Solid Electrolytes: Extremely Fast Charge Carriers in Garnet-Type Li$_6$La$_3$ZrTaO$_{12}$ Single Crystals

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The development of all-solid-state electrochemical energy storage systems, such as lithium-ion batteries with solid electrolytes, requires stable, electronically insulating compounds with exceptionally high ionic conductivities. Considering ceramic oxides, garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ and derivatives, see Zr-exchanged Li$_6$La$_3$ZrTaO$_{12}$ (LLZTO), have attracted great attention due to its high Li$^+$ ionic conductivity of $10^{-3}$ S cm$^{-1}$ at ambient temperature. Despite numerous studies focussing on conductivities of powder samples, only few use time-domain NMR methods to probe Li ion diffusion parameters in single crystals. Here we report on temperature-variable NMR relaxometry measurements using both laboratory and spin-lock techniques to probe Li jump rates covering a dynamic temperature window spanning several decades. Both techniques revealed a consistent picture of correlated Li ion jump diffusion in the single crystal; the data perfectly mirror a modified BPP-type relaxation response being based on a Lorentzian-shaped relaxation function. The rates measured could be parameterized with a single set of diffusion parameters. Results from NMR are completely in line with ion transport parameters derived from conductivity spectroscopy.
temperatures in the rigid lattice regime, are fully averaged at ambient temperature. Fast Li ion exchange is corroborated by NMR spin-lattice relaxation measurements carried out at a Larmor frequency of 116 MHz and at a spin-locking frequency of 25 kHz. From the diffusion-induced rate peaks recorded jump rates, activation energies and pre-factors of the underlying Arrhenius relation were deduced. Correlated motion is found clearly revealing that short-range motion is quite different from long-range ion transport to which AC conductivity measurements are sensitive. Activation energies from AC conductivity measurements are fully consistent with that deduced from a global fit analysis of the diffusion-controlled $^7$NMR relaxation rates measured.

2. Experiment

2.1. Preparation of the Single Crystals

LLZTO single crystals with the nominal composition Li$_6$La$_3$ZrTaO$_{12}$ were grown by the conventional Czochralski technique. The starting materials were Li$_2$CO$_3$, La$_2$O$_3$, ZrO$_2$, and Ta$_2$O$_5$. Carbonates and oxides were dried and mixed in the required stoichiometry with a 10% excess of Li$_2$CO$_3$. Afterwards the powders were uniaxial pelletized, isostatically pressed at 2800 kbar and finally sintered at 1373 K for 16 h in air. Capped magnesia crucibles were used while covering the pellets with the respective LLZTO powder to avoid Li-loss during sintering.

Because of the high melting temperature the sintered LLZTO samples were molten by radio frequency induction heating using a 25 kW microwave generator. An iridium seed (pulling rate 1.5 mm h$^{-1}$, rotation speed 1 rpm) was used for the crystal growth performed under dinitrogen atmosphere. An active afterheater was applied to adjust the temperature gradient in the set up. Thermal insulation was established by an outer alumina ceramic tube filled with zirconia granules. Inductively coupled plasma optical emission spectroscopy corroborated that the LLZTO single crystal obtained has indeed the composition Li$_6$La$_3$ZrTaO$_{12}$. For NMR and impedance measurements a single crystal with the following dimensions was used: 5 mm × 5 mm × 6 mm.

2.2. Characterization via Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX CCD-diffractometer. A single crystal was selected on the basis of its optical properties (sharp extinctions, regular shape and homogeneity in colour) and glued on top of a glass capillary (0.1 mm in diameter). Intensity data were collected with graphite-monochromatized Mo K$_\alpha$ X-ray radiation (50 kV, 30 mA). The crystal-to-detector distance was 30 mm and the detector positioned at $\phi$ = 0°, 90°, 180° and 270°. 630 frames with $\Delta \omega$ = 0.3° were acquired for each run. 3D data were integrated and corrected for Lorentz-, polarization and background effects using the APEX3 software. Structure solution using direct methods and subsequent weighted full-matrix least-squares refinements on F2 were carried out with SHELX-2012 as implemented in the program suite WinGX 2014.

Details on data collection and results of structure refinement of selected samples are given in Table 1, the fractional atomic coordinates, anisotropic and equivalent isotropic atomic displacement parameters are compiled in Tables 2 and 3.

