**Investigation of Li ions in garnet LLZO solid electrolytes via impedance spectroscopy, X-ray and neutron scattering**

**Authors:** T. Reppert,a,b S. O. Diallo,2 A. Huq,2 Y-J. Sohn,a,b L. Daemen,2 G. M. Veith,1 M. Bram,a,b M. Finsterbusch.a,b

a Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-1), Materials Synthesis and Processing, 52425 Jülich, Germany

b Jülich Aachen Research Alliance: JARA-Energy, Germany

1 Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

2 Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Inhalt

[Abstract 2](#_Toc466215088)

[1. Introduction 2](#_Toc466215089)

[2. Experimental 4](#_Toc466215090)

[General LLZO electrolyte synthesis: 4](#_Toc466215091)

[LLZO powder X-ray diffraction 4](#_Toc466215092)

[POWGEN, VISON and BASIS Experiments: 4](#_Toc466215093)

[HT-Impedance measurements: 5](#_Toc466215094)

[3. Results and Discussion 6](#_Toc466215095)

[Elementary and phase composition 6](#_Toc466215096)

[Results HT-electrochemical impedance spectroscopy 9](#_Toc466215097)

[Measuring lithium compounds with neutron techniques in the presence of hydrogen 10](#_Toc466215098)

[Vibrational spectra by INS measurement 11](#_Toc466215099)

[Determination Li self-diffusion constant 12](#_Toc466215100)

[Comparison HT-EIS to QENS 14](#_Toc466215101)

[4. Conclusion 16](#_Toc466215102)

[Acknowledgements 16](#_Toc466215103)

[References 17](#_Toc466215104)

## Abstract

The solid Li ion conductor Li7La3Zr2O12 (LLZO) and its derivatives are promising oxide electrolytes for all-solid-state batteries (ASB). When doped with supervalent cations such as aluminum or tantalum, reasonably high ionic conductivities can be reached to make it an attractive choice for ASB fabrication. In this work, the structure of tetragonal LLZO, cubic Al substituted LLZO (AL-LLZO), and Ta substituted LLZO (Ta-LLZO), has been investigated using x-ray diffraction (PXRD) and neutron diffraction (ND). Using a specially developed synthesis and handling route to avoid water contamination, we unambiguously determine the Li self-diffusion constant for the cubic LLZO compounds via quasi-elastic neutron scattering (QENS) experiments. The results were then compared to activation energies measured via high-temperature impedance measurements (HT-EIS) to correlate the determined self-diffusion coefficients with the ionic conductivity of the materials.

## 1. Introduction

With a growing demand for energy storage of intermittent renewable energies such as wind and solar power[1-5](#_ENREF_1), for transportation, e.g. in electric vehicles (EV),[5-8](#_ENREF_5), and for a myriad of portable electronic devices[9-11](#_ENREF_9) battery development has become a large scale commercial endeavor.[12](#_ENREF_12),[13](#_ENREF_13) Since the commercialization of the first lithium ion batteries (LIB) by Sony in 1991, rechargeable lithium and lithium ion batteries are heavily focused on in research and development, especially in order to improve energy and power densities, as well as to solve serious safety concerns when scaling up LIBs for vehicle and stationary storages applications.[11](#_ENREF_11),[14-18](#_ENREF_14)

Over the last years, ceramic all-solid-state batteries (ASBs) became one of the most promising battery concepts for post Li-ion cells, especially, since ceramics have a much higher intrinsic stability than commonly used liquids or polymers. Furthermore, without a leaking fluid, they are in general less toxic and fulfill the targeted safety requirements. Some of the available ceramic electrolytes are (electro-) chemical compatible to lithium metal, offering even higher energy and power densities when Li is used as anode. In addition, degradation caused by electrolyte-consumption will be minimized, e.g. as shown for thin-film ASBs having very high cycling stability.[19-22](#_ENREF_19) Furthermore, ceramic Li ion conductors may not only be an interesting option for ASB, but also application in other future battery concepts like Li-air and Li-S.[15](#_ENREF_15)

One of the first solid electrolytes, lithium phosphorous oxynitride (LIPON), has been discovered and investigated over the last two decades at Oak Ridge National Laboratory (ORNL).[21](#_ENREF_21) LIPON is an amorphous material with a relatively narrow electrochemical stability window[23](#_ENREF_23) and an average ionic conductivity on the order of σION ~10‑6 S/cm but forms a stable SEI when in contact with lithium metal. Using physical vapor deposition (PVD) techniques like sputtering, it was successfully implemented into a thin film lithium battery[21](#_ENREF_21),[24](#_ENREF_24) with current research focusing on increasing the surface area, and thus the overall capacity, via 3-D structuring[25](#_ENREF_25).

To improve conductivity and manufacture self-supporting cells, the garnet structured oxide ceramic lithium lanthanum zirconate (LLZO) is one of the most promising candidates and researched worldwide[26-35](#_ENREF_26). LLZO combines a higher total ionic conductivity at room temperature (σION > 10-4 S/cm,[28](#_ENREF_28) two orders of magnitude higher than LIPON) with true (electro-) chemically stability against lithium metal.[23](#_ENREF_23) After its discovery, the LLZO crystal structure was identified to be in a cubic space group (, No. 230) like its mother compound Li5La3Ta2O12 . However, in air more often a subgroup, the tetragonal phase (I41/acd, No. 146) with two orders of magnitude lower conductivity[36](#_ENREF_36" \o "Matsui, 2014 #220) was also observed,. To stabilize the highly conductive phase, substitutions with super-valent cations like Al on the Li site or Ta on the Zr site are commonly made.[37-40](#_ENREF_37) Al substituted LLZO has already been investigated manifold and the limit of aluminum incorporation is reported to be between 0.32 and 0.38 mol of Al per mole of LLZO.[38](#_ENREF_38) Ta substituted LLZO shows one of the highest total ionic conductivity (higher than 10‑3 S cm-1 [41](#_ENREF_41)) and Wang et al. showed that 0.60 mol of Ta per mole of LLZO is necessary to obtain pure cubic Ta substituted LLZO[40](#_ENREF_40).

For this work, 0.36 mol Al and 0.60 mol Ta substituted LLZO was synthesized, as well as pure tetragonal un-substituted LLZO for comparison. The LLZO structure and phase purity was investigated using x-ray diffraction (PXRD) and neutron diffraction (ND). In addition, neutron scattering is used as complementary method to investigate the Li diffusion in the material. The Li self-diffusion constant was determined for all three materials using quasi-elastic neutron scattering (QENS) at the BASIS beamline at ORNL. As QENS is much more sensitive to H than to Li, proton exchange during manufacturing and handling of the material in air can be detrimental in observing Li mobility. Therefore, proton free LLZO was prepared with a specially developed synthesis and handling route in Argon and confirmed by inelastic neutron scattering (INS), one of the most proton sensitive techniques, on the VISION spectrometer at ORNL. To correlate the self-diffusion to the ionic conductivity of the material, the activation energies obtained from QENS are compared to the activation energy for total Li-Ion conductivity measured via high-temperature impedance spectroscopy between 300-600 K.

