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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Thermal Transport and Lattice Dynamics in
Solid Electrolytes

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Electrical Engineering

by

Yitian Wang

June 2026

Dissertation Committee:

Dr. Xi Chen, Chairperson

Dr. Roger Lake

Dr. Chen Li

The Dissertation of Yitian Wang is approved by:

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University of California, Riverside

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Acknowledgement of Previously Published Materials

The text of this dissertation, in part or in full, is a reprint of material as it appears in the following publications:

- Chapter 1 includes material from: Yitian Wang, Handing Wang, and Xi Chen, “Thermal Transport Mechanisms in Electrolytes for All-Solid-State Batteries: A Review” (Submitted 2026).
- Chapter 3 includes material from: Yitian Wang*, Yaokun Su*, Jesús Carrete*, Huanyu Zhang, Nan Wu, Yutao Li, Hongze Li, Jiaming He, Youming Xu, Shucheng Guo, Qingan Cai, Douglas L. Abernathy, Travis Williams, Kostiantyn V. Kravchyk, Maksym V. Kovalenko, Georg K. H. Madsen, Chen Li, and Xi Chen, “Origin of Intrinsically Low Thermal Conductivity in a Garnet-Type Solid Electrolyte: Linking Lattice and Ionic Dynamics with Thermal Transport,” *PRX Energy* **4**, 033004 (2025). (*contributed equally)
- Chapter 4 includes material from: Yitian Wang[‡], Shuchen Li[‡], Nan Wu, Qianru Jia, Thomas Hoke, Li Shi, Yutao Li, and Xi Chen, “Thermal properties and lattice anharmonicity of Li-ion conducting garnet solid electrolyte $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$,” *Journal of Materials Chemistry A* **12**, 18248–18257 (2024). ([‡]contributed equally)
- Chapter 5 includes material from: Yitian Wang, Qianru Jia, Shuchen Li, Li Shi, Yutao Li, and Xi Chen, “Glass-like thermal transport in polycrystalline perovskite lithium-ion conductor $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$,” *Chemical Communications* **61**, 17125–17128 (2025).

- Chapter 6 includes material from: Yi-Tian Wang, Qian-Ru Jia, Shu-Chen Li, Li Shi, Yu-Tao Li, and Xi Chen, “Low thermal conductivity and lattice anharmonicity of NaSICON-type solid electrolyte $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$,” *Tungsten* **8**, 52–61 (2026).

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To the people whose support carried me through my life,
to those who are with me, and to those who are not.

ABSTRACT OF THE DISSERTATION

Thermal Transport and Lattice Dynamics in Solid Electrolytes

by

Yitian Wang

Doctor of Philosophy, Graduate Program in Electrical Engineering
University of California, Riverside, June 2026
Dr. Xi Chen, Chairperson

All-solid-state batteries replace flammable liquid electrolytes with inorganic solid electrolytes, yet the thermal properties of these ion conductors remain less understood than their ionic conductivity. Because solid electrolytes form continuous heat pathways between electrodes, their thermal conductivity (κ) governs temperature profiles, degradation, and cycling safety. This dissertation examines thermal transport and lattice dynamics in oxide solid electrolytes and explains low, glass-like heat transport in ion conductors.

Single-crystal $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) was grown by floating zone method. Thermal measurements show an intrinsically low room-temperature κ of $1.59(33) \text{ W m}^{-1} \text{ K}^{-1}$. Inelastic neutron scattering observes acoustic phonons, while first-principles calculations reproduce the spectra and reveal dense optical modes with acoustic-optical avoided crossings near 7 meV. Quasielastic neutron scattering reveals fast local Li hopping, connecting mobile-ion dynamics with heat-suppressing lattice dynamics. A two-channel analysis links weak temperature dependence to diffuson-mediated transport.

Polycrystalline LLZTO exhibits a low-temperature κ peak near 50 K, followed by weak temperature dependence above 200 K. Thermal expansion and mechanical testing yield a

Grüneisen parameter of 1.63(4), quantifying strong lattice anharmonicity. Aging in air increases κ by $\sim 75\%$ at room temperature due to Li_2CO_3 formation and modified thermal boundary resistance.

The perovskite lithium-ion conductor $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$ (LSHT) displays glass-like thermal transport, with $\kappa = 1.7(5) \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. The data indicate strong disorder-driven scattering and a significant diffuson contribution, showing similar heat-transport suppression in perovskites.

The NaSICON-type electrolyte $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) has a Debye temperature of 370 K, sound velocity of 2962 m s^{-1} , and room-temperature κ of $1.01(6) \text{ W m}^{-1} \text{ K}^{-1}$. Its κ shows a low-temperature peak near 95 K and a plateau above ~ 200 K. Its Grüneisen parameter of 0.70 indicates intermediate anharmonicity relative to related NaSICON compositions.

Together, these studies establish lattice-dynamics principles for thermal management and materials design in all-solid-state batteries, positioning solid electrolytes as a platform for studying and controlling heat transport.

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Chapter 1

Introduction

1.1 All-Solid-State Batteries and Solid Electrolytes

The rapid electrification of transportation and the growth of grid-scale renewable energy storage have created an urgent demand for safer, higher-energy-density rechargeable batteries [15–17]. Conventional lithium-ion batteries (LIBs) have dominated the portable electronics and electric vehicle markets for over three decades. However, they rely on flammable organic liquid electrolytes that present intrinsic safety hazards. These hazards include electrolyte leakage, dendrite-induced internal short circuits, and thermal runaway, a cascading exothermic failure that can lead to fire or explosion [18, 19]. The energy density of LIBs is also approaching its theoretical ceiling, because conventional graphite anodes and intercalation cathodes offer limited specific capacity [15]. Replacing the liquid electrolyte with an inorganic solid electrolyte (SE) yields an all-solid-state battery (ASSB). ASSBs promise inherently safer designs, wider electrochemical windows, and compatibility with high-voltage cathodes and lithium-metal anodes [20–22]. The use of a solid separator also enables bipolar stacking of cells, which can increase the volumetric energy density of battery packs. As a result, ASSBs have emerged as one of the most actively pursued platforms for next-generation energy storage. Figure 1.1 schematically contrasts a conventional liquid-electrolyte battery with an all-solid-state battery, where the liquid electrolyte and separator are replaced by a solid electrolyte layer.

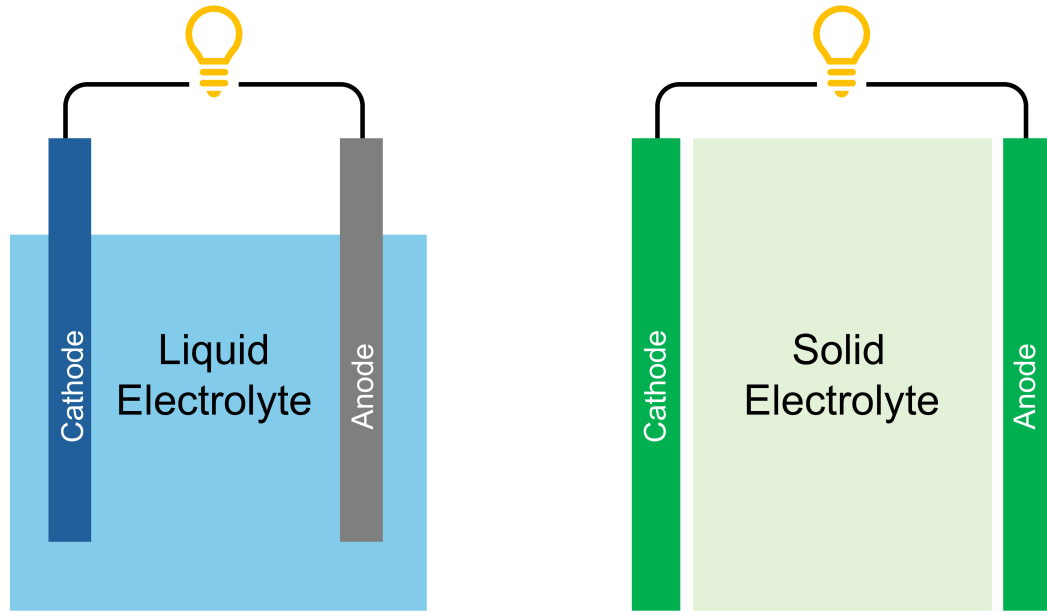


Figure 1.1: Comparison of conventional and all-solid-state battery architectures. Left: conventional liquid-electrolyte battery. Right: all-solid-state battery with inorganic solid electrolyte serving as ion conductor and separator simultaneously.

Heat generation is unavoidable in any operating battery. Joule heating from ionic migration, polarization losses, and exothermic side reactions all contribute to a continuous thermal load during charge and discharge [23, 24]. In the ASSB architecture, the SE occupies a large volume fraction and forms a continuous thermal pathway between electrodes. The thermal conductivity (κ) of the SE therefore controls the temperature profile of the cell under load. Poor heat dissipation leads to localized hot spots, which accelerate interfacial degradation, promote nonuniform lithium plating, and can trigger thermal runaway [18, 25]. Conversely, low temperatures impede ionic transport and reduce usable capacity [26]. Fast charging compounds both problems by concentrating heat generation into short time windows [23]. Effective thermal management is therefore essential for realizing the safety and performance advantages of ASSBs. Agne *et al.* [23] discussed the theoretical role of thermal transport in solid-state battery design, emphasizing that a

detailed understanding of heat evolution and transport mechanisms is needed to enhance battery safety and performance.

Despite the central role of heat transport, the thermal properties of SEs have received far less attention than their ionic conductivity. Early surveys of SE materials focused almost exclusively on ionic transport and electrochemical stability [22]. Only in recent years has the thermal behavior of SEs begun to receive systematic attention [3, 27]. Understanding these properties requires a general overview of the materials themselves. Inorganic SEs fall into three broad chemical families: oxides, sulfides, and halides. Each family offers distinct compromises among ionic conductivity, electrochemical stability, mechanical stiffness, and ambient stability. Over the past two decades, intense research efforts have produced several SE compositions with room-temperature ionic conductivities that rival those of liquid electrolytes.

Oxide SEs have been studied since the mid-twentieth century and remain the most chemically and electrochemically stable family [28]. They offer wide electrochemical windows, high mechanical stiffness, and good compatibility with high-voltage cathodes. Three dominant subfamilies exist among oxide SEs: garnet-type, NaSICON, and perovskite.

Garnet-type materials are exemplified by $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), first stabilized in the cubic $Ia\bar{3}d$ phase by Murugan *et al.* [29]. The garnet structure consists of a rigid framework of corner-sharing ZrO_6 octahedra and LaO_8 dodecahedra, within which Li^+ ions occupy tetrahedral and distorted octahedral interstitial sites with partial occupancy [12]. Doping with Al, Ga, or Ta further increases ionic conductivity. The Ta-doped composition $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) reaches $10^{-3} \text{ S cm}^{-1}$ at room temperature [30, 31].

NaSICON (Na Super Ionic CONductor) materials were discovered in 1976 by Hong [32] and Goodenough *et al.* [33]. The parent compound $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) crystallizes in the rhombohedral $R\bar{3}c$ space group. Its framework of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra creates interconnected channels for three-dimensional Na^+

transport. Substitution of Si for P produces the compositional series $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, with NZSP ($x = 2$) showing the highest ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ [34].

Perovskite-type SEs adopt the ABO_3 structure with corner-sharing BO_6 octahedra. The most studied composition, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO), can exhibit bulk ionic conductivities up to $10^{-3} \text{ S cm}^{-1}$, but high grain boundary resistance reduces the total conductivity [35]. The composition $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$ (LSHT) crystallizes in cubic $Pm\bar{3}m$ symmetry and exhibits an ionic conductivity of $3.8 \times 10^{-4} \text{ S cm}^{-1}$ with a low activation energy of 0.36 eV [36].

The main limitation of oxides is their high interfacial resistance due to poor physical contact with electrodes, and the need for high-temperature sintering to achieve dense pellets.

Sulfide SEs substitute sulfur for oxygen and deliver the highest ionic conductivities among inorganic SEs [37, 38]. The larger ionic radius and lower electronegativity of S^{2-} compared to O^{2-} widen diffusion channels and weaken the framework-ion interaction, lowering the activation energy for ionic transport. The 2011 discovery of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) by Kamaya *et al.* [39] produced an SE with 12 mS cm^{-1} at room temperature, matching liquid electrolytes. LGPS crystallizes in a tetragonal structure that hosts one-dimensional conduction channels along the c -axis. Glass-ceramic systems such as $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ and the argyrodite family $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl, Br, I}$) further expand the landscape of viable lithium sulfide SEs [40, 41]. Sulfides are also mechanically soft, which eases densification by cold pressing without the high-temperature sintering required for oxides. Their main drawbacks are poor ambient stability (reaction with moisture to form H_2S) and narrower electrochemical windows.

Halide SEs form a rapidly growing family following the 2018 report by Asano *et al.* [42] of room-temperature conductivities above $10^{-3} \text{ S cm}^{-1}$ in Li_3YCl_6 and Li_3YBr_6 . These materials consist of layers of corner-sharing YCl_6 octahedra with partially occupied Li^+

sites in the interstitial space [43]. The high polarizability of Cl^- softens the local potential and reduces the activation energy for Li^+ migration. Subsequent studies introduced composition-tunable systems such as $\text{Li}_x\text{ScCl}_{3+x}$ [44], while oxyhalides such as LiTaOCl_4 achieve $10^{-2} \text{ S cm}^{-1}$ [45]. Halides combine high voltage stability with tunable compositions, which positions them well for high-voltage cathode compatibility [46, 47].

Despite their chemical and structural diversity, many SEs share a broad architectural motif: a comparatively rigid anion framework supports mobile cations that occupy partially filled sites or migration channels. This motif motivates studying SEs as a related group of ion-conducting materials in which mobile-ion disorder, framework complexity, and lattice dynamics can all influence heat conduction.

1.2 Phonon Thermal Transport

In electrically insulating solids such as SEs, electronic contributions to thermal conductivity are negligible. Heat is carried primarily by phonons, the quantized modes of lattice vibration [48]. This section introduces the phonon gas model, the Debye framework, and the scattering mechanisms that limit thermal conductivity. These concepts provide the theoretical foundation for the thermal transport analyses in Chapters 3–6.

1.2.1 Phonons and Debye Model

Atoms in a crystalline solid are bound to their equilibrium positions by interatomic forces. At finite temperature, they vibrate about these positions. These vibrations are collective: the motion of one atom is coupled to its neighbors through the bonding network. The quantum-mechanical treatment of these collective vibrations yields phonons, which are bosonic quasiparticles characterized by a wavevector $\mathbf{q}$, a branch index, and a frequency

ω . Phonons are directly related to the thermodynamic properties of solids, including heat capacity, thermal expansion, and thermal conductivity.