2.3. NMR and AC Conductivity Measurements

$^7$Li NMR spectra and relaxation rates were recorded at $\omega_0/2\pi$ = 116 MHz with an Avance III Bruker digital NMR spectrometer that is connected to a shimmmed 7-Tesla wide-bore magnet (Bruker). We used a Bruker NMR probe that is capable to reach temperatures as high as 573 K. The temperature in the sample chamber was adjusted with a stream of dry, freshly evaporated dinitrogen gas. The Avance III is equipped with a Eurotherm controller to set the temperature. Further details of the experimental setup and the measuring techniques can be found elsewhere.

While the solid-echo NMR pulse sequence was used to acquire the NMR spectra at different temperatures, spin-lattice relaxation rates in the rotating ($R_{\text{rel}}$) and laboratory ($R_1$) frame of reference were measured with the spin-lock technique and the saturation recovery method, respectively. The pulse sequences employed are as follows: (i) $10 \times \pi/2 - t_d - \pi/2 - \text{acq.}$ for the $R_1$ measurements and (ii) $\pi/2 - p_{\text{lock}} - \text{acq.}$ to measure $R_{\text{rel}}$. The lengths of the radio frequency pulse ($\pi/2$) to excite the spins slightly varied with temperature and ranged from 2 to 3 $\mu$s.

In the case of (i) the initial pulse train, consisting of ten $\pi/2$ pulses separated by 80 $\mu$s, is used to destroy any longitudinal magnetization ($M_0 = M_{\text{eq}}$), $M_0 = 0$ at $t_d = 0$ prior to recording its recovery as a function of the delay time $t_d$. To get access to $R_{\text{rel}}$ (see (ii)), immediately after the $\pi/2$-pulse the magnetization $M_0$
pointing along the \((−y/2, y, 0)\) axis is locked by the field \(B_z = a_1 \gamma/\gamma\). \(\gamma\) denotes the magnetogroic ratio. Note that \(B_z\) is much lower than the corresponding \(B_y\) field determining \(a_1\). The subsequent transversal decay of \(M_y(−y/2)\) is then probed by plotting the height (or area) of the free induction decay (FID) as a function of the locking pulse length \(T_{\text{lock}}\). In the present case, the power level of the locking pulse was adjusted such that \(a_1 \gamma/\gamma \approx 25 \text{ kHz}\).

The recycle delay for the \(R_{\text{ref}}\) experiments was set to at least 5 \(\times T_{\text{ref}}\). Both, \(R_{\text{ref}}\) and \(R_{\text{lock}}\) were obtained by parameterizing the magnetic transients \(M_y(t)\) and \(M_x(t_{\text{lock}})\), respectively, by stretched exponentials: \(M_y(t) \propto 1 - \exp\left(−(t/T_1)^\gamma\right)\) and \(M_x(t_{\text{lock}}) \propto \exp\left(−(t_{\text{lock}}/T_0)^\gamma\right)(0 < \gamma \leq 1)\).

For the AC conductivity measurements we applied Au electrodes on a flat piece of the single crystal with polished surfaces.

### Table 1. Fractional atomic coordinates as obtained from structure refinement of the single crystal studied.

| Atom     | x/a   | y/b   | z/c   | Occ. |
|----------|-------|-------|-------|------|
| O1 (96e) | 0.10299(17) | 0.19773(17) | 0.28027(17) | 1    |
| La1 (24c) | 0.125 | 0    | 0.25  | 0.9748(8) |
| Zr1 (16a) | 0    | 0    | 0    | 0.455(8)  |
| Ta1 (16e) | 0    | 0    | 0    | 0.545(8)  |
| Li1 (24d) | 0.375 | 0    | 0.75  | 0.75(2)   |
| Li2 (96e) | 0.1470(16) | 0.1760(17) | 0.4387(17) | 0.25(3) |

We used a Novocontrol broadband impedance spectrometer with an Alpha impedance analyzer and a QUATRO temperature unit to measure conductivities as a function of temperature. Experimental details and the exact setup have already been described elsewhere, see Refs. [22–24].

### 3. Results and Discussion

#### 3.1. NMR Motional Narrowing

First insights into Li ion dynamics in single crystaline LLZTO are provided by \(^7\)Li NMR line shape measurements, see Ref. [25] for a short introduction. Usually, for Li-Li dipolar interactions in oxide materials, such as LLZO, the width of the lithium resonance is in the order of 8 to 10 kHz.\(^{26–28}\) With increasing Li ion hopping among the crystallographic inequivalent sites dipole-dipole interactions are averaged. This averaging results in line narrowing that can be observed as a function of temperature (see Figure 2).\(^{26}\)