## 2. Experimental

### General LLZO electrolyte synthesis:

Unsubstituted lithium lanthanum zirconate (LLZO) Li7La3Zr2O12, aluminum substituted LLZO (36Al-LLZO) Li5.92Al0.36La3Zr2O12 and tantalum substituted LLZO (60Ta-LLZO) Li6.4La3Zr1.4Ta0.6O12 were synthesized via a three step solid-state reaction in argon atmosphere.[28](#_ENREF_28) They were prepared in 50 g batches from LiOH ∙ H2O (98%; Merck), La2O3 (99.9%, dried at 900 °C, 10 h; Merck), ZrO2 (99.5%, Treibacher), Al2O3 (99.9%, Inframat) and Ta2O5 (99.5%, Inframat). The educts were mixed in stoichiometric amounts with an excess of 15% of LiOH ∙ H2O 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 a uniaxial press into pellets to reduce the diffusion pathways of educts metal atoms to their final lattice positions during solid-state reaction and to reduce lithium evaporation. A subsequent calcination at 850 °C for 20 h in argon was done using graphite crucibles to avoid aluminum uptake. Two more cycles of grinding, pellet pressing and calcination at 1000 °C for 20 h in argon were done. After calcination the LLZO pellets were transferred immediately into an argon glove box and again ground to a fine powder.

### LLZO powder X-ray diffraction

The powder x-ray diffraction (PXRD) structure analysis and phase characterization was done with a Bruker D4 Endeavour spectrometer equipped with a 1D detector LYNXEY and a DIFFRACplus BASIC package 2009 using Cu-Kα radiation. The synthesized LLZO powders were analyzed at room temperature in a 2θ range of 10° to 130° with a Δ2θ =0.02° and 2 s per step.

### POWGEN, VISON and BASIS Experiments:

To assure that the electrolyte powders are free of any moisture or crystal water, they were stored at all times in an Ar filled glove box. Furthermore, for every measurement 10 g of each LLZO powder batch were calcined in a furnace inside the glove box at 450 °C for 3 h. The vanadium cans for the POWGEN and VISION experiments and the aluminum cans for the BASIS experiment were also stored inside the glove box at 200 °C for 7 to 12 h. After the calcination and cool down of the powder, it was loaded into the sample cans and sealed. Vanadium cans were sealed by a copper gasket and aluminum cans were sealed by using a 200 µm aluminum foil as gasket.

The time-of-flight neutron powder diffraction data was collected at the POWGEN beam line at the ORNL’s SNS at 300 K and 10 K for all garnets (LLZO, 36Al-LLZO, and 60Ta-LLZO). The data sets’ adjusted incident wavelength of 1.333 Å covers a broad 2θ range from 10° to 80°. The refinement was done with the crystallographic program GSAS.[42](#_ENREF_42),[43](#_ENREF_43)

To prove that the LLZO samples were not contaminated by water or underwent a lithium-proton exchange, inelastic neutron spectroscopy (INS) was performed at 5 K at the vibrational neutron spectrometer VISION at the Spallation Neutron Source (SNS) at ORNL over a broad energy range (5 to 600 meV). The use of neutrons rather than photons as a probe of molecular vibrations provides a high sensitivity to hydrogen. Water shows a very strong signal between 60 and 120 meV[44](#_ENREF_44), which were not observed in our samples.

QENS experiments were performed at the time-of-flight near-backscattering spectrometer BASIS[45](#_ENREF_45) at the ORNL’s SNS. This crystal analyzer provides a very fine energy resolution as low as 3.0 to 3.5 µeV at the elastic peak. Thigh quality quasi-elastic neutron scattering data were collected In the range ±100 µeV around the elastic peak to determine the Li+ ions self-diffusion rate. The measurements were taken in the temperature range from 300 K to 600 K. The incident neutron wavelength used was 6.4 Å (with a bandwidth of about 0.5 Å). The BASIS detector covers a 2θ range from about 11 to 165°.

### HT-Impedance measurements:

For comparison, high-temperature impedance measurements (HT-EIS) were performed at the same temperatures as the neutron backscattering experiments at the BASIS beam line. An “Alpha A High Performance Frequency Analyzer” (Novocontrol Technologies, furnace included) was used to measure the conductivity of pellets from each LLZO 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 mV mm-1. About 6 g of calcined LLZO powder were taken from each LLZO batch and uniaxial pressed in a 13 mm die with 115 MPa to a pellet (pellet thickness?). A MgO substrate was used as a sample holder to avoid reactions with or sticking to the substrate during the sintering process.[46](#_ENREF_46) A small amount of LLZO 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 in argon. A ramp rate of 5 K min-1 was used for heating and cooling to room temperature. Subsequently, 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 LLZO. 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.

## 3. Results and Discussion

### Elementary and phase composition

For any research on ionic dynamics it is crucial that the investigated specimens are without impurities, that measured results refer to the materials properties and are not influence by anything else. The purity of garnet electrolytes like LLZO can for example be compromised if the samples synthesis was done grubby, that Al-contaminations occur or the samples get exposed to air moisture and underwent a lithium-proton exchange.[47](#_ENREF_47) If pure tetragonal LLZO is aimed, like in one of our samples, it is necessary to avoid contamination by other cations like aluminum or yttrium. Yttrium or aluminum as abrasion from milling media, or by diffusion from crucibles are incorporated into the crystal structure. In most cases the intended incorporation of super-valent cations is aimed as it is shown by many research groups like Hubaud et al.[38](#_ENREF_38) or Murugan et al.[48](#_ENREF_48) that these cations stabilize the much better conductive cubic LLZO phase during heat treatment down to room temperature. In comparison to Shimonishi et al. who prepared unsubstituted LLZO at 1180 °C in an Al2O3 crucible, obtaining unintentionally 0.23 mol of Al[49](#_ENREF_49), or the sample of Geiger et al. containing 0.20 mol of Al[50](#_ENREF_50), it is shown that the use of suitable crucibles is unavoidable to avoid contamination. We prevent these effects by using graphite crucibles and heat-treatment in argon atmosphere. Al2O3 impurities are often indicated by discoloration of LLZO samples, but in this work no discoloration was observed. First step of confirming was to determine the elemental composition, which was done by ICP-OES. In a broad search for impurities any other elements then expected were detectable. In table 3.1 the composition of the investigated unsubstituted lithium lanthanum zirconate (LLZO) Li7La3Zr2O12, aluminum substituted LLZO (36Al-LLZO) Li5.92Al0.36La3Zr2O12 and tantalum substituted LLZO (60Ta-LLZO) Li6.4La3Zr1.4Ta0.6O12 are compared in their stoichiometry. For that purpose, the mass percentage of each element is converted into the amount of substance and normalized to three mole of lanthanum which value should stay constant in each LLZO composition during doping Al or Ta. If we compare our aimed sum formula with the data of table 3.1 it is shown that every value fits the statistical spread except of 36Al-LLZO’s amount of lithium, which is about 10 percent above expectation. This may be due to the intentional excess of lithium during synthesis.

