

Non-Arrhenius Lithium Diffusion With Temperature-Independent Haven Ratio in Garnet-Type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ Single Crystals

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(Received 24 April 2026; revised 5 August 2026; accepted 4 September 2026; published 21 October 2026)

Lithium-ion dynamics of garnet-type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ single crystals were investigated using pulsed field gradient (PFG) NMR and impedance spectroscopy over a wide temperature range up to 700 K. The diffusion coefficient measured by PFG-NMR exhibits non-Arrhenius behavior at elevated temperatures (> 400 K). The conductivity diffusion coefficient is consistently higher than the PFG-NMR diffusion coefficient across the entire temperature range, with a Haven ratio of 0.3–0.4, indicating that the motion of mobile Li^+ ions is correlated. Remarkably, the Haven ratio exhibits little temperature dependence despite the non-Arrhenius behavior, representing the first experimental observation in garnet-type electrolytes and consistent with the molecular dynamics simulations. This indicates that ion-ion correlations remain essentially unchanged over a wide temperature range. Combined with the local Li^+ ion dynamics obtained from spin-lattice relaxation analysis, these results suggest that long-range diffusion is suppressed at low temperatures due to short-range ordering of Li^+ ions.

DOI: [10.1103/zld4-bjxp](https://doi.org/10.1103/zld4-bjxp)

I. INTRODUCTION

High-performance solid-state lithium-ion batteries are strongly desired to replace conventional liquid electrolytes. A key requirement is the development of solid electrolytes with high ionic conductivity and electrochemical stability [1,2]. With a focus on chemically stable oxides, materials having a garnet-type structure with a space group $Ia\bar{3}d$, such as Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), have attracted significant attention in the last decade [3,4]. Ta-doped LLZO, for instance, $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO), is one of the most promising candidates for an electrolyte due to its high Li-ion conductivity reaching $\sim 1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ [5,6].

Recently, Kataoka *et al.* successfully grew large single crystals of cubic garnet-type electrolytes [5–9]. Figure 1(a)

shows a photograph of the grown single crystal. A key advantage of single crystals is the absence of grain boundaries, enabling direct access to intrinsic bulk transport properties. The determined structure of the LLZTO single crystal is illustrated in Fig. 1(b) [5]. In cubic LLZO, Li^+ ions occupy tetrahedral (*Td*) and octahedral (*Oh*) sites, forming a disordered network. When two adjacent *Td* sites are occupied, it is difficult for other Li^+ ions to reside in the adjacent *Oh* sites because of the Coulomb repulsion [see Fig. 1(c)]. This can induce short-range ordering of the trapped Li^+ ions, particularly at low temperatures. At high temperatures, the Li ordering is disrupted because the thermal energy overwhelms the activation energy of hopping events [10,11]. The temperature dependence of the conductivity (σ) of Li-ion conductors frequently exhibits non-Arrhenius behavior at elevated temperatures, resulting in an upward or downward curvature in Arrhenius plots [12–16]. Many ionic solids, such as AgCl, exhibit upward curvature in their Arrhenius plots. This behavior has often been attributed to a transition from extrinsic to intrinsic diffusion regimes [17,18]. In contrast, downward curvature has also been observed in several ionic conductors, including cubic

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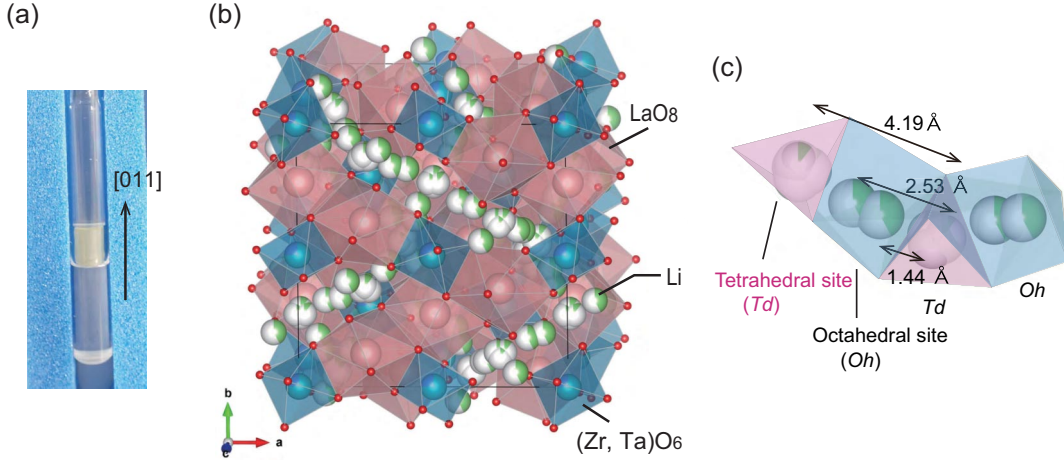


FIG. 1. (a) A photograph of an LLZTO single crystal in an NMR tube. (b) Crystal structure of LLZTO, adapted from Ref. [5], showing Li^+ ions occupying tetrahedral (Td) and octahedral (Oh) sites. (c) A schematic view of Li sites and lengths between several Li sites and selected site-site distances.

LLZTO polycrystals [19], although its origin remains unclear. Several mechanisms have been proposed, including fluctuations in activation energy and the coordination number of Li^+ ions [13] and collective correlations among ions [20]. Nevertheless, a unified understanding remains lacking, and experimental validation is scarce.

