al-O with the addition of more Al_2O_3 .

Based on the SEM and EDS results, we provide an explanation for the morphology differences in the samples with various amounts of Al_2O_3 . The Al-free sample had an almost pure garnet phase with a large number of pores distributed at the grain boundaries. With the additions of 0.02 and 0.05 mol Al, the Al_2O_3 might react with excessive Li_2O existing in the sample, which would form $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3$ liquid phases. According to the phase diagram between Li_2O and Al_2O_3 [46], a eutectic composition with 23 mol% Al_2O_3 is formed that has a melting

temperature of 1055°C, which is lower than the sintering temperature (i.e., 1100°C) in our study. The formation of liquid phases helps to densify the samples, which leads to the higher density compared to that without the addition of Al₂O₃. With the additions of 0.1 and 0.2 mol Al, the amount of liquid phases further increased, and that facilitated fast movement of the grain boundaries and rapid grain growth, which led to the observed exaggerated grain growth. Based on all of these observations, we can conclude that the addition of 0.05 mol Al to the sample yielded an optimal microstructure (e.g., well-connected particles, no obvious porosity, and no exaggerated grain growth). As shown in Figure 5, that sample exhibited the highest relative density among all of the compositions.

To understand the effect of prolonged sintering time on the microstructure, we further sintered samples with 0.1 and 0.2 mol Al at 1100°C for 18 and 24 h. As shown in Figure 6, the larger particles continued to grow at the cost of the smaller particles and the amount of pores inside the large particles also decreased.

3.3 Ionic conductivity

The ionic conductivity of the samples was measured using impedance spectroscopy. Typical impedance plots at room temperature are shown in Figure 7a. In polycrystalline ion-conducting ceramics, the impedance plots typically consist of two semicircles corresponding to the intragrain (bulk) and intergrain (grain boundary) processes. In this study, only one semicircle was observed for the measured frequency range. We attributed this semicircle to the intergrain process, as the left intercept was non-zero. The frequency associated with the intragrain process was too high to be measured. At high frequencies, the semicircles bent below the real axis, which is likely because of an inductance effect. To obtain bulk and grain-boundary resistances, fitting using an equivalent circuit (shown in the inset of Figure 7a) was performed. The terms L and R_b

represent the stray inductance and bulk resistance, and two R-Q (constant phase elements) circuits correspond to the intergrain process and the electrode process.

The bulk and total conductivities of various samples at room temperature are plotted in Figure 7b and c. Without addition of Al_2O_3 sintering aid, the sample showed poor bulk and total conductivities. They were significantly increased with addition of 0.02 mol Al. These results were consistent with the observed changes in the morphology in Fig. 2. Samples with 0.05 and 0.2 mol Al had a similar total conductivity (i.e., $\sim 0.5 \text{ mS cm}^{-1}$), but the grain-boundary resistance was slightly higher in the sample with 0.2 mol Al. The higher grain-boundary resistance might be related to segregation of secondary phases such as Li-Al-O compounds at the grain boundaries, as discussed earlier. These phases typically have lower ionic conductivity compared to the garnet phase so existence of these phases at the grain boundaries might be detrimental to ionic conduction. It was interesting that double-maxima were observed in the plot of conductivity vs. Al content (Figure 7d). We cannot conclusively interpret this trend because the Li-ion transport or conduction is a complex process, which is affected by a number of factors such as phase composition and microstructure (e.g., grain size, porosity, impurity, etc.). The low conductivity in the sample with 0.1 mol Al may be the result of the coarsening of the grains and pores, whereas the low conductivity in the sample with 0.3 mol Al can be explained by a large amount of impurity phases, as discussed earlier. Nevertheless, combining the morphological and electrochemical characterizations, we can conclude that 0.05 mol is the optimal amount of Al sintering aid in this system.