Table 3.1: Stoichiometric elemental composition of the LLZO samples by ICP-OES, normalized to 3 mol of La (by FZJ, ZEA-3).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Li** | **La** | **Zr** | **Al** | **Ta** | **Sample** |
| **6.94 ± 0.21** | **3.00** | **1.98 ± 0.06** | **< 0.01** | **< 0.01** | LLZO (THRO26) |
| **6.58 ± 0.20** | **3.00** | **1.96 ± 0.06** | **0.33 ± 0.03** | **< 0.01** | 36Al-LLZO (THR029) |
| **6.22 ± 0.19** | **3.00** | **1.38 ± 0.04** | **< 0.02** | **0.57 ± 0.02** | 60Ta-LLZO (THRO25) |

t-(400)

t-(004)

c-(400)



Figure 3.1: (Left) PXRD pattern and comparison of unsubstituted LLZO, 36Al-LLZO and 60Ta-LLZO to cubic and tetragonal LLZO references. (Right) Magnified PXRD pattern of chosen region reveals splitting of c-(400) Bragg peak into t-(004) and t-(400).

Next to the stoichiometry the phase purity is even more important. By intention unsubstituted LLZO should be in a tetragonal phase and both Al or Ta substituted LLZOs in a cubic phase. In figure 3.1 the measured PXRD patterns of LLZO, 36Al-LLZO and 60Ta-LLZO are compared to each other and to reference data taken from inorganic crystal structure database (ICSD, FIZ Karlsruhe). On the left-hand side it is shown, that all three PXRD pattern match with the references, but there are differences in between the samples. 36Al-LLZO and 60Ta-LLZO show the LLZO in cubic space group and no impurity phases, but a broadening of peaks is observed, too. If there is a zoom on the characteristic Bragg peak c-(400) in the PXRD pattern, the 36Al-LLZO shows a splitting into two equal very close peaks and 60Ta-LLZO shows a shoulder at lower 2ϴ degree. It is possible that the shift in 36Al-LLZO is due to a second cubic LLZO phase, as there was an intended substitution on the tetrahedral Li(1) *24d* site (B position) into the LLZO lattice with its A3B2C3O12 garnet structure.[51](#_ENREF_51),[52](#_ENREF_52) Because of PXRD pattern correction by subtraction of Kβ, an effect of the Kβ rays can be neglected. In literature it is shown, that substitution of super-valent cations into the LLZO crystal lattice effects the lattice parameter *a* to decrease. And this decrease causes a shift of all Bragg peaks to higher 2ϴ degree.[53](#_ENREF_53)  Additionally a small amount of tetragonal LLZO phase might contributing, but the typical splitting of the cubic c-(400) Bragg peak into the tetragonal subgroup t-(400) and t-(004) peak did not appear significantly like it is clearly shown in the PXRD magnification in figure 3.1 on the right hand side for unsubstituted LLZO, that exists only in a pure tetragonal LLZO phase. 60Ta-LLZO behaves in its Bragg reflection like 36Al-LLZO but with a minor and a major phase. In Ta substituted LLZO the effect of shifting Bragg peaks is even stronger then in aluminum substitution, because Ta replaces zirconium on its octahedral *24c* site (C position), . If fully replaced cubic Li5La3Ta2O12 would be obtained, which has a much smaller lattice parameter *a* then cubic Li7La3Zr2O12, causing a bigger shift to higher 2ϴ degree.

Table 3.2: Overall phase data and atomic parameters from LLZO and 60Ta-LLZO. Tetragonal phase in LLZO and 60Ta-LLZO assumed to be equal.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Phase data** | | | | | | |
| **Sum formula** | Li6.31La3Zr1.4Ta0.6O12 | | Li7La3Zr2O12 | | | |
| **Crystal system** | cubic | | tetragonal | | | |
| **Space-group** | I a -3 d (230) | | I 41/a c d (142) | | | |
| **Cell parameters** | a=12.9117(1) Å | | a=13.1270(1) Å  c=12.6626(1) Å | | | |
| **Cell volume** | 2152.53(7) Å3 | | 2182.00(3) Å3 | | | |
| **Atomic parameters** | | | | | | |
| **60Ta-LLZO cubic phase** | | | | | | |
| **Atom** | **Wyck.** | **S.O.F.** | **x/a** | **y/b** | **z/c** | **U [Å2]** |
| Li1 | 24d | 0.520(27) | 3/8 | 0 | 1/4 | 0.036(4) |
| Li2 | 96h | 0.396(11) | 0.0995(4) | 0.6871(5) | 0.5747(5) | 0.0160(21) |
| La | 24c | 1 | 1/8 | 0 | 1/4 | 0.0069(2) |
| Zr1 | 16a | 0.3 | 0 | 0 | 0 | 0.0047(2) |
| Ta | 16a | 0.7 | 0 | 0 | 0 | 0.0047(2) |
| O1 | 96h | 1 | -0.03108(6) | 0.05244(7) | 0.14786(6) | 0.0115(2) |
| **60Ta-LLZO and LLZO tetragonal phase** | | | | | | |
| **Atom** | **Wyck.** | **S.O.F.** | **x/a** | **y/b** | **z/c** | **U [Å2]** |
| La1 | 8b | 1 | 0 | 1/4 | 1/8 | 0.0027(1) |
| La2 | 16e | 1 | 0.12709 | 0 | 1/4 | 0.0027(1) |
| Zr1 | 16c | 1 | 0 | 0 | 0 | 0.0024(1) |
| Li1 | 8a | 1 | 0 | 1/4 | 3/8 | 0.0080(8) |
| Li2 | 16f | 1 | 0.1799 | 0.4299 | 1/8 | 0.0165(8) |
| Li3 | 32g | 1 | 0.08169 | 0.08782 | 0.80576 | 0.0140(5) |
| O1 | 32g | 1 | -0.03424 | 0.05450 | 0.15254 | 0.0040(1) |
| O2 | 32g | 1 | 0.05373 | 0.85294 | 0.53414 | 0.0051(1) |
| O3 | 32g | 1 | 0.14958 | 0.02756 | 0.44677 | 0.0043(1) |

