

Origin of Intrinsically Low Thermal Conductivity in a Garnet-Type Solid Electrolyte: Linking Lattice and Ionic Dynamics with Thermal Transport

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Understanding thermal transport in solid electrolytes is essential for improving the performance, reliability, and safety of all-solid-state batteries. Garnet-type lithium-ion conductors are promising candidates for solid electrolytes, yet their thermal-transport mechanisms remain poorly understood. Here, we connect the lattice and ion dynamics of single-crystal garnet-type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ to its intrinsically low thermal conductivity. Our study reveals that the single crystals grown by the floating-zone method exhibit remarkably low glasslike thermal conductivity. Using first-principles calculations and inelastic-neutron-scattering measurements, we identify both the acoustic and numerous optical phonon modes, which stem from the complex crystal structure of the material. Notably, a low-energy optical branch exhibits an avoided crossing with acoustic phonons near 7 meV. These optical modes can enhance the scattering of heat-carrying acoustic phonons and reduce thermal conductivity. Furthermore, the calculated Grüneisen parameters are large, especially for the vibrational modes around 6 meV, indicating strong anharmonicity, with a noticeable contribution from lithium-ion vibrations. A two-channel thermal-transport model is employed to describe the weak temperature dependence of the thermal conductivity, which can be attributed to the substantial contribution of diffuson transport facilitated by the abundance of optical phonons and intrinsic anharmonicity. These results offer valuable insights into the thermal transport in a broad class of ionic conductors of interest for energy conversion and storage applications.

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I. INTRODUCTION

As battery applications push charge-discharge rates and voltages to their limits, increased Joule heating becomes

inevitable, potentially disrupting operational conditions due to the accumulated heat not promptly dissipating within the battery [1–3]. Thermal management is crucial for controlling the operating temperature of the battery due to the strong effect of temperature change on ion transport and interfacial chemical stability. The heat dissipation rate and temperature profile depend on the thermal conductivity (κ) of several components in the battery [2,4]. Therefore, understanding heat-transport mechanisms and accurately characterizing thermal properties of battery materials are pivotal in enhancing the performance and lifespan of battery systems [5].

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Ion-conducting materials have attracted increasing interest due to their potential applications in enhancing the safety of rechargeable batteries by serving as solid electrolytes [6–9]. These materials exhibit well-defined crystalline structures and the capacity for extensive ionic diffusion over long distances, comparable to the movement of ions in liquid salts [10]. A comprehensive understanding of thermal transport in ionic conductors, which typically have low κ , remains elusive. On the one hand, the phonon-liquid–electron-crystal (PLEC) picture of ionic conductors implies a blockage for shear waves, which has been used to explain the breakdown of transverse acoustic (TA) phonons observed above the superionic transition in Cu_2Se [11,12]. On the other hand, in other superionic conductors such as CuCrSe_2 [13], AgCrSe_2 [14], and Ag_8SnSe_6 [15], the persistence of TA phonons beyond the superionic transition points to a more complex selective breakdown picture, where the anharmonicity of the ion-related modes plays an important role in suppressing κ . In addition, weak bonding and low sound velocity [16], the low cutoff frequency of acoustic phonons [17], and rattlinglike thermal damping [18] have also been proposed as the origin of low κ in various ionic conductors.

Garnet-type ionic conductors based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) are promising solid electrolytes for all-solid-state batteries due to their good stability against electrode materials and their relative high ionic conductivity (σ) among solid electrolytes [19,20]. Notably, Ta-doped LLZO with the composition of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) exhibits a high σ of $10^{-3} \text{ S cm}^{-1}$ at room temperature [21]. Despite extensive studies on ionic transport in garnet-type solid electrolytes, their thermal properties, which play a crucial role in determining the overall performance, safety, and reliability of battery devices, remain poorly understood [22–28]. Recently, the κ of LLZO polycrystals has been found to be low and to show glasslike behavior [8,29,30]. However, the presence of grain boundaries and defects in these samples can obscure the intrinsic thermal-transport properties of the material. To uncover the fundamental mechanisms governing heat conduction in garnet-type solid electrolytes, it is essential to investigate high-quality single crystals, where the effects of microstructural imperfections are minimized. Despite their significance, the thermal-transport properties of single-crystal garnet electrolytes remain unexplored and the underlying mechanisms responsible for their thermal behavior have yet to be thoroughly investigated. While previous neutron studies [26,31] have primarily focused on the crystal structure and ionic transport in garnet-type solid electrolytes, the phonon dispersion of LLZTO—which is essential for understanding its phonon dynamics—has not yet been reported.

In this work, we investigate the heat-transport mechanisms and the origin of the low κ in LLZTO by combining single-crystal growth, thermal and ionic

transport measurements, molecular-dynamics (MD) simulations, density-functional theory (DFT), and inelastic neutron scattering (INS). The measured κ of LLZTO crystals exhibits a weak temperature dependence above 100 K and an intrinsically low value of $(1.59 \pm 0.33) \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. The DFT calculations together with INS measurements reveal both longitudinal and transverse acoustic phonon branches, along with multiple optical branches. In particular, a low-energy optical branch shows an avoided crossing with acoustic phonons near 7 meV. Furthermore, the calculated Grüneisen parameters are large, especially for the vibrational modes below 10 meV, suggesting strong phonon anharmonicity in this material. Additionally, the ionic transport has been studied by quasielastic neutron scattering (QENS) and impedance measurements. A two-channel model is employed to explain the temperature dependence of thermal conductivity in LLZTO.

II. METHODS

A. Material synthesis

Single crystals of LLZTO were grown by the floating-zone method. We followed the procedure reported by Kataoka *et al.* [23], with some modifications. The starting materials were Li_2CO_3 (Thermo Fisher Scientific, 99%), La_2O_3 (Sigma-Aldrich, 99.99%), ZrO_2 (Sigma-Aldrich, 99%), and Ta_2O_5 (Thermo Fisher Scientific, 99%). These materials were mixed according to the nominal composition of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$, with a 40% excess of Li_2CO_3 to account for lithium volatilization during the growth. The mixed powders were fired for 60 h at 1123 K in air. The obtained powder was ground and then pressed into cylindrical rods with a diameter of 6 mm by isostatic pressing in hydraulic oil at 30 MPa for 12 min. The rods were subsequently sintered at 1223 K for 4 h in air and used as feed rods for crystal growth. Single-crystal growth was carried out using the floating-zone method in an optical-image furnace (Quantum Design, IRF01-001-05, two-mirror configuration), equipped with two 1000-W halogen lamps. The growth was performed under an air flow of 7 L min^{-1} at a rate of 10 mm h^{-1} . The high airflow is necessary to flush away evaporated lithium and make the crystal growth stable, as otherwise the evaporated lithium oxide can be deposited on the inner surface of the growth chamber and block the heat input from the infrared light. For the purpose of a comparative study, a polycrystal LLZTO sample was prepared by spark-plasma sintering under 50 MPa in vacuum at 1373 K for 15 min [30]. The density of the obtained pellet was $(4.78 \pm 0.02) \text{ g cm}^{-3}$, which is about 89% of the theoretical density.