To gain insight into the averaged effects of many-body interactions among mobile ions, it is useful to measure and compare both the self-diffusion coefficient (D_{self}) and the conductivity diffusion coefficient (D_{σ}) [12,14]. D_{self} can be determined by pulsed-field gradient nuclear magnetic resonance (PFG-NMR), which measures the displacement of NMR-active ions undergoing thermal diffusion through magnetic field gradient encoding. D_{σ} , on the other hand, is derived from σ measurements, such as impedance spectroscopy, and reflects the displacement of the center of mass of ions in the entire sample [21,22]. The ratio between D_{self} and D_{σ} , known as the Haven ratio ($H_R \equiv D_{\text{self}}/D_{\sigma}$), is a robust measure of ion-ion correlations. If the non-Arrhenius behavior originates from changes in diffusion mechanisms or Li ordering, the H_R is expected to exhibit temperature dependence [18,23–25]. Therefore, it is imperative to accurately determine D_{self} and σ in order to comprehensively investigate the ion diffusion mechanism. However, given that these high-precision measurements require high-quality single crystals, such experimental examples are extremely rare.

In this work, we investigated the Li^+ ion diffusion in garnet-type LLZTO single crystals using PFG-NMR and impedance spectroscopy for a wide temperature range up to 700 K. The diffusion coefficient (D_{NMR}) demonstrates non-Arrhenius temperature dependence at elevated temperatures, as exhibited by σ . H_R was approximately 0.3 and exhibited little temperature dependence, indicating persistent ion-ion correlations over the entire temperature range. Combined with spin-lattice relaxation time (T_1) analysis,

these results suggest that the non-Arrhenius behavior originates from short-range ordering of Li^+ ions at low temperatures. The findings of this study offer crucial insights into the diffusion mechanism in garnet-type electrolytes.

II. METHODS

Single crystals of LLZTO were grown by the Czochralski method [7,8], in accordance with the preceding report by Redhammer *et al.* [26]. Single crystals were cut into a block or a column shape in order to be used for NMR measurements. A typical shape of a block is $2.8 \times 2.8 \times 4$ mm. In previous NMR studies [27,28], samples were prepared by the floating-zone method. Crystal structure refinement using single-crystal x-ray diffraction revealed that the crystal structure of the sample was identical to that previously reported. Because the crystals were grown by the Czochralski method using an iridium crucible, trace amounts of iridium contamination are possible.

D_{NMR} of ^7Li was measured using an ECA-400 NMR spectrometer (JEOL, Japan) in a low-temperature (LT) range from 263 to 393 K. The resonance frequency of ^7Li nucleus was 155.4 MHz. A pulsed gradient stimulated echo (PGSTE) method, as illustrated in Fig. S1(a) in Supplemental Material [29], was used to obtain D_{NMR} [21]. A single crystal of LLZTO was placed in an NMR tube, BMS-005J (SHIGEMI, Japan). The ^7Li diffusion along the [011] direction of the single crystal was observed. The chemical shift of ^7Li was calibrated by using 1 mol L^{-1} LiCl solution (0 ppm). The decay of the PFG echo signal can be described by the Stejskal-Tanner equation [22],

$$S = S_0 \exp[-\gamma^2 g^2 \delta^2 (\Delta - \delta/3) D_{\text{NMR}}], \quad (1)$$

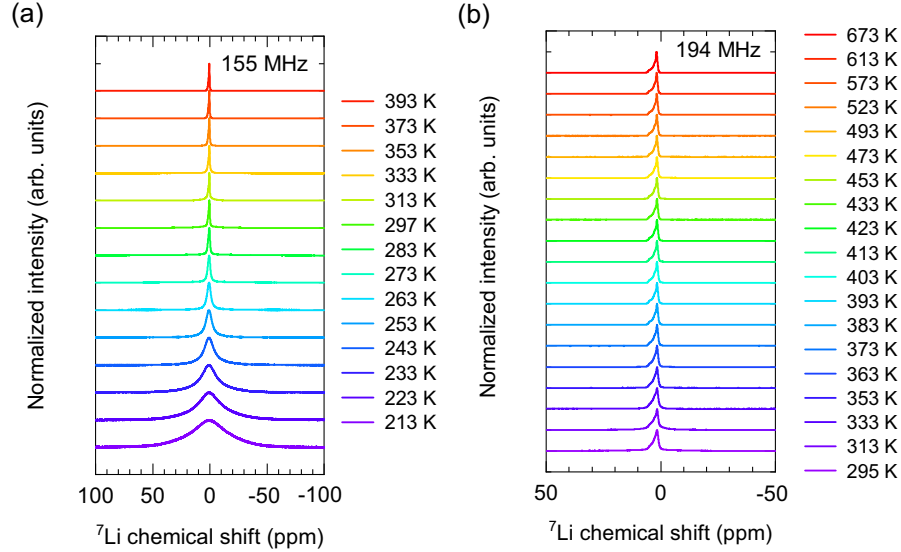


FIG. 2. Temperature dependence of the ^7Li NMR spectra of LLZTO, normalized by maximum height: (a) spectra obtained at low temperatures (155 MHz) and (b) spectra obtained at high temperatures (194 MHz), respectively.

where S is the signal intensity, S_0 is the initial signal intensity, γ is the gyromagnetic ratio, g is the gradient field strength ($0.1\text{--}13\text{ T m}^{-1}$), δ is the pulse field gradient time ($2\text{--}5\text{ ms}$), and Δ is the diffusion time (200 ms). The 90° pulse length is $16\text{ }\mu\text{s}$. T_1 was measured by the conventional saturation-recovery method. The spin-spin relaxation time (T_2) was measured by the spin-echo method.

