Investigation of ionic mobility in NASICON-type solid electrolytes

A Vyalikh¹⁴, V Vizgalov², D M Itkis²³, D C Meyer¹
¹ Institut für Experimentelle Physik, Technische Universität Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany
² Department of Materials Science, Moscow State University, Leninskie gory, 119991 Moscow, Russian Federation
³ Department of Chemistry, Moscow State University, Leninskie gory, 119991 Moscow, Russian Federation

Abstract. Impedance spectroscopy and ⁷Li NMR have been applied to characterize the lithium conducting glass-ceramics membranes of the Li₅Al₅Ge₅(PO₄)₁₃ composition with the NASICON-type structure. The ⁷Li NMR spectra and T₁ relaxation times have been compared for the precursor glass and two glass-ceramics annealed for 2 and 6 hours, and analysed with respect to the ionic conductivity in these materials. The ⁷Li static NMR spectra reveal two components in the glass-ceramics samples: A quadrupole pattern with C_Q of 38.7 kHz and 32.5 kHz, and a narrow signal of the Lorentzian or Gaussian lineshape for the samples annealed for 2 and 6 hours, respectively. Variation of the lineshape and the deconvolution parameters point out to the modification of the NASICON framework in the former, which affects the conductivity channels towards improved movement of lithium ions. The NMR data correlate with the conductivity measurements demonstrating enhanced ionic mobility in the glass-ceramics annealed for 2 hours. The ⁷Li NMR relaxation data seem to be very sensitive to the species with different mobility and reveal the presence of an additional minor component, which can be responsible for decrease of conductivity at longer thermal treatment.

Introduction
Highly demanded high-voltage and safe lithium-based energy storage is associated today with all-solid state lithium-ion batteries. All-solid-state batteries utilize solid electrolytes, which demonstrate a sufficiently high ionic conductivity (> 10⁻⁴ S/cm), good chemical stability and an electrochemical stability window, which is significantly broader than in liquid electrolytes. Due to an unmatchable combination of their chemical and electrical properties, materials with the NASICON-type structure have been proposed as optimum candidate structures for ion migration in Na- or Li-based all-solid-state batteries. [1] By a partial replacement of the structural elements and a total charge balance, one can vary carrier concentration and therefore tailor the electrical properties. In the present work we focus on the Li₅Al₅Ge₅(PO₄)₁₃ composition (LAGP) with a stoichiometric value of x=0.5, as this NASICON-type material is reported to demonstrate particular stability against lithium metal. [2, 3] Since conducting properties are related to the crystalline phase and microstructures of the materials, development of improved ceramics-based electrode materials is focused today on optimising the morphology of their microstructure, which is influenced by the composition, the choice of nucleating

¹ To whom any correspondence should be addressed, email: Anastasia.Vyalikh@physik.tu-freiberg.de.
agents and the heat treatment processes used. As sintering behaviour has a strong effect on phase formation and thus on electrical characteristics, a detailed characterisation of the amounts of the phases and their ionic dynamics on an atomic level is of great importance for gaining understanding of structure-property relationships.

Among the existing analytical tools able to characterize the complex morphology of ceramic materials, NMR has an important advantage as it can probe each phase directly through differences in chemical shift and relaxation behaviour. [4,5] Moreover, NMR as being reflecting short-to-medium-range-order is more sensitive to the very local structure, and is particularly useful in the cases, where X-Ray and other diffraction techniques are limited due to a lack of long-range order.

The NMR relaxation times of nuclear spins are sensitive to a number of parameters including degree of crystallinity, presence of impurity phases, morphology of the ceramics system and molecular mobility. Depending on the relaxation kind (spin-spin or spin-lattice relaxation in the laboratory or rotating frame) under study, different motional time scales can be investigated. [6] The spin-lattice or longitudinal relaxation characterized by the time constant $T_1$ describes the recovery of the magnetisation along the axis of the magnetic field and has been frequently applied to correlate the structure [7, 8] and morphology [9, 10] of solid electrolyte materials with their conducting properties. In the present work, we apply solid-state nuclear magnetic resonance (NMR) in order to characterize LAGP glass and glass-ceramics as a function of sintering conditions and to reveal a relationship between the microstructure and ionic conductivity towards further development of materials for sustainable energy.