For further phase information, the samples were investigated by POWGEN neutron powder diffraction at ORNL. The data refinement was done using the Rietveld method.[54](#_ENREF_54),[55](#_ENREF_55) The more phases are present in an ND pattern the more difficult is to obtain a trustful refinement. Unsubstituted LLZO was confirmed to be a single tetragonal phase LLZO where the Li positions are fully occupied, with a minor impurity phase (<1.8 percent) of Li2O, that might be residual lithium educt, used as excess during synthesis. Rietveld refinement revealed that the 60Ta-LLZO sample is made up of 78 percent cubic LLZO and 22 percent tetragonal LLZO phase and that the refined sum formula is Li6.31La3Zr1.4Ta0.6O12, because in agreement with actual opinion in literature the cubic LLZO phase is not fully occupied (compare table 3.2).[53](#_ENREF_53),[56](#_ENREF_56),[57](#_ENREF_57) 36Al-LLZO contains at least two cubic LLZO phases and a third tetragonal LLZO phase, that it was not possible to get trustful data from Rietveld refinement. In table 3.2 the overall phase data and atomistic parameters from unsubstituted LLZO tetragonal phase and 60Ta-LLZO cubic phase are listed. The tetragonal phase of 60Ta-LLZO was assumed from unsubstituted LLZO, after equality was shown by Rietveld refinement.

Summarized, all samples are free from significant impurities, unsubstituted LLZO is in a pure tetragonal phase, but 36Al-LLZO and 60Ta-LLZO show in their PXRD pattern a contribution of second cubic or tetragonal LLZO phase, which might be caused by not perfectly matching stoichiometry like intended. This is covered by the statistical deviation of elemental composition, determined by ICP-OES. ND and Rietveld refinement confirmed phases of all three garnets, but only for LLZO and 60Ta-LLZO trustful crystal structure data with atom positions and occupation could be obtained. 36Al-LLZO consisting two cubic and one tetragonal LLZO phase is too complex for trustful refinement. All three garnet samples can be used for further HT- impedance and QENS measurements.

### Results HT-electrochemical impedance spectroscopy

HT-impedance provides macroscopic total ionic conductivity and its related activation energy. The Nyquist-plots from each measurement were characterized by Z-View to determine the total ionic conductivity, because it was not possible to distinguish between bulk and grain boundary resistance. The conductivity values are plotted against 1000 / T in Figure 3.2. At 300 K 36Al-LLZO has a total ionic conductivity of σION,300K=0.24 mS cm‑1. It is a factor of 3 lower than the value of 60Ta-LLZO (σION,300K=0.68 mS cm-1) at the same temperature, but three orders of magnitude higher than tetragonal LLZO (2.2x10-5 mS cm-1). The values for the conductivity of the cubic and tetragonal compositions are in good agreement with literature values.[36](#_ENREF_36),[37](#_ENREF_37),[41](#_ENREF_41),[58-62](#_ENREF_58) With increased temperature, the conductivity increases to σION,650K=440 mS cm-1. From the slope of a linear fit through these data points the activation energy was calculated. The activation energy of 36Al-LLZO (EA=0.37 eV) is comparable to 60Ta-LLZO (EA=0.36 eV), but much lower compared to tetragonal LLZO’s (EA=0.66 eV) activation energy.



Figure 3.2: Arrhenius plot of the total Li ionic conductivity of the three LLZO samples and the derived activation Energy *EA*.

### Measuring lithium compounds with neutron techniques in the presence of hydrogen

Neutron techniques are interesting to investigate structures and dynamics of condensed matters’ bulk samples. Since neutrons are electrically neutral they penetrate samples more deeply where they interact with the atoms nuclei and magnetic fields of unpaired electrons. This causes pronounces interference and energy transfer effects in neutron scattering experiments.[63](#_ENREF_63) The neutrons scattering and absorption cross section vary widely from element to element and even from isotope to isotope. A big advance in investigation of lithium compounds is the fact that Li is one of the best incoherent neutron scatterer in between elements with a small atomic number. But hydrogen has a much larger incoherent scattering cross section *sinc* (*sinc,Li* =0.92 barns;*sinc,H*=80.26 barns).[64](#_ENREF_64) For this reason it is critical that dry lithium compounds be prepared for probing Li diffusivity with neutron techniques. For the very sensitive BASIS instrument with its very fine energy resolution, it is essential that samples are not only dry, but essentially free of hydrogen. Most Li components’ proposals are rejected because of the believe there will be too many residual protons. To perform this experiment, it was necessary to prove, that quasi-elastic signal from Li be determined reliably and quantitatively.

### Vibrational spectra by INS measurement

As mentioned above for the investigations it is essential that the samples be free from any residual protons, since they are compared to Li much stronger neutron scatterer and would have contributed a strong quasi-elastic signal overwhelming the Li quasi-elastic signal. VISION is sensitive to a fraction of a mmol of hydrogen. This proof is provided by the inelastic neutron scattering at VISON experiment, which measured a neutron vibrational spectrum for each of the measured composites. In addition, one sample was opened after the measurement and exposed to air for few minutes and measured again. The vibrational band of water appears in the range of 60 to 120 meV[44](#_ENREF_44) and, when present, always shows a very intense band compared to the garnets vibrational modes.



Figure 3.3: INS pattern of sealed unsubstituted tetragonal LLZO, and the difference of a LLZO sample after exposition to air moisture for few minutes.

In figure 3.3 are the intensities from INS measurement of the LLZO powders that were measured subsequently in the BASIS experiment compared to a sample exposed to air moisture for few minutes. The sealed LLZO sample has no significant peaks in the range of 60 to 120 meV, proving that the samples are dry enough for the BASIS experiment. This is in contrast with the signal from the sample exposed to air moisture for a few minutes (red line in Figure 3.3).

### Determination Li self-diffusion constant

In contrast to HT-impedance, the self-diffusion constant describes the hopping of ions from one lattice site to another when the chemical potential gradient equals zero.[65](#_ENREF_65) In our LLZO powders, Li self-diffusion constants were determined with the neutron backscattering spectrometer, BASIS.