In the kinetic-theory picture, phonons behave as a gas of quasiparticles that carry energy from hot to cold regions. For a single phonon mode with group velocity v and mean free path ℓ , the thermal conductivity takes the form

$$\kappa = \frac{1}{3} C_v v \ell, \quad (1.1)$$

where C_v is the volumetric heat capacity. Substituting $\ell = v\tau$, where τ is the phonon relaxation time, yields

$$\kappa = \frac{1}{3} C_v v^2 \tau. \quad (1.2)$$

In a real crystal, this same physical picture applies mode by mode across the phonon spectrum [48]. Equation 1.2 therefore emphasizes the three ingredients that control thermal conductivity: the heat capacity carried by thermally populated modes, their group velocities, and their lifetimes. Suppressing any one of these quantities suppresses thermal transport.

The Debye model approximates the acoustic phonon dispersion as linear, with a single sound velocity v_s and a cutoff frequency ω_D [48]. The Debye temperature is defined as $\Theta_D = \hbar\omega_D/k_B$. At temperatures far below Θ_D , the lattice specific heat approaches the Debye T^3 form:

$$C_v(T) = \frac{12\pi^4}{5} nk_B \left(\frac{T}{\Theta_D} \right)^3, \quad (1.3)$$

where n is the atomic number density. At high temperatures ($T \gg \Theta_D$), the specific heat saturates at the Dulong–Petit limit of $3nk_B$. The Debye temperature can be extracted from low-temperature specific-heat measurements. It is directly related to the Debye-averaged sound velocity through [49]

$$\frac{3}{v_s^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}, \quad (1.4)$$

where v_L and v_T are the longitudinal and transverse sound velocities. Sound velocities connect to elastic moduli through the bulk modulus B , the shear modulus G , and the mass density ρ . For an isotropic solid, $v_L = \sqrt{(B + \frac{4}{3}G)/\rho}$ and $v_T = \sqrt{G/\rho}$. Low sound velocities and low Debye temperatures generally correlate with low thermal conductivities, because both signal soft bonding and limited phonon dispersion [50, 51]. Slack showed that the Umklapp-limited thermal conductivity of nonmetallic crystals can be estimated from the average atomic mass, the Debye temperature, and the lattice anharmonicity [50]. This relation provides a useful rule of thumb: heavy atoms, soft bonds, and strong anharmonicity all suppress κ .

Several scattering processes limit the phonon relaxation time τ . Under Matthiessen's rule, the total scattering rate is the sum of independent contributions [48]:

$$\tau^{-1} = \tau_U^{-1} + \tau_D^{-1} + \tau_B^{-1} + \dots, \quad (1.5)$$

where τ_U describes Umklapp phonon–phonon scattering, τ_D describes point-defect and mass-disorder scattering [52], and τ_B describes boundary scattering. Umklapp scattering is the dominant intrinsic mechanism at temperatures above Θ_D . In an Umklapp process, two phonons combine to produce a third whose wavevector falls outside the first Brillouin zone. The resulting wavevector must be folded back by a reciprocal lattice vector, which does not conserve crystal momentum and therefore creates thermal resistance. As temperature increases, the population of high-frequency phonons grows, and Umklapp scattering intensifies. This produces the characteristic $\kappa \propto 1/T$ decay observed in many crystalline solids at high temperatures.

Point-defect scattering arises from substitutional atoms, vacancies, or interstitial atoms that locally change the mass and bonding of the lattice. Klemens showed that the defect scattering rate scales as $\tau_D^{-1} \propto \omega^4$, where ω is the phonon frequency [52]. This strong fre-

quency dependence means that defect scattering preferentially suppresses high-frequency phonons. In SEs, point-defect scattering is particularly relevant because many SE compositions involve extensive substitution on cation sites (e.g., Ta for Zr in LLZTO, Si for P in NZSP), which introduces substantial mass and bond disorder.

Boundary scattering becomes significant when the phonon mean free path approaches the sample dimensions or the grain size. In polycrystalline ceramics, grain boundaries act as scattering centers for phonons. The boundary scattering rate is approximately $\tau_B^{-1} \approx v/L$, where L is the characteristic grain size or sample dimension. This mechanism dominates at low temperatures where Umklapp and defect scattering are weak and mean free paths are long.

The combined effect of these mechanisms produces the characteristic $\kappa(T)$ curve observed in crystalline solids. At low temperatures, κ rises with temperature as the heat capacity grows following the Debye T^3 law. It reaches a peak, typically between 20 K and 100 K, where boundary and defect scattering balance the increasing heat capacity. Above the peak, Umklapp scattering becomes dominant and κ decreases, often following a $1/T$ dependence at high temperatures.

1.2.2 Beyond the phonon gas: diffusons and two-channel models

A more rigorous treatment starts from the phonon Boltzmann transport equation (BTE) [48, 53]. In modern first-principles studies, the BTE is often solved using phonon frequencies, group velocities, and scattering matrix elements obtained from density functional theory [54].

This approach is powerful but is traditionally based on the phonon-gas picture, where heat is carried by well-defined phonon wave packets with meaningful group velocities and lifetimes; in materials with large unit cells, strong disorder, or strong anharmonicity those assumptions can fail. Modern solutions of the BTE and its Wigner/generalized formula-

tions, however, explicitly recover additional, mode-coupling contributions to heat transport by introducing off-diagonal terms in the transport matrix [55, 56].

A useful way to describe this mode-coupling is the classification of vibrational excitations into propagons, diffusons, and locons [57]. Propagons are ideal gas-like phonon modes that transport heat through wave-like propagation. Locons are strongly localized modes and contribute little to long-range heat flow. Diffusons occupy the intermediate regime: they are extended vibrational modes, but they do not carry heat through a well-defined group velocity. Instead, energy moves through mode-to-mode coupling and spatial diffusion among a dense set of overlapping vibrations [55, 57].

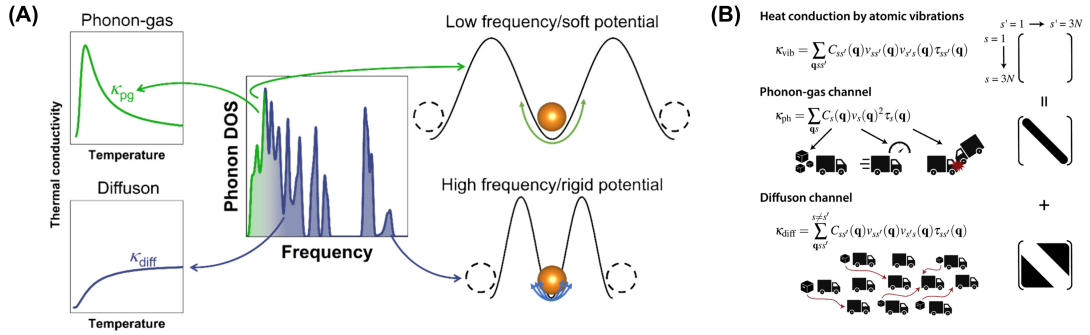


Figure 1.2: Propagon and diffuson mechanisms in thermal transport. Schematic illustration of propagon and diffuson thermal transport. (A) Temperature dependence of the phonon-gas and diffuson contributions, together with the frequency cutoff separating low-frequency propagons from high-frequency diffusons. Adapted from Böger *et al.* [1]. (B) Microscopic two-channel picture in which diagonal terms of the vibrational transport matrix describe phonon-gas propagation, while off-diagonal coupling between vibrational modes gives the diffuson channel. Adapted from Hanus *et al.* [2]. Both panels are adapted under the Creative Commons Attribution 4.0 International License (CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>).

Although diffusons were first introduced for amorphous solids, recent theoretical work has broadened this idea beyond a purely glass-based picture. Simoncelli *et al.* developed a unified theory of thermal transport that connects the Peierls–Boltzmann description for propagating phonons with the Allen–Feldman description for diffusons, allowing both particle-like and wave-like heat conduction to coexist in complex crystals [55]. Their later

Wigner formulation further showed that, when the phonon-gas picture fails, heat can still be carried through wave-like tunneling and interference between nearly degenerate vibrational eigenstates [56]. These theories provide a microscopic foundation for treating glass-like thermal conductivity in crystalline materials with large unit cells, strong disorder, or highly anharmonic dynamics.

Several complementary analytical frameworks have been developed from this perspective. The analysis used in this dissertation follows the analytical two-channel model introduced by Bernges *et al.*, which was developed to interpret materials where both phonon-gas and diffuson channels contribute to thermal conduction [14]. In this model, the lattice thermal conductivity is separated into a low-frequency propagon channel and a high-frequency diffuson channel:

$$\kappa_L(T) = \kappa_{\text{pr}}(T) + \kappa_{\text{diff}}(T). \quad (1.6)$$

The propagon part is treated with a relaxation-time phonon-gas expression, while the diffuson part uses a diffusive transport expression based on the vibrational density of states, following the diffuson-mediated minimum-thermal-conductivity framework of Agne *et al.* [14, 58]. The boundary between the two regimes is often associated with the Ioffe–Regel limit, where the phonon mean free path becomes comparable to its wavelength and the phonon-gas description loses validity [59, 60]. Below this limit, propagons show the familiar crystalline behavior: a low-temperature peak followed by decreasing κ as phonon–phonon scattering increases. Above it, diffuson modes contribute through non-propagating energy diffusion, often producing a weakly temperature-dependent background that can help explain glass-like thermal conductivity in crystalline solid electrolytes.

This framework is particularly relevant to solid electrolytes. Their open frameworks, partially occupied mobile-ion sublattices, large primitive cells, and strong local disorder

der can suppress wave-like phonon propagation while leaving many extended vibrational modes available for diffuson-mediated heat flow. A separate Onsager-based framework for superionic crystals has also emphasized that the apparent thermal conductivity can include both vibrational heat conduction and enthalpy diffusion associated with mobile ions, helping rationalize weak or even positive temperature dependence in systems with fast ion motion [61]. Together, these recent theoretical developments show why a crystalline solid electrolyte can exhibit thermal transport closer to a glass than to a simple phonon gas, while also highlighting that mobile ions may modify heat flow beyond the conventional lattice-only picture. The detailed implementation of the two-channel fit used in this dissertation is described in Chapter 2, and its material-specific consequences are discussed in Chapters 3–6.

1.3 Thermal Transport in Solid Electrolytes

Sections 1.1 and 1.2 established that SEs are essential components of ASSBs and that phonons carry heat in these electrically insulating solids. As summarized in Figure 1.3, many representative SEs combine high ionic conductivity with relatively low thermal conductivity, making them attractive for electrochemical function but potentially challenging for heat dissipation.

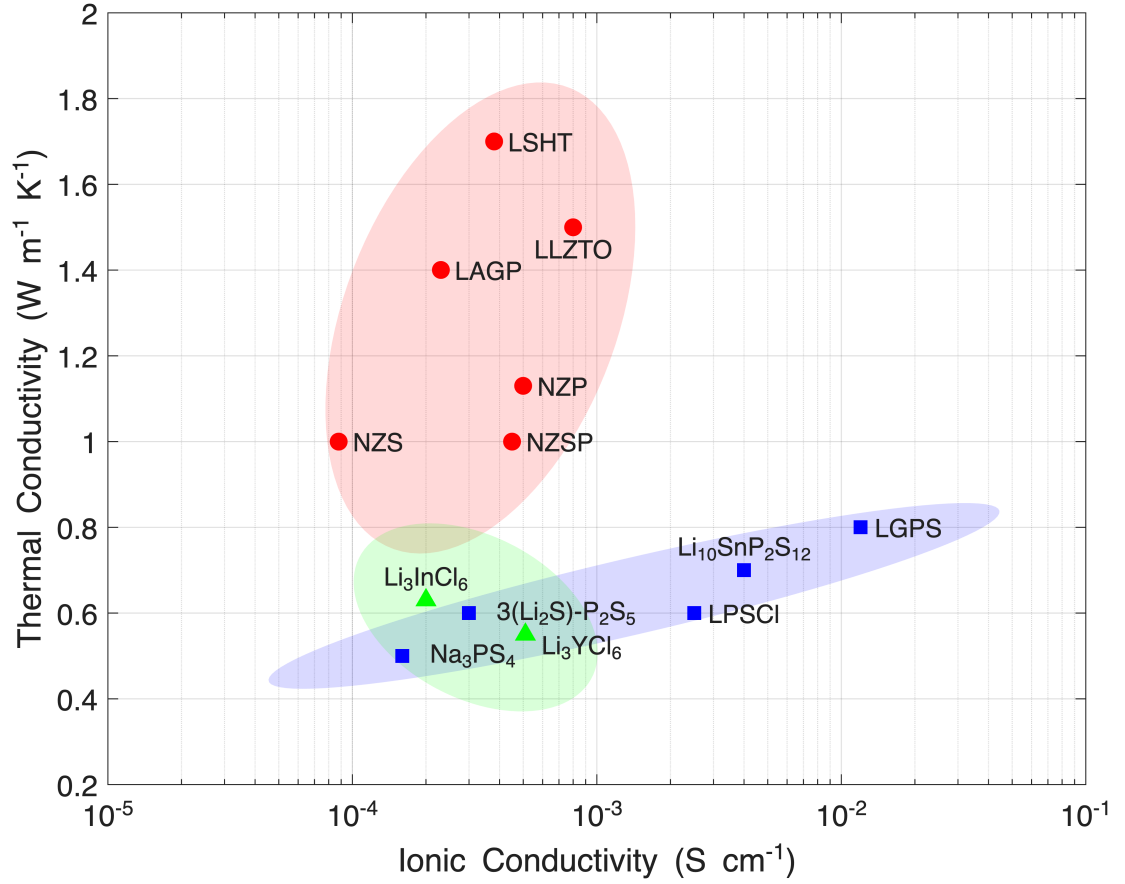


Figure 1.3: Reported ionic and thermal conductivities of representative solid electrolytes. Room-temperature ionic vs thermal conductivity showing solid electrolytes as both ion conductors and thermal materials. Data compiled from representative literature [1, 3–8].

Cheng *et al.* [3] conducted the first systematic study of SE thermal properties and showed that representative oxide, sulfide, and halide SEs often exhibit thermal conductivities close to amorphous limits, despite their crystalline structures. Reported room-temperature κ values fall below $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ for oxides and below $1 \text{ W m}^{-1} \text{ K}^{-1}$ for sulfides and halides [1, 3, 4]. For comparison, typical crystalline oxides such as Al_2O_3 and MgO exhibit κ values one to two orders of magnitude higher at room temperature [50].

Figure 1.4 shows that many representative SEs cluster near the Cahill minimum-thermal-conductivity line, meaning their measured κ values are already close to the diffuse-limit lower bound where phonon mean free paths approach the interatomic spacing

and heat transport becomes strongly diffusive. In the figure, the oxides sit somewhat above the $\kappa = \kappa_{\min}$ line, while the sulfides and halides fall close to or slightly below it, reinforcing the view that these materials already approach the minimum lattice thermal conductivity expected for disordered solids.