High-temperature (HT) measurements of D_{NMR} up to 700 K were performed using an ECA-500 NMR spectrometer (JEOL, Japan) equipped with a high-temperature diffusion probe [30]. The resonance frequency of ^7Li nucleus was 194.4 MHz . The sample was placed in a quartz tube, and the temperature was controlled using nitrogen gas. During the high-temperature measurements, g ranged from 0.2 to 3 T m^{-1} , $\Delta = 100\text{ ms}$, and $\delta = 5\text{ ms}$, and the 90° pulse length was $30\text{ }\mu\text{s}$. The same sample was used for the ECA-400 and ECA-500 measurements. We note that the PFG strengths of both spectrometers were calibrated independently according to the manufacturers' recommended procedures using the known D_{self} of D_2O at 30°C . The D_{NMR} obtained in the LT and HT measurements are therefore considered quantitatively comparable within the experimental uncertainty, although minor systematic differences arising from the probe configuration, sample tube geometry, and shimming conditions cannot be completely excluded.

σ was measured by impedance spectroscopy using a high-frequency impedance system (4990EDMS-120K, TOYO, Japan) in the temperature range of $200\text{--}470\text{ K}$. Gold electrodes were sputtered onto two polished sides of the sample. High-temperature impedance measurements were performed using a system (HT-Z2-HF, TOYO, Japan) in the temperature range of $300\text{--}700\text{ K}$. The samples were measured in a sealed Ar cell or in an air atmosphere during

the low- and high-temperature measurements, respectively. In both measurements, an impedance analyzer (E4990A, KEYSIGHT, USA) was used over a frequency range of $20\text{ Hz--}100\text{ MHz}$. The same sample was used for two impedance measurements.

III. RESULTS

A. ^7Li NMR spectra and relaxations

Figures 2(a) and 2(b) show temperature variations of ^7Li NMR spectra of LLZTO obtained using ECA-400 and ECA-500 spectrometers, respectively. The spectrum undergoes a substantial change at low temperatures; however, the change becomes negligible above $\sim 350\text{ K}$. A representative spectrum is shown in Fig. 3(a). The NMR spectrum consists of two or three components. The sharp main peak is assigned to the central transition ($-1/2 \leftrightarrow 1/2$) of ^7Li (nuclear spin $I = 3/2$), whereas the broadest component is attributed to quadrupolar interactions; the latter is also observed in the spin-echo spectrum at 213 K [Fig. 3(b)] [27,31]. The negligible change in the spectrum above 350 K suggests that the carrier density remains constant.

The temperature dependence of full width at half maximum (FWHM) and the chemical shift of ^7Li NMR spectra are shown in Figs. 3(c) and 3(d), respectively. The main peak becomes sharper with increasing temperature due to the faster motion of the dipole-coupled Li^+ ions, resulting in motional narrowing. At high temperatures above 400 K , the FWHM demonstrates minute temperature variations. The chemical shift of all the peaks exhibits negligible change in temperature dependence over a wide temperature range. The precise origin of the side peak remains under discussion. Previous studies have

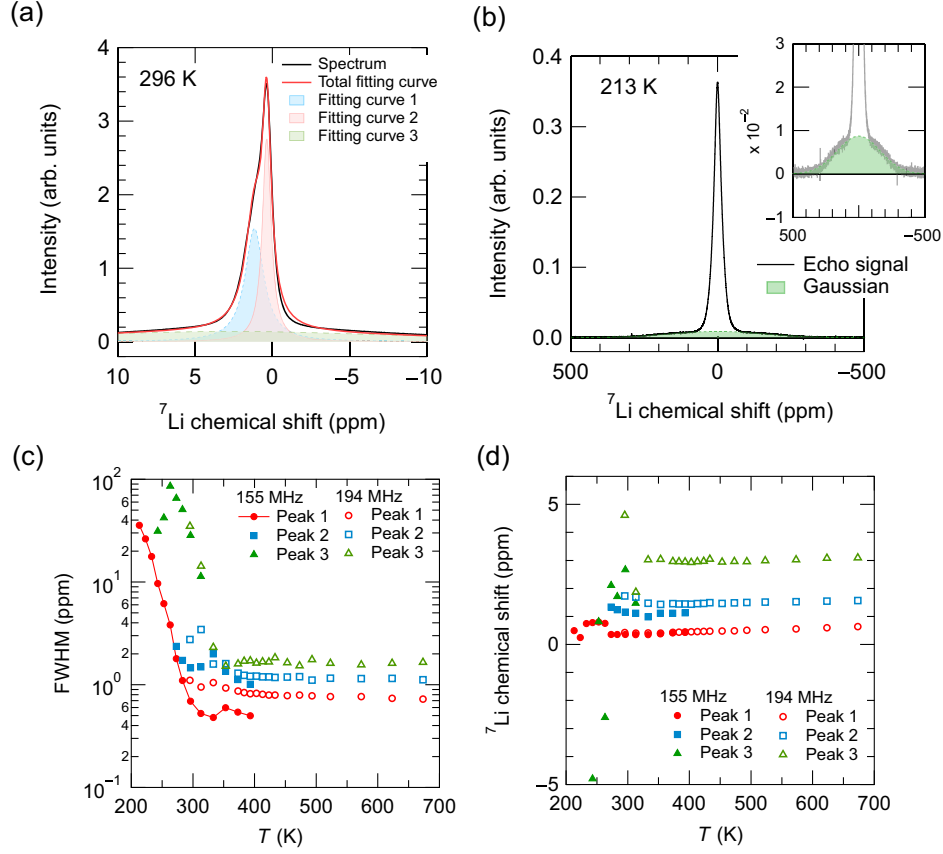


FIG. 3. (a) ${}^7\text{Li}$ NMR spectrum at 296 K, showing three components; the broadest component arises from quadrupole interactions. (b) Spin-echo spectrum at 213 K; the inset shows a magnified view. The green Gaussian curve is attributed to the quadrupole interaction. Temperature dependence of (c) FWHM and (d) the chemical shift of three components. The filled and open symbols represent the results obtained using ECA-400 (155 MHz) and ECA-500 (194 MHz), respectively. The solid curve in (c) is a guide for the eyes.