The activation energy was calculated based on the Arrhenius equation, $\sigma = \sigma_0/T \exp(-E_a/kT)$, and listed in Table 1. It can be seen that the values fell in the range of 0.32 to 0.45 eV except for the Al-free sample. Such a high variation with different amounts of Al content

suggested a strong influence of microstructure on the transport properties. From Figure 7d, it also can be seen that the activation energies and ionic conductivities are correlated with each other, and the samples with a higher ionic conductivity had lower activation energy and vice versa (with the exception of the sample with 0.3 mol Al). This was not surprising, as the microstructure affected both ionic conductivities and activation energies. It was interesting that the sample with 0.3 mol Al had the lowest grain interior activation energy among all of the samples sintered for 12 h, possibly because the bulk composition had been significantly altered by the high level of Al doping. For the sample with 0.05 mol Al, the activation energy value of 0.37 eV was comparable to those reported in the literature [19,29,41,47].

Comparing the samples with different sintering times, we concluded that prolonged sintering over 12 h in general led to poor transport properties (see Table 1). For the samples with addition of 0.1 mol Al, the total conductivity remained almost unchanged while the bulk conductivity decreased with longer holding time. For the samples with 0.2 mol Al, both total and bulk conductivities decreased with prolonged sintering time. Although longer sintering time yielded slightly higher density, it was expected to increase the level of Li and O deficiency, which could explain the deteriorating transport properties. For most of the samples, the conductivity generally followed Arrhenius's relation in the measured temperature range between 25 and 150°C. However, the sample with 0.2 mol Al sintered for 24 h clearly showed a higher activation energy below 50°C than that in the high-temperature regions (refer to Figure 7e). This is likely due to the ion-trapping phenomenon that has been documented for Li garnets [48,49] and other ionic conductors [50,51]. It is curious that the non-Arrhenius behavior was observed only for sample #8. While it is possible that other samples also may show non-Arrhenius behaviors at lower temperatures (below 273 K), the subject of ion trapping is not the focus of this

study. According to the molecular dynamic simulation reported by Wang et al. [52], **the Li ion conduction is strongly influenced by short-range Li-Li interactions**. Percival et al. [48] showed that the activation energy of $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ changed from 0.67 eV to 0.35 eV at around 250°C, which is very similar to our observation, except that the transition temperature is higher. Note that the Li content in the samples with 0.2 mol Al is higher than that in $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$. Given that there are no reports of the ion-trapping phenomenon in high Li-content garnet (Li content higher than 6.5), we postulate that the transition temperature for the non-Arrhenius behavior decreases with increasing Li content.

Conclusion

In this study, we have systematically investigated sintering effects of $\gamma\text{-Al}_2\text{O}_3$ on the garnet-type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$. Al-free crucibles were used to eliminate any contamination from the crucibles. While the sample without sintering aid cannot be successfully densified at 1100°C, 0.05 mol Al sintering aid per mol of LLZT0.5 significantly enhanced the densification. Further addition of Al led to rapid grain growth and formation of secondary phases, which were detrimental to the densification process. The different morphology of samples with various amounts of Al was explained by a liquid-phase sintering mechanism based on the $\text{Li}_2\text{O-Al}_2\text{O}_3$ eutectic system. Our EDS analysis showed that Al preferentially stayed at the grain boundaries rather than entering the garnet lattice. Uneven Al distribution in high Al-content samples was observed, as Al predominately exists in small, concentrated areas as secondary phases. Transport properties characterized by impedance spectroscopy are largely consistent with the morphology results that the sample with 0.05 mol of Al showed the best densification. Therefore, 0.05 mol Al in the form of $\gamma\text{-Al}_2\text{O}_3$ is the optimal amount of sintering aid for this system. This study clarifies

the role of Al as a sintering aid and will be useful for harnessing the sintering power of Al in a controllable manner.

Acknowledgments

This work was supported by the U.S. Department of Energy's (DOE's) Office of Electricity Delivery & Energy Reliability (OE). We appreciate the useful discussions with Dr. I. Gyuk of the DOE-OE Grid Storage Program. PNNL is a multiprogram laboratory operated by Battelle Memorial Institute for the DOE under Contract DE-AC05-76RL01830.