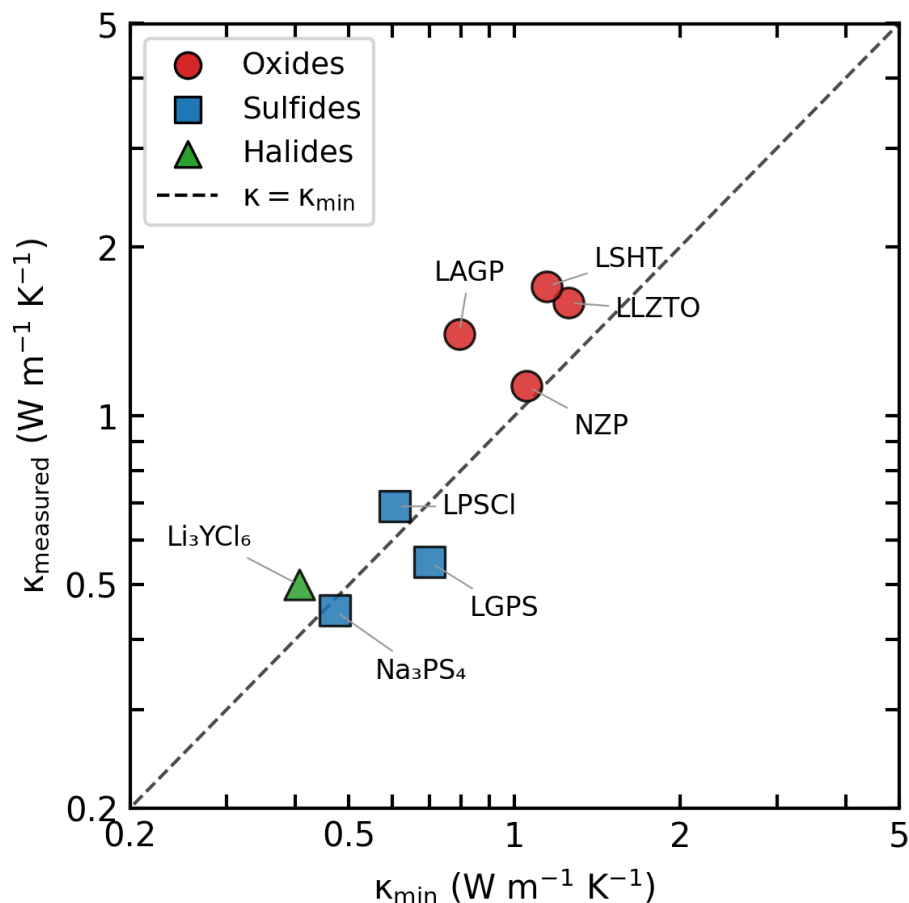


Figure 1.4: Reported solid-electrolyte thermal conductivities compared with minimum thermal conductivity. Thermal conductivities of solid electrolytes compared with Cahill minimum ($\kappa_{\min}$). Data from representative reports [1, 3–8].

The temperature dependence of κ in SEs is also unusual. Instead of the $1/T$ decay expected for crystalline solids, SEs show a weak, near-plateau behavior above 200 K. This glass-like temperature dependence is characteristic of amorphous or highly disordered materials and is unexpected for compounds with well-defined long-range crystalline order.

Several mechanisms have been proposed to explain this glass-like behavior. These include strong lattice anharmonicity that enhances phonon–phonon scattering [1], complex phonon dispersions arising from large unit cells that suppress acoustic phonon velocities [62], and liquid-like dynamics of the mobile-ion sublattice that disrupt wave-like phonon propagation [63].

As introduced in Section 1.2, this behavior can be viewed as a crossover from propagon-dominated heat conduction to a mixed propagon–diffuson regime. In SEs, the same structural features that promote fast ionic conductivity—open frameworks, partially occupied mobile-ion sublattices, and strong local disorder—can also suppress wave-like phonon propagation and enhance diffuson-mediated heat flow.

1.4 Motivation of This Dissertation

Despite growing interest in the thermal properties of SEs, several gaps limit the current understanding. First, the existing literature is fragmented across isolated material systems and measurement techniques. A complete picture of how intrinsic lattice dynamics, mobile-ion disorder, and microstructure contribute to low κ across different SE families is still lacking [23, 27]. Second, most existing measurements are performed on polycrystalline pellets, where grain boundaries, porosity, and secondary phases can obscure intrinsic behavior [13, 64]. Separating intrinsic from extrinsic contributions requires single-crystal measurements, which have been scarce. Third, direct probes of lattice dynamics—such as the phonon dispersion—are largely absent for most SE compositions, leaving the microscopic origin of the glass-like behavior untested. Fourth, cross-family comparisons under a common experimental and analytical framework are rare, making it difficult to distinguish material-specific effects from broader trends.

Addressing these gaps is essential for understanding thermal transport in SEs and for informed thermal design of ASSBs. Here, we systematically investigate the thermal transport properties of three structurally distinct oxide SE families: garnet LLZTO, perovskite LSHT, and NaSICON NZSP. These three systems span the major oxide SE subfamilies and exhibit distinct crystal structures, unit cell sizes, and ionic conduction mechanisms. By studying them under a common experimental and analytical framework, we can separate material-specific effects from recurring thermal-transport features. We combine single-crystal and polycrystalline measurements, cryogenic-to-high-temperature thermal transport data, inelastic neutron scattering, and first-principles lattice dynamics to identify mechanisms that suppress thermal conductivity in these materials. This dissertation addresses whether the low κ of SEs is intrinsic or dominated by microstructural features such as grain boundaries and porosity, identifies the microscopic mechanisms that give rise to glass-like thermal transport in crystalline SEs, and compares the features shared among garnet, perovskite, and NaSICON oxide SEs with those that remain material-specific.

1.5 Structure of the Dissertation

This dissertation is organized as follows. Chapter 2 describes the experimental and computational methods used throughout the work. Chapter 3 presents the flagship study of single-crystal LLZTO, combining thermal conductivity, heat capacity, and ionic transport measurements with inelastic neutron scattering and first-principles lattice dynamics to identify the intrinsic mechanism of glass-like transport in garnet SEs [6]. Chapter 4 presents the parallel polycrystalline LLZTO study, which established baseline thermal properties and revealed a counterintuitive aging response [5]. Together, these two chapters demonstrate that the low κ of garnet SEs is intrinsic rather than microstructural. Chapter 5 extends the analysis to perovskite LSHT and shows that the glass-like transport picture applies to a

chemically distinct SE family [7]. Chapter 6 completes the cross-family comparison with NaSICON NZSP, connecting the lattice anharmonicity to the mobile-ion site occupancy across the NZP–NZSP–NZS compositional series [8]. Chapter 7 summarizes the findings, compares recurring and material-specific features of glass-like thermal transport across the studied SE families, and discusses implications for thermal management in ASSBs.

Chapter 2

Experimental Methods

This chapter describes the experimental methods used throughout this dissertation. The techniques cover sample synthesis, structural and compositional characterization, thermal property measurements, and inelastic neutron scattering. Generic procedures and instrument specifications are given here. Material-specific parameters, nominal compositions, precursor excesses, sintering temperatures, and similar details, are reported in the relevant results chapters.

2.1 Sample Synthesis

Polycrystalline samples were prepared by solid-state reaction. Single crystals were grown from polycrystalline feed rods using the optical floating zone technique. The following subsections describe the generic protocols used for both routes and the Archimedes method used to measure the density of sintered pellets.

2.1.1 Solid-State Reaction

Polycrystalline oxide solid electrolytes were synthesized by a conventional solid-state reaction. The starting materials were high-purity oxides, carbonates, or ammonium salts of the constituent cations. Precursor powders were weighed according to the nominal target composition. An excess of the volatile alkali-metal carbonate precursor, such as Li_2CO_3 or Na_2CO_3 , was added when required to compensate for alkali loss during high-temperature processing. The exact excess used for each composition is reported in the corresponding results chapter.

Depending on the material, the weighed powders were either thoroughly ground or mixed with ethanol and ball-milled for several hours to ensure homogeneous mixing. When wet milling was used, the resulting slurry was dried overnight in an oven at approximately 80 °C until all solvent had evaporated. The dried cake or mixed powder was ground manually in an agate mortar to produce a fine, homogeneous powder.

The mixed powder was then calcined in air at an elevated temperature to drive off CO₂ (from carbonate precursors) and to promote solid-state reaction between the constituent oxides. Calcination temperatures and durations were chosen based on the target phase and are specified in the results chapters. After calcination, the reacted powder was reground to break up any agglomerates.

The powder was uniaxially cold-pressed into pellets under pressures of about 300 MPa. For isostatic pressing of cylindrical rods used in floating zone growth, hydraulic oil was used as the pressure-transmitting medium at pressures of about 30 MPa. The green pellets or rods were then sintered in air at a temperature close to the solidus of the target compound. To minimize alkali loss during sintering, pellets were either covered with sacrificial mother powder of the same composition or enclosed in a crucible with a tight-fitting lid. Heating and cooling rates were typically 1 °C min⁻¹ to 5 °C min⁻¹ to avoid thermal shock.

For density measurement, the bulk density of each sintered pellet was measured by the Archimedes method. The mass of the pellet was first measured in air (m_{air}). The pellet was then suspended in the immersion liquid (deionized (DI) water or isopropanol) and weighed while fully submerged (m_{liq}). The bulk density was calculated as

$$\rho = \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{liq}}} \rho_{\text{liq}}, \quad (2.1)$$

where ρ_{liq} is the density of the immersion liquid at the measurement temperature. The theoretical density ρ_{th} was computed from the lattice parameters and unit-cell content obtained by Rietveld refinement (Section 2.2.1). The porosity was then estimated as

$$\Phi = 1 - \frac{\rho}{\rho_{\text{th}}}. \quad (2.2)$$

The porosity enters the correction of the measured thermal conductivity to the intrinsic solid value, as discussed in the results chapters.

2.1.2 Floating Zone Crystal Growth

Single crystals were grown by the optical floating zone method. Polycrystalline feed material was first prepared by solid-state reaction as described in Section 2.1.1. The reacted powder was loaded into a thin rubber tube, evacuated, and pressed into cylindrical rods using a cold isostatic press. The as-pressed rods had diameters of 5 mm to 7 mm and lengths of 50 mm to 70 mm. The rods were then pre-sintered in air at a temperature slightly below the final sintering temperature to improve their mechanical strength and to reduce shrinkage during growth.

Crystal growth was carried out in an optical image furnace (Quantum Design IRF01-001-05, two-mirror configuration) equipped with two 1000 W halogen lamps. The feed rod and a seed rod were mounted on the upper and lower shafts of the furnace, respectively. The lamps focused infrared radiation onto a small volume of the feed rod, forming a molten zone that was held in place by surface tension. By translating the feed and seed rods downward at a controlled rate, the molten zone swept along the feed rod, and a single crystal solidified from the melt at the trailing edge of the zone. Figure 2.1 schematically illustrates this floating zone growth process.

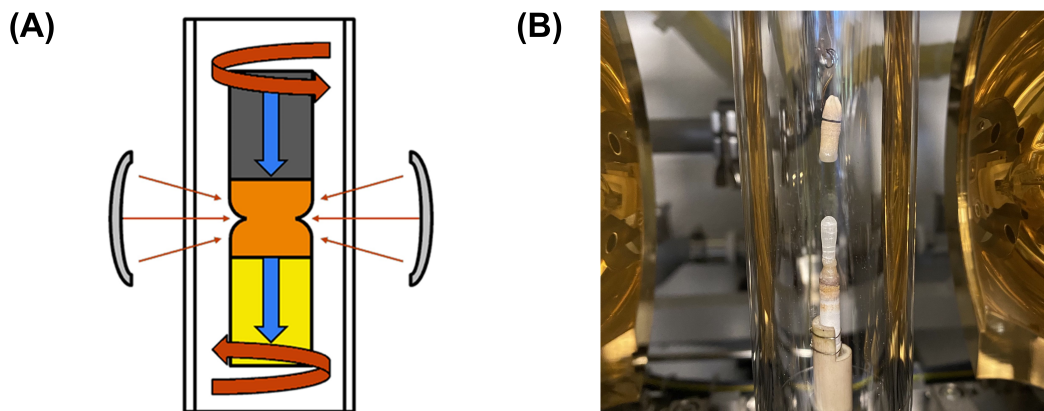


Figure 2.1: Optical floating zone single-crystal growth schematic. Optical floating zone single-crystal growth. (A) Schematic of the feed rod, molten zone, and growing crystal during floating zone growth. (B) Photograph of the growth chamber.

The key operating parameters were the growth rate, the atmosphere, and the rotation rates of the two shafts. Growth rates were in the range of 1 mmh^{-1} to 15 mmh^{-1} , depending on the material system. Growths were performed under dried air flow of about 5 Lmin^{-1} to 10 Lmin^{-1} to maintain oxygen stoichiometry and to flush away evaporated volatile species that would otherwise deposit on the quartz growth chamber and destabilize the molten zone. The feed and seed rods were counter-rotated at rates of 10 rev min^{-1} to 30 rev min^{-1} to promote mixing in the melt and to maintain a symmetric zone shape. Material-specific growth conditions are reported in the corresponding results chapters.

After growth, the as-grown boules were characterized using backscattering Laue X-ray diffraction to identify the crystallographic orientation. Oriented slices were then cut from the boule using a diamond saw. The cut surfaces were polished with aluminum oxide sandpaper down to approximately $0.3 \mu\text{m}$ grit for subsequent surface-sensitive characterization. Bar-shaped specimens for thermal transport measurements were cut to the geometry required by the Physical Property Measurement System (Section 2.3.1).

2.2 Structural and Compositional Characterization

2.2.1 X-Ray Diffraction and Rietveld Refinement

Powder X-ray diffraction (XRD) was used to confirm phase purity and to refine the crystal structure of the synthesized samples. Measurements were performed on a laboratory diffractometer with a Cu $K\alpha$ source ($\lambda = 1.54 \text{ \AA}$) operating in Bragg-Brentano geometry. Samples were prepared either as finely ground powder on a low-background sample holder, or as a polished sintered pellet mounted in a standard holder. Patterns were typically collected over a broad 2θ range of about 10° to 80° , with a step size of about 0.02° and counting times of about 1 min to 2 min to achieve a signal-to-noise ratio adequate for Rietveld refinement.

Rietveld refinement of the collected patterns was performed using GSAS-II [65]. A literature structural model was used as the starting point, with the background described by a shifted 5-term Chebyshev polynomial and the peak profile modeled by a pseudo-Voigt function. Refined parameters included the instrument factors, lattice constants, atomic positions (when allowed by symmetry), isotropic thermal displacement parameters. The quality of the refinement was assessed using the weighted profile reliability factor R_{wp} and the goodness-of-fit χ^2 . The refined lattice parameters were also used to compute the theoretical density ρ_{th} required for the porosity analysis (Equation 2.2).

High-temperature XRD measurements were performed on a similar instrument equipped with a high-temperature XRD stage. Patterns were collected in air over material-specific temperature ranges, for example 323 K to 523 K for LLZTO. The refined lattice parameter $a(T)$ was used to extract the linear thermal expansion coefficient $\alpha_l(T)$ from the definition $\alpha_l = (1/a)(da/dT)$, as described in the relevant results chapters.

2.2.2 Scanning Electron Microscopy and Energy-Dispersive Spectroscopy

The microstructure and chemical composition of the sintered pellets were examined by field-emission scanning electron microscopy (SEM). Two kinds of surfaces were imaged: fracture surfaces, which reveal the grain morphology and intergranular porosity; and polished surfaces, which permit quantitative measurement of pore fraction and EDS mapping of the bulk microstructure. Polished surfaces were prepared using successive aluminum oxide sandpaper down to approximately 0.3 μm grit. Non-conductive samples were sputter-coated with a thin layer of carbon or gold (5 nm to 10 nm) to prevent charging.