suggested that the three components of the ${}^6\text{Li}$ magic-angle spinning-NMR spectrum correspond to the Li^+ ions occupying the different sites [32,33]. However, such assignments are uncertain in cubic LLZTO due to rapid Li^+ exchange between *Oh* and *Td* sites. Another work on a tetragonal ${}^6\text{Li}$ -hydrogarnet and tetragonal ${}^6\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ refers to the small signal at ~ 0 ppm as Li_2CO_3 and/or LiOH peaks [34]. In the present single crystal, the two observed components (peaks 1 and 2) exhibit identical relaxation times and diffusion coefficients (Figs. S2(a) and S2(b) in Supplemental Material [29]). This indicates that both signals originate from the same phase rather than impurities. Although the origin of the peak separation remains unclear, it may reflect long-range structural disorder within the single crystal, consistent with the presence of unassigned diffuse scattering features observed in x-ray diffraction [6] and the intrinsic anharmonicity of structure observed in the thermal conductivity [35]. Minor discrepancies between the datasets obtained using the two NMR spectrometers are attributed to differences in the probe configuration and sample tubes as explained in the Methods part.

The ${}^7\text{Li}$ NMR T_1 and T_2 were measured, and the experimental results are shown in Figs. 4(a) and 4(b), respectively. The temperature dependence of T_1 is analyzed using the Bloembergen-Purcell-Pound (BPP) model [36],

$$\frac{1}{T_1} = C[J(\omega_0) + 4J(2\omega_0)], \quad (2)$$

where C is a constant factor, ω_0 is the Larmor frequency. $J(\omega_0)$ is the Lorentzian-shaped spectral density function given by $J(\omega_0\tau_c) = \tau_c/(1 + \omega_0^2\tau_c^2)$, where τ_c is the correlation time. The temperature dependence of τ_c is given by an Arrhenius relationship, $\tau_c = \tau_0 \exp(E_a/k_B T)$, where τ_0 is the preexponential factor, k_B is the Boltzmann constant, and E_a is the activation energy. At intermediate temperatures ($\omega_0\tau_c \approx 1$), the temperature dependence of T_1 shows a minimum [37]. For LLZTO, a minimum of T_1 is observed in the high-temperature measurements, as shown in Fig. 4(a). The temperature dependence of T_1 is fitted by a two-component BPP model, in which the total relaxation time is expressed as the sum of low- and

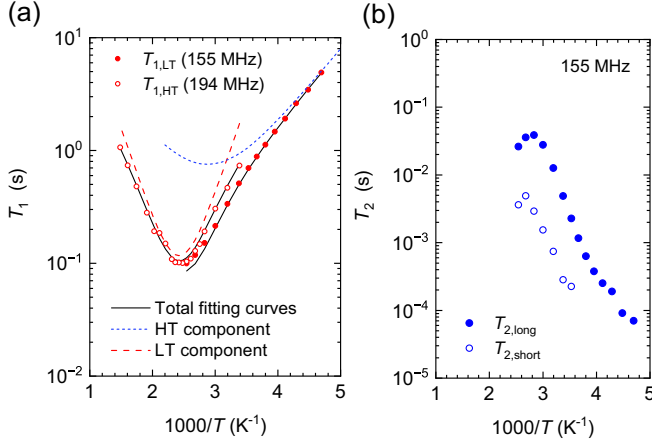


FIG. 4. (a) Temperature dependence of the spin-lattice relaxation time T_1 . The high-temperature measurements (194 MHz) are shown as open red circles, while the low-temperature measurements (155 MHz) are shown as filled red circles. The fitting results using the two-component BPP model [36] are also shown as black solid lines. The dotted blue and dashed orange lines correspond to the low-temperature and high-temperature components, respectively. (b) Temperature dependence of spin-spin relaxation time T_2 . The exponential decay of spin echo signals at each temperature is fitted by two components, resulting in two relaxation times ($T_{2,\text{long}}$ and $T_{2,\text{short}}$).

high-temperature contributions:

$$T_1^{-1} = T_{1,\text{HT}}^{-1} + T_{1,\text{LT}}^{-1}. \quad (3)$$

A single BPP-type contribution could not reproduce the experimental temperature dependence. It should be emphasized that the two terms in this model do not represent two separately resolved T_1 components in the saturation-recovery curves. At each temperature, the recovery curve was well described by a single-exponential function, and only a single effective T_1 value was obtained (Fig. S3 in Supplemental Material [29]). The two BPP terms should therefore be regarded as phenomenological contributions to the total relaxation rate.

The fitting results using this two-component BPP model are shown by black solid curves in Fig. 4(a) and reproduce the T_1 data reasonably well. Fitting parameters are $C = 9.1 \times 10^8 \text{ s}^{-2}$, $\tau_0 = 8.5 \times 10^{-12} \text{ s}$, and $E_a = 0.13 \text{ eV}$ for the low-temperature component and $C = 7.3 \times 10^9 \text{ s}^{-2}$, $\tau_0 = 7.4 \times 10^{-14} \text{ s}$, and $E_a = 0.31 \text{ eV}$ for the high-temperature component, respectively. The low-temperature contribution, characterized by an activation energy of 0.13 eV, is tentatively associated with localized Li-ion motion such as short-range site-to-site jumps or forward-backward fluctuations. Because no corresponding feature is observed in the long-range diffusion data, this process is unlikely to contribute significantly to macroscopic Li-ion transport. However, its microscopic origin cannot be determined unambiguously from the present T_1 data alone.