Each BASIS spectrum was fitted to a resolution-convoluted model function consisting of a delta function, δ (ω), and a single Lorentzian function, together with a linear background at each momentum transfer *Qi*: [66](#_ENREF_66),

(1)

in which is the relative intensity associated with the delta function and the width of the Lorentzian at Q=, is the reduced Planck constant, and are respectively the energy transfer and the best fit position of the elastic line. Figure 3.4 shows versus energy transfer for 60Ta-LLZO at 400 K as an example. The red line is a least-squares fit to the data. In the same figure on the right-hand side the contribution of each fit and the full-width at half-maximum (FWHM) is drafted. From the temperature dependence of the width (HWHM) of the Lorentzians, the diffusion coefficient can be extracted. Only lower momentum transfers *Q*, between 0.3 A-1 and 0.9 A-1 were used due to the strong coherent signal from the garnets’ Bragg reflections above 0.9 A-1. As a resolution function the lowest temperature dataset (here 300 K) is taken, as there was no observable difference between this signal and the empty vanadium can response, and essentially identical to a vanadium run. There was also no observable QENS signal in the low-conductivity tetragonal LLZOat any temperature compared to the empty vanadium can’s signal. This might be due to its very low self-diffusion rate. This observation is supported by the total ionic conductivity measured by EIS being one order of magnitude lower than for 60Ta-LLZO and 36Al-LLZO. To get a better resolved QENS measurement of tetragonal LLZO a more intense Li scattering is necessary. This can be provided by using isotopically pure 7Li, instead of natural Li resources, containing a 6Li fraction, which is absorbing a bigger part of neutrons. Another possibility is to extend measuring time manifold in future experiments.

**Figure 3.4:** (**Left**) Sinc (Q,ω) for 60Ta-LLZO measured at 400 K at its lowest exchange momentum Q = 0.3 Å-1 and its resolution convoluted fit (red line). (**Right**) Schematic of least-squares fitting (black line) QENS data (grey dots). Being composed of delta function (red dotted line), Lorentzian fit (orange line) and background (green dashes). Peak broadening ins measured as full-with half maximum (FWHM).

-1 0 1

Energy Transfer

**FWHM**

Finally, the self-diffusion constant *D*can be calculated from the expression (2) [Cerclier] over the whole range of momentum transfers *Q*, in which τ0 is the characteristic residue time between ion jumps and is the reduced Planck constant:

(2)

But if only lower momentum transfers are used to calculate the Li ion self-diffusion constant *DLi*, the expression can be simplified assumed to:

(3)

To extract the Li ion self-diffusion constant *DLi*the expression *DLi x Q²* was fitted to the low *Q* section of the HWHM *Γ*. The graphical extraction of DLi is shown in figure 3.5 for 60Ta-LLZO QENS measurements between 450 K and 600 K on the left-hand side, and for 36Al-LLZO in the same temperature segments on the right-hand side.

As inlays in the figure 3.5 the self-diffusion constants DLi are plotted for each temperature to obtain the activation energy EA, which is correlated to the self-diffusion constant DLi by Arrhenius equation. In this equation (4) **σ** is the material specific diffusion coefficient, ***kB***the Boltzmann constant, **T** the temperature.

(4)

As a result, the self-diffusion of Li ions in the two solid electrolytes exhibits an activation energy of EA(60Ta‑LLZO) =13.6 kJ/mol [0.14 eV] and of EA(36Al-LLZO) =10.1 kJ/mol [0.10 eV].

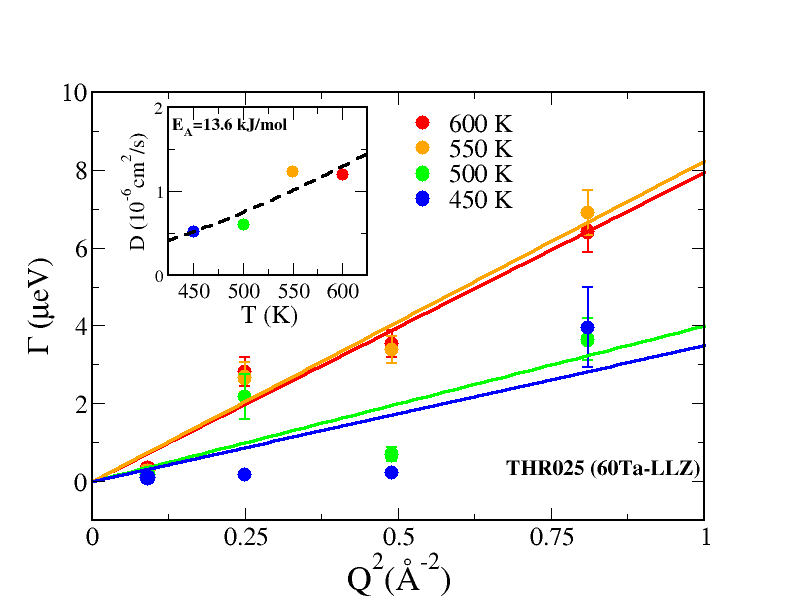
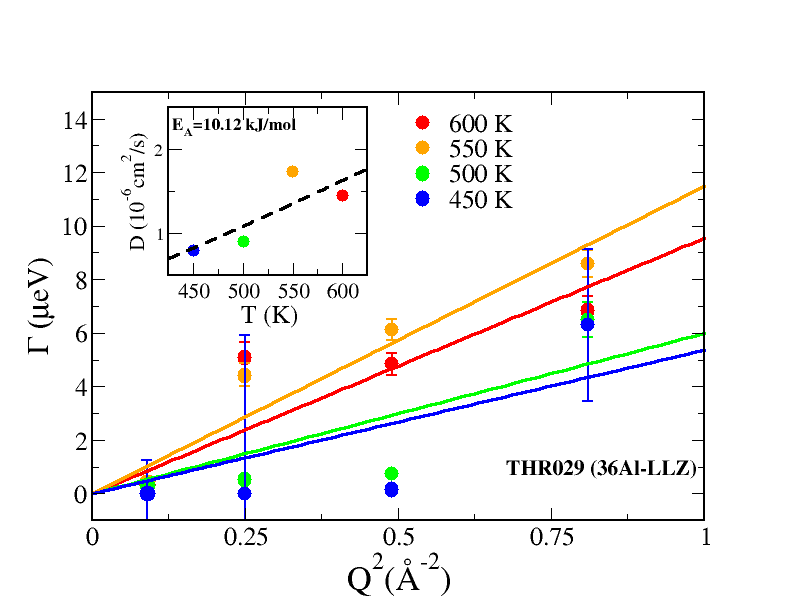


Figure 3.5: HWHM *Γ* plotted against Q2 for temperatures 450 K to 600 K to derivate Li self-diffusion constant *D* of **(Left)** 60Ta-LLZO and (**Right**) 36Al-LLZO. In each graph a plot of *D* against T is inlayed to determine self-diffusion’s activation Energy *EA*.

### Comparison HT-EIS to QENS

*- ionic conductivity from QENS (Nernst-Einstein)*[*67*](#_ENREF_67) *vs. ionic conductivity by HT-impedance*

*- In pellets or film samples larger influence by grain boundary resistance*

HT-impedance spectroscopy and neutron backscattering spectrometry both provide an activation energy EA, but the focus on the investigated reaction is different. HT-EIS measures the total ionic conductivity of lithium ions, that are forced by AC current. QENS measurements were focused on the investigation of neutron induced Li ion self-diffusion inside of LLZO grains. HT-EIS and QENS activation energies are plotted for comparison in figure 3.6. In addition, the ionic conductivity of all three samples is plotted right-hand side (red stars).