References

- [1] A. Kraytsberg, Y. Ein-Eli, *Adv Energy Mater*, 2 (2012) 922-939.
- [2] K. Xu, *Chem Rev*, 114 (2014) 11503-11618.
- [3] J.B. Goodenough, Y. Kim, *Chem Mater*, 22 (2010) 587-603.
- [4] B. Scrosati, J. Hassoun, Y.K. Sun, *Energ Environ Sci*, 4 (2011) 3287-3295.
- [5] N.S. Choi, Z.H. Chen, S.A. Freunberger, X.L. Ji, Y.K. Sun, K. Amine, G. Yushin, L.F. Nazar, J. Cho, P.G. Bruce, *Angew Chem Int Edit*, 51 (2012) 9994-10024.
- [6] Y.S. Jung, D.Y. Oh, Y.J. Nam, K.H. Park, *Isr J Chem*, 55 (2015) 472-485.
- [7] K. Takada, *Acta Mater*, 61 (2013) 759-770.
- [8] J.W. Fergus, *J Power Sources*, 195 (2010) 4554-4569.
- [9] Y. Ren, K. Chen, R. Chen, T. Liu, Y.H. Zhang, C.W. Nan, *J Am Ceram Soc*, (2015) 1-21.
- [10] V. Thangadurai, S. Narayanan, D. Pinzar, *Chem Soc Rev*, 43 (2014) 4714-4727.
- [11] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, *Nat Mater*, 10 (2011) 682-686.
- [12] Y. Seino, T. Ota, K. Takada, A. Hayashi, M. Tatsumisago, *Energ Environ Sci*, 7 (2014) 627-631.
- [13] Y.F. Mo, S.P. Ong, G. Ceder, *Chem Mater*, 24 (2012) 15-17.
- [14] E. Rangasamy, Z.C. Liu, M. Gobet, K. Pilar, G. Sahu, W. Zhou, H. Wu, S. Greenbaum, C.D. Liang, *J Am Chem Soc*, 137 (2015) 1384-1387.
- [15] A. Sakuda, A. Hayashi, M. Tatsumisago, *Chem Mater*, 22 (2010) 949-956.
- [16] J.S. Thokchom, B. Kumar, *J Power Sources*, 185 (2008) 480-485.
- [17] J. Fu, *Solid State Ionics*, 96 (1997) 195-200.
- [18] Y. Inaguma, L.Q. Chen, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, M. Wakihara, *Solid State Commun*, 86 (1993) 689-693.