For LLZO with tetragonal symmetry motional narrowing (MN) sets in at ca. 280 K.\(^{29}\) If Li ions are partly substituted with trivalent cations such as Al\(^{3+}\) or Ga\(^{3+}\), LLZO with cubic symmetry is obtained for which the onset of MN is shifted by approximately 100 K toward lower temperature.\(^{19}\) Since both (i) the shape of the curves and (ii) their rigid-lattice line widths, \(\nu_{\text{li}}\), are almost the same the shift directly reflects the increase in conductivity by at least two orders of magnitude when going from tetra-LLZO to its cubic relatives.\(^{21}\) The same increase in diffusivity is found when \(\text{Zr}^{4+}\) ions are partly replaced with higher valent ions such as Mo\(^{5+}\) or, as it is in the present case, by Ta\(^{5+}\). For the reason of charge neutrality, the number of Li ions per unit cell is reduced in LLZTO. The additional vacant Li sites introduced enable the remaining ions to quickly jump from site to site. From the point of view of NMR line narrowing, the highest diffusivity is found for Ga-stabilized c-LLZO.\(^{19}\) The diffusivity of single crystalline c-LLZTO turns out to be only slightly lower. At temperatures above the inflection point \(T_{\text{inf}}\) of the MN curve of c-LLZO the jump rate \(\tau_{\text{MN}}^{-1}\) can be estimated according to \(\tau_{\text{MN}}^{-1} = 2\pi \nu_{\text{li}}\) with \(\nu_{\text{li}} = 9 \text{ kHz}\) this estimation yields \(T_{\text{inf}} = 5.6 \times 10^4 \text{ s}^{-1}\) at 235 K to 250 K. For comparison, for Ga-bearing c-LLZO, which may serve as benchmark for cubic garnets with extraordinary high Li diffusivity, the same jump rate is reached at \(T_{\text{inf}} = 200 \text{ K}\). Hence, Li diffusion in LLZTO is only slightly less than in the best Ga-LLZO samples known.\(^{19}\)

With respect to Li-containing sulfides, on the other hand, even lower temperatures \(T_{\text{inf}}\) have been found.\(^{27}\) As an example, in Figure 2 the \(^7\)Li NMR MN curve of argyrodite-type Li\(_3\)PS\(_4\)Br is shown for which the beginning of line narrowing is seen at temperatures as low as 80 K.\(^{27}\) The lower \(^7\)Li NMR rigid-lattice line width of polycrystalline Li\(_3\)PS\(_4\)Br reflects somewhat weaker dipole-dipole interactions the Li spins are exposed to in the sulfide structure. In general, \(\nu_{\text{li}}\) depends on both homonuclear and heteronuclear spin-spin interactions. While the strength of the first depend on the mean Li-Li distance, heteronuclear dipolar interactions are governed by the coupling of the \(^7\)Li nuclei with other spin-carrying ions in the direct neighborhood.

Regarding the uniform shape of the MN curves of the garnet-based electrolytes (see Figure 2) one might speculate whether...
**Table 3.** Corresponding anisotropic and equivalent isotropic atomic displacement parameters, continuation of Table 2.

| Atom       | \( U_{11} \)   | \( U_{22} \)   | \( U_{33} \)   | \( U_{12} \)   | \( U_{13} \)   | \( U_{23} \)   | \( U_{44} \)   |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| O (96\(h\)) | 0.0092(8)      | 0.0117(9)      | 0.0120(9)      | 0.0012(6)      | 0.0004(6)      | −0.0005(6)     | 0.0110(4)     |
| La (24\(c\)) | 0.00958(13)    | 0.0070(1)      | 0.0070(1)      | 0.00225(9)     | 0              | 0              | 0.00786(9)    |
| Zr (16\(a\)) | 0.00499(11)    | 0.00499(11)    | 0.00499(11)    | −0.00003(5)    | −0.00003(5)    | −0.00003(5)    | 0.00499(11)   |
| Ta (16\(a\)) | 0.00499(11)    | 0.00499(11)    | 0.00499(11)    | −0.00003(5)    | −0.00003(5)    | −0.00003(5)    | 0.00499(11)   |
| Li (7\(a\)) | 0.025(12)      | 0.056(13)      | 0.056(13)      | 0              | 0              | 0              | 0.046(10)     |
| Li (96\(h\)) |                |                |                |                |                |                | 0.011(6)      |

![Figure 2. 7Li NMR line width as a function of temperature. c-LLZTO denotes the single crystal investigated in this study. Tetra-LLZO refers to Li7La3Zr2O12 with tetragonal symmetry.](Image)