60Ta-LLZO and 36Al-LLZO activation energy EA derivated from the HT-EIS Arrhenius plot (EA0.36-0.37 eV) is about three times the value of EA calculated from the quasi-elastic neutron backscattering experiment (EA0.10-0.14 eV). But tetragonal LLZO provided an even higher activation energy (EA0.66 eV). of Unfortunately, it was not possible to determine EA for tetragonal LLZO by QENS because of bad resolution and to compare it to HT-EIS. It would be interesting to compare differences like monitored for the cubic garnets.

As there is almost no difference between 60Ta-LLZO and 36Al-LLZO in HT-EIS activation energy, there is a significant one in QENS determined EA. 60Ta-LLZO needs a 0.04 eV higher EA to initiate Li ion movement than 36-Al-LLZO. This might be due to the 22 percent tetragonal phase fraction or because of the broad deviation of HWHM values provided by QENS.

The difference between QENS and HT-EIS is on the one hand due to the different reactions, as QENS measurements only look on the diffusivity when Li+ ions hop from one site to the next vacancy inside of a crystal lattice regardless of which direction. It is possible that ions just move back and forth. Contrary to that, in EIS Li+ ions move along an applied current between both electrodes, through the sintered LLZO bulk pellet, conducting through grains and have to overcome grain boundary resistances. That might be a reason for the observed higher activation energy in HT-EIS.



Figure 3.6: Comparison of all three garnet LLZO EA (DLi) by QENS and EA (σLi ION) by HT-EIS. EA(DLi) was not determinable for tetragonal LLZO. Right-hand side the total ionic conductivity σLi ION at room temperature (lined red stars) measured by HT-EIS is correlated.

## 4. Conclusion

We reported about hurdles like hydrogen and phase purity to overcome, necessary for trustful QENS measurements of lithium compounds. But it was successful to synthesize tetragonal LLZO, cubic 36Al- or 60Ta- substituted LLZO in Argon and proof absence of hydrogen by INS. Structure and phases were investigated by XRD and ND. We were able to determine the Li ion self-diffusion constant DLi for both 36Al- and 60Ta-LLZO in a temperature range from 450 K to 600 K and extrapolated their activation energy EA. We compared these results to the ionic conduction activation energy EA provided by HT-EIS measurements. We observed that EA for Li ionic movement initiated by AC current was three times higher than the EA for Li ion self-diffusion. Next to the activation energy it was possible to show that the ionic conductivity from 60Ta-LLZO was more than three times higher compared to 36Al-LLZO. We want to highlight, that QENS is a very interesting and powerful method in research of electrolyte materials. In future it might be interesting to investigate lithium solid-electrolytes with perfectly resolved structures to get the density of mobile Li ions, and to calculate by Nernst-equation [Lit] diffusion constant DLi and ionic conductivity coefficient σION for QENS and HT-EIS measurements and to compare both to get a deeper insight into ionic kinetics.

As it is difficult to get much more extended beam time it might be interesting to synthesize isotopically pure 7Li containing garnets for further investigations.

## Acknowledgements

We thank all contributing members of FZJ IEK-1 and ORNL MS&T Division for help and support with experiments, especially we thank the staff of SNS for all support and contribution with neutron experiments and furthermore. Work at SNS is supported by the Scientific User Facilities Division, Office of Basis Energy Sciences, US Department of Energy.

Financial support by Helmholtz Gemeinschaft Deutscher Forschungszentren e.V., by the Bundesministerium für Bildung und Forschung under support code 03X4634C under project no. 03EK3032 is gratefully acknowledged.

## 

## References

1 Diouf, B. & Pode, R. Potential of lithium-ion batteries in renewable energy. *Renewable Energy* **76**, 375-380, doi:10.1016/j.renene.2014.11.058 (2015).

2 Darcovich, K., Kenney, B., MacNeil, D. D. & Armstrong, M. M. Control strategies and cycling demands for Li-ion storage batteries in residential micro-cogeneration systems. *Applied Energy* **141**, 32-41, doi:<http://dx.doi.org/10.1016/j.apenergy.2014.11.079> (2015).

3 Darcovich, K. *et al.* Higher-capacity lithium ion battery chemistries for improved residential energy storage with micro-cogeneration. *Applied Energy* **111**, 853-861, doi:10.1016/j.apenergy.2013.03.088 (2013).

4 Bruce, P. G., Freunberger, S. A., Hardwick, L. J. & Tarascon, J. Li-O2 and Li–S batteries with high energy storage. *Nature materials* **11**, 19-29., doi:10.1038/nmat319110.1038/NMAT3191 (2012).

5 Fergus, J. W. Ceramic and polymeric solid electrolytes for lithium-ion batteries. *Journal of Power Sources* **195**, 4554-4569, doi:10.1016/j.jpowsour.2010.01.076 (2010).

6 Zeng, X. L., Li, J. H. & Liu, L. L. Solving spent lithium-ion battery problems in China: Opportunities and challenges. *Renew Sust Energ Rev* **52**, 1759-1767, doi:10.1016/j.rser.2015.08.014 (2015).

7 Kim, J. G. *et al.* A review of lithium and non-lithium based solid state batteries. *Journal of Power Sources* **282**, 299-322, doi:10.1016/j.jpowsour.2015.02.054 (2015).

8 Ren, Y. Y. *et al.* Oxide Electrolytes for Lithium Batteries. *Journal of the American Ceramic Society* **98**, 3603-3623, doi:10.1111/jace.13844 (2015).

9 Janek, J., Schmitz, R. & Winter, M. Functional materials and analytics for high performance lithium ion batteries. *Progress in Solid State Chemistry* **42**, 37-38, doi:10.1016/j.progsolidstchem.2014.05.002 (2014).

10 Whittingham, M. S. Introduction: batteries. *Chem Rev* **114**, 11413, doi:10.1021/cr500639y (2014).

11 Wang, Y. X. *et al.* Lithium and lithium ion batteries for applications in microelectronic devices: A review. *Journal of Power Sources* **286**, 330-345, doi:10.1016/j.jpowsour.2015.03.164 (2015).

12 Gholam-Abbas, N. & Gianfranco, P. *Lithium batteries : science and technology*. (Springer, 2009).

13 Winter, M. & Brodd, R. What Are Batteries, Fuel Cells, and Supercapacitors? *Chemical Reviews* **104** (2004).

14 Kozinsky, B. *et al.* Effects of Sublattice Symmetry and Frustration on Ionic Transport in Garnet Solid Electrolytes. *Phys Rev Lett* **116**, 055901, doi:10.1103/PhysRevLett.116.055901 (2016).

