



Microstructure and properties investigation of garnet structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ as electrolyte for all-solid-state batteries

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ABSTRACT

Garnet structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is investigated in its pure, tetragonal phase and its stabilized cubic phase by substitution with different amounts of Ta and Al. The effect of substitution and sintering conditions on phase composition, microstructure, electrical properties and, as main focus, the mechanical properties are investigated. Sintering is carried out in air and argon atmosphere at temperatures of 1150 and 1200 °C. The Ta substitution ranges up to 60% and the Al substitution up to 36% to obtain fully cubic samples. The mechanical properties were assessed via depth-sensitive indentation testing and interpreted in terms of properties of the material and effective properties of the porous specimens. Complementary, ab initio calculations were performed to determine the structural and mechanical properties. The study verifies the strong dependency of the ionic conductivity on substitution, phase composition and materials density. Overall, the effect of substitution and phase composition can be mostly seen in changes in the intrinsic materials properties, whereas the effects of sintering conditions and porosity can mostly be seen in the change in effective mechanical properties.

1. Introduction

All-solid-state batteries (ASBs) based on inorganic ceramic Li-ion conductors are promising as next generation batteries due to their potential high energy densities and cycle life as well as high intrinsic safety [1,2], especially if used in combination with Li metal negative electrodes [3] and high voltage positive electrodes [4]. The extent of their advantages in comparison with conventional, organic liquid based Li-ion batteries depends strongly on the used electrolyte material and thus a very detailed understanding of the solid electrolyte materials properties is a prerequisite for cell design and engineering.

To achieve application relevant high energy densities, for example by increasing the anode capacity, the garnet structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) is one of the few solid state electrolyte materials that is stable in contact with Li metal [5,6]. It is thus a promising candidate as solid state electrolyte and possibly even as ionic conductive phase in mixed cathodes, even if some manufacturing limitations have to be overcome [7,8].

However, recent observations of Li-metal dendrite growth through the LLZ electrolyte raised questions with respect to the mechanical stability of the material [9–11], especially since obtaining necessary highly dense LLZ based ceramic electrolytes is still a manufacturing challenge [12] and up-scaling using industrial relevant manufacturing

processes also needs to be demonstrated yet.

Additionally, a large variety of substituents for LLZ might be considered to stabilize the highly conductive cubic phase [13–17]. On one hand, Al substitution (Al:LLZ) on the Li site is a low cost method to (at least partially) stabilize the cubic phase. By substitution Li with Al having a 3+ oxidation state, the double amount of Li vacancies is created. Vacancy densities above 0.4 per LLZ formula unit lead to an additional stabilization of the cubic phase, as shown by density functional and molecular dynamics calculations [18,19]. The resulting gain in conductivity is partially lost due to the blockage of the Li conduction pathways [20]. Ta substitution on the other hand, will stabilize the cubic phase without this blocking effect [21], but increases the material cost even further. Furthermore, the phase purity and sinter-ability of the two materials depends strongly on the synthesis route and the resulting mechanical properties might be affected. Only a limited number of studies on the mechanical properties of LLZ exist, where the elastic modulus E at different densities and grain sizes varies from ~130 to 150 GPa [9,22–26]. For Al:LLZ the single crystal hardness was measured by nanoindentation to be around 9.1 GPa, decreasing as the porosity increases to ~5.2 GPa [22,23]. A summary of experimental and numerical results on LLZ mechanical properties can also be found in our previous work [27], where a novel technique was applied to determine the fracture toughness of LLZ, being important in the framework of a

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Table 1
Substitution, sintering conditions, relative density, total Li-ion conductivity and composition.

Substitution [mol%]	Sintering atm./temp. [°C] / dwell time [h]	Relative density [%]	Li-ion conductivity [RT] [$S\text{ cm}^{-1}$]	ICP-OES elements				
				Li	La	Zr	Al	Ta
Un-substituted LLZ_Ar	Ar/1150/10	77	2.23E-08	6.94	3	1.98	–	–
Al-substituted								
20Al:LLZ	Ar/1150/10	90	1.89E-04	7.42	3	1.97	0.14	–
20Al:LLZ	Ar/1200/20	90	2.21E-05	7.05	3	1.98	0.16	–
20Al:LLZ	Air/1200/20	93	2.08E-05	6.91	3	1.98	0.13	–
36Al:LLZ	Ar/1150/10	90	2.45E-04	6.58	3	1.96	0.32	–
Ta-substituted								
20Ta:LLZ	Ar/1150/20	92	2.97E-04	6.79	3	1.76	0.05	0.21
40Ta:LLZ	Ar/1150/10	91	4.73E-04	6.22	3	1.53	0.07	0.40
60Ta:LLZ	Ar/1150/10	98	6.80E-04	6.35	3	1.35	0.04	0.57

reliability oriented mechanical characterization. Overall, due to this scarce literature data, a thorough investigation of the sinter-ability and final mechanical properties is still missing, especially for Ta substituted LLZ (Ta:LLZ). This is extremely important, since the mechanical properties, both intrinsic and effective (affected by grain boundaries and pores), are highly relevant for assessing the mechanical stability and avoiding possible degradation mechanisms in full cells, e.g. via dendrite growth as described in [28,29].

Therefore, the effect of various amounts of Ta and Al substitution of LLZ specimens is investigated under various sintering conditions to determine their impact on the mechanical and electrical properties of the final samples.