Imaging conditions were selected according to the sample conductivity and the feature size of interest. The average grain size was estimated by the linear-intercept method applied to calibrated SEM micrographs. Energy-dispersive X-ray spectroscopy (EDS) was performed using a silicon-drift detector attached to the SEM column. Point spectra, line scans, and two-dimensional elemental maps were collected to assess elemental composition and spatial homogeneity. The EDS yields semiquantitative atomic ratios with a typical uncertainty of a few percent, sufficient for confirming nominal stoichiometry and for identifying secondary phases.

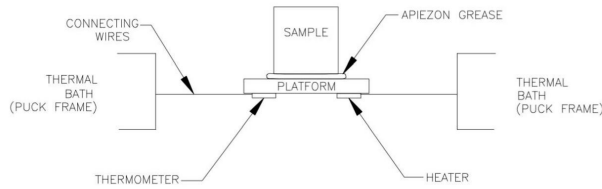
2.3 Thermal Property Measurements

2.3.1 Heat Capacity Option with Physical Property Measurement System

Low-temperature thermal measurements were performed on a Quantum Design Physical Property Measurement System (PPMS), generally over a range of approximately 2 K to 400 K, with the exact range depending on the measured property and material. The PPMS provides a cryostat with active temperature control and a high-vacuum sample space, which

together allow specific heat and thermal conductivity to be measured with minimal radiative losses.

(A)



(B)

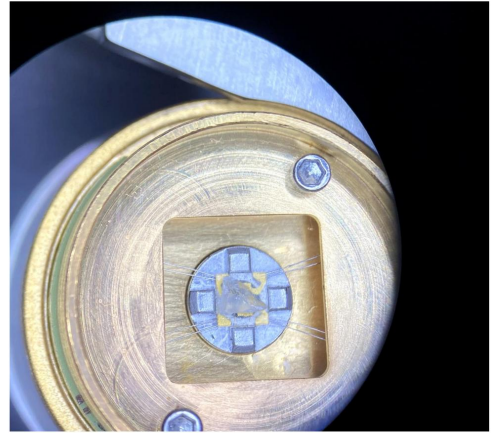


Figure 2.2: Heat-capacity relaxation method and sample mounting. (A) Schematic of thermal relaxation method: heat pulse applied, temperature decay measured, sample contribution extracted [9]. (B) Sample mounted on PPMS heat-capacity puck.

For specific heat measurements, the specific heat at constant pressure (C_p) was measured using the thermal relaxation method in the PPMS. The sample was mounted on the calorimeter puck to ensure good thermal contact, and an addenda measurement was collected before the sample measurement. The addenda contribution was subtracted from the total heat capacity measured with the sample in place.

Figure 2.2 illustrates the relaxation method and shows a representative heat-capacity puck with a mounted sample. The uncertainty on C_p is typically about 3-5% over most of the measured range, increasing at the lowest temperatures where the addenda contribution becomes comparable to that of the sample.

Low-Temperature Heat Capacity Analysis

At sufficiently low temperature, the heat capacity was also analyzed by plotting C_p/T versus T^2 and fitting the data to a straight line. This procedure follows from the same low-temperature relation[66]:

$$C_p(T) = \frac{12\pi^4 k_B N}{5\rho V} \left(\frac{T}{\theta_D} \right)^3 + \lambda T, \quad (2.3)$$

so that

$$\frac{C_p}{T} = \lambda + \frac{12\pi^4 k_B N}{5\rho V} \frac{T^2}{\theta_D^3}. \quad (2.4)$$

In this expression, λ captures the linear contribution, while the T^3 term is the leading phonon contribution predicted by the Debye model. In a plot of C_p/T versus T^2 , the slope is proportional to θ_D^{-3} and the intercept is λ , from which we can extract the Debye temperature θ_D .

For the oxide solid electrolytes studied in this dissertation, which are primarily insulating, the intercept λ was typically small and the slope was used to extract the Debye temperature, allowing direct comparison with the thermal-analysis values reported in the results chapters.

2.3.2 Thermal Transport Option with Physical Property Measurement System

Thermal conductivity (κ) was measured using the Thermal Transport Option (TTO) of the PPMS, which implements a steady-state four-probe technique. Bar-shaped samples were cut to typical dimensions of about $2 \text{ mm} \times 2 \text{ mm} \times 10 \text{ mm}$, with the exact geometry adjusted for the PPMS thermal transport puck. Four gold-coated copper leads were attached to the sample with silver epoxy: one lead at each end served as the heater and heat sink, and two leads defined a central temperature-gradient region. A known electrical power $\dot{Q}$ was

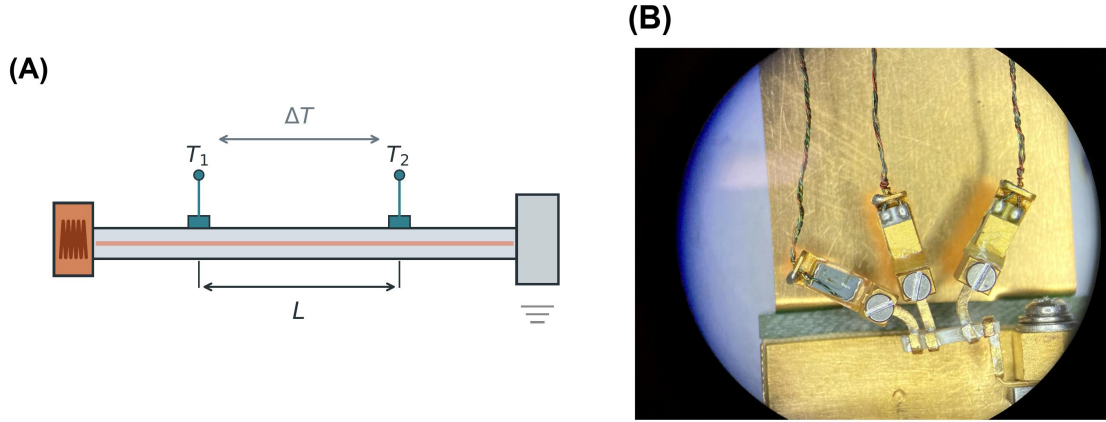


Figure 2.3: TTO measurement principle and sample mounting. (A) Four-probe steady-state geometry: heat applied at one end, sunk at opposite end, temperature difference measured over separation L . (B) Sample mounted on TTO puck with gold-coated copper leads and silver-epoxy contacts.

applied through the heater, and the steady-state temperature difference ΔT between the two intermediate thermometers was measured after the sample had equilibrated. The thermal conductivity was then computed from Fourier's law:

$$\kappa = \frac{\dot{Q} L}{\Delta T A}, \quad (2.5)$$

where L is the separation between the two thermometers and A is the sample cross-sectional area. Figure 2.3 summarizes the measurement geometry and shows a representative mounted sample.

The uncertainty on κ is typically about 5% at low temperatures and increases to about 10-20% near room temperature due to radiative losses from the heater and sample surfaces.

Thermal Transport Fitting and Analysis

The measured thermal conductivity was analyzed using a common set of phenomenological models. The purpose of this analysis was to place the measured $\kappa(T)$ values on the same basis before comparing different materials and sample forms.

Porosity Correction

For porous pellets, the measured thermal conductivity was first corrected to the solid value κ_s using the Maxwell-Eucken relation [67, 68]:

$$\kappa_s = \kappa \frac{\kappa_p + 2\kappa_s - \Phi(\kappa_p - \kappa_s)}{\kappa_p + 2\kappa_s + 2\Phi(\kappa_p - \kappa_s)}, \quad (2.6)$$

where κ is the measured thermal conductivity, κ_p is the thermal conductivity of the pores, and Φ is the porosity. For measurements performed under high vacuum, κ_p was taken to be zero. The porosity-corrected value was then compared with the Cahill minimum thermal conductivity [69],

$$\kappa_{\min} = \frac{\pi^{1/3}}{6} k_B \left(\frac{N}{V} \right)^{2/3} 3v_b \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx, \quad (2.7)$$

where N/V is the atomic number density, v_b is the average sound velocity, and θ_D is the Debye temperature. This comparison provides a reference for assessing whether the measured thermal conductivity approaches the amorphous-limit value.

Phonon Mean Free Path Calculation

At temperatures well below θ_D , the average phonon mean free path ℓ was estimated from the Debye approximation [70]:

$$\ell = \kappa_s \left[\frac{k_B^4 T^3}{2\pi^2 v_b^2 \hbar^3} \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \right]^{-1}. \quad (2.8)$$

This estimate was used only as an average transport length scale, rather than as a mode-resolved phonon lifetime.

Two-Channel Model Analysis

For selected materials with weak temperature dependence in κ , the full $\kappa(T)$ curve was fitted using an analytical two-channel model [14]. The model separates lattice thermal conductivity into a low-frequency propagon contribution and a high-frequency diffuson contribution:

$$\kappa_L(T) = \kappa_{\text{pr}}(T) + \kappa_{\text{diff}}(T). \quad (2.9)$$

The propagon term describes phonon-gas transport below the Ioffe-Regel limit:

$$\kappa_{\text{pr}}(T) = nk_B \int_0^{\omega_{\text{IR}}} \frac{g(\omega)}{3n} C(\omega, T) v_s^2 \tau(\omega, T) d\omega, \quad (2.10)$$

where n is the atomic density, $g(\omega)$ is the vibrational density of states, v_s is the sound velocity, and τ is the propagon lifetime. The lifetime was parameterized as

$$\tau^{-1}(\omega, T) = C_1 \omega^2 T + A\omega + C_2 \omega^4, \quad (2.11)$$

where C_1 , A , and C_2 represent phonon-phonon, boundary, and point-defect scattering terms, respectively. The diffuson term describes non-propagating energy transfer above the Ioffe-Regel limit:

$$\kappa_{\text{diff}}(T) = \frac{n^{1/3}k_B}{\pi} \int_{\omega_{\text{IR}}}^{\infty} \frac{g(\omega)}{3n} C(\omega, T) P \omega d\omega, \quad (2.12)$$

where P is a fitted diffuson parameter that represents the average strength of energy transfer between nearby vibrational modes. The spectral heat-capacity factor $C(\omega, T)$ follows Agne *et al.* [58]:

$$C(\omega, T) = \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}. \quad (2.13)$$

The cutoff frequency ω_{IR} was estimated from the Debye frequency as

$$\omega_{\text{IR}} = \omega_D N^{1/3}, \quad (2.14)$$

where N is the number of atoms in the primitive unit cell and $\omega_D = (6\pi^2 n)^{1/3} v_s$.

In practice, the measured $\kappa(T)$ curve was fitted by evaluating the propagon and diffuson integrals over the vibrational density of states and optimizing the adjustable parameters. Material-specific values of ω_{IR} and the fitted parameters are reported in the corresponding results chapters.

2.3.3 Differential Scanning Calorimetry

High-temperature specific heat was measured using differential scanning calorimetry (DSC) on two complementary instruments: a Netzsch DSC 214 Polyma and a Netzsch DSC 404. Both instruments operate in heat-flux mode, in which the temperature difference between the sample crucible and a reference crucible is recorded as both are subjected to a common temperature program. Measurements typically began near room temperature

(about 300 K) and extended up to about 960 K, with heating rates of about 10 K min⁻¹ to 20 K min⁻¹.

For specific heat determination, the three-curve method was used. In sequence, a baseline curve (empty crucibles), a reference curve (with a sapphire standard), and a sample curve were collected under identical conditions. The specific heat of the sample was then obtained by scaling the heat-flow ratios against the known C_p of the sapphire standard. Samples were loaded in alumina crucibles and measured under a protective gas flow of ultra-high-purity Ar or N₂ to prevent oxidation and moisture uptake. The typical uncertainty on C_p obtained by DSC is approximately 5% in this temperature range.

2.3.4 Laser Flash Analysis

High-temperature thermal conductivity (κ) was determined using a Netzsch LFA 457 laser-flash apparatus. Thermal diffusivity (α) was measured over the material-dependent high-temperature range (typically 300 K to 825 K), and κ was calculated from

$$\kappa = \alpha C_p \rho, \quad (2.15)$$

where C_p is the specific heat (from DSC or PPMS as appropriate) and ρ is the bulk density measured by the Archimedes method (Section 2.1.1). Samples were coated with a thin graphite layer when necessary to ensure uniform absorbance and emissivity, and were measured under inert gas or vacuum to minimize convective losses. The temporal response was analyzed using standard laser-flash routines appropriate to the sample geometry and heat-loss conditions. Typical uncertainties on α are about 3–5%, propagating to a similar uncertainty on κ when combined with C_p and density uncertainties.

2.4 Inelastic Neutron Scattering

Inelastic neutron scattering (INS) was used to characterize both the phonon dispersion and the ionic dynamics of selected samples. Two complementary classes of spectrometers were employed: triple-axis spectrometers, which measure the dynamical structure factor $S(\mathbf{Q}, E)$ at a single $(\mathbf{Q}, E)$ point at a time with high energy resolution, and time-of-flight spectrometers, which survey a wide range of $(\mathbf{Q}, E)$ simultaneously. Quasielastic neutron scattering (QENS), a specialization of either geometry focused on the low-energy region around the elastic line, was used to probe diffusive ionic motion. Figure 2.4 shows the instrument geometries used for these measurements.

2.4.1 Triple-Axis Spectrometry

Triple-axis measurements were performed on the HB-3 thermal triple-axis spectrometer (TAX) at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). In a triple-axis spectrometer, the incident neutron energy is selected by Bragg reflection from a monochromator crystal. The selected neutrons are scattered by the sample mounted on a goniometer, and the final neutron energy is selected by a second Bragg reflection from an analyzer crystal before detection. The three axes, monochromator, sample, and analyzer, can be rotated independently to access any point in the four-dimensional $(\mathbf{Q}, E)$ phase space allowed by the kinematic conditions [11].