- [19] Y.T. Li, J.T. Han, C.A. Wang, H. Xie, J.B. Goodenough, *J Mater Chem*, 22 (2012) 15357-15361.
- [20] V. Thangadurai, H. Kaack, W.J.F. Weppner, *J Am Ceram Soc*, 86 (2003) 437-440.
- [21] R. Murugan, V. Thangadurai, W. Weppner, *Angew Chem Int Edit*, 46 (2007) 7778-7781.
- [22] F. Du, N. Zhao, Y. Li, C. Chen, Z. Liu, X. Guo, *J Power Sources*, 300 (2015) 24-28.
- [23] L. Cheng, W. Chen, M. Kunz, K. Persson, N. Tamura, G.Y. Chen, M. Doeff, *Acs Appl Mater Inter*, 7 (2015) 2073-2081.
- [24] Y.Y. Ren, Y. Shen, Y.H. Lin, C.W. Nan, *Electrochem Commun*, 57 (2015) 27-30.
- [25] K. Ishiguro, Y. Nakata, M. Matsui, I. Uechi, Y. Takeda, O. Yamamoto, N. Imanishi, *J Electrochem Soc*, 160 (2013) A1690-A1693.
- [26] J.L. Allen, J. Wolfenstine, E. Rangasamy, J. Sakamoto, *J Power Sources*, 206 (2012) 315-319.
- [27] C.A. Geiger, E. Alekseev, B. Lazic, M. Fisch, T. Armbruster, R. Langner, M. Fechtelkord, N. Kim, T. Pettke, W. Weppner, *Inorg Chem*, 50 (2011) 1089-1097.
- [28] S. Ohta, T. Kobayashi, T. Asaoka, *J Power Sources*, 196 (2011) 3342-3345.
- [29] Y.X. Wang, W. Lai, *Electrochem Solid St*, 15 (2012) A68-A71.
- [30] E. Rangasamy, J. Wolfenstine, J. Sakamoto, *Solid State Ionics*, 206 (2012) 28-32.
- [31] A.A. Raskovalov, E.A. Il'ina, B.D. Antonov, *J Power Sources*, 238 (2013) 48-52.
- [32] Y. Jin, P. McGinn, *J Power Sources*, 196 (2011) 8683-8687.
- [33] Y.Y. Ren, H. Deng, R.J. Chen, Y. Shen, Y.H. Lin, C.W. Nan, *J Eur Ceram Soc*, 35 (2015) 561-572.
- [34] S. Ohta, J. Seki, Y. Yagi, Y. Kihira, T. Tani, T. Asaoka, *J Power Sources*, 265 (2014) 40-44.
- [35] S. Kumazaki, Y. Iriyama, K.H. Kim, R. Murugan, K. Tanabe, K. Yamamoto, T. Hirayama, Z. Ogumi, *Electrochem Commun*, 13 (2011) 509-512.
- [36] S.W. Baek, J.M. Lee, T.Y. Kim, M.S. Song, Y. Park, *J Power Sources*, 249 (2014) 197-206.
- [37] A.A. Hubaud, D.J. Schroeder, B. Key, B.J. Ingram, F. Dogan, J.T. Vaughey, *J Mater Chem A*, 1 (2013) 8813-8818.
- [38] H. Buschmann, J. Dolle, S. Berendts, A. Kuhn, P. Bottke, M. Wilkening, P. Heitjans, A. Senyshyn, H. Ehrenberg, A. Lotnyk, V. Duppel, L. Kienle, J. Janek, *Phys Chem Chem Phys*, 13 (2011) 19378-19392.
- [39] T. Thompson, J. Wolfenstine, J.L. Allen, M. Johannes, A. Huq, I.N. David, J. Sakamoto, *J Mater Chem A*, 2 (2014) 13431-13436.
- [40] Y.X. Wang, W. Lai, *J Power Sources*, 275 (2015) 612-620.
- [41] Y.Q. Li, Z. Wang, C.L. Li, Y. Cao, X.X. Guo, *J Power Sources*, 248 (2014) 642-646.
- [42] A. Duvel, A. Kuhn, L. Robben, M. Wilkening, P. Heitjans, *J Phys Chem C*, 116 (2012) 15192-15202.
- [43] A. Logeat, T. Koehler, U. Eisele, B. Stiaszny, A. Harzer, M. Tovar, A. Senyshyn, H. Ehrenberg, B. Kozinsky, *Solid State Ionics*, 206 (2012) 33-38.
- [44] R. German, *Sintering: From Empirical Observations to Scientific Principles*, Butterworth-Heinemann, 2014.
- [45] R.L. Coble, *J Am Ceram Soc*, 45 (1962) 123-127.
- [46] N.S. Kulkarni, T.M. Besmann, K.E. Spear, *J Am Ceram Soc*, 91 (2008) 4074-4083.
- [47] H. Buschmann, S. Berendts, B. Mogwitz, J. Janek, *J Power Sources*, 206 (2012) 236-244.
- [48] J. Percival, E. Kendrick, P.R. Slater, *Solid State Ionics*, 179 (2008) 1666-1669.
- [49] V. Thangadurai, W. Weppner, *J Am Ceram Soc*, 88 (2005) 411-418.
- [50] Q. Mei, B. Meyer, D. Martin, S.W. Martin, *Solid State Ionics*, 168 (2004) 75-85.

- [51] J.A. Kilner, R.J. Brook, Solid State Ionics, 6 (1982) 237-252.
- [52] Y.X. Wang, M. Klenk, K. Page, W. Lai, Chem Mater, 26 (2014) 5613-5624.