15 Scrosati, B. & Garche, J. Lithium batteries: Status, prospects and future. *Journal of Power Sources* **195**, 2419-2430, doi:10.1016/j.jpowsour.2009.11.048 (2010).

16 Sullivan, J. L. & Gaines, L. A review of battery life-cycle analysis : state of knowledge and critical needs. (2010).

17 Armand, M. & Tarascon, J. M. Building better batteries. *Nature* **451**, 652-657, doi:10.1038/451652a (2008).

18 Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* **414**, 359-367, doi:10.1038/35104644 (2001).

19 Takada, K. Progress and prospective of solid-state lithium batteries. *Acta Materialia* **61**, 759-770, doi:10.1016/j.actamat.2012.10.034 (2013).

20 Hausbrand, R. *et al.* Fundamental degradation mechanisms of layered oxide Li-ion battery cathode materials: Methodology, insights and novel approaches. *Materials Science and Engineering: B* **192**, 3-25, doi:10.1016/j.mseb.2014.11.014 (2015).

21 Dudney, N. J. Thin Film Microbatteries. *Interface* (2008).

22 Bates, J. B., Dudney, N. J., Neudecker, B., Ueda, A. & Evans, C. D. Thin-film lithium and lithium-ion batteries. *Solid State Ionics* **135**, 33-45, doi:Doi 10.1016/S0167-2738(00)00327-1 (2000).

23 Richards, W. D., Miara, L. J., Wang, Y., Kim, J. C. & Ceder, G. Interface Stability in Solid-State Batteries. *Chemistry of Materials* **28**, 266-273, doi:10.1021/acs.chemmater.5b04082 (2016).

24 Dudney, N. J., West, W. C. & Nanda, J. *Handbook of solid state batteries*. Second edition edn, Vol. 6 (World Scientific, 2016).

25 Xu, F. *et al.* Properties of lithium phosphorus oxynitride (Lipon) for 3D solid-state lithium batteries. *Journal of Materials Research* **25**, 1507-1515, doi:10.1557/jmr.2010.0193 (2011).

26 Thangadurai, V., Narayanan, S. & Pinzaru, D. Garnet-type solid-state fast Li ion conductors for Li batteries: critical review. *Chemical Society reviews* **43**, 4714-4727, doi:10.1039/c4cs00020j (2014).

27 Murugan, R., Thangadurai, V. & Weppner, W. Fast Lithium Ion Conduction in Garnet-Type Li7La3Zr2O12. *Angewandte Chemie International Edition* **46**, 7778-7781, doi:10.1002/anie.200701144 (2007).

28 Tsai, C. L. *et al.* High conductivity of mixed phase Al-substituted Li7La3Zr2O12. *Journal of Electroceramics* **35**, 25-32, doi:10.1007/s10832-015-9988-7 (2015).

29 Rao, R. P. *et al.* In Situ Neutron Diffraction Monitoring of Li7La3Zr2O12 Formation: Toward a Rational Synthesis of Garnet Solid Electrolytes. *Chemistry of Materials. Apr2015, Vol. 27 Issue 8, p2903-2910. 8p.* **27**, Start Page: 2903, doi:10.1021/acs.chemmater.5b00149 (2015).

30 Matsuyama, T., Takano, R., Tadanaga, K., Hayashi, A. & Tatsumisago, M. Fabrication of all-solid-state lithium secondary batteries with amorphous TiS4 positive electrodes and Li7La3Zr2O12 solid electrolytes. *In Solid State Ionics Jan 2015*, doi:10.1016/j.ssi.2015.05.025 (2015).

31 Cheng, L. *et al.* Effect of surface microstructure on electrochemical performance of garnet solid electrolytes. *In: ACS Applied Materials and Interfaces. (ACS Applied Materials and Interfaces, 28 January 2015, 7(3):2073-2081)* **7**, Start Page: 2073, doi:10.1021/am508111r (2015).

32 Buschmann, H. *et al.* Lithium metal electrode kinetics and ionic conductivity of the solid lithium ion conductors ''Li7La3Zr2O12'' and Li7-xLa3Zr2-xTaxO12 with garnet-type structure. *Journal of Power Sources 15 May 2012, vol.206, pp. 236-44. ISSN: 0378-7753 (print), CODEN: JPSODZ Publisher: Elsevier Sequoia S.A Country of Publication: Switzerland* **206**, Start Page: 236, doi:10.1016/j.jpowsour.2012.01.094 (2012).

33 Hubaud, A. A., Ingram, B. J., Vaughey, J. T., Schroeder, D. J. & Okasinski, J. S. Thermal expansion in the garnet-type solid electrolyte (Li7-xAlx/3)La3Zr2O12 as a function of Al content. *In: Journal of Alloys and Compounds. (Journal of Alloys and Compounds, 25 September 2015, 644:804-807)* **644**, Start Page: 804, doi:10.1016/j.jallcom.2015.05.067 (2015).

34 Gu, W., Ezbiri, M., Prasada Rao, R., Avdeev, M. & Adams, S. Effects of penta- and trivalent dopants on structure and conductivity of Li7La3Zr2O12. *In Solid State Ionics June 2015 274:100-105* **274**, Start Page: 100, doi:10.1016/j.ssi.2015.03.019 (2015).

35 Thompson, T. *et al.* Tetragonal vs. cubic phase stability in Al - free Ta doped Li7La3Zr2O12 (LLZO). *Journal of Materials Chemistry A 7 Sept. 2014, vol.2, no.33, pp. 13431-6. ISSN: 2050-7488 (print), Publisher: Royal Society of Chemistry Country of Publication: UK* **2**, Start Page: 13431, doi:10.1039/c4ta02099e (2014).

36 Matsui, M. *et al.* Phase stability of a garnet-type lithium ion conductor Li7La3Zr2O12. *Dalton Trans* **43**, 1019-1024, doi:10.1039/c3dt52024b (2014).

37 Murugan, R., Thangadurai, V. & Weppner, W. Fast lithium ion conduction in garnet-type Li(7)La(3)Zr(2)O(12). *Angewandte Chemie* **46**, 7778-7781, doi:10.1002/anie.200701144 (2007).

38 Hubaud, A. A. *et al.* Low temperature stabilization of cubic (Li7-xAlx/3) La3Zr2O12: role of aluminum during formation. *Journal of Materials Chemistry A* **1**, 8813-8818, doi:10.1039/c3ta11338h (2013).

39 Xu, B. Y. *et al.* Multistep sintering to synthesize fast lithium garnets. *Journal of Power Sources* **302**, 291-297, doi:10.1016/j.jpowsour.2015.10.084 (2016).