3.2. NMR Relaxometry

If recorded as a function of temperature, the spin-lattice relaxation rates \( R_1 \) and \( R_2 \) contain information on short- as well as long-range ion hopping processes in solids.\(^{[20,32]}\) Besides non-diffusive effects, usually showing up at low temperatures, longitudinal as well as transversal relaxation is induced by internal fluctuating fields. Such fluctuations are caused by the temperature dependent motion of the nuclei. These fields may be dipolar magnetic or quadrupolar electric in nature.\(^{[33]}\) In the case of \(^7\)Li with its spin quantum number \( I = 3/2 \) the quadrupole moment can interact with static local electric field gradients in the direct neighborhood of the spin. Quadrupole relaxation represents a strong relaxation source. For \(^7\)Li the two types of relaxation usually superimpose. In most NMR relaxation experiments they cannot be treated separately; thus, longitudinal relaxation is commonly approximated with a single spectral density function \( J(\omega) \) to which the rates \( R_1 \) and \( R_2 \) are proportional, see below.

The fluctuations of the internal fields the ions are subjected to are generally described with the help of a correlation function \( G(t) \). According to the model introduced by Bloembergen, Purcell and Pound (BPP),\(^{[34]}\) for random jump diffusion \( G(t) \) is assumed to be a simple exponential

\[
G(t) = G(0) \exp\left(-|t|/\tau_c\right),
\]

where \( \tau_c \) is the correlation time which is within a factor of the order of unity equal to the mean residence time \( \tau \) between two successive jumps of the nucleus. The Fourier transform of \( G(t) \) is the spectral density function \( J(\omega) \). It has a Lorentzian shape when \( G(t) \) is an exponential. Most importantly, spin-lattice relaxation becomes effective when \( J(\omega) \) has intensities at the resonance frequency \( \omega_0 \):\(^{[35]}\)

\[
1/T_1 \approx R_1 \propto J(\omega_0) \approx G(0)\frac{\tau_c}{1 + (\omega_0\tau_c)^2} = \frac{\tau_c}{1 + (\omega_0\tau_c)^2}.
\]

\[
J(\omega_0) \text{ represents the first term of the full expression for } J. \text{ In most cases it is sufficient to approximate } J \text{ with the first term. For } R_{1c} \text{ we obtain}
\]

\[
1/T_{1c} \approx R_{1c} \propto J(2\omega_0) \approx G(0)\frac{\tau_c}{1 + (2\omega_0\tau_c)^2} = \frac{\tau_c}{1 + (2\omega_0\tau_c)^2}.
\]

The temperature dependence of \( \tau_c \) in eq. 2 is typically given by an Arrhenius relation

\[
\tau_c = \tau_0 \exp\left(E_a/(k_B T)\right),
\]

where \( \tau_0 \) is the pre-exponential factor and \( E_a \) the activation energy of the diffusion process. \( T \) is the absolute temperature and \( k_B \) denotes Boltzmann's constant. Thus, for a given Larmor frequency \( \omega_0 \), the so-called diffusion induced relaxation rate \( R_{1c(\omega)} \), measured at \( \omega = \omega_0 \), first increases with increasing \( T \) (low-\( T \) range, \( \omega_0\tau_c \gg 1 \), passes through a maximum at a specific temperature \( T_{\max} \) and then decreases with still increasing temperature (high-\( T \) range, \( \omega_0\tau_c \ll 1 \)). With eqs. 2 and 3 fully symmetric rate peaks are obtained. Correlation effects caused by structural...
disorder and/or Coulomb interactions of the jumping ions lead to asymmetric peaks with a smaller slope in the regime $\omega_0 \tau \gg 1$, i.e., we have to deal with $E'_a$ (low-$T$) $< E''_a$ (high-$T$). To take into account this finding the quadratic dependence of $R_1(\varrho)$ on $\omega_0^{(1)}$ is replaced by a sub-quadratic one resulting with $\beta_0(\varrho) < 2$, in $R_1^{\text{diff}}(\omega_0, T) \propto \tau_c^{1 - \beta_0(\varrho)\omega_0^{(0)}}$ and $R_1^{\text{diff}}(\omega_0, T) \propto \tau_c^{1 - \beta_0(\varrho)\omega_0^{(0)}}$.