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

Sample ID	Al content (mol)	Al ₂ O 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

Figure Captions

Figure 1. XRD patterns of the samples with various amounts of Al_2O_3 sintered at 1100°C for 12 h. Measurements were taken on powders ground from sintered pellets.

Figure 2. SEM images of fractured surfaces of the samples sintered at 1100°C for 12 h: (a) no Al (# 1), (b) 0.02 mol Al (#2), (c) 0.05 mol Al (#3), (d) 0.1 mol Al (#4), (e) 0.2 mol Al (#7), and (f) 0.3 mol Al (#10).

Figure 3. EDS mapping on the fractured surfaces of the sample with 0.2 mol Al sintered at 1100°C for 18 h (#8): (a) mapping area, (b) Al, (c) La, (d) O, (e) Zr, and (f) Ta.

Figure 4. EDS mapping at high magnification for sample #8 (0.2 mol Al, 1100°C , 18 h): (a) mapping area and (b) Al. EDS mapping at high magnification for sample #3 (0.05 mol Al, 1100°C , 12 h): (c) mapping area and (d) Al.

Figure 5. Relative densities and open porosities of samples sintered at 1100°C for 12 h as a function of Al_2O_3 amount.

Figure 6. SEM images of fractured surfaces of the sintered samples: (a) #5 (0.1 mol Al, 1100°C , 18 h), (b) #6 (0.1 mol Al, 1100°C , 24 h), (c) #8 (0.2 mol Al, 1100°C , 18 h), and (d) #9 (0.2 mol Al, 1100°C , 24 h).

Figure 7. Transport properties of sintered samples with different Al quantities: (a) Nyquist plots, (b) and (c) bulk and total conductivities of samples sintered at 1100°C for 12 h, (d) conductivity and activation energy trend at room temperature, and (e) Arrhenius plots for LLZT0.5 with 0.2 mol Al sintered at 1100°C for 24 h.

Figure 1

Figure 1. XRD patterns of the samples with various amounts of Al₂O₃ sintered at 1100°C for 12 h. Measurements were taken on powders ground from sintered pellets.

Figure 2

Figure 2. SEM images of fractured surfaces of the samples sintered at 1100 °C for 12 h: (a) no Al (# 1), (b) 0.02 mol Al (#2), (c) 0.05 mol Al (#3), (d) 0.1 mol Al (#4), (e) 0.2 mol Al (#7), and (f) 0.3 mol Al (#10).

Figure 3

Figure 3. EDS mapping on the fractured surfaces of the sample with 0.2 mol Al sintered at 1100 °C for 18 h (#8): (a) mapping area, (b) Al, (c) La, (d) O, (e) Zr, and (f) Ta.

Figure 4

Figure 4. EDS mapping at high magnification for sample #8 (0.2 mol Al, 1100 °C, 18 h): (a) mapping area and (b) Al. EDS mapping at high magnification for sample #3 (0.05 mol Al, 1100 °C, 12 h): (c) mapping area and (d) Al.

Figure 5

Figure 5. Relative densities and open porosities of samples sintered at 1100°C for 12 h as a function of Al_2O_3 amount.

Figure 5

Figure 5. Relative densities and open porosities of samples sintered at 1100°C for 12 h as a function of Al_2O_3 amount.

Figure 6

Figure 6. SEM images of fractured surfaces of the sintered samples: (a) #5 (0.1 mol Al, 1100 °C, 18 h), (b) #6 (0.1 mol Al, 1100 °C, 24 h), (c) #8 (0.2 mol Al, 1100 °C, 18 h), and (d) #9 (0.2 mol Al, 1100 °C, 24 h).

Figure 7

Figure 7. Transport properties of the sintered samples with different amounts of Al: (a) Nyquist plots, (b) and (c) bulk and total conductivities of samples sintered at 1100°C for 12 h, (d) conductivity and activation energy trend at room temperature, and (e) Arrhenius plots for LLZT0.5 with 0.2 mol Al sintered at 1100°C for 24 h.