Phonon dispersion measurements were carried out in constant- $\mathbf{Q}$ scan mode, in which the momentum transfer $\mathbf{Q}$ is held fixed while the energy transfer E is scanned. A fixed final neutron energy of $E_f = 14.7$ meV was used, with pyrolytic graphite (PG) monochromator and analyzer crystals and a PG filter in the scattered beam to suppress higher-order harmonics. The single-crystal sample was oriented with a selected crystallographic plane

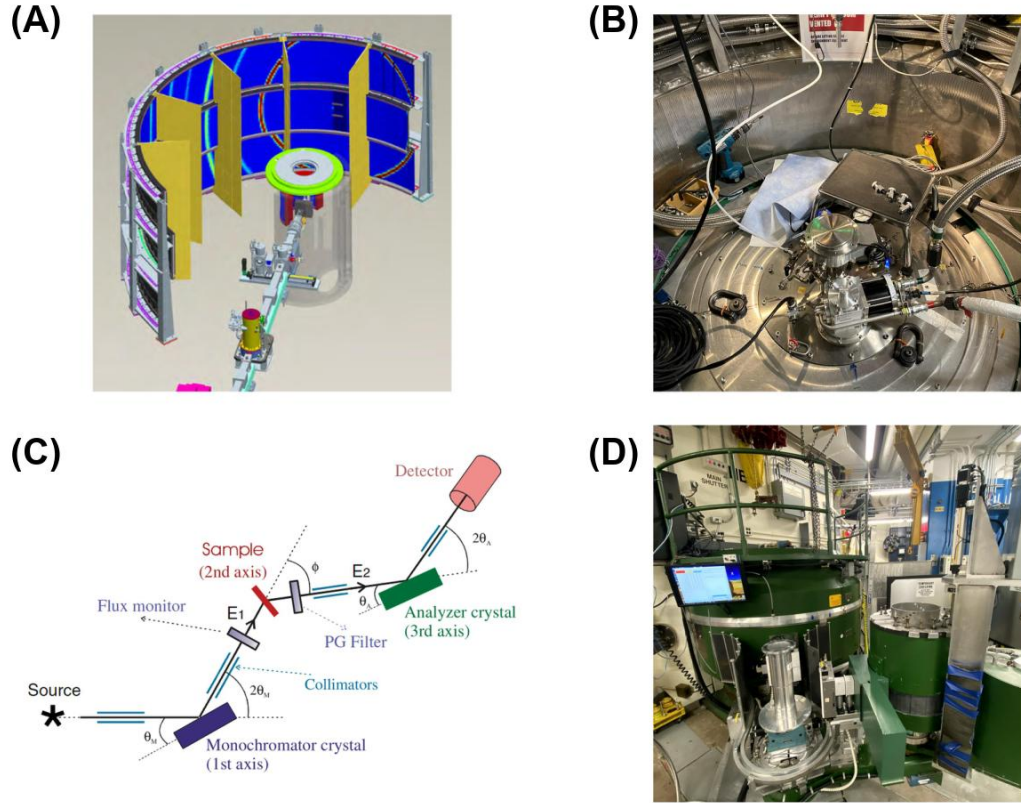


Figure 2.4: Triple-axis and time-of-flight neutron scattering instruments. (A) Wide Angular-Range Chopper Spectrometer (ARCS) time-of-flight spectrometer schematic at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) [10]. (B) ARCS photograph showing position-sensitive detector array. (C) Triple-axis spectrometer layout with monochromator, sample, and analyzer stages [11]. (D) HB-3 thermal triple-axis at HFIR.

horizontal, and scans were taken from chosen reciprocal lattice points along high-symmetry directions.

The structure factor for one-phonon scattering scales as $|\mathbf{Q} \cdot \mathbf{e}|^2$, where $\mathbf{e}$ is the phonon polarization vector. This selection rule was exploited to distinguish between predominantly transverse and predominantly longitudinal acoustic modes by choosing $\mathbf{Q}$ points with $\mathbf{Q} \cdot \mathbf{e}$ parallel or perpendicular to $\mathbf{q}$, respectively.

2.4.2 Time-of-Flight Spectrometry

Time-of-flight (TOF) INS measurements were performed on the Wide Angular-Range Chopper Spectrometer (ARCS) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory [71]. ARCS operates with a pulsed white beam of neutrons that is monochromated by a Fermi chopper synchronized to the source pulse. The incident neutron energy E_i is set by the chopper phase and was chosen in the range of 30 meV to 80 meV depending on the energy window of interest. The final energy of each scattered neutron is determined by its arrival time at a large array of position-sensitive ^3He detectors that cover a wide solid angle around the sample. This geometry allows the full dynamical structure factor $S(\mathbf{Q}, E)$ to be mapped over a large volume of reciprocal space and a broad energy window in a single measurement.

Single crystals were mounted on aluminum holders with a selected crystallographic plane horizontal, oriented with backscattering Laue X-ray diffraction prior to the measurement. The sample was rotated about the vertical axis in angular steps of about 1° to access additional reciprocal-space orientations. The raw TOF data were reduced to $S(\mathbf{Q}, E)$ using the instrument-specific data reduction software and then folded into the crystal's irreducible Brillouin zone to improve statistics.

To compare the experimental $S(\mathbf{Q}, E)$ with density functional theory (DFT) calculations, the neutron-weighted one-phonon structure factor was simulated from the calculated

force constants and eigenvectors using the Euphonic package [72]. Euphonic computes the coherent one-phonon cross section including the $|\mathbf{Q} \cdot \mathbf{e}|^2$ selection rule, the Debye-Waller factor, and the Bose population factor. This simulation allows a direct, quantitative comparison between the measured and calculated dispersion and intensity.

2.4.3 Quasielastic Neutron Scattering

Quasielastic neutron scattering (QENS) probes diffusive atomic motions on picosecond timescales and Ångström length scales [73]. A diffusing atom broadens the elastic line of $S(\mathbf{Q}, E)$ by an energy width that depends on the characteristic jump distance and residence time. For lithium-containing samples, QENS is sensitive to lithium-ion dynamics through the quasielastic broadening associated with diffusive motion.

QENS data were extracted from the low-energy region of the ARCS TOF measurements described in Section 2.4.2. At each selected $\mathbf{Q}$ point, the quasielastic line was fitted using a Gaussian function to represent the instrumental elastic resolution and a Lorentzian function to describe the quasielastic signal. The fitted peak was treated as the convolution of these two functions. For the LLZTO analysis, fitted elastic-resolution widths were approximately 0.4 meV to 0.8 meV; for TAX, the elastic resolution of the specific setup was estimated from sharp elastic peaks to be approximately 0.3 meV. The half width at half maximum (HWHM) of the Lorentzian, $\Gamma_{1/2}(\mathbf{Q})$, was then tracked as a function of $|\mathbf{Q}|$.

The $\Gamma_{1/2}(\mathbf{Q})$ data were analyzed using jump-diffusion models. The Chudley-Elliott model [74] describes diffusion as discrete jumps of fixed length d between well-defined sites with a mean residence time τ :

$$\Gamma_{1/2}(\mathbf{Q}) = \frac{\hbar}{\tau} \left(1 - \frac{\sin(|\mathbf{Q}|d)}{|\mathbf{Q}|d} \right). \quad (2.16)$$

The Singwi-Sjölander model [75] and the single-diffusion model [76] were used as cross-checks. From the fitted hopping distance d and residence time τ , the microscopic diffusivity was estimated as $D_{\text{QENS}} = d^2/6\tau$ and compared with macroscopic diffusivities obtained from ionic-conductivity measurements through the Nernst-Einstein relation.

Chapter 3

Phonon Dispersion and Thermal Transport in Garnet-Type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ Single Crystals

3.1 Introduction

As battery applications push charge-discharge rates and voltages to their limits, increased Joule heating becomes inevitable. The accumulated heat, if not promptly dissipated, can disrupt operational conditions and compromise both performance and safety [23–25]. Thermal management is therefore crucial for controlling the operating temperature of all-solid-state batteries, given the strong effect of temperature on ion transport kinetics and interfacial chemical stability. The rate of heat dissipation and the resulting temperature profile depend critically on the thermal conductivity (κ) of the constituent battery materials [24, 77]. A comprehensive understanding of heat transport mechanisms and accurate characterization of thermal properties are thus pivotal for enhancing the performance and lifespan of next-generation battery systems.

Ion-conducting materials have attracted increasing interest as solid electrolytes that can improve the safety of rechargeable batteries by replacing flammable liquid electrolytes [3, 39, 78, 79]. These materials exhibit well-defined crystalline structures while supporting extensive ionic diffusion over long distances, comparable to the movement of ions in liquid salts [80]. Despite their technological importance, a comprehensive understanding of thermal transport in ionic conductors, which typically exhibit low κ , remains elusive.

Several competing physical pictures have been proposed to explain the low thermal conductivity observed in superionic conductors. The phonon-liquid/electron-crystal (PLEC)

model implies a blockage of shear waves, which has been invoked to explain the breakdown of transverse acoustic (TA) phonons observed above the superionic transition in Cu_2Se [81, 82]. On the other hand, in other superionic conductors such as CuCrSe_2 [83], AgCrSe_2 [84], and Ag_8SnSe_6 [85], the persistence of TA phonons beyond the superionic transition points to a more nuanced selective breakdown picture, in which the anharmonicity of ion-related vibrational modes plays a central role in suppressing κ . Additional mechanisms that have been proposed include weak bonding and low sound velocity [86], low cutoff frequencies of acoustic phonons, and rattling-like thermal damping [87].

Garnet-type ionic conductors based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ are among the most promising solid electrolytes for all-solid-state batteries, owing to their good stability against electrode materials and relatively high ionic conductivity (σ) [29, 88]. In particular, Ta-doped garnet LLZTO exhibits a high σ of $10^{-3} \text{ S cm}^{-1}$ at room temperature [30] (for the full formula, see Chapter 1). Despite extensive studies on ionic transport in garnet-type solid electrolytes, their thermal properties, which play a crucial role in determining overall battery performance, safety, and reliability, remain poorly understood [89–95].

Our previous work on LLZTO polycrystals (Chapter 4) established that the thermal conductivity is low and exhibits glass-like temperature dependence [5], consistent with other reports [3, 13]. However, the presence of grain boundaries and defects in polycrystalline samples can obscure the intrinsic thermal transport properties. To uncover the fundamental mechanisms governing heat conduction in garnet-type solid electrolytes, it is essential to investigate high-quality single crystals, where microstructural imperfections are minimized. Furthermore, while previous neutron scattering studies [93, 96] have focused on crystal structure and ionic transport in garnet-type solid electrolytes, the phonon dispersion of LLZTO, which is essential for understanding phonon dynamics and thermal transport, had not been reported prior to this work.

In this chapter, we present a comprehensive investigation of the heat transport mechanisms and the origin of the intrinsically low κ in LLZTO [6]. We combine single-crystal growth via the floating zone method, thermal and ionic transport measurements, molecular dynamics (MD) simulations, DFT calculations, and INS. The single crystals exhibit remarkably low, glass-like thermal conductivity of $\kappa = 1.59(33) \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K, confirming that the low κ is an intrinsic material property. DFT calculations and INS measurements reveal both acoustic and numerous optical phonon modes, with a low-energy optical branch that exhibits an avoided crossing with acoustic phonons near 7 meV, reducing the group velocity of heat-carrying acoustic modes. The calculated Grüneisen parameters are large, especially for vibrational modes around 6 meV, indicating strong anharmonicity with a noticeable contribution from lithium-ion vibrations. A two-channel thermal transport model, incorporating both propagon and diffuson contributions, successfully describes the weak temperature dependence of κ .

3.2 Crystal Structure and Thermal Conductivity

Single crystals of LLZTO were grown by the floating zone method, following the procedure reported by Kataoka *et al.* [90] with modifications optimized in our laboratory. The starting materials, Li_2CO_3 (99%), La_2O_3 (99.99%), ZrO_2 (99%), and Ta_2O_5 (99%), 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 compensate for lithium volatilization during growth. The mixed powders were fired for 60 h at 1123 K in air. The resulting powder was ground and 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.

Crystal growth was carried out using an optical image furnace (Quantum Design, IRF01-001-05, two-mirror configuration) equipped with two 1000 W halogen lamps. Growth was performed under an air flow of 7 L min^{-1} at a rate of 10 mm h^{-1} . The high airflow rate is critical: it flushes away evaporated lithium that would otherwise deposit on the inner surface of the growth chamber and block the infrared heat input, destabilizing the molten zone. The as-grown crystals have a cylindrical shape with approximate dimensions of 5 mm in diameter and 20 mm in length, and are semitransparent with a characteristic white color (Figure 3.1).

For comparative studies, a polycrystalline LLZTO sample was prepared by spark plasma sintering (SPS) under 50 MPa in vacuum at 1373 K for 15 min [5]. The density of the obtained pellet was $(4.78(2) \text{ g cm}^{-3})$, approximately 89% of the theoretical density.

Figure 3.1 illustrates the crystal structure of LLZTO at room temperature. LLZTO adopts a cubic garnet structure with $Ia\bar{3}d$ symmetry and a lattice parameter of $12.94 \text{ \AA}$, as determined by Rietveld refinement of the X-ray diffraction pattern. The $(\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12})^{6.5-}$ framework contains two kinds of interstitial lithium sites: tetrahedral Li1 sites (Wyckoff position 24d) with approximately 62% occupancy, and octahedral Li2 sites (96h) with approximately 38% occupancy [12]. The higher-occupancy Li1 sites serve as junctions, while the Li2 sites function as pathways within the three-dimensional Li-ion transport network.

The structural relationship between the tetragonal and cubic phases of LLZO is important for understanding the lithium sublattice. During the tetragonal-to-cubic phase transition, a pair of neighboring Li2 sites split from a single octahedral position [90, 97], which accounts for the short distance between Li2 sites in the cubic phase. This splitting creates the partially occupied, disordered lithium network that is responsible for the high ionic conductivity of the cubic garnet.

The phase purity and crystal quality of the single-crystal samples were confirmed using powder X-ray diffraction, backscattering Laue patterns, and elastic neutron scattering. To examine the surface morphology and chemical composition, SEM analysis was conducted on a polished crystal surface (Figure 3.1). No discernible impurities or grain boundaries were observable within the scanning range, confirming the single-crystalline nature of the sample. Energy-dispersive X-ray spectroscopy (EDS) mapping indicated an even distribution of constituent elements with a stoichiometric ratio of La:Zr:Ta = 3.0:1.7:0.5, in good agreement with the nominal composition of 3.0:1.5:0.5.

High-resolution transmission electron microscopy (TEM) revealed lattice fringes with a spacing of approximately 0.52 nm, matching the d -spacing of 0.53 nm for the (211) lattice plane of LLZTO. The selected-area electron diffraction (SAED) pattern further confirmed the monocrystalline nature of the sample.

The thermal conductivity of single-crystal LLZTO was measured using the PPMS TTO (see Section 2.3.1) over the temperature range from 2 K to 300 K. The results are presented in Figure 3.1(F), alongside previously reported data for polycrystalline samples [3, 5, 13].

Because LLZTO is electronically insulating with high resistivity [13], the electronic contribution to thermal transport is negligible. The measured total κ is therefore attributed entirely to the lattice contribution (κ_L). Several notable features emerge from the temperature-dependent data:

First, the single crystal exhibits a κ peak near 22 K, arising from the competition between increasing phonon population (which raises κ) and increasing phonon-phonon scattering (which lowers κ) as temperature rises. In the polycrystalline sample, this peak is significantly suppressed and shifted to higher temperature (~ 50 K) due to enhanced defect and boundary scattering. The average grain size of the polycrystal was determined to be 5.4 μm from SEM analysis.