The local diffusion coefficient is estimated as $D_{\text{local}} = l_{\text{hop}}^2 / 2d\tau_c$, where l_{hop} is the effective hopping distance, d is the dimension ($d = 3$ for LLZTO), and τ_c is evaluated from Eq. (2). Here, we adopted the average interatomic distance between Li^+ ions as, $l_{\text{hop}} = 1.99 \text{ \AA}$. The high-temperature component of the local diffusion coefficient ($D_{\text{local,HT}}$) is shown by a dashed curve in Fig. 5(c). Here, we show only $D_{\text{local,HT}}$ because the low-temperature component is caused by local hopping and may not be essential for the long-range diffusion. The comparison of $D_{\text{local,HT}}$ and D_{NMR} will be discussed later.

Over a wide temperature range, T_2 exhibits two components ($T_{2,\text{long}}$ and $T_{2,\text{short}}$) as shown in Fig. 4(b), consistent with a previous study [38]. Both components decrease with decreasing temperature below 353 K, following typical BPP behavior.

B. ^7Li PFG-NMR

The echo attenuation plots as a function of gradient strength (g) at various temperatures are shown in Figs. 5(a) and 5(b). D_{NMR} is obtained by fitting the data to Eq. (1). Figure 5(c) shows the temperature dependence of D_{NMR} in LLZTO. At low temperatures, D_{NMR} obeys the Arrhenius relationship, $D_{\text{NMR}} = D_0 \exp(-E_a/k_B T)$, where D_0 is the preexponential factor. The obtained activation energy (E_a) is 0.46 eV, which is in good agreement with previous reports [27,38]. Above 400 K, however, D_{NMR} deviates from Arrhenius behavior, with E_a gradually decreasing as the temperature increases. The fitted E_a decreases to below 0.31 eV at $\sim 500 \text{ K}$. A similar curved behavior of D_{NMR} has also been reported in $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ [14].

As shown in Fig. 5(c), $D_{\text{local,HT}}$ calculated from T_1 in the high temperatures above 400 K agrees with the PFG-NMR results (D_{NMR}). These observations indicate that the long-range diffusion coefficients obtained from PFG-NMR measurements agree with the local Li^+ ion migrations at high temperatures for LLZTO. On the other hand, as the temperature decreases, long-range diffusion is disturbed, resulting in lower D_{NMR} and the higher E_a than would be expected based solely on local motions. The underlying mechanism responsible for this suppression will be discussed in the last discussion section.

To verify the reliability of the PFG-NMR measurements, g -array and δ -array methods were compared (Fig. S1(a) in Supplemental Material [29]). Figures S1(b) and S1(c) in Supplemental Material [29] show the Δ dependence of D_{NMR} at 303 and 393 K, respectively. At both temperatures, D_{NMR} exhibits a variation in the region of $\Delta \leq 50 \text{ ms}$, but above $\Delta \geq 75 \text{ ms}$, D_{NMR} is independent of Δ . Therefore, in this study, D_{NMR} is evaluated at $\Delta = 100$ or 200 ms . The anomalous behavior previously reported [38] is not observed in the present study. The discrepancies are likely due to differences in the