**Experimental part**

*1.1. Sample preparation*

For preparation of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ glass ceramics 1.2420 g of $\text{Li}_2\text{CO}_3$ (99.9%, Sigma-Aldrich), 0.5713 g of $\text{Al}_2\text{O}_3$ (99.9%, Sigma-Aldrich), 3.5162 g of $\text{GeO}_2$ (99.9%, SMI Ltd.), 8.8801 g of $(\text{NH}_4)_2\text{HPO}_4$ (99.9%, Sigma-Aldrich) and 0.3189 g (5 vol. % or 12 mol. %) of $\text{Y}_2\text{O}_3$ (99.99%, Sigma-Aldrich) were mixed in required molar ratios in an agate mortar without any additional purification. Stoichiometric mixtures of precursors were preannealed at 500°C for 5 hours. Resulting powder was placed into a platinum crucible and melted at 1300°C for 2 hours. The melt was quenched between two steel plates preheated at 450°C, forming 500 or 1000 µm thick discs, and then cooled down to room temperature for 3 hours. The glass discs were then tempered at 500°C and 400°C subsequently. For crystallisation, glass was rapidly heated to 650°C and annealed for 2 hours and 6 hours with subsequent cooling in air yielding the samples LAGP-2h and LAGP-6h, respectively. Finally, glass-ceramic membranes were obtained by rapid heating and crystallization at 750°C. For impedance spectroscopy, as-obtained glass-ceramic membranes were polished down to 300 – 350 µm using Struers Tegrapol-11 polishing machine and DiaDur abrasives. For NMR measurements the samples were ground to powder and filled into zirconia rotors.

*1.2. Impedance spectroscopy*

Ionic conductivity of the resulting samples was characterized by electrochemical impedance spectroscopy (EIS). Nickel blocking electrodes were sputtered on both sides of a glass-ceramic membrane using Quorum Technologies Q150T Turbo-Pumped Sputter Coater / Carbon Coater. Electric contacts were fixed on sputtered electrodes using EPO-TEK H20S conductive epoxy. The ac impedance measurements were conducted in the frequency range of 7 MHz to 100 Hz with an amplitude of 50 mV using Bio-Logic SP-300 with a frequency response analyzer. The obtained Niquist plots generally consist of one or two semicircles in a higher frequency region typical for bulk and grain boundary resistance of electrolyte and a spike at the lower frequency corresponding to diffusion due to the blocking electrodes.
1.3. NMR measurements
Static $^7$Li NMR measurements were performed on a BRUKER AVANCE III 400 MHz spectrometer operating at a resonance frequency of 155.5 MHz employing a 2.5 mm MAS probe head. Static $^7$Li NMR spectra were recorded at a single pulse of 1 $\mu$s pulse duration ($\pi/12$), a recycle delay of 1 s and 4096 repetitions. The spectra were referenced to 1M solution of LiCl at 0 ppm. The spectra were fitted using Dmfit. [11] $^7$Li NMR spin-lattice relaxation times were recorded with the standard saturation recovery pulse sequence employing a saturation pulse train of 50 pulses separated by 0.0002 s. The duration of the 90° pulse of 5 $\mu$s, 128 repetitions and the repetition delay of 1 s were applied. 16 increments in the range from 0.05 s to 150 s and 22 increments in the range from 0.002 s to 50 s were used for the studies of glass and glass-ceramics samples, respectively. The magnetization decay profiles were analysed with a double and triple exponential functions with Bruker TopSpin 3.2 software.

Results and Discussion
Figure 1(a) shows the static $^7$Li NMR spectra of LAGP glass and glass-ceramics annealed at 2 hours and 6 hours. The spectrum of glass is represented by a single line inhomogeneously broadened due to a long-range disorder typical for the glass structure. The spectra of both glass-ceramics demonstrate the characteristic $I=3/2$ quadrupolar lineshape formed by the central line, whose linewidth is significantly narrower as compared to glass, and the satellite transitions. [6] Fit shows two overlapping spectral components for both LAGP-2h and LAGP-6h spectra, their fit parameters are given in Table 1. The major spectral component in both cases shows the quadrupolar pattern and can be attributed to Li ions surrounded by six oxygens (component I) [8], while the minor component does not show a quadrupolar splitting and can be described by a Lorentzian or Gaussian lineshape (component II). Such lineshape for quadrupolar nuclei arises, either in the symmetrical local environment, or when quadrupolar interactions are averaged out on the timescale of the NMR experiment due to fast atomic motion. We assume that the component II is attributed to more mobile Li ions accommodated within the interstitial channels formed by the NASICON framework.

Analysis of the deconvolution parameters helps to correlate the local structure with the conducting properties. A drastic change is observed for the lineshape of the component II, which transforms from the pure Lorentzian in LAGP-2h to the pure Gaussian one in LAGP-6h, which is known to be responsible for slower motions with correlation times. A similar lineshape transformation has been observed for LiHf$_2$(PO$_4$)$_3$ with the NASICON structure and associated with a transition from the triclinic phase characterized by very low ionic conductivity to the rhombohedral symmetry with significantly higher conductivity. [7] It is worth mentioning that such a transformation in LiHf$_2$(PO$_4$)$_3$ has been accompanied by an enormous increase of the T$_1$ relaxation time. Considerable increase of the linewidth values in LAGP-2h as compared to LAGP-6h is observed for both spectral components. Such behaviour has been reported previously for LAGP glass-ceramics of the same composition, where Li$_2$O was used as a nucleating agent to considerable promote crystallisation during heat treatment that resulted in a dense microstructure with a uniform grain size and therefore in an enhanced ionic conductivity. [12] The main cause of the linewidth increase is likely to be an increase in the strength of the dipole-dipole interactions (most likely Li-P) associated to the incorporation of a part of excess lithium into the crystal lattice of the NASICON-type structure. Variations of the other deconvolution $^7$Li spectral parameters such as chemical shift, quadrupole coupling constant C$_Q$ and asymmetry parameter at different thermal treatment points out to changes in the local environment around $^7$Li, which are not directly related to the ionic conductivity, but suggests a modification of the conducting channels that favour the movement of lithium ions.