For all samples the environmental conditions during sintering were kept as similar as possible, hence, systematically varying one parameter at the time. This way, the effect of the substituents and sintering conditions on the final mechanical and electrical properties was considered to be most obvious. It has to be noted though, that in each case the sintering process might be optimized further in the framework of future research (e.g. using hot pressing [22]) to reduce residual porosity and to improve the properties of the respective substituted material further (e.g. for industrial cell fabrication). In the current initial study, the resulting variations (e.g. microstructure and porosity) were taken into account when drawing conclusions from experimental results and derived values represent either the pure materials properties (e.g. close to single crystal values) or the effective ones, respective to the microstructure. The interpretation of the experimental results is supported by density functional theory (DFT). Mechanical and microstructural parameters were predicted, which can be directly related to the measured values and show good agreement for the various levels of substitution.

2. Experimental

Unsubstituted lithium lanthanum zirconate $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ), Al substituted LLZ (Al:LLZ) $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ ($x = 0.2, 0.36$) (20Al:LLZ and 36Al:LLZ) and Ta substituted LLZ (Ta:LLZ) $\text{Li}_{7-y}\text{La}_3\text{Zr}_2\text{Ta}_y\text{O}_{12}$ ($y = 0.2, 0.40, 0.60$) (20Ta:LLZ, 40Ta:LLZ and 60Ta:LLZ) powders were synthesized via a three step solid-state reaction in argon atmosphere. They were prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ (98%; Merck), La_2O_3 (99.9%, dried at 900 °C, 10 h; Merck), ZrO_2 (99.5%, Treibacher), Al_2O_3 (99.9%, Inframat) and Ta_2O_5 (99.5%, Inframat). The educts were mixed in stoichiometric amounts with an excess of 15% of $\text{LiOH}\cdot\text{H}_2\text{O}$ to compensate the lithium loss during the calcination processes. They were homogenized by grinding in a mortar (Retsch RM 200) for 1 h and pressed with an uniaxial press into pellets. A subsequent calcination at 850 °C for 20 h in argon was done using graphite crucibles to avoid additional aluminum uptake. Two more cycles of grinding, pellet pressing and calcination at 1000 °C for 20 h in argon were done. After calcination the LLZ pellets were transferred immediately into an argon

glove box and again ground into a fine powder.

For the final sintering, about 6 g of calcined LLZ powder were taken from each LLZ batch and uniaxial pressed in a 13 mm die with 115 MPa to a pellet (ca. 12 mm in diameter). A MgO substrate was used as a sample holder to avoid reactions with or sticking to the substrate during the sintering process. A small amount of LLZ powder was placed between pellet and substrate to prevent possible cross contamination from MgO. The pellets were then sintered at 1150 °C for 10 h dwell time in argon. A ramp rate of 5 K min^{-1} was used for heating and cooling to room temperature. For the $x = 0.2$ Al and Ta substitutions, the sintering temperature and dwell time was then increased to 1200 °C and 20 h in order to investigate the effect on density and composition. Finally, the sintering atmosphere was also changed for the 20 mol% Al-LLZ sample from Ar to Air. The resulting dense pellets were then used for the subsequent investigations and all sample parameters are comprised in Table 1.

The relative densities of the sintered samples were obtained via Archimedes method and their elemental composition via inductively-coupled plasma optical emission spectroscopy (ICP-OES; Thermo Elemental, IRIS Intrepid). The grain size was estimated using AnalySIS Pro®, based on the circular intercept segment method.

The X-ray diffraction (XRD) structure analysis and phase characterization was done with a Bruker D4 Endeavour spectrometer equipped with a 1D detector LYNXEY and a DIFFRAC^{plus} BASIC package 2009 using $\text{Cu-K}\alpha$ radiation. The synthesized LLZ powders were analyzed at room temperature in a 2θ range of 10° to 130° with a $\Delta_{2\theta} = 0.02^\circ$ and 2 s per step. The lattice parameters were determined via Rietveld refinement using the profile analysis software TOPAS (Version 4.2, Bruker AXS GmbH, Karlsruhe Germany) and the crystal structures were extracted from the Inorganic Structure Database (ICSD, FIZ Karlsruhe, Germany). Tetragonal and cubic proportions below 10% by weight are not detectable, therefore are not presented here, as well as small amounts of secondary phases that are below the detection limit of XRD.

An “Alpha A High Performance Frequency Analyzer” (Novocontrol Technologies, furnace included) was used to measure the conductivity of pellets from each LLZ composition between 300 K and 650 K in steps of 50 K in a frequency range from 1 Hz to 20 MHz with an electrical field perturbation of $20\text{ mV}\cdot\text{mm}^{-1}$. For this test, the top and bottom of the cylindrical pellets were polished with 250, 400, 800 and 1200 grid sandpapers to remove any contamination and to flatten the surface. As blocking electrodes, thin Au layers were sputtered on both sides, providing a good contact to the LLZ. Silver paste was then painted onto the Au electrodes and annealed at 600 °C for 30 min to provide a stable contact to the impedance system. For simplicity and relevance reasons, only the room temperature conductivities are report here.

Polished cross-sections of the LLZ, Al:LLZ and Ta:LLZ disks were used for indentation measurements. Specimens were polished using #400 to #1000 grit sandpaper and water-free Polyethylene Glycol

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