B. X-ray diffraction (XRD)

To examine the purity and crystal structure of the samples, the XRD patterns were measured with an x-ray

diffractometer (Empyrean, Malvern Panalytical), using graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 45 kV and 40 mA. The Rietveld refinement was performed using the GSAS-II software. The orientation and crystal quality were examined with Laue back reflection.

C. Microstructure characterization

Structural and compositional information were obtained by scanning electron microscopy (SEM) (TESCAN Vega3). Energy-dispersive x-ray spectroscopy (EDS) was conducted on the sample surface to obtain the atomic ratio and element distribution. Scanning-transmission-electron-microscopy (STEM) characterization was performed in a probe-side aberration-corrected FEI Titan Themis STEM with a 200-kV 150-pA electron beam.

D. Raman-scattering measurement

The Raman spectrum of the LLZTO crystals was measured with a HORIBA LabRam (HORIBA, Hyoto, Japan), using a 532-nm solid-state green laser. The laser power was set to 30 mW to minimize sample damage. The Raman spectrum was acquired at room temperature.

E. Thermal and ionic property measurements

The low-temperature specific heat C_p was measured in the Physical Property Measurement System (PPMS) (Quantum Design, DynaCool-9). The high-temperature C_p was measured using differential scanning calorimetry (DSC) (Neztech, model 214 Polyma), using the C_p -ratio method. A standard sapphire pellet with comparable mass to the sample was used in the DSC measurement, with a heating rate of 10 K min^{-1} and a nitrogen gas flow of 40 L min^{-1} . κ was measured in the PPMS using the thermal-transport option in the temperature range of 2–300 K. Then, ac impedance measurements were conducted to determine the ionic conductivity of an LLZTO single crystal from 233 to 323 K.

F. Inelastic neutron scattering

Inelastic-neutron-scattering measurements were conducted on an LLZTO single crystal with the Wide Angular-Range Chopper Spectrometer (ARCS) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). The incident neutron energy was 30 meV, with the beam incident on a crystal mounted with the ($H0L$) crystallographic plane horizontal. The obtained data were plotted along the phonon wave vector $\mathbf{q} = [H00]$, $[HH0]$, and $[HHH]$ from different Brillouin zones, which are indexed by the reciprocal lattice vector $\mathbf{G}_{\text{HKL}}$. In addition, the phonon dispersion was also measured using

the triple-axis spectrometer (TAX) at the High Flux Isotope Reactor (HFIR) at ORNL. We used the constant-momentum-transfer ($\mathbf{Q}$) scan mode and limited the output neutron energy to a constant value $E_f = 14.7 \text{ meV}$. The INS measurements at TAX originated at the (008) point in reciprocal space. Different $\mathbf{Q}$ points along the $[00L]$, $[HH0]$, and $[HHH]$ directions were selected for the constant- $\mathbf{Q}$ scans.

G. Calculation of phonon dispersions and thermal conductivity

The phonon dispersion was calculated with the PHONOPY [32] and HIPHIVE [33] software, with the Vienna *ab initio* simulation package (VASP) as backend for electronic calculations [34–36]. In our simulation, a $2 \times 2 \times 2$ supercell with 1504 atoms was used. To compare the calculated phonon dispersion with the INS data, we simulated the neutron-weighted structure factors by employing the EUPHONIC software [37].

The MD component of this work comprised the development of a neural-network (NN) potential to describe the garnet [38] as well as the MD runs used to extract the transport properties and the vibrational density of states (DOS) of the material. The training data were also generated using VASP. The phonon DOS result was calculated as the power spectrum of the velocity autocorrelation function computed over a 1-million-step MD trajectory using the PWTOOLS software [39]. For the thermal-conductivity calculation, we used the Green-Kubo formula for the time autocorrelation function of the thermal flux. Further calculation details are provided in the Supplemental Material [40] (see also Refs. [8,23,29,34–36,38,39,41–54] therein).

III. RESULTS AND DISCUSSION

A. Crystal structure and thermal conductivity

In Fig. 1(a), we illustrate the crystal structure of LLZTO at room temperature. LLZTO exhibits a cubic structure with $Ia\bar{3}d$ symmetry, with a lattice parameter of 12.94 Å based on the Rietveld refinement (see Fig. S1 in the Supplemental Material [40]). The $(\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12})^{6.5-}$ framework contains two kinds of interstitial sites: Li1 tetrahedral sites ($24d$), with about 62% occupancy, and Li2 octahedral sites ($96h$), with about 38% occupancy [46]. The higher-occupancy Li1 sites work as junctions, while the Li2 sites serve as pathways of the three-dimensional Li-ion network in LLZTO. Previous studies [23,55] have revealed that during the transition from the tetragonal phase to the cubic phase, a pair of neighboring Li2 sites are split from one octahedra site, which explains the short distance between Li2 sites. In Fig. 1(b), we show photographs of single crystals grown using the floating-zone method. The as-grown crystals have a cylindrical shape with approximate dimensions of 5 mm in diameter and