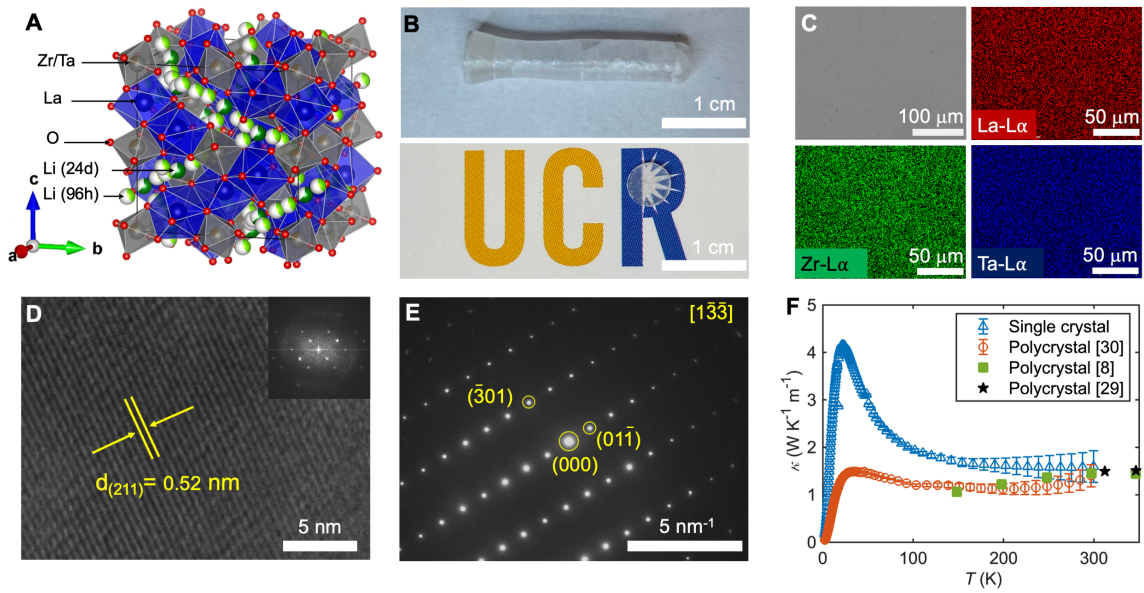


Figure 3.1: Structure and thermal conductivity of LLZTO crystals. (A) Crystal structure of LLZTO (ICSD-894) [12] showing the lithium transport network consisting of two types of lithium sites. (B) Photographs of as-grown LLZTO single crystals produced by the floating zone method. (C) SEM image of a polished LLZTO crystal surface with EDS elemental mapping results. (D) High-resolution TEM micrograph with fast Fourier transform pattern (inset). (E) Selected-area electron diffraction pattern. (F) Thermal conductivity of single-crystal LLZTO compared with polycrystalline data from our previous study [5] and from Cheng *et al.* [3] and Neises *et al.* [13].

At higher temperatures, as the temperature increases above 100 K, the κ of both single-crystal and polycrystalline LLZTO exhibits a remarkably weak temperature dependence, a hallmark of disordered or glass-like materials [98]. This behavior contrasts sharply with conventional crystalline solids, where κ typically decreases as $1/T$ due to Umklapp scattering at elevated temperatures.

Finally, at room temperature, the single-crystal value is only $\kappa = 1.59(33) \text{ W m}^{-1} \text{ K}^{-1}$, intrinsically low and comparable to some of the best thermoelectric materials, including PbTe [99], PbSe [100], and SnSe [101]. The fact that the single crystal, free from grain boundaries and extrinsic defects, still exhibits such low κ demonstrates that the low thermal conductivity is an intrinsic property of the LLZTO lattice rather than an artifact of microstructural scattering.

These observations raise fundamental questions about the underlying mechanisms responsible for the intrinsically low and weakly temperature-dependent thermal conductivity. In the following sections, we address these questions through a combined experimental and computational investigation of the lattice dynamics, phonon anharmonicity, ionic dynamics, and thermal transport channels in LLZTO.

3.3 Lattice Dynamics of LLZTO

To understand the origin of the low κ in LLZTO, we calculated the phonon dispersion relations using density functional theory. The calculations employed the VASP code as backend for electronic structure calculations, with phonon dispersions extracted using Phonopy and hiPhive on a $2 \times 2 \times 2$ supercell containing 1504 atoms. This large supercell is necessary to capture the complex vibrational spectrum of the garnet structure, which contains 188 atoms per primitive unit cell, giving rise to $3 \times 188 - 3 = 561$ optical phonon branches in addition to the 3 acoustic branches, for a total of 564 branches. In practice, due to the par-

tial occupancy of lithium sites and the resulting symmetry reduction in the computational supercell, we obtained 282 branches below 90 meV for the modeled configuration.

Figure 3.2(A) presents the full phonon dispersion along the $[H00]$ direction. The phonon spectrum reveals several important features that are directly relevant to thermal transport.

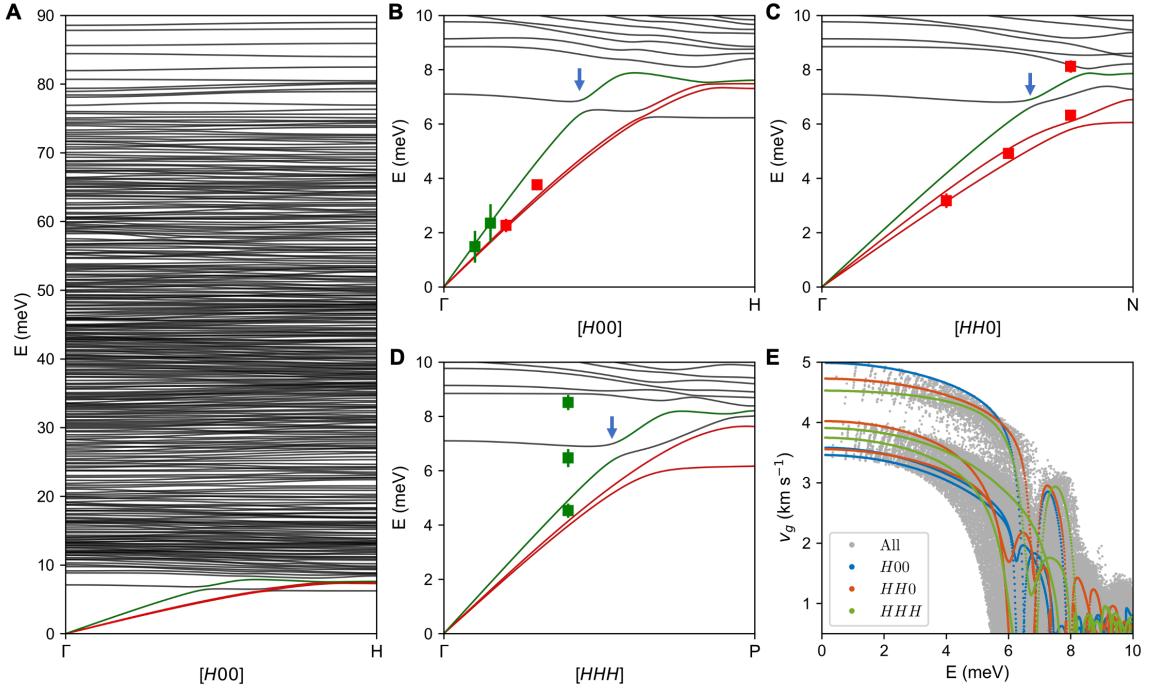


Figure 3.2: Calculated phonon dispersion of LLZTO from DFT. (A) Full harmonic phonon dispersion along $[H00]$ showing all branches up to 90 meV. (B-D) Enlarged views of the low-energy phonon modes along the $[H00]$, $[HH0]$, and $[HHH]$ directions, respectively. Avoided crossings at ~ 7 meV are marked with blue arrows. Square markers represent data collected with the triple-axis spectrometer at ORNL. Acoustic branches and TAX data are categorized by polarization: red for transverse modes and green for longitudinal modes. (E) Group velocity of phonon modes calculated from DFT, with data along the three high-symmetry directions highlighted in color.

The DFT calculations reveal well-defined longitudinal acoustic (LA) and transverse acoustic (TA) phonon branches extending from the zone center up to energies of ~ 7 meV. However, it is important to note that in a complex system with many atoms per unit cell, and for an arbitrary point in the Brillouin zone, acoustic modes can only be labeled as

predominantly longitudinal or transverse. The displacement of individual atoms generally has components both parallel and perpendicular to the wave vector.

The LA modes exhibit group velocities in the range of 4.5 km s^{-1} to 5.0 km s^{-1} , while the TA modes are slower at 3.5 km s^{-1} to 4.0 km s^{-1} . From the low-temperature specific heat analysis using a Debye model [66], we extracted a Debye temperature of 498 K and an average sound velocity of 3781 m s^{-1} , in excellent agreement with the DFT-calculated average sound velocity of 3742 m s^{-1} .

The large and complex crystal structure of LLZTO gives rise to a dense manifold of optical phonon branches above 7 meV. Among these, a particularly important feature is a low-energy optical branch at $\sim 7 \text{ meV}$. As shown in Figure 3.2(B-D), this optical branch exhibits an *avoided crossing* with the LA branch in all three high-symmetry directions ([H00], [HH0], and [HHH]).

The avoided crossing has two important consequences for thermal transport. First, as the phonon energy approaches $\sim 7 \text{ meV}$, there is a pronounced drop in the group velocities of the acoustic modes, as shown in Figure 3.2(E). Since thermal conductivity scales as v^2 in kinetic theory, this velocity reduction directly suppresses the heat-carrying capacity of acoustic phonons. The reduction in phonon group velocity due to avoided crossings has been associated with the suppression of thermal conductivity in several other material systems [102].

Second, the avoided crossing flattens the acoustic branch near the hybridization energy, creating a larger phase space for three-phonon scattering processes [103, 104]. When phonon branches become flat (i.e., when the group velocity approaches zero), many states share similar energies, increasing the probability of finding energy- and momentum-conserving scattering channels. Similar avoided-crossing behavior has been identified as a key contributor to the low κ in several thermoelectric materials [103, 105].

Elemental analysis of this low-lying optical branch reveals a dominant contribution from La atoms. At the Brillouin zone center, the 7 meV optical mode is primarily characterized by localized vibrations of La atoms, which are heptacoordinated by O atoms, with minimal contributions from surrounding atoms. The avoided crossing effectively transfers the flat, La-dominated character of the optical branch onto the LA branch, further suppressing phonon transport.

To experimentally verify the calculated phonon dispersion, we performed inelastic neutron scattering measurements on a LLZTO single crystal using two complementary instruments at ORNL.

For TAX, measurements on the HB3 triple-axis spectrometer used constant- $\mathbf{Q}$ scan mode with a fixed final neutron energy of $E_f = 14.7$ meV. The scans originated from the (008) reciprocal lattice point, and different $\mathbf{Q}$ -points along the $[00L]$, $[HH0]$, and $[HHH]$ directions were selected. The resulting phonon peak positions, shown as markers in Figure 3.2(B-D), demonstrate excellent agreement with the DFT calculations. For a net momentum transfer $\mathbf{Q} = \mathbf{G}_{HKL} + \mathbf{q}$, the INS intensity for a given polarization scales as $|\mathbf{Q} \cdot \mathbf{e}|^2$, where $\mathbf{e}$ is the phonon polarization vector. This selection rule allowed us to distinguish between transverse (red markers) and longitudinal (green markers) modes.

For ARCS time-of-flight spectrometry, the Wide Angular-Range Chopper Spectrometer at the Spallation Neutron Source provided a comprehensive view of the dynamical structure factor $S(\mathbf{Q}, E)$ across a broad range of momentum and energy transfers. The incident neutron energy was 30 meV, with the crystal mounted with the $(H0L)$ crystallographic plane horizontal. To compare with the calculations, we simulated neutron-weighted structure factors using Euphonic.

Figure 3.3 presents the measured $S(\mathbf{Q}, E)$ alongside the calculated results for three slices through reciprocal space, indexed by the reciprocal lattice vectors $\mathbf{G}_{HKL} = (008)$, $(\bar{5}50)$, and $(\bar{6}60)$. Clear TA modes with $\mathbf{q}$ along $[H00]$ and $[HH0]$ are observed in Fig-

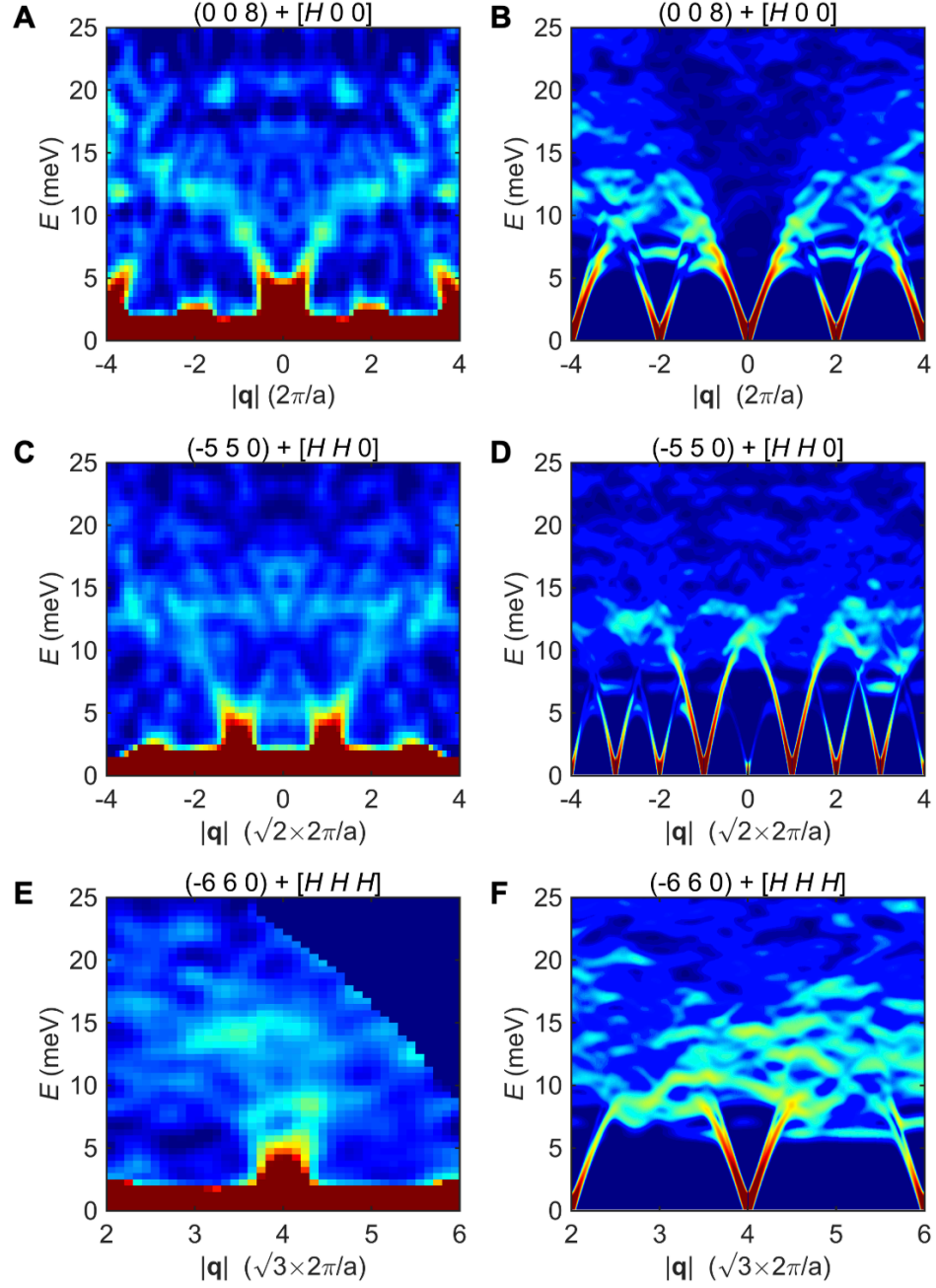


Figure 3.3: Dynamical structure factor $S(\mathbf{Q}, E)$ measured with ARCS compared with DFT simulations for LLZTO at 300 K. (A, C, E) Experimental $S(\mathbf{Q}, E)$ along the $[H00]$, $[HH0]$, and $[HHH]$ directions, respectively. (B, D, F) The corresponding calculated dynamical structure factor from DFT.

ures 3.3A and 3.3C, originating from the zone center at 0 meV and extending to the zone boundary at ~ 7 meV. Along the $[HHH]$ direction, both TA and LA modes are visible, as shown in Figure 3.3E. Optical modes with energies ranging from 10 meV to 25 meV are observed along all three directions, consistent with the DFT calculations. A critically important observation is that the TA modes persist in all three high-symmetry directions. This finding rules out the PLEC mechanism, involving a complete breakdown of transverse phonons, as the explanation for the low κ in LLZTO. Unlike Cu_2Se , where TA phonons are suppressed above the superionic transition [81], the garnet LLZTO maintains well-defined transverse acoustic phonons at room temperature. The origin of its low thermal conductivity must therefore lie in other mechanisms, which we explore in the following sections.