Characterization of the NMR relaxation times may give independent estimation on the number of the components with different mobility. Figure 1(b) shows the experimental relaxation curves for three samples under study. It is obviously that the relaxation time for LAGP-glass deviates strongly from
Figure 1. (a) Static $^7$Li NMR spectra of LAGP-glass (top), LAGP glass-ceramic annealed at 2 hours (middle) and LAGP glass-ceramic annealed at 6 hours (bottom) with their fit sum and fit components; (b) $^7$Li relaxation curves for three samples. The insert shows the best fits to LAGP-2h and LAGP-6h in the zoomed region.

those for LAGP glass-ceramics. The fit parameters of the experimental data are indicated in Table 2. While the relaxation in glass dominates by a contribution (97 %) with a long $T_1$ of 4.38 s characteristic for the glassy structure, in glass-ceramics it shows a multicomponent character reflecting a heterogeneous nature of ionic dynamics in Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$. In LAGP-2h two relaxation components of 0.23 s (81%) and 0.06 s (19%) are found, their fractions are in good agreement with the quantitative relationship of both spectral components reported in Table 1. In LAGP-6h, while two relaxation components deviate only slightly in magnitude (0.19 s and 0.05 s) from those in LAGP-2h, but their fractions change (68 % and 30 %, respectively) and an additional slow component (7.45 s, 2 %) appears. Although, the fractions of former two contributions agree with the deconvolution data in Table 1, the fraction of the latter is too small to be resolved in the $^7$Li NMR spectrum as well as to be detected by other characterization techniques. The formation of the phase with the slow $T_1$ component at longer crystallization time can be associated with the grain growth and appearance of cracks, in which a new phase is formed, which interrupts the conduction pathways and therefore suppresses ionic conductivity in these materials.

Although the chemical composition and morphology of the phase, which suppresses conductivity, cannot be determined from the data available, the systematic study in the LAGP glass-ceramics prepared at different annealing conditions using the complementary methods will help in understanding the factors that influence the ionic conductivity in the materials with the NASICON-type structure and therefore contribute to the design of new solid electrolyte materials.
Table 1. $^7$Li NMR fit parameters with their experimental errors.

| Sample   | component I | component II |
|----------|-------------|--------------|
|          | $\delta(^7\text{Li})$ (±0.1, ppm) | $C_0$ (±0.5, kHz) | $\eta$, (±0.05) | width (±0.2, ppm) | %, | $\delta(^7\text{Li})$ (±0.1, ppm) | G/L ratio, (±0.1) | width (±0.3, ppm) | %, |
| LAGP-2h  | 0.1         | 38.7         | 0.35       | 6.8         | 78          | -3.2       | 0         | 9.0         | 22 |
| LAGP-6h  | 0.4         | 32.5         | 0.20       | 4.5         | 64          | -0.9       | 1         | 6.4         | 36 |

Table 2. $^7$Li spin-lattice relaxation $T_1$ parameters. Fraction of each component is indicated in parentheses relative to the sum. The experimental uncertainty is ±0.01 s for $T_1$ and ±1 % for the fraction.

| Sample   | conductivity (mScm$^{-1}$) | I component (s) | II component (s) | III component (s) |
|----------|---------------------------|-----------------|------------------|-------------------|
| Glass    | $<10^{-9}$                | 4.38 (97%)      | 0.49 (3%)        | -                 |
| LAGP-2h  | 0.5                       | -               | 0.23 (81%)       | 0.06 (19%)        |
| LAGP-6h  | 0.3                       | 7.45 (2%)       | 0.19 (68%)       | 0.05 (30%)        |

Conclusions

The structure and mobility in NASICON-like glass-ceramics electrolyte membranes of a $\text{Li}_{1+x}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ composition have been studied and analyzed in respect to ionic conductivity. We have shown that NMR spin-lattice relaxation time measurement is a simple non-destructive analytical tool, which is sensitive to morphological changes that occur in glass-ceramics due to thermal treatment. Quantitative analysis of the relaxation data has shown a multicomponent character of the relaxation behavior associated with different mobility of lithium ions accommodated within interstitial channels formed by the NASICON framework. In the sample with the longer crystallization time an additional slow relaxing component appears, which is indistinguishable in the $^7$Li NMR spectrum, and which is believed to account for the decrease of the ionic conductivity.

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