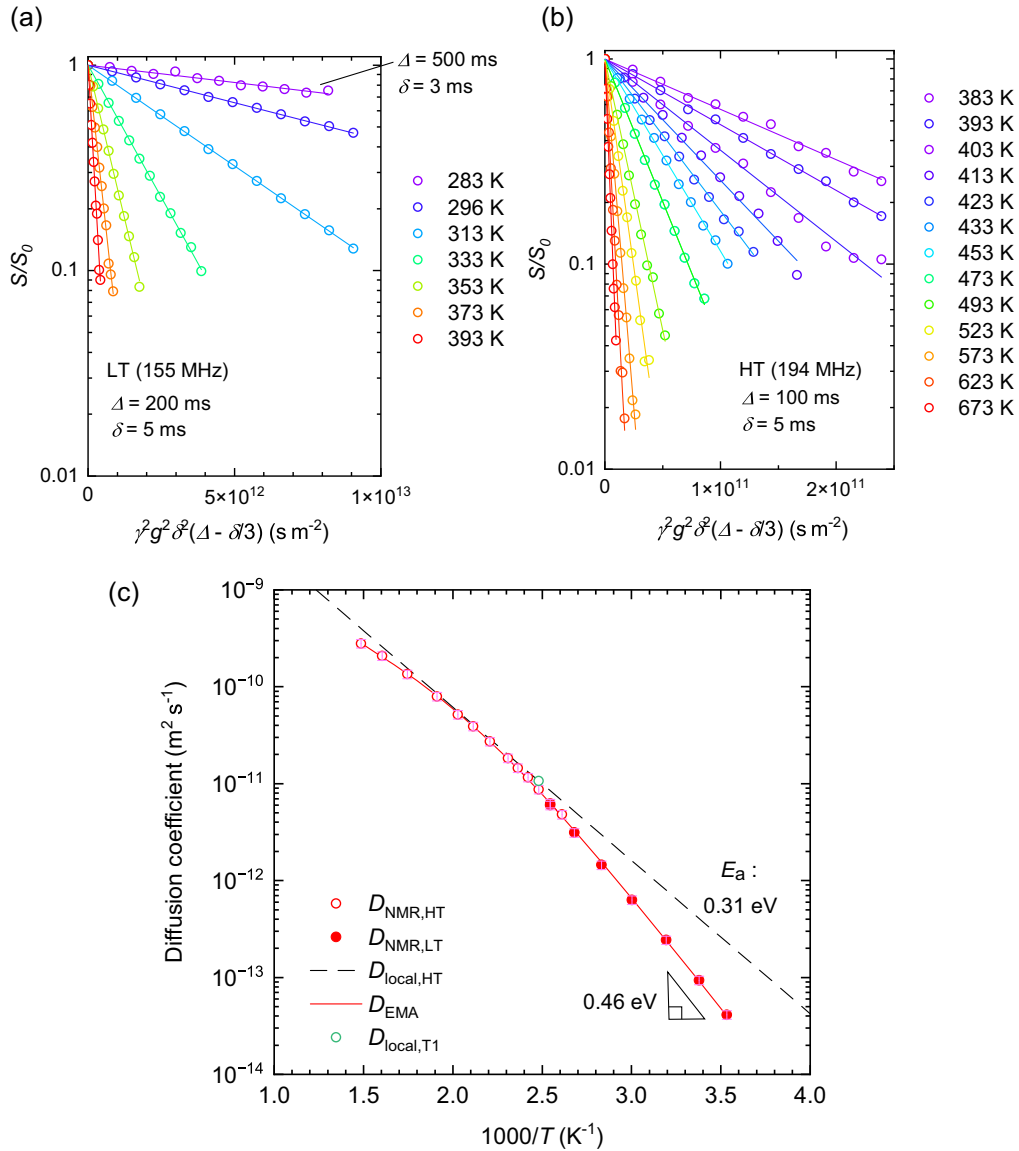


FIG. 5. Echo attenuation plots of LLZTO single crystal measured by PFG-NMR using (a) ECA-400 (155 MHz) and (b) ECA-500 (194 MHz). The normalized integrals are fitted by the Stejskal-Tanner equation denoted by the solid lines. (c) Temperature dependence of the diffusion coefficient D_{NMR} . The filled circles represent the low-temperature measurements (155 MHz) and the open circles represent the high-temperature measurements (194 MHz), respectively. The local diffusion coefficient ($D_{\text{local,HT}}$) estimated from the fitting of T_1 is shown by the dashed line. The $D_{\text{local,HT}}$ well agrees with the experimental result D_{NMR} at high temperatures. The fitting curve calculated by using the effective medium approximation (EMA) method [39] is shown by the red solid curve. The local diffusion coefficient estimated from the minimum T_1 ($D_{\text{local,T1}}$) is also shown by a green symbol [29,40].

experimental setup and the different influence of eddy currents [12,27].

C. Impedance spectroscopy

The temperature and frequency dependence of the real part of the conductivity (σ_{real}) of LLZTO is shown in Fig. 6(a). The bulk conductivity is extracted from the frequency-independent plateau in σ_{real} . The Nyquist plots of LLZTO at 280–460 K are shown in Fig. S4(a) in

Supplemental Material [29]. In general, the ionic conductivity of a solid electrolyte is expressed by the Arrhenius equation, $\sigma T = \sigma_0 \exp(-E_a/k_B T)$, where σ_0 is the pre-exponential factor. At low temperatures ($T < 400$ K), σ obeys the Arrhenius equation with an activation energy of 0.46 eV, consistent with the previous reports [27,38] and the PFG-NMR results in Fig. 5(c). On the other hand, above 400 K, σ deviates from the Arrhenius behavior, exhibiting a similar curved temperature dependence to D_{NMR} . It is noteworthy that trace Ir contamination

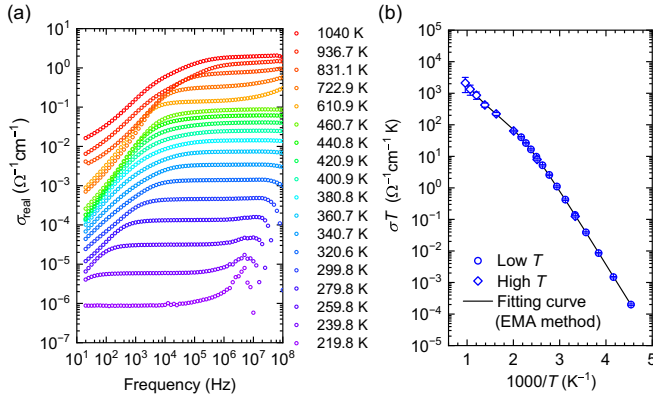


FIG. 6. (a) Frequency dependence of the real part of ionic conductivity σ_{real} of LLZTO single crystal at various temperatures. (b) Arrhenius plot of σT as a function of $1000/T$. The circle and diamond symbols represent the low- and high-temperature measurements, respectively. The solid curve represents the fitting result using the EMA method [29].

(0.18 wt% by ICP-AES (Inductively coupled plasma atomic emission spectroscopy)) was detected, but it is unlikely to be responsible for the observed non-Arrhenius

diffusion behavior. Such non-Arrhenius ionic conductivity has been reported in cubic LLZO, LLZTO, and other solid electrolytes [12–14,19,41]. MD simulation has also reported similarly curved ionic conductivity in LLZTO [19] (see Fig. S5 in Supplemental Material [29]).

The conductivity diffusion coefficient (D_σ) is obtained using the Nernst-Einstein equation,

$$D_\sigma = \frac{k_B T}{n(z e)^2} \sigma, \quad (4)$$

where n is the number density of ions, z is the valence of the ions, and e is the elementary charge. For LLZTO, assuming that all the Li^+ ions contribute to conduction, $n = 2.4 \times 10^{22} \text{ cm}^{-3}$, the temperature dependence of D_σ is calculated, as shown in Fig. 7(a). Over the entire temperature range, $D_\sigma > D_{\text{NMR}}$ holds, and both D_σ and D_{NMR} exhibit similar non-Arrhenius temperature dependence. These findings indicate that the curved temperature variations of D_σ and D_{NMR} should originate from a common underlying factor, namely a change in mobility rather than carrier density.