The Raman spectrum of single-crystal LLZTO, measured at 300 K using a 532 nm laser, provides complementary information about the zone-center optical phonon energies. Based on previous Raman studies of LLZTO [96, 106, 107], the La contribution can be identified as the feature centered at 15.3 meV, while the Li contribution exhibits three peaks at 24.8 meV, 46.6 meV, and 63.4 meV in the spectrum. The O contribution appears as two peaks at 33.5 meV and 49.6 meV. These peak positions from Raman spectroscopy agree well with the projected phonon density of states (DOS) calculated using molecular dynamics, as shown in Figure 3.4(B). The phonon DOS was computed as the power spectrum of the velocity autocorrelation function from a 1,000,000-step MD trajectory using a neural-network potential. The phonon cutoff energy is approximately 100 meV. Overall, the phonon modes are dominated by Li and O vibrations, while the vibrations of Zr, Ta, and La contribute primarily to modes below ~ 20 meV.

The temperature dependence of the specific heat (C_p) of single-crystal LLZTO was measured using two complementary techniques: the PPMS (see Section 2.3.1) from 1.8 K to 381 K and DSC (see Section 2.3.3) from 294 K to 800 K. As shown in Figure 3.4(C), both datasets exhibit a consistent and continuous trend with no indication of a first-order

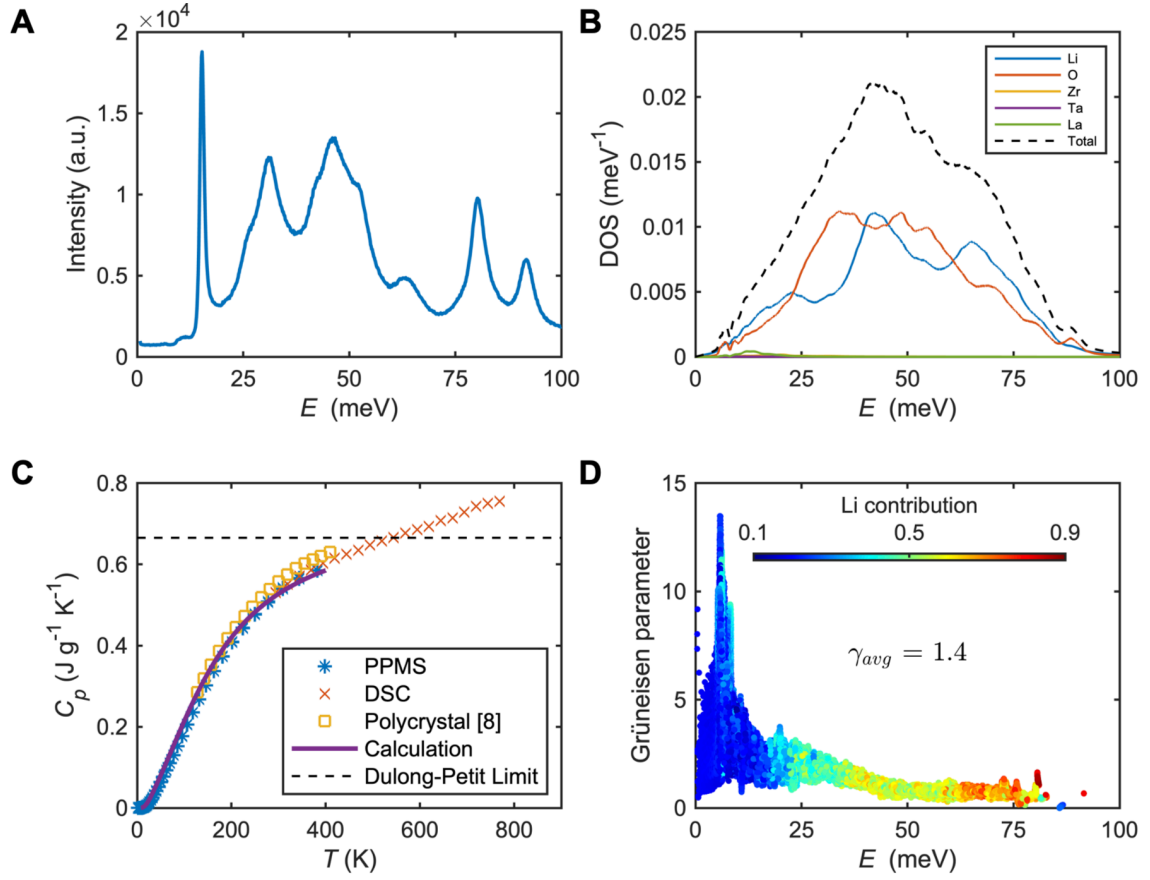


Figure 3.4: Raman spectrum, phonon density of states (DOS), specific heat, and Grüneisen parameter of LLZTO. (A) Raman spectrum of single-crystal LLZTO at 300 K. (B) Phonon DOS calculated by MD simulation showing element-projected contributions. (C) Specific heat measured experimentally and calculated using DFT, compared with data from Cheng *et al.* [3]. (D) Grüneisen parameter (γ) calculated for different phonon modes using DFT, with colormap indicating lithium atom contribution.

phase transition up to 800 K. The measured data agree well with prior reports by Cheng *et al.* [3].

The calculated phonon contribution to the specific heat shows excellent agreement with the experimental data from 8 K to 400 K. This agreement can be attributed to the electronically insulating nature of LLZTO: because there are no free carriers, the specific heat is well described by considering only the phonon contribution. The low-temperature C_p data were analyzed using a Debye model [66], yielding a Debye temperature of $\theta_D = 498$ K and an average sound velocity of 3781 m s^{-1} , in agreement with the DFT value of 3742 m s^{-1} .

The Grüneisen parameter (γ) quantifies the anharmonicity of phonon modes by relating the shift in phonon frequency to changes in lattice volume. Large values of γ indicate that the interatomic potential deviates substantially from the harmonic approximation, leading to strong phonon-phonon scattering and reduced thermal conductivity.

The mode-resolved γ calculated via DFT is presented in Figure 3.4(D). Several striking features emerge:

First, the Grüneisen parameter reaches a remarkable peak value of 13.5 near 6 meV, far exceeding the typical values found in conventional crystalline materials. This sharp peak aligns with the flat phonon bands arising from the avoided crossing discussed in Section 3.3, suggesting that phonon hybridization between the low-lying optical branch and acoustic phonons enhances the anharmonicity in this energy region.

Beyond this peak, the Grüneisen parameter maintains a baseline of approximately 2.0 for phonons below 30 meV, with an average value of $\gamma_{\text{avg}} = 1.4$. This average value is consistent with experimental Grüneisen parameters of 1.3-1.6 derived from the thermodynamic properties of LLZO-based compounds [5, 108–111], supporting the reliability of the calculation.

In addition, analysis of the Li character of individual phonon modes reveals an anomalous feature near the 6 meV peak. While the Li contribution to phonon modes is generally

low at low energies and increases at higher energies, the modes at ~ 6 meV exhibit a significantly higher Li contribution than other low-energy modes. This localized enhancement suggests that lithium dynamics play a critical role in amplifying anharmonic scattering in the vicinity of the avoided crossing. The coupling between Li vibrations and framework modes near this energy creates an effective channel for phonon scattering that is absent in garnet compositions without mobile ions.

These findings are consistent with observations in other ionic conductors. Anharmonic scattering associated with avoided crossings has been reported in Fe_2Ge_3 [112], and Böger *et al.* [1] similarly found that NaSICON-type electrolytes exhibit strong anharmonicities driven by low-frequency Na vibrational modes. This parallel suggests that coupling between mobile-ion vibrations and framework modes may be one recurring mechanism contributing to low κ in some solid electrolytes.

3.4 Ionic Conductivity and Dynamics in LLZTO

To characterize the ionic transport properties of the single crystal, AC impedance measurements were conducted over the temperature range from 233 K to 323 K using a Au/LLZTO/Au symmetric cell configuration. A representative Nyquist plot at 273 K is shown in Figure 3.5(A). The measured ionic conductivity at 295 K is $\sigma = 1.77 \text{ mS cm}^{-1}$, in agreement with the previously reported value of 1.27 mS cm^{-1} for a single crystal [90].

The Arrhenius plot of the ionic conductivity is presented in Figure 3.5(B), yielding an activation energy of 0.484 eV, similar to the reported value of 0.44 eV [90]. Using the measured ionic conductivity and the Nernst-Einstein relation [113], the ionic diffusivity was estimated to be $D_{\text{ionic}} = 1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

Quasielastic neutron scattering (QENS) provides a microscopic probe of atomic diffusion dynamics on picosecond timescales and Ångström length scales [73]. In a QENS

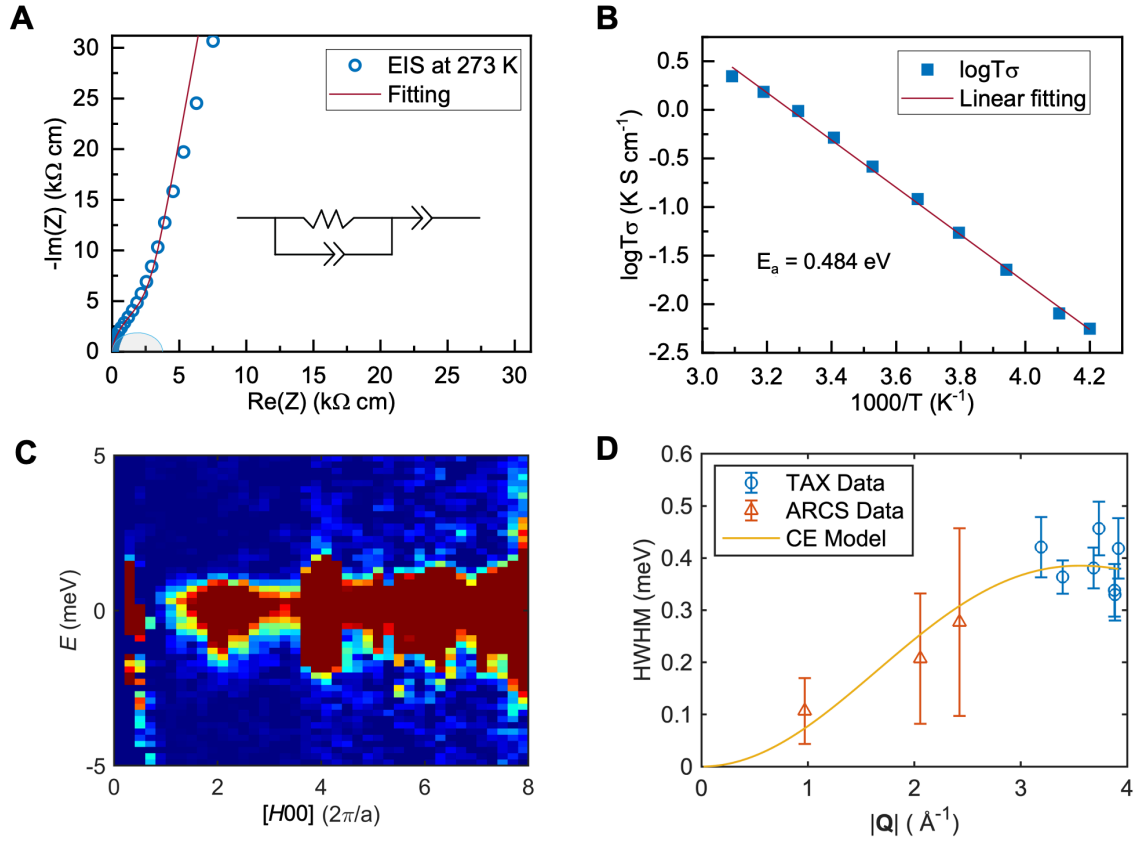


Figure 3.5: Ionic conductivity and dynamics of LLZTO. (A) Nyquist diagram of the single-crystal pellet measured at 273 K through a Au/LLZTO/Au symmetric cell. (B) Arrhenius plot of the ionic conductivity. (C) Dynamical structure factor $S(\mathbf{Q}, E)$ showing an increasing energy width with larger $|\mathbf{Q}|$ along the $[H00]$ direction. The notably large energy width at $\mathbf{Q} = (400)$ is caused by elastic scattering. (D) Chudley-Elliott fitting of the half width at half maximum (HWHM) vs. $|\mathbf{Q}|$.

measurement, the broadening of the elastic line in the dynamical structure factor $S(\mathbf{Q}, E)$ directly reflects the diffusive motion of atoms. For LLZTO, QENS provides a direct way to probe lithium-ion dynamics through the quasielastic broadening associated with diffusive motion.

The $\mathbf{Q}$ - E slice presented in Figure 3.5(C) demonstrates that the energy width of the quasielastic signal increases with rising $|\mathbf{Q}|$, a clear signature of diffusive behavior. Multiple $\mathbf{Q}$ points along the $[H00]$, $[HH0]$, and $[HHH]$ directions were selected for the QENS analysis.

The extracted half widths at half maximum (HWHM), denoted $\Gamma_{1/2}$, are plotted as a function of $|\mathbf{Q}|$ in Figure 3.5(D). The $\Gamma_{1/2}$ - Q relation was fitted to the Chudley-Elliott (CE) model [74], which describes diffusion as a series of discrete jumps between well-defined sites:

$$\Gamma_{1/2}(Q) = \frac{\hbar}{\tau} \left(1 - \frac{\sin(|\mathbf{Q}| d_{\text{CE}})}{|\mathbf{Q}| d_{\text{CE}}} \right), \quad (3.1)$$

where $\hbar$ is the reduced Planck constant, τ is the residence time between hops, and d_{CE} is the average hopping distance. The fitting yielded $\tau = 2.1(2)$ ps and $d_{\text{CE}} = 1.3(3)$ Å. The analysis was cross-validated using the Singwi-Sjölander model and the single-diffusion model [76], both of which gave consistent results.