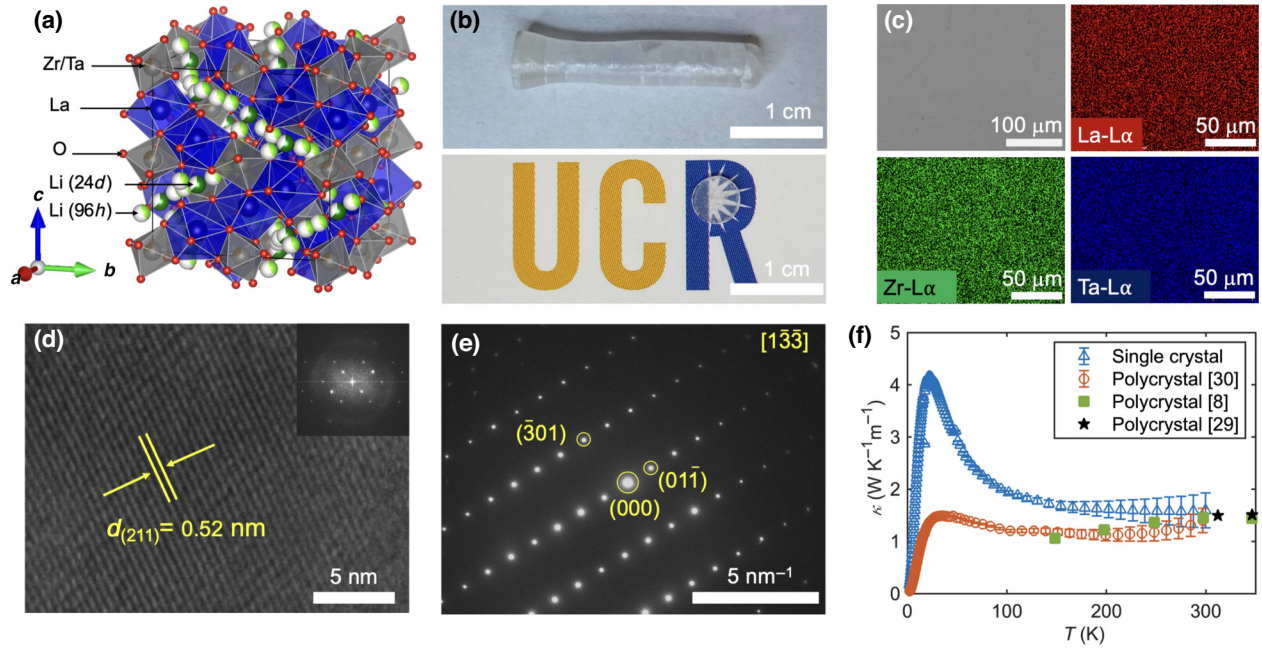


FIG. 1. The structure and thermal conductivity of LLZTO crystals. (a) The crystal structure of LLZTO (ICSD-894) [46], showing the lithium transport network consisting of two types of lithium sites. (b) Photographs of as-grown LLZTO single crystal using the floating-zone method. (c) A scanning-electron-microscopy (SEM) image of an LLZTO crystal showing the polished surface, with EDS elemental mapping results on the same sample. (d) A high-resolution transmission-electron-microscopy (TEM) micrograph of an LLZTO crystal. The inset shows the fast-Fourier-transform pattern. (e) The selected-area electron diffraction (SAED) of an LLZTO crystal. (f) The thermal conductivity of a single-crystal LLZTO. Shown for comparison are the polycrystal data reported in our previous study [30] and those by Cheng *et al.* [8] and Neises *et al.* [29].

20 mm in length. The crystals are semitransparent, with a characteristic white color. The phase purity and crystal quality of our single-crystal samples were confirmed using XRD, backscattering Laue patterns, and elastic neutron scattering (see Fig. S2 in the Supplemental Material [40]).

To study the surface features and chemical composition of the obtained crystals, SEM analysis was conducted on a polished surface of the single-crystal sample, as shown in Fig. 1(c). No discernible impurities or grain boundaries are observable within the scanning range. The EDS mapping indicates an even distribution of the constituent elements in the material with a stoichiometric ratio of La:Zr:Ta = 3.0:1.7:0.5, which agrees with the nominal composition of 3.0:1.5:0.5. A high-resolution transmission electron microscopy (TEM) image of an LLZTO sample is shown in Fig. 1(d). The spacing of the lattice fringes was measured to be around 0.52 nm, which matches the d spacing of 0.53 nm for the (211) lattice plane of LLZTO. The selected-area electron diffraction (SAED) of LLZTO in Fig. 1(e) indicates the monocrystalline nature of the sample.

The κ of the single-crystal LLZTO is displayed in Fig. 1(f), along with reported data for polycrystals [8,29,30]. The electronic contribution to thermal transport is negligible due to the high resistivity of the material [29].

Consequently, the total κ measured is primarily attributed to the lattice contribution (κ_L). The single crystal exhibits a κ peak near 22 K, while this peak is suppressed in the polycrystalline sample due to the increased defect and boundary scattering. The average grain size of the polycrystal is found to be 5.4 μm (see Fig. S3 in the Supplemental Material [40]). As the temperature increases over 100 K, the κ of both single-crystal and polycrystal LLZTO exhibits a weak temperature dependence, characteristic of disordered materials [56]. The measured room-temperature κ of the single-crystal LLZTO is only $(1.59 \pm 0.33) \text{ W m}^{-1} \text{ K}^{-1}$, an intrinsically low value comparable to some good thermoelectric materials [57–59]. The low value and weak temperature dependence of the single-crystal thermal conductivity require further investigation into the underlying mechanisms of thermal transport in LLZTO.

B. Lattice dynamics of LLZTO

In order to understand the origin of the low κ in LLZTO, we calculated its phonon dispersions using DFT. In Fig. 2(a), we present the full phonon dispersion along $[H00]$. The full dispersion contains 282 total bands below 90 meV. The full calculation results along $[HH0]$ and $[HHH]$, together with the identification process for the