40 Wang, Y. X. & Lai, W. Phase transition in lithium garnet oxide ionic conductors Li7La3Zr2O12: The role of Ta substitution and H2O/CO2 exposure. *Journal of Power Sources* **275**, 612-620, doi:10.1016/j.jpowsour.2014.11.062 (2015).

41 Tsai, C. L. *et al.* Li7La3Zr2O12 Interface Modification for Li Dendrite Prevention. *ACS applied materials & interfaces* **8**, 10617-10626, doi:10.1021/acsami.6b00831 (2016).

42 Toby, B. H. & Von Dreele, R. B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *J Appl Crystallogr* **46**, 544-549, doi:doi:10.1107/S0021889813003531 (2013).

43 Toby, B. H. EXPGUI, a graphical user interface for GSAS. *J Appl Crystallogr* **34**, 210-213, doi:Doi 10.1107/S0021889801002242 (2001).

44 Amann-Winkel, K. *et al.* X-ray and Neutron Scattering of Water. *Chem Rev* **116**, 7570-7589, doi:10.1021/acs.chemrev.5b00663 (2016).

45 Mamontov, E. & Herwig, K. W. A time-of-flight backscattering spectrometer at the Spallation Neutron Source, BASIS. *The Review of scientific instruments* **82**, 085109, doi:10.1063/1.3626214 (2011).

46 Tietz, F., Wegener, T., Gerhards, M. T., Giarola, M. & Mariotto, G. Synthesis and Raman micro-spectroscopy investigation of Li7La3Zr2O12. *Solid State Ionics* **230**, 77-82, doi:10.1016/j.ssi.2012.10.021 (2013).

47 Yow, Z. F., Oh, Y. L., Gu, W., Rao, R. P. & Adams, S. Effect of Li+/H+ exchange in water treated Ta-doped Li7La3Zr2O12. *Solid State Ionics* **292**, 122-129, doi:10.1016/j.ssi.2016.05.016 (2016).

48 Murugan, R., Ramakumar, S. & Janani, N. High conductive yttrium doped Li7La3Zr2O12 cubic lithium garnet. *Electrochemistry Communications* **13**, 1373-1375, doi:10.1016/j.elecom.2011.08.014 (2011).

49 Shimonishi, Y. *et al.* Synthesis of garnet-type Li7-xLa3Zr2O12-1/2x and its stability in aqueous solutions. *Solid State Ionics* **183**, 48-53, doi:10.1016/j.ssi.2010.12.010 (2011).

50 Geiger, C. A. *et al.* Crystal chemistry and stability of "Li7La3Zr2O12" garnet: a fast lithium-ion conductor. *Inorganic chemistry* **50**, 1089-1097, doi:10.1021/ic101914e (2011).

51 Cussen, E. J. Structure and ionic conductivity in lithium garnets. *Journal of Materials Chemistry* **20**, 5167-5173, doi:10.1039/b925553b (2010).

52 Meier, K., Laino, T. & Curioni, A. Solid-State Electrolytes: Revealing the Mechanisms of Li-Ion Conduction in Tetragonal and Cubic LLZO by First-Principles Calculations. *J Phys Chem C* **118**, 6668-6679, doi:10.1021/jp5002463 (2014).

53 Wang, Y., Huq, A. & Lai, W. Insight into lithium distribution in lithium-stuffed garnet oxides through neutron diffraction and atomistic simulation: Li7-xLa3Zr2-xTaxO12 (x=0–2) series. *Solid State Ionics* **255**, 39-49, doi:10.1016/j.ssi.2013.11.017 (2014).

54 Awaka, J. *et al.* Neutron powder diffraction study of tetragonal Li7La3Hf2O12 with the garnet-related type structure. *Journal of Solid State Chemistry* **183**, 180-185, doi:10.1016/j.jssc.2009.10.030 (2010).

55 Rietveld, H. M. The Rietveld Method: a retrospection. *Zeitschrift Fur Kristallographie* **225**, 545-547, doi:10.1524/zkri.2010.1356 (2010).

56 Abreu-Sepúlveda, M. *et al.* Synthesis and characterization of substituted garnet and perovskite-based lithium-ion conducting solid electrolytes. *Ionics* **22**, 317-325, doi:10.1007/s11581-015-1556-2 (2015).

57 Mukhopadhyay, S. *et al.* Structure and Stoichiometry in Supervalent Doped Li7La3Zr2O12. *Chemistry of Materials* **27**, 3658-3665, doi:10.1021/acs.chemmater.5b00362 (2015).

58 Li, Y. T., Han, J. T., Wang, C. A., Xie, H. & Goodenough, J. B. Optimizing Li+ conductivity in a garnet framework. *Journal of Materials Chemistry* **22**, 15357-15361, doi:10.1039/c2jm31413d (2012).

59 Kokal, I., Somer, M., Notten, P. H. L. & Hintzen, H. T. Sol-gel synthesis and lithium ion conductivity of Li7La3Zr2O12 with garnet-related type structure. *Solid State Ionics* **185**, 42-46, doi:10.1016/j.ssi.2011.01.002 (2011).

60 Buschmann, H., Berendts, S., Mogwitz, B. & Janek, J. Lithium metal electrode kinetics and ionic conductivity of the solid lithium ion conductors "Li7La3Zr2O12" and Li7-xLa3Zr2-xTaxO12 with garnet-type structure. *Journal of Power Sources* **206**, 236-244, doi:10.1016/j.jpowsour.2012.01.094 (2012).

61 Xia, W. *et al.* Ionic Conductivity and Air Stability of Al-Doped Li7La3Zr2O12 Sintered in Alumina and Pt Crucibles. *ACS applied materials & interfaces* **8**, 5335-5342, doi:10.1021/acsami.5b12186 (2016).

62 Awaka, J., Kijima, N., Hayakawa, H. & Akimoto, J. Synthesis and structure analysis of tetragonal Li7La3Zr2O12 with the garnet-related type structure. *Journal of Solid State Chemistry* **182**, 2046-2052, doi:10.1016/j.jssc.2009.05.020 (2009).

63 Jin, X. *Neutron Diffraction : Principles, Instrumentation and Applications*. (2013).

64 Sears, V. F. Neutron scattering lenghts and cross sections. *Neutron news* **3**, 26 (1992).

65 Everett, D. H. in *Pure and Applied Chemistry* Vol. 31 577 (1972).

66 Kamazawa, K. *et al.* Interrelationship between Li+diffusion, charge, and magnetism inLi7Mn2O4andLi71.1Mn1.9O4spinels: Elastic, inelastic, and quasielastic neutron scattering. *Physical Review B* **83**, doi:10.1103/PhysRevB.83.094401 (2011).

67 Heitjans, P. & Indris, S. Diffusion and ionic conduction in nanocrystalline ceramics. *Journal of Physics: Condensed Matter* **15**, R1257 (2003).