For $R_1^{\text{diff}}$, as well as for $R_{1\varrho}^{\text{diff}}$, this behaviour can be summarized as follows:

$$R_1^{\text{diff}}(\omega_0, T) \sim \begin{cases} \tau_c, & \text{if } T \gg T_{\text{max}}(\omega_0) \\ \tau_c^{1 - \beta_0(\varrho)\omega_0^{(0)}}, & \text{if } T \ll T_{\text{max}}(\omega_0). \end{cases}$$

In the (ideal) BPP case the exponent $\beta$ is 2; deviations from this ideal behaviour have soon be recognized.\cite{35} Several models for NMR spin-lattice relaxation in disordered ion conductors predict, however, that $1 < \beta \leq 2$. $\beta$ values smaller than 2 are, for example, derived from the coupling concept,\cite{36} the jump relaxation model,\cite{37} and the dynamic structure model.\cite{38} Similarly, an assumption of a distribution of jump correlation times $\tau_0^{(0)}$ would be consistent with $1 < \beta \leq 2$. The parameter $\beta$ does not only describe the frequency dependence of $R_1^{\text{diff}}$ it also links the two activation energies $E'_s$ (low-$T$) and $E''_s$ (high-$T$) according to:

$$E'_s = (\beta - 1) E''_s.$$  

Eq. 7 clearly illustrates and quantifies the asymmetry of a given NMR rate peak. In the present case, the $^7\text{Li}$ NMR SLR rates, which were extracted from the magnetization transients shown in Figure 3, also reveal an asymmetric peak characterized by $\beta$ significantly smaller than 2. The temperature dependence of the rates $R_1$ and $R_{1\varrho}$ is shown in the Arrhenius diagram of Figure 4. Below 250 K the $R_1$ rates are governed by so-called non-diffusive relaxation effects, i.e., lattice vibrations or couplings of the spins to paramagnetic centers are responsible for longitudinal relaxation. The temperature dependence in this regime can often be described with a power law ansatz according to $R_1 \propto T^\beta$. Above 250 K the rates start to be directly induced by lithium diffusion. From the slope of the corresponding Arrhenius line we obtain an activation energy of ca. 0.24 eV. Approximating the non-diffusive rates with $R_1 \propto T^{3.9}$ and subtracting the...
extrapolated values from the measured ones purely diffusion-induced \( R \) NMR rates are obtained (see the data points marked with a dot). These corrected values yield 0.28 eV. Thus, due to any uncertainties of the extrapolation short-range Li ion diffusion in single crystalline Li\(_6\)La\(_3\)ZrTaO\(_{12}\), to which the \( R \) rates in the limit \( \omega_0\tau \gg 1 \) are sensitive, has to be characterized by activation energies ranging from 0.24 to 0.28 eV.

At higher \( T \) the rates pass through a maximum and reach the high-temperature flank for which \( \omega_0\tau \ll 1 \); in our experimental setup the flank is, however, only partly accessible since we restricted the measuring temperature to be below 550 K. Fortunately, the complete flank is seen in \(^7\)Li NMR spin-lock NMR, i.e., when transversal relaxation of the spins is watched at lowing frequencies in the kHz range (see Figure 4). \( R_\omega(1/T) \) reveals the whole diffusion-induced rate peak. Because of \( R_\omega > R_1 \) for \( T > 440 \) K any undesired non-diffusive contributions to \( R_\omega \) are completely absent. Independent of any relaxation model the flanks of the asymmetric \( R_\omega(1/T) \) rate peak are characterized by \( E_1' = 0.48 \) eV (\( \omega_0\tau \ll 1 \)) and \( E_1'' = 0.24 \) eV (\( \omega_0\tau \gg 1 \)). According to eq. 7 we end up with \( \beta \approx 1.5 \). Almost the same result is obtained when the two data sets of \( R_\omega \) and \( R_1 \) are analyzed with a so-called joint fit, see the dashed lines in Figure 4. For this fitting procedure a single activation energy \( (E_1 = E_1') \), a joint pre-factor \( (\tau_0^{-1}) \), see eq. 4) and a joint \( \beta \) was used. The fit, which is based on a Lorentzian-type spectral density function (see eq. 5) yields \( E_1 = 0.51(3) \) eV, \( \tau_0^{-1} = 1.5 \times 10^{15} \) s\(^{-1} \) and \( \beta = 1.47 \approx 1.5 \).