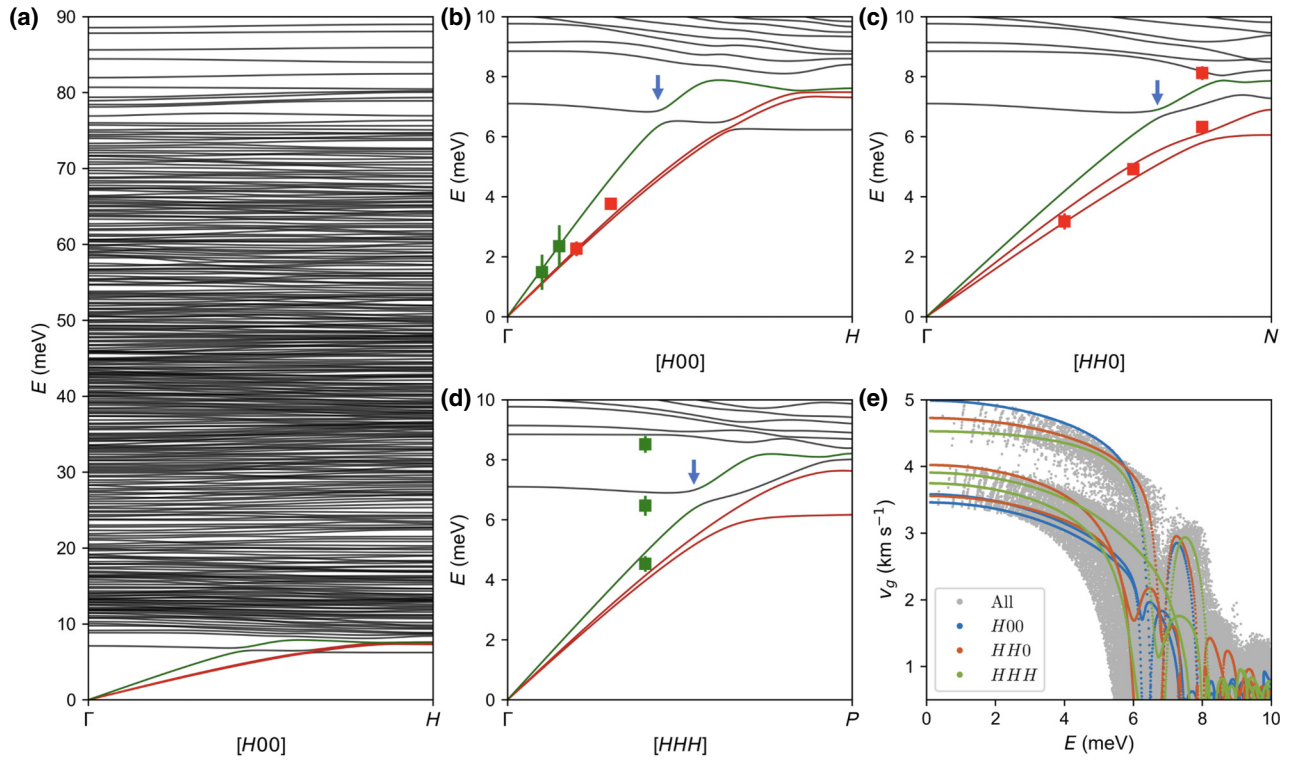


FIG. 2. The calculated phonon dispersion of LLZTO by DFT. (a) The calculated harmonic phonon dispersion of LLZTO along [H00] in the full energy range. (b)–(d) Enlarged views of the low-energy phonon modes along the [H00], [HH0], and [HHH] directions, respectively. The avoided crossing at 7 meV is marked with blue arrows. The square markers represent the data collected with the triple-axis spectrometer (TAX) at ORNL. The acoustic bands and TAX data are categorized by their polarizations: red for transverse modes and green for longitudinal modes. (e) The group velocity of phonon modes calculated from DFT, with data along the three high-symmetry directions highlighted in color.

polarization of acoustic modes, can be found in Figs. S4 and S5 in the Supplemental Material [40]. It should be noted that in a complex system and for an arbitrary point in the Brillouin zone, the acoustic modes can only be labeled as predominantly longitudinal or transverse, with the movement of individual atoms having, in general, components both parallel and perpendicular to the wave vector.

The DFT calculations reveal numerous optical phonon branches above 7 meV, which can be attributed to the large and complex crystal structure of LLZTO. Among the many optical phonon branches, there is a low-energy band with an energy (E) of approximately 7 meV. As shown in Figs. 2(b)–2(d), this optical branch shows an avoided crossing with the longitudinal acoustic (LA) branch in all three directions. As the energy approaches approximately 7 meV, there is a noticeable drop in the group velocities of the acoustic modes, as presented in Fig. 2(e). The reduction in phonon group velocity due to the avoided crossing has been associated with the suppression of thermal conductivity in some materials [60]. Elemental analysis on this low-lying optical branch indicates a dominant contribution from La atoms (see Fig. S6 in the Supplemental

Material [40]). At the Brillouin-zone center, this low-lying optical branch at 7 meV is primarily characterized by localized vibrations of La atoms, which are heptacoordinated by O atoms. Contributions from surrounding atoms are minimal. The avoided crossing appears to transfer the flat La-dominated character of the optical branch onto the LA branch. Furthermore, the acoustic band becomes flat due to the avoided crossing, creating a larger phase space for three-phonon scattering [61,62]. Similar avoided-crossing behavior has been observed in some thermoelectric materials and is considered a contributing factor to their low thermal conductivity [61,63]. This low-lying optical phonon, along with other optical phonons, can provide a large phase space for scattering acoustic phonons.

To verify the calculated phonon dispersion, we performed INS to determine the dynamical structure factor $S(\mathbf{Q}, E)$ across a range of $\mathbf{Q}$ and E , utilizing both TAX and a time-of-flight wide-angular-range chopper spectrometer (ARCS). The resulting $S(\mathbf{Q}, E)$ data from TAX, shown in Figs. 2(b)–2(d), display the phonon peaks extracted from constant- $\mathbf{Q}$ scans. For a net momentum transfer $\mathbf{Q} = \mathbf{G}_{\text{HKL}} + \mathbf{q}$, the intensity of the INS signal for certain polarization increases with $|\mathbf{Q} \cdot \mathbf{e}|^2$, where $\mathbf{e}$ is the