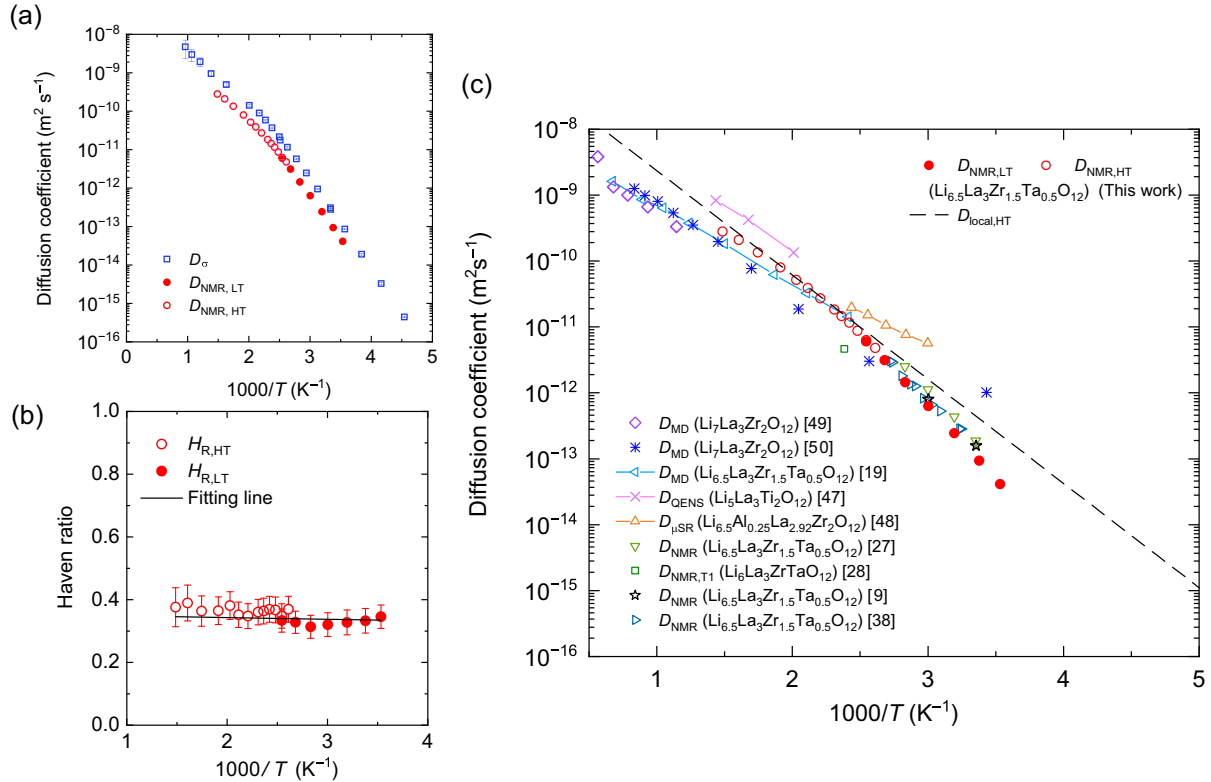


FIG. 7. (a) Comparison of the diffusion coefficients obtained from PFG-NMR (D_{NMR}) and ionic conductivity (D_σ) for LLZTO. (b) Temperature dependence of the Haven ratio $H_R (= D_{\text{NMR}}/D_\sigma)$. The black line represents a linear fit, whose slope is not significantly different from zero within the experimental uncertainty. (c) Comparison of diffusion coefficients of cubic garnet-type solid-state electrolytes reported in previous studies [9,27,28,38,47,48]. $D_{\text{local,HT}}$ estimated from T_1 by using the BPP model, and results from MD simulations [19,49,50] are also shown.

IV. DISCUSSION

A. Haven ratio

Self-diffusion coefficient (D_{self}) is described as

$$D_{\text{self}} = \lim_{t \rightarrow \infty} \left[\frac{1}{2dtN} \sum_{i=1}^N \langle |\Delta \mathbf{R}_i(t)|^2 \rangle \right] \\ = \frac{1}{2d} \lim_{t \rightarrow \infty} \left(\frac{d \text{MSD}(t')}{dt'} \bigg|_{t'=t} \right), \quad (5)$$

where i is the index number of Li^+ ions, $\frac{1}{N} \sum_{i=1}^N \langle |\Delta \mathbf{R}_i(t)|^2 \rangle$ is the mean square displacement, d is the dimension, N is the number of ions. Here, since D_{NMR} represents the diffusion coefficient of labeled ions, it is identical to D_{self} .

In contrast, the conductivity diffusion coefficient is described by

$$D_{\sigma} = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \left\langle \frac{1}{N} \left(\sum_{i=1}^N (\Delta \mathbf{R}_i(t)) \right)^2 \right\rangle \right], \quad (6)$$

where $\sum_{i=1}^N (\Delta \mathbf{R}_i(t))$ is the sum of displacement of all ions. From two diffusion coefficients, the Haven ratio is calculated as

$$H_R \equiv \frac{D_{\text{NMR}}}{D_{\sigma}} = \left[1 + \frac{1}{N} \lim_{t \rightarrow \infty} \frac{\sum_{i \neq j} \langle \Delta \mathbf{R}_i(t) \cdot \Delta \mathbf{R}_j(t) \rangle}{\langle \Delta R^2(t) \rangle} \right]^{-1}, \quad (7)$$

where $\sum_{i \neq j} \langle \Delta \mathbf{R}_i(t) \cdot \Delta \mathbf{R}_j(t) \rangle$ is the ensemble-averaged cross-correlation term of different ions [42–44]. H_R quantifies the degree of correlation among mobile ions [20,25,42,45,46]. Independent motion of mobile Li^+ ions results in H_R of unity, whereas correlated motion of Li^+ ions leads to H_R values smaller than unity.

Figure 7(b) shows the temperature dependence of H_R of the LLZTO single crystal. The H_R values range from 0.3 to 0.4, which is significantly smaller than unity, demonstrating strong correlations among mobile Li^+ ions. These values are consistent with previous simulations reporting $H_R \approx 0.3$ –0.4 for LLZTO [20,44]. This reflects the collective motion of ions, which enhances conductivity more than uncorrelated hopping does.