In order to interpret the dynamic parameters as seen by diffusion-induced NMR relaxometry we compare our present results for in \( \text{Li}_{6}\text{La}_{3}\text{ZrTaO}_{12} \) with those of other solid electrolytes, particularly garnet-type oxides, studied over the last couple of years in our group. Figure 5 shows an overview; in Figure 5a) the \( R_\omega(1/T) \) peak of single crystalline LLZTO \((\omega_0/2\pi = 20 \) kHz\) is shown together with that of tetragonal LLZO \((\omega_0/2\pi = 30 \) kHz\) in the same Arrhenius plot. Both rate peaks do not differ much in shape; \( \beta \) being a measure for the deviation from symmetric behaviour, differs by only 0.2 revealing a slighter stronger asymmetry for LLZTO. Interestingly, \( E_1 \) as obtained from BPP-type fits is almost the same. Hence, in the present case the higher Li ion bulk diffusivity seen in LLZTO can, most likely, be explained by an increase of the pre-factor \( \tau_0^{-1} \) when going from tetra LLZ to the single-crystal with cubic symmetry. Indeed while LLZTO is characterized by \( \tau_0^{-1} = 1.5 \times 10^{15} \) s\(^{-1} \) the corresponding value for tetra LLZO is by 1 to 2 orders of magnitude lower. The same feature is also valid for the two \( R(1/T) \) rate peaks of tetragonal LLZO and LLZTO, see Figure 5b). Note that the difference in absolute rates is most likely due to weaker homonuclear dipole-dipole interactions in \( \text{Li}_{6}\text{La}_{3}\text{ZrTaO}_{12} \) with a lower Li content as compared to tetragonal \( \text{Li}_{6}\text{La}_{3}\text{ZrO}_{12} \). According to the relation introduced by van Vleck this will influence the underlying \(^7\)Li-\(^7\)Li dipolar coupling constant to which \( R_\omega \) is directly proportional.

Thus, although the ions seem to have access to a very similar potential landscape in tetra LLZO and LLZTO, the increased number fraction of vacant Li sites in LLZTO leads to more frequent Li jump processes shifting its \( R_\omega(1/T) \) peak clearly towards lower \( T_{\max} \). Of course, even lower values for \( T_{\max} \), as indicated in Figure 5a) at the top axis, are found for sulfides; as examples, the peaks for argyrodite-type \( \text{Li}_{6}\text{PS}_{5}\text{Cl} \) and \( \text{Li}_{6}\text{PSe}_{5}\text{Br} \) are shown. The latter examples clearly show lower activation energies (0.35 eV, 0.2 eV) while the corresponding \( \beta \) values are similar. Values of 1.4 seem to be a lower limit, even for extremely fast ion conductors with liquid-like diffusion behaviour. The interpretation of \( \beta \) still remains a fundamental question. In some cases \( \beta = 1.5 \) is expected for Li ion diffusion when influenced by...
coupling of the spins with paramagnetic impurities; on the other hand, any asymmetry of a given rate peaks can be traced back to short-range (or localized) ion dynamics being different from long-range ion transport. Several models have been proposed attributing the asymmetry to correlation effects arising from both structural disorder and Coulomb interactions the moving spins are subjected to. In general, the parameter is a measure for the extent of correlated motion, i.e., if not attributed to specific spin interactions with the surroundings, it directly reflects the degree of heterogeneity of the underlying potential landscape the ions are exposed to.

In Figure 5b) the present results are also compared with those of another garnet oxide viz. Li$_{7}$La$_{2}$Zr$_{1.7}$Mo$_{0.25}$O$_{12}$ (LLZMO) that is stabilized in its cubic form through the introduction of Mo ions residing on the Zr sites. In contrast to LLZTO two distinct Li ion diffusion processes have been observed for LLZMO. The broad $R_0$ $(1/T)$ peak can be best parameterized with two sub-peaks. For single crystalline LLZTO the $R_0$ rate peak with its narrow shape clearly points to a single diffusion mechanism being valid over the entire temperature range covered. What is common for LLZMO and all of the LLZO, when stabilized in its cubic modification via doping mit trivalent cations such as Al$^{3+}$ and Ga$^{3+}$, see Figure 5c), are the shallowly sloping low-$T$ fanks of the $R_0$ peaks. In most cases activation energies equal or even lower than 150 meV are obtained. This feature definitely points to local hopping processes, which, at least in the case of Al- and Ga-stabilized LLZO, are controlled by the disordered Li sub-lattice hosting the immobile Al$^{3+}$ and Ga$^{3+}$ ions. Although the foreign ions open many pathways for the lithium ions to jump between the 24d and 96h sites, forming a 3D diffusion network, they also block some of paths because of their immobilities. In contrast to Mo and Ta replacing some of the Zr ions, the trivalent cations prefer to reside on the same sites as the Li ions thus directly influencing the Li sublattice.