The fitted hopping distance can be compared with the known lithium site geometry in LLZTO [12]. The distance between Li1 (tetrahedral) and Li2 (octahedral) sites is $d_{12} = 1.51$ Å, while the distance between adjacent Li2 sites is $d_{22} = 1.01$ Å. Each Li1 site connects to each of its four neighboring Li1 sites through a pair of Li2 sites [114]. The numerically weighted average distance between adjacent lithium sites is $d_{\text{avg}} = 1.32$ Å, which agrees well with the CE-fitted value of $d_{\text{CE}} = 1.3$ Å. This agreement indicates that the dominant diffusion process observed by QENS involves hopping between nearest-neighbor lithium sites.

From the hopping parameters, we estimated a QENS diffusivity of

$$D_{\text{QENS}} = \frac{d_{\text{CE}}^2}{6\tau} = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}. \quad (3.2)$$

This value is approximately three orders of magnitude larger than the diffusivity estimated from ionic conductivity ($D_{\text{ionic}} = 1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$) or from MD simulations ($D_{\text{MD}} = 1.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$).

This discrepancy points to the existence of a local fast-hopping mode. Such a mode involves lithium ions hopping back and forth between nearby sites without contributing to long-range diffusion. Because QENS is sensitive to all atomic motion on the relevant timescale, it captures both productive (long-range) and non-productive (local) hops, while ionic conductivity measurements reflect only the net long-range transport. A similar phenomenon was previously observed in Cu_2Se [82], where QENS-derived diffusivities exceeded macroscopic values.

One possible structural explanation invokes the difference between local and average crystal structure. In sodium-ion conductors [115, 116], doping induces a transition in the average structure from tetragonal to cubic symmetry, while the local structure dynamically preserves the tetragonal phase. A similar scenario may occur in LLZTO: although the average structure is cubic $Ia\bar{3}d$, a local tetragonal framework could persist and support fast back-and-forth Li hopping that does not contribute to macroscopic diffusion but broadens the QENS signal.

3.5 Two-Channel Model Analysis of Thermal Transport

In materials with intrinsically low κ , strong phonon scattering and narrow interband spacings fundamentally alter the nature of heat transport. Each phonon branch acquires a

linewidth determined by anharmonicity and defect scattering. When phonon branches are closely spaced in energy and exhibit large linewidths, modes at the same $\mathbf{q}$ -point overlap substantially. Under these conditions, energy transfer between adjacent phonon modes creates a second channel for heat transport, mediated by *diffusons* [2, 55, 59, 103].

Diffusons are fundamentally distinct from *propagons* [57, 117], the conventional gas-like phonon quasiparticles. While propagons carry heat through coherent wave-like propagation with well-defined group velocities, diffusons transport energy through incoherent hopping between vibrational modes. Diffuson-mediated thermal transport has been identified in glasses, strongly disordered materials, and crystalline compounds with complex unit cells [2, 59, 103]. LLZTO, with its disordered lithium sublattice and 282 phonon branches, is a natural candidate for significant diffuson contributions.

We employ the analytical two-channel model developed by Bernges *et al.* [14] to decompose the lattice thermal conductivity into propagon and diffuson contributions, following the formulation summarized in Chapter 2 (Equations 2.9-2.14). Here, n is the atomic density, $g(\omega)$ is the phonon DOS from calculation, v_s is the sound velocity, τ_p is the propagon lifetime, and P describes the average probability of energy transfer between adjacent phonon modes (the “diffuson parameter”).

The boundary between propagon and diffuson regimes is set by the Ioffe-Regel limit [59, 60], which defines the frequency above which the mean free path of a phonon becomes comparable to its wavelength. At this threshold, the concept of a phonon as a propagating wave packet breaks down, and transport transitions from ballistic to diffusive. Using the method described in Chapter 2 (Equation 2.14), the Ioffe-Regel cutoff for LLZTO is $\omega_{\text{IR}} = 7.8 \text{ meV}$, which aligns remarkably well with the energy at which the dense cluster of optical modes appears in the phonon dispersion (above $\sim 8 \text{ meV}$). This correspondence reinforces the physical picture: below 7.8 meV, phonons propagate as

coherent wave packets; above this energy, the closely packed optical modes facilitate diffuson-mediated transport.

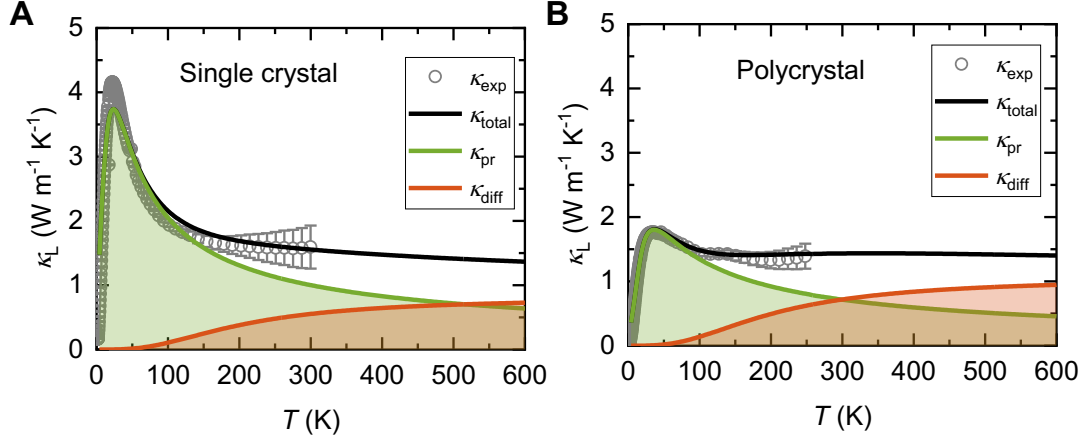


Figure 3.6: Two-channel model analysis of the thermal conductivity. (A) Single-crystal LLZTO showing propagon (κ_{pr}) and diffuson (κ_{diff}) contributions. (B) Polycrystalline LLZTO with the same decomposition. In both cases, the opposing temperature dependences of propagons (decreasing) and diffusons (increasing) produce the observed plateau in total κ above 100 K.

As shown in Figure 3.6, the two-channel model accurately captures the temperature dependence of κ for both the single crystal and the polycrystal. The key findings from the model analysis are:

First, at low temperatures ($T < 200$ K), thermal transport is dominated by propagons, which follow the conventional phonon gas model. As temperature increases, Umklapp scattering intensifies and the propagon contribution decreases. Simultaneously, the diffuson contribution increases as more high-energy modes become thermally populated.

At room temperature, diffusons contribute approximately 30% of the total κ in the single crystal and approximately 50% in the polycrystal. The larger diffuson fraction in the polycrystal arises because grain boundary and defect scattering preferentially suppress

propagons (which require coherent long-range propagation) while leaving diffusons (which involve local energy transfer) largely unaffected.

The origin of the κ plateau is clarified by the opposing temperature dependences of propagons (decreasing with T) and diffusons (increasing with T), which produce a near-cancellation that manifests as the observed plateau in total κ above 100 K. This explains the glass-like thermal conductivity behavior without requiring structural disorder.

Finally, the fitted scattering and diffuson parameters listed in Table 3.1 support this interpretation. The phonon-phonon scattering parameter is comparable between the single crystal and polycrystal, as expected for an intrinsic property of the material. The point-defect term is small in both cases, while the boundary-scattering coefficient is larger in the polycrystal, consistent with stronger microstructural scattering of long-wavelength propagons. The fitted diffuson parameter P remains of the same order in both samples, supporting the view that diffuson-mediated transport is governed primarily by local vibrational-mode coupling rather than long-range grain structure.

Table 3.1: Two-channel model fitting parameters for single-crystal and polycrystalline LLZTO from the supporting analysis of Ref. [6]. Here, C_1 describes phonon-phonon scattering, C_2 describes point-defect scattering, A describes boundary scattering, and P is the diffuson coupling parameter.

Sample	C_1 (10^{-16} s K $^{-1}$)	C_2 (10^{-40} s 3)	A	P
Single crystal	0.1419	5.6×10^{-9}	0.0009	0.5733
Polycrystal	0.1118	9.5×10^{-9}	0.0039	0.7449

This finding is physically intuitive: grain boundaries and defects scatter long-wavelength propagating phonons more effectively than they affect diffusons, which transport energy over shorter, more local length scales.

A significant diffusion contribution to thermal transport has also been reported in NaSICON-type solid electrolytes [1], supporting the generality of this two-channel framework for understanding thermal transport in ionic conductors.

3.6 Summary

This chapter presented a comprehensive investigation of the thermal transport mechanisms in single-crystal LLZTO, revealing the origin of its intrinsically low thermal conductivity. Single-crystal LLZTO exhibits an intrinsically low thermal conductivity of $\kappa = 1.59(33) \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K and a weak temperature dependence above 100 K, deviating from conventional crystalline behavior. Because this behavior is observed in a single crystal, the low κ is an intrinsic material property rather than an artifact of grain boundaries or processing defects.

Phonon band-structure calculations and INS measurements reveal acoustic phonons co-existing with a dense cluster of optical phonon branches, reflecting the complex garnet unit cell with 282 phonon branches below 90 meV. A low-energy optical branch dominated by La vibrations exhibits an avoided crossing with acoustic phonons near 7 meV. This avoided crossing reduces the group velocity of heat-carrying acoustic modes and, together with the many other optical phonons, provides abundant scattering channels for acoustic phonons. At the same time, INS measurements confirm that both TA and LA phonons remain present in the measured crystallographic directions, ruling out the PLEC mechanism based on complete TA phonon breakdown as the origin of the low κ in this garnet-type solid electrolyte.

DFT calculations further show large Grüneisen parameters for the low-energy modes, with a peak of 13.5 near 6 meV and an average value of $\gamma_{\text{avg}} = 1.4$. The peak in anharmonicity coincides with enhanced lithium character in the phonon modes, indicating that

Li dynamics contribute significantly to anharmonic scattering around the avoided-crossing region. Complementary QENS measurements reveal lithium hopping with a residence time of 2.1 ps and a hopping distance of 1.3 Å, consistent with nearest-neighbor site-to-site jumps. The three-order-of-magnitude discrepancy between QENS and macroscopic diffusivity suggests the presence of a local fast-hopping mode that broadens the QENS signal without contributing substantially to long-range ionic transport.

Finally, the measured thermal conductivity can be reproduced by a two-channel model that accounts for contributions from propagons and diffusons. Diffusons contribute $\sim 30\%$ of κ at room temperature in the single crystal and $\sim 50\%$ in the polycrystal, while the opposing temperature dependences of the two channels produce the characteristic κ plateau. Taken together, these results establish that the intrinsically low thermal conductivity of LLZTO arises from its complex crystal structure and strong lattice anharmonicity. The large number of optical phonon modes provides abundant scattering channels for acoustic phonons, while the avoided crossing near 7 meV reduces phonon group velocities. The lithium sublattice disorder and associated anharmonicity further suppress heat transport. These findings offer a framework for understanding thermal conduction in garnet LLZTO and motivate the thermal transport studies shown in the subsequent chapters.

Chapter 4

Thermal Properties, Lattice Anharmonicity, and Aging Effects in Garnet-Type $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ Polycrystals

4.1 Introduction

The successful deployment of all-solid-state batteries hinges not only on achieving high ionic conductivity in the solid electrolyte but also on understanding and managing the thermal properties of each battery component [4, 23]. Among these thermal properties, the thermal conductivity (κ), specific heat (C_p), and thermal expansion coefficient (α) of the solid electrolyte are of paramount importance. The thermal conductivity governs the rate at which internally generated heat, from Joule heating during ion transport and from exothermic side reactions, is dissipated through the electrolyte [3]. If the thermal conductivity of the solid electrolyte is low, as is typical for many ionic conductors, the electrolyte can become a thermal bottleneck that limits the overall heat dissipation of the cell, particularly under high-rate cycling conditions [23]. The resulting temperature gradients can promote inhomogeneous lithium deposition, accelerate degradation at electrode–electrolyte interfaces, and in extreme cases trigger thermal runaway [18, 118].

The specific heat determines how much thermal energy the electrolyte can absorb per unit temperature rise, directly influencing the transient thermal response of the cell during rapid charge–discharge cycles. Meanwhile, the thermal expansion coefficient controls the thermomechanical stresses that develop at the electrode–electrolyte interface during thermal cycling [119]. Because solid-state batteries involve rigid ceramic–ceramic or ceramic–metal interfaces, even modest differences in thermal expansion between the electrolyte

and adjacent components can generate interfacial stresses sufficient to cause delamination, crack formation, or loss of electrical contact. Understanding the thermal expansion behavior is therefore essential for designing mechanically reliable battery architectures.

Despite the critical importance of these thermal properties, systematic characterization of garnet-type solid electrolytes, particularly over a broad temperature range, has been lacking. Prior to this work, only a few studies had addressed the thermal properties of garnet electrolytes. Cheng *et al.* [3] measured the specific heat and thermal conductivity of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ from 150 K to 500 K and observed a low κ of $1.4 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, approaching the calculated minimum value. Neises *et al.* [13] studied the thermal conductivity of Ta^{5+} - and Al^{3+} -doped LLZO with different grain sizes from 300 K to 1225 K and observed that thermal transport is independent of grain size. However, these studies did not analyze the lattice dynamics aspect behind the thermal transport behavior, and the potential aging effects on thermal properties were not explored.

In this chapter, we present a comprehensive investigation of the thermal properties and lattice anharmonicity of LLZTO polycrystals [5]. The thermal conductivity is measured over a wide temperature range from 5 K to 824 K, revealing a peak near 50 K and a weak temperature dependence above 200 K that approaches the calculated minimum thermal conductivity. The average phonon mean free path is extracted from the low-temperature data and reaches approximately 500 nm at 5 K. High-temperature X-ray diffraction measurements from 323 K to 523 K yield the linear thermal expansion coefficient and, together with the measured specific heat and the reported bulk modulus [119], allow us to determine the Grüneisen parameter as $\gamma = 1.63 \pm 0.04$ at 300 K, indicating relatively strong phonon anharmonicity. Finally, the thermal conductivity of aged LLZTO samples is found to increase by 70–80% compared to pristine samples, an unexpected result that is attributed to the formation of Li_2CO_3 impurities with higher thermal conductivity than LLZTO. These

results establish the baseline polycrystalline thermal properties that motivated the single-crystal investigation presented in Chapter 3.

4.2 Phase and Microstructure

Polycrystalline LLZTO samples were synthesized by a conventional solid-state reaction method. The starting materials, Li_2CO_3 (99%), La_2O_3 (99.99%), ZrO_2 (99%), and Ta_2O_5 (99%), 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 20% excess of Li_2CO_3 to compensate for lithium loss during high-temperature processing. The mixture was fired in air at 1123 K for 60 h. The resulting LLZTO powders were cold pressed into pellets under 300 MPa and sintered in LLZTO bed powder at 1173 K for 8 h, designated as sample #1. A second polycrystalline sample (sample #2) was prepared by spark plasma sintering (SPS) under 50 MPa in vacuum at 1373 K for 15 min. The densities of the samples were measured using the