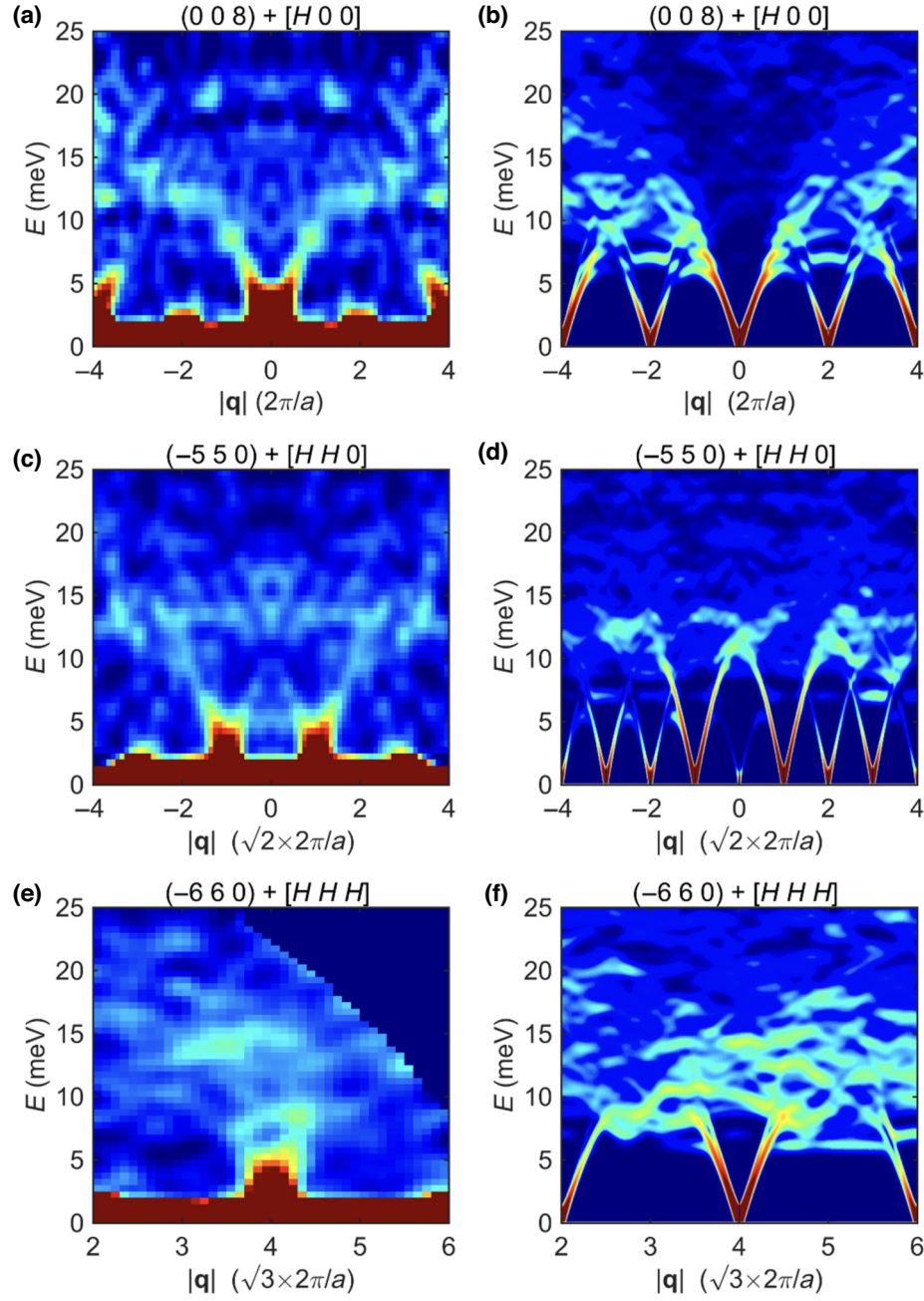


FIG. 3. The dynamical structure factor $S(\mathbf{Q}, E)$ measured with ARCS compared with the simulated results for LLZTO at 300 K. (a),(c),(e) The experimental dynamical structure factor $S(\mathbf{Q}, E)$ along the $[H00]$, $[HH0]$, and $[HHH]$ directions, respectively. (b),(d),(f) The corresponding calculated dynamical structure factor from DFT.

polarization vector of the atoms for a phonon mode. The color of the data points indicates the polarization of the measured phonon signals. The red markers align with the calculated TA modes, while the green markers correspond to the LA and longitudinal optical modes. The LA modes have higher group velocities, ranging from 4.5 to 5.0 km s^{-1} , compared to the TA modes, which range from 3.5 to 4.0 km s^{-1} . These sound velocities are in agreement with the calculated values based on

DFT, as listed in Table S2 in the Supplemental Material [40].

In Fig. 3, we present the phonon dynamical structure factor $S(\mathbf{Q}, E)$ of LLZTO measured using the ARCS, compared with the calculated results. Three slices of data were plotted along three directions in reciprocal space, $\mathbf{q} = [H00]$, $[HH0]$, and $[HHH]$. These slices correspond to distinct regions of the Brillouin zone, indexed by the reciprocal lattice vectors $\mathbf{G}_{\text{HKL}} = (008)$, $(\bar{5}50)$, and $(\bar{6}60)$,

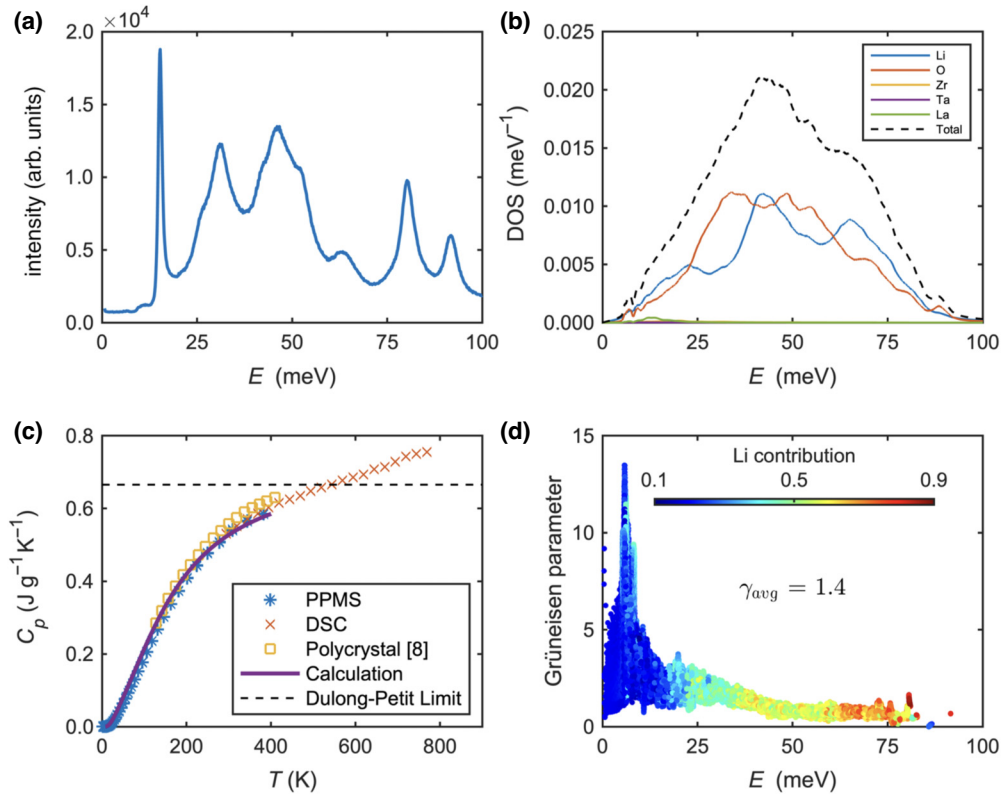


FIG. 4. The Raman spectrum, calculated phonon DOS, specific heat, and Grüneisen parameter. (a) The Raman spectrum of the single-crystal LLZTO at 300 K. (b) The DOS of LLZTO calculated by MD simulation. (c) The specific heat measured experimentally and calculated using DFT, compared with data from Cheng *et al.* [8]. (d) The Grüneisen parameter (γ) calculated for different phonon modes using DFT, with a color map indicating the lithium-atom contribution.