Comparing the $R_0$ $(1/T)$ rate peaks (see Figure 5c)) structural disorder turns out to be the most probable origin that produces anomaly broad diffusion-induced $^7$Li NMR rate peaks. These peaks can on the one hand be understood as a superposition of multiple hopping processes that are visible when the spins have to relax in weak locking fields with frequencies of 35 kHz or lower. At much higher frequencies, i.e., those in the MHz range of the experiments in the laboratory frame of reference, only the local jump processes are seen that produce a single rate peak with a very shallow low-$T$ flank. A similar picture, but even more pronounced and resembling that of Al-stabilized LLZO, has recently been found for the fast ion conductor Li$_7$P$_3$S$_{11}$.[44] On the other hand, heterogeneous dynamics might be the result of an inhomogeneous distribution of Al cations in the sample. Whereas local dynamics seem, in this scenario, to be very similar, long-range ion dynamics are able to distinguish Al-rich from Al-poor regions.

Most importantly, with respect to Al-LLZO (see Figure 5c)) the single crystal LLZTO shows remarkably fast Li ion diffusion. Since we deal with both a relatively high activation energy and a large pre-factor the jump rate reaches values in the order of $10^9$ s$^{-1}$ just slightly above 400 K, i.e., $T_{\text{max}}$ of its $R_0$ peak is even lower than that of Al-LLZO (550 K, see Figure 6a) or Ga-LLZO. Of course, at very low temperatures the diffusivity in the doped samples with Al$^{3+}$ and Ga$^{3+}$ is higher due to the low activation energy. In the next section we will briefly compare the jump rates and activation energies deduced from NMR with those from conductivity measurements.
3.3. Li Jump Rates: Comparison with AC Conductivity Measurements

NMR relaxation entails an almost model independent access to diffusion parameters if \( \tau_\nu \) is read out via the maximum condition, \( \omega_0 \tau_\nu = 0.62 \), this condition is valid for \( R_\parallel \) rates following BPP behavior. With \( \tau = \tau_\nu \) (see above) a microscopic self-diffusion coefficient, for 3D diffusion, can be calculated via the Einstein-Smoluchowski relation

\[
D_{\text{NMR}} = \frac{a^2}{6\tau} \tag{8}
\]

where \( a \) denotes the average jump distance which can be estimated from the lattice parameters of the crystals. In our case we chose a mean distance of 2 Å to take into account jumps between the 24d and 96h sites. \( D \) values obtained from NMR can be compared with those estimated from AC conductivity measurements. The conductivity \( \sigma_{\nu \rightarrow 0} \), if recorded at low frequencies, is directly related to the long-range solid-state diffusion coefficient, \( D_\nu \), via the well-known Nernst-Einstein relation

\[
D_\nu = \frac{\sigma_{\nu \rightarrow 0} k_B T}{N q^2} \tag{9}
\]

where \( q \) denotes the charge and \( N \) the number density of charge carriers. \( \sigma_0 \) usually follows Arrhenius behavior according to

\[
\sigma_{\nu \rightarrow 0} = A \exp\left(-\frac{E_{\nu,\text{AC}}}{k_B T}\right). \tag{10}
\]

The relationship between \( D \) and \( D_\nu \) is seen when the tracer diffusion coefficient, \( D_{\text{tracer}} \), is introduced. The self-diffusion coefficient \( D \) is linked to \( D_{\text{cond}} \) via the relations \( D_{\text{tracer}} = H_f D_{\text{cond}} \) and \( D_{\text{tracer}} = f D \). While \( H_f \) represents the Haven ratio, \( f \) denotes the so-called correlation factor that depends on the exact diffusion pathway. A good approximation is given by \( f = 1 \) and \( H_f \approx 1 \); the latter is acceptable for an almost pure ionic conductor. For \( D_{\text{tracer}} \) one obtains

\[
D_{\text{tracer}} = H_f \frac{\sigma_{\nu \rightarrow 0} k_B T}{N q^2} = f \frac{a^2}{6\tau} \tag{11}
\]

which gives

\[
\tau^{-1} = \left(H_f / f\right) \frac{6k_B T}{N q^2 a^2} \cdot \sigma_{\nu \rightarrow 0} \approx \frac{6k_B T}{N q^2 a^2} \cdot \sigma_{\nu \rightarrow 0} \tag{12}
\]

directly linking the motional correlation rate \( \tau^{-1} \) available by NMR with \( \sigma \). In Figure 6a) the jump rates \( \tau^{-1} \) deduced from the two NMR SLR maxima of Figure 4 are shown; the left axis refers to the corresponding diffusion coefficients according to eq. 8. Figure 6a) also includes \( D_\nu \); the solid line represents a linear fit taking into account both \( D_\nu \) and \( D_{\text{NMR}} \). Conductivities \( \sigma_{\nu \rightarrow 0} \), from which \( D_{\text{cond}} \) values were calculated, were read off from the frequency independent plateaus of the \( \sigma(v) \) isotherms. In Figure 6b) \( \sigma_{\nu \rightarrow 0} \) is plotted in an Arrhenius diagram; the insets show \( \sigma(v) \) and the corresponding Nyquist plot at 298 K. The latter is obtained when the imaginary part \( -Z' \) of the complex AC impedance \( Z \) is plotted against its real part \( Z' \).