Remarkably, H_R demonstrates negligible temperature dependence even when the non-Arrhenius behavior is observed in D_{NMR} and D_{σ} . The temperature-independent H_R implies that the correlation between Li^+ ions remains essentially unchanged with temperature and that the underlying conduction mechanism is preserved. This behavior may appear inconsistent with the expected enhancement of short-range ordering of Li^+ ions at low temperatures, because a previous study has observed a slight decrease in H_R during order-disorder transition [23]. However, unlike systems undergoing structural phase transitions, LLZTO

retains its cubic structure, suggesting a crossover rather than a transition even when the area of the Li short-range ordering spreads.

According to the MD simulations of Dai *et al.*, while H_R of LLZTO increases with rising temperature, the change of H_R is minimal [19], which is consistent with our result. The Monte Carlo calculations have indicated that the concentration of Li^+ ions and the bottleneck structure of the Li^+ ion pathway primarily determine H_R [20]. These theoretical indications offer a rational explanation for the constant H_R of LLZTO.

B. Comparison with other works

Figure 7(c) presents a comparison of the diffusion coefficients of LLZTO with those of other garnet-type solid electrolytes [9,27,28,38,47,48]. At low temperatures, previous PFG-NMR data [9,27,38] agree well with the present results. At high temperatures, the experimental data approach the values obtained from MD simulations [19,49,50]. The diffusion coefficient obtained from the QENS of $\text{Li}_3\text{La}_3\text{Ti}_2\text{O}_{12}$ [47] shows comparable activation energy to those of LLZTO. The μSR results for $\text{Li}_{6.5}\text{Al}_{0.25}\text{La}_{2.92}\text{Zr}_2\text{O}_{12}$ [48] are higher than D_{NMR} of LLZTO. The discrepancy can be attributed to the variation in the length scale of each experiment. The PFG-NMR measurement observes diffusion on a length scale of 10^2 – 10^5 nm. The NMR T_1 measurements observe a length scale of about 0.1–1 nm, similar to μSR (1–10 nm) and QENS (0.1–10 nm). Therefore, these methods observe more local diffusion than PFG-NMR. As previously discussed, the long-range diffusion (D_{NMR}) at low temperatures differs from the local diffusion observed by T_1 and μSR . This phenomenon suggests a mechanism common to garnet-type electrolytes.

What factors impede the long-range diffusion of Li^+ ions specifically at low temperatures? The formation of a short-range ordered phase of Li^+ ions at low temperatures is presumed to be the most significant factor. As previously mentioned in the Introduction, it is expected that the area of Li ordering will expand as the temperature decreases, leading to suppressed Li mobility. If we further assume that the ordered and disordered phases form microdomains on the order of a few micrometers, D_{NMR} may be described using the effective medium approximation (EMA) model [39]. To simplify the matter, we will consider a system in which two regions coexist: one with a low diffusion coefficient where Li^+ ions are trapped and another with a high diffusion coefficient. At low temperatures, regions with small diffusion coefficients are assumed to be dominant. As the temperature increases, regions with a large diffusion coefficient will increase and become dominant. The details of the calculations are presented in Supplemental Material [29]. As shown in Figs. 5(c) and S6(a) in Supplemental Material [29], the fitting result

using the EMA model (D_{EMA}) reproduces the experimental results.

Despite extensive research, no direct evidence of Li short-range ordering at low temperatures has yet been found in LLZTO, and this is still a major obstacle in future research. Further structural investigations using neutron or x-ray diffuse scattering and pair-distribution-function analysis would be valuable for obtaining direct evidence for the proposed short-range ordering of Li ions and the formation of ordered and disordered microdomains.

Furthermore, the bond strength-coordination number fluctuation (BSCNF) model [13] can also provide a qualitative explanation for the temperature dependence of σ (see Fig. S6(b) in Supplemental Material [29]). Thus, both the EMA and BSCNF models provide plausible phenomenological descriptions of the experimental results, although they are based on different physical pictures. The present data do not uniquely support either model, and therefore, the interpretation in terms of ordered and disordered microdomains proposed within the EMA framework should be regarded as one possible explanation rather than a definitive description. Further structural and theoretical studies are required to distinguish between these models and to clarify how their underlying parameters are related to atomistic simulations.

V. CONCLUSIONS

The self-diffusion coefficient (D_{NMR}) of cubic garnet-type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ single crystals has been investigated up to 700 K. D_{NMR} shows non-Arrhenius temperature dependence in the same way as ionic conductivity (σ). Notably, the Haven ratio exhibits no statistically significant temperature dependence, indicating that the correlation between the conducting Li^+ ions remains essentially unchanged in the wide temperature range. This finding aligns with the predictions from the molecular dynamics simulations. The activation energy of both D_{NMR} and σ decreases with elevating temperature, reaching ~ 0.3 eV. The local diffusion coefficient ($D_{\text{local,HT}}$) estimated from the spin-lattice relaxation time agrees with D_{NMR} only at high temperatures. The substantial suppression of D_{NMR} at low temperatures is consistent with the development of Li ordering that would form a short-range order. The effective medium approximation provides one plausible phenomenological description of D_{NMR} , suggesting that heterogeneous Li-ion dynamics may be a general feature of garnet-type electrolytes. To our knowledge, this is the first experimental study elucidating the temperature dependence of H_{R} over a broad temperature range within the garnet-type electrolytes. Our findings will provide a more profound understanding of the Li^+ ion dynamics within solid electrolytes.

ACKNOWLEDGMENTS

This work was supported by the GteX program Japan (Grant No. JPMJGX23S6), the MEXT program “Materealize” (JPMXP0219207397), the JSPS KAKENHI “Ion Jamology” (24H02205), and the JST COI-NEXT program (JPMJPF2016). This work was partly supported by the NIMS All-Solid-State Battery Materials Open Platform (MOP).

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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