respectively. Clear TA modes with $\mathbf{q}$ along $[H00]$ and $[HH0]$ are observed in Figs. 3(a) and 3(c). The branches originate from the zone center at 0 meV and end at the zone boundary at approximately 7 meV. Along the $[HHH]$ direction [Fig. 3(e)], both the TA and LA modes are present. Notably, the TA modes are present in all three directions, suggesting that the inherently low κ in LLZTO is unlikely to be attributed to the complete breakdown of TA phonons, as observed in some other ionic conductors [11]. Furthermore, optical modes with energies ranging from 10 to 25 meV are observed in the measurements along all directions, consistent with the calculations. The extracted ARCS signals show good agreement with the calculated phonon dispersion, as shown in Fig. S7 in the Supplemental Material [40].

The Raman spectrum of LLZTO was measured to better understand its phonon energy, as shown in Fig. 4(a). From previous Raman studies [31,64,65] on LLZTO, we can identify the contribution of La centered at 15.3 meV. The Li contribution exhibits three peaks at 24.8, 46.6, and 63.4 meV in the spectrum. The O contribution shows two peaks at 33.5 and 49.6 meV. The peak locations corresponding to each element agree well with the projected phonon DOS of LLZTO using MD, as shown in Fig. 4(b).

The phonon cutoff energy is found to be approximately 100 meV. Overall, the phonon modes are dominated by Li and O vibrations, while the vibrations associated with Zr, Ta, and La mainly contribute to the phonon modes below approximately 20 meV.

The temperature dependence of the C_p of single-crystal LLZTO was measured using the PPMS from 1.8 to 381 K and DSC from 294 to 800 K, as shown in Fig. 4(c). Both data sets exhibit a consistent and continuous trend, with no indication of a first-order phase transition up to 800 K. Our data agree well with the previous study from Cheng *et al.* [8]. The calculated specific heat due to phonons also shows good agreement with the experimental data in the range of 8–400 K. It is worth mentioning that the calculation only considered the phonon contribution to the specific heat here. The good agreement can be attributed to the electron-insulating nature of LLZTO, which allows the specific heat to be accurately modeled by considering only the phonon contribution in the DFT calculation. The low-temperature data of C_p were analyzed using a Debye model [45], yielding a Debye temperature of 498 K and an average sound velocity of 3781 m s $^{-1}$. This value agrees with the average sound velocity of 3742 m s $^{-1}$ from DFT. Further details of

the analysis are provided in Fig. S8 in the Supplemental Material [40].

The Grüneisen parameter (γ) calculated via DFT highlights significant anharmonicity in the phonon band structure of LLZTO. As shown in Fig. 4(d), the Grüneisen parameter reaches a peak value of 13.5 near 6 meV, with an average value (γ_{avg}) of 1.4 and a baseline of approximately 2.0 for phonons below 30 meV. The average value is consistent with experimental γ values of 1.3–1.6, derived from the thermodynamic properties of LLZO-based compounds [30,66–69], supporting the reliability of the calculated phonon anharmonicity. This result indicates that low-energy phonons, which are typically responsible for heat conduction, deviate substantially from harmonic behavior and are strongly scattered. The sharp peak at approximately 6 meV aligns with flat phonon bands arising from an avoided crossing, suggesting that phonon hybridization enhances anharmonicity in this region. We further analyzed the Li contribution to individual phonon modes. While the Li character is generally low at low phonon energies and increases at higher energies, an anomalous feature emerges near the 6-meV peak: the phonon modes at this energy exhibit significantly higher Li contributions than other low-energy modes. This localized enhancement suggests that the Li dynamics play a critical role in

amplifying the anharmonic scattering in the vicinity of the avoided-crossing region. Previously, anharmonic scattering associated with avoided crossings has been observed in Fe_2Ge_3 [70]. Böger *et al.* [71] have similarly found that NASICON-type electrolytes exhibit strong anharmonicities, evoked by low-frequency Na vibrational modes.

C. Ionic conductivity and dynamics in LLZTO

To gain deeper insights into the ionic properties of LLZTO, we measured the ionic conductivity of a single crystal from 233 to 323 K, with a representative result at 273 K shown in Fig. 5(a). The measured ionic conductivity is 1.77 mS cm^{-1} at 295 K, which agrees with the previously reported value of 1.27 mS cm^{-1} for a single crystal [23]. The calculated activation energy is 0.484 eV, as shown in Fig. 5(b), similar to the reported value of 0.44 eV [23]. Using the measured ionic conductivity and a previously reported relation [72], the ionic diffusivity is estimated to be $1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

Quasielastic neutron scattering (QENS) is a useful technique to study the dynamic behavior of atoms within materials [73]. The $\mathbf{Q}$ - E slice presented in Fig. 5(c) demonstrates that the energy width increases with rising $\mathbf{Q}$, reflecting the diffusion behavior of lithium ions