Around ambient temperature \( \sigma_{\nu \rightarrow 0} T(1/T) \) is best described with an Arrhenius law governed by \( E_{\nu,\text{AC}} = 0.48 \) eV. This activation energy, which has to be identified with the that describing long-range ion dynamics, is close to that seen via SLR NMR relaxometry at high \( T \). The good agreement clarifies that the dynamic process seen by NMR is also of long-range nature. Almost the same activation energy has been found for tetragonal LLZO through conductivity spectroscopy (0.47 eV). At room temperature we obtain \( \sigma_{\nu \rightarrow 0} = 3 \times 10^{-4} \) S cm\(^{-1}\) for LLZO. This translates into \( D \approx 10^{-14} \) m\(^2\) s\(^{-1}\). For comparison, while for tetragonal LLZO the diffusion coefficient is by two orders of magnitude lower, that of Al-doped cubic LLZO is somewhat larger nearly reaching \( 10^{-13} \) m\(^2\) s\(^{-1}\) (see Figure 6).

The higher diffusivity in LLZTO as compared to that of tetragonal LLZO is, since the activation energies for long-range ion transport are almost identical, mainly given by the larger prefactor of the underlying Arrhenius relation, as suggested above. Besides other factors, the pre-factor is determined by entropic contributions including those of configurational and/or vibrational nature. Hence, besides \( E \), its influence on ion dynamics should by no means underestimated and need to be considered if we want to understand Li ion self-diffusivity and ionic transport in oxide garnets comprehensively.

4. Summary

Single crystalline LLZTO with the nominal composition Li\(_6\)La\(_3\)ZrTaO\(_{12}\) was prepared via the Czochralski technique. Li ion dynamics in LLZTO was investigated by both time-domain NMR spin-lattice relaxation and AC conductivity measurements. We observed extremely fast ion exchange processes with jump rates in the order of approximately \( 10^7 \) s\(^{-1}\) at 298 K; at elevated \( T \), e.g., at 400 K the rate increased to \( 10^9 \) s\(^{-1}\). This translates into average diffusion coefficients of \( 10^{-14} \) m\(^2\) s\(^{-1}\) and \( 10^{-12} \) m\(^2\) s\(^{-1}\), respectively. The associated activation energy \( (E) \) from both spin-lock NMR and our conductivity study is ca. 0.5 eV. This similarity reveals that through NMR relaxation we probed a single long-range ion transport process in LLZTO. Short-range motions, seen on the low-\( T \) side of the NMR diffusion induced rate peaks, are to be described with 0.24 eV.

Although the ionic diffusivity is by two orders of magnitude higher in LLZTO as compared to tetragonal LLZO, the two compounds have to be described by almost the same \( E \). The high Arrhenius pre-factor of LLZTO, \( \tau_0^{-1} = 1.5 \times 10^{15} \) s\(^{-1}\), is responsible for rapid ion exchange seen by NMR and conductivity spectroscopy.

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Conflict of Interest

The authors have declared no conflict of interest.
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Solid Electrolytes, Li Ion Mobility, Garnets, NMR, Relaxometry

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[1] J. C. Bachman, S. Muy, A. Grimaud, H. H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, and Y. Shao-Horn, Chem. Rev. 116(1), 140–162 (2016).
[2] V. Thangadurai, S. Narayanan, and D. Pinzaru, Chem. Soc. Rev. 43, 4714 (2014).
[3] J. Sakamoto, Handbook of Solid State Batteries, (World Scientific, Singapore, 2015), chap. Super-ionic conducting oxide electrolytes.
[4] F. Mizuno, C. Yada, and H. Iba, Solid-state lithium-ion batteries for electric vehicles, in: Lithium-Ion Batteries, edited by G. Pistoia, (Elsevier, Amsterdam, 2014), pp. 273–291.
[5] P. Knauth, Solid State Ion. 180, 911 (2009).
[6] V. Epp and M. Wilkening, Handbook of Solid State Batteries, (World Scientific, Singapore, 2015), chap. Li ion dynamics in solids as seen via relaxation NMR.