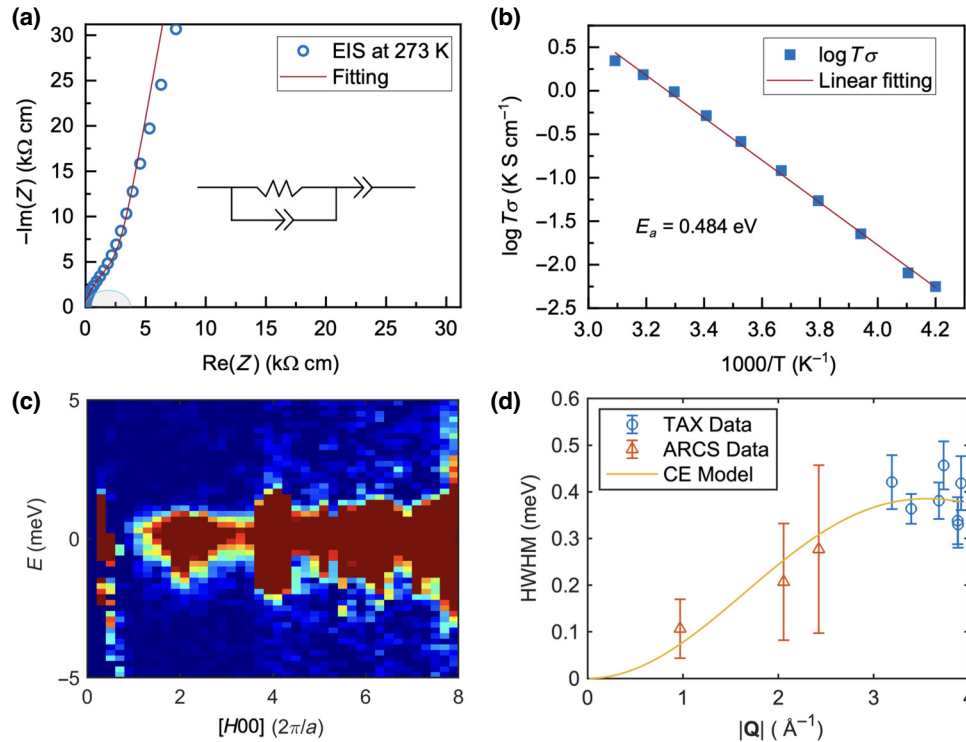


FIG. 5. The ionic conductivity and dynamics of LLZTO. (a) The Nyquist diagram of the cut single-crystal pellet measured at 273 K through the Au/LLZTO/Au symmetrical cell configuration. (b) The Arrhenius plot of the measured ionic conductivity. (c) The dynamical structure factor $S(\mathbf{Q}, E)$, showing an increasing energy width with larger $\mathbf{Q}$ along the $[H00]$ direction. The notably large energy width observed at $\mathbf{Q} = (400)$ is caused by elastic scattering. (d) Chudley-Elliott (CE) fitting of the half width at half maximum (HWHM) versus the $\mathbf{Q}$ relation.

in LLZTO. For QENS analysis, multiple $\mathbf{Q}$ points along the $[H00]$, $[HH0]$, and $[HHH]$ directions were selected. The instrument resolution was fitted accordingly, as detailed in Fig. S10 of the Supplemental Material [40]. The obtained half widths at half maximum (HWHMs), denoted as $\Gamma_{1/2}$, at different $\mathbf{Q}$ are displayed in Fig. 5(d). The $\Gamma_{1/2}$ - $\mathbf{Q}$ relation can be fitted to the Chudley-Elliott (CE) model [74] as

$$\Gamma_{1/2}(\mathbf{Q}) = \frac{\hbar}{\tau} \left(1 - \frac{\sin(|\mathbf{Q}|d_{\text{CE}})}{|\mathbf{Q}|d_{\text{CE}}} \right), \quad (1)$$

where $\hbar$ is the Planck constant, τ is the hopping time, and d_{CE} is the hopping distance. The obtained fitting results are $\tau = (2.1 \pm 0.2)$ ps and $d_{\text{CE}} = (1.3 \pm 0.3)$ Å. The analysis of QENS data using the CE model is consistent with the analysis using the Singwi-Sjölander model and the single-diffusion model [49] (see the Supplemental Material [40]).

The hopping distance of lithium ions was analyzed based on a previously reported LLZTO structure [46]. The distance between the Li1 and Li2 sites is $d_{12} = 1.51$ Å, while the distance between the Li2 sites is $d_{22} = 1.01$ Å. Each Li1 site is connected to each of its four neighboring Li1 sites by a pair of Li2 sites, as reported by a previous study [75]. The numerically weighted average distance between adjacent lithium sites is calculated as $d_{\text{avg}} = 1.32$ Å, which shows good agreement with $d_{\text{CE}} = 1.3$ Å fitted from the CE model. Based on our analysis, the observed lithium diffusion in the QENS data can be attributed predominantly to the hopping of lithium ions between the nearest sites.

We estimated a diffusivity of $D_{\text{QENS}} = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ from the hopping time and distance using the relation $D_{\text{QENS}} = d_{\text{CE}}^2/6\tau$ [74]. However, this value is much larger than the diffusivity values estimated from ionic conductivity measurement (D_{ionic}) and MD simulations (D_{MD}), which are $1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $1.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, respectively. This discrepancy could be attributed to the existence of a local fast-hopping mode. Such a local mode contributes little to long-range diffusion and therefore does not significantly increase ionic conductivity, yet it still contributes to QENS, as previously observed in Cu_2Se [12]. Despite not having a crystal structure indicating a local mode, one possible explanation is the difference between the local structure and the average structure. This phenomenon has been observed in sodium-ion conductors [76,77], where doping induces a transition in the average structure from tetragonal to cubic, while dynamically preserving the local tetragonal phase. A similar scenario may occur in LLZTO, derived from LLZO, where a local tetragonal framework could persist and account for the observed disparity between D_{QENS} and D_{ionic} or D_{MD} .

D. Two-channel model analysis of thermal transport

In materials with intrinsically low κ , strong phonon scattering and narrow interband spacings suppress the phonon contribution. Each phonon branch has a linewidth affected by the anharmonicity of, and defects in, the material. When phonon branches are closely spaced in energy and exhibit large linewidths, modes at the same $\mathbf{q}$ -point overlap. Under these conditions, energy channeling between adjacent phonon modes can create a second channel for energy transfer, mediated by diffusons [61,78–80], which are distinct from propagons [81,82], the classic gaslike phonons. Diffuson-contributed thermal transport has been observed in glasses, strongly disordered materials, and crystals with complex unit cells [61,78,79]. Since LLZTO exhibits disordered lithium atoms and numerous optical phonons, we use an analytical two-channel model [53] to analyze its thermal-transport behavior. κ_L consists of contributions from propagons (κ_{pr}) and diffusons (κ_{diff}), which are modeled separately as

$$\kappa_L = \kappa_{\text{pr}} + \kappa_{\text{diff}} = \frac{3nk_B}{3} \int_0^{\omega_{\text{IR}}} \frac{g(\omega)}{3n} C(\omega) v_s^2(\omega) \tau_p(\omega) d\omega + \frac{n^{1/3}k_B}{\pi} \int_{\omega_{\text{IR}}}^{\infty} \frac{g(\omega)}{3n} C(\omega) P\omega d\omega, \quad (2)$$

where n is the atomic density, k_B is the Boltzmann constant, $g(\omega)$ is the phonon DOS from calculation, v_s is the sound velocity, τ_p is the phonon lifetime, and P describes the average diffusivity of diffusons. The spectral heat capacity $C(\omega)$ is defined [83] as

$$C(\omega) = \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}. \quad (3)$$

The cutoff frequency ω_{IR} , also known as the Ioffe-Regel limit [78,84], marks the threshold at which phonons are scattered so frequently that the gaslike propagation model breaks down. This limit is approximated as

$$\omega_{\text{IR}} = \omega_D N^{1/3}, \quad (4)$$

where N is the number of atoms in the unit cell and ω_D is the Debye frequency, given by $\omega_D = (6\pi^2 n)^{1/3} v_s$. In this model, only extended modes below this threshold exhibit behavior characteristic of gaslike phonons, while diffuson transport predominates above this threshold. The obtained ω_{IR} for LLZTO is 7.8 meV, which aligns well with the dense cluster of optical modes observed above 8 meV in the phonon dispersion. The closely packed optical modes in energy space reinforce the transition from gaslike phonon thermal transport to a two-channel thermal-transport mechanism, where diffusons and propagons coexist to govern the thermal conductivity.

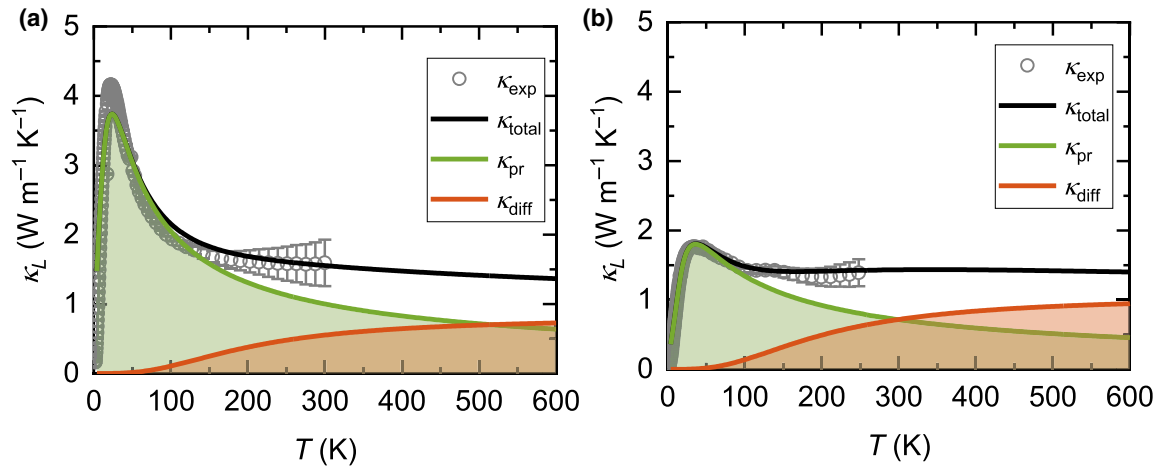


FIG. 6. Two-channel model analysis for thermal conductivity. An analysis of the thermal conductivity of the LLZTO (a) single crystal and (b) polycrystal using the two-channel model with propagon (κ_{pr}) and diffuson (κ_{diff}) contributions.

As shown in Fig. 6, the two-channel model accurately captures the temperature dependence of the thermal conductivity for both the single crystal and the polycrystal. Details of the fitting are provided in the Supplemental Material [40]. Despite thermal transport being dominated by propagons below approximately 200 K, diffusons play a significant role at elevated temperature, contributing approximately 30% and approximately 50% of the total thermal conductivity at room temperature in the single crystal and the polycrystal, respectively. Since the propagons and diffusons exhibit opposite temperature dependence, a plateau in thermal conductivity as a function of temperature is observed above 100 K. A significant diffuson contribution to thermal transport has also been observed in NASICON-type materials [71], consistent with the findings of the present study.

The obtained fitting parameters are listed in Table S3 in the Supplemental Material [40]. The phonon-phonon scattering parameter is comparable between the two samples, as this type of scattering is an intrinsic property of the material. Similarly, the diffuson parameter P , which represents the average probability of energy transfer between adjacent phonon modes, is close between two samples. This suggests that diffuson-mediated thermal transport is not significantly affected by defects or grain boundaries. In contrast, the boundary and impurity scattering parameters in the polycrystalline sample are approximately 2 and 4 times higher, respectively, than those in the single-crystal sample. This finding is consistent with the accumulated contributions to thermal conductivity versus phonon energy in Fig. S13 in the Supplemental Material [40]. In the polycrystal, increased defect and boundary scattering suppress the contribution of propagons, while the diffuson contribution remains similar in both single-crystal and polycrystalline samples.

IV. CONCLUSIONS

The thermal conductivity of single-crystalline LLZTO exhibits an intrinsically low value and a weak temperature dependence above 100 K, deviating from conventional crystalline behavior. Phonon band-structure calculations and INS measurements reveal acoustic phonons and a dense cluster of optical phonon branches, which are attributed to the complex crystal structure of LLZTO. Notably, the avoided crossing between a low-lying optical mode and acoustic modes near 7 meV reduces the group velocity of acoustic phonons. This low-lying mode, along with other optical phonons, provides scattering channels for acoustic phonons. DFT calculations further suggest large Grüneisen parameters, especially for the vibrational modes below 10 meV. A peak in the Grüneisen parameter appears at an energy of 6 meV and is associated with a significant contribution from Li vibrations. Additionally, combined QENS and ionic conductivity measurements suggest the presence of a local Li hopping mode that contributes to the QENS signal but does not significantly contribute to bulk diffusion. The thermal conductivity can be modeled using a two-channel model, accounting for contributions from propagons and diffusons. Therefore, the intrinsically low thermal conductivity in LLZTO stems from its complex crystal structure and strong lattice anharmonicity. These findings offer valuable insights into the unique thermal-transport properties in solid electrolytes, with implications for advancing energy-conversion and -storage technologies.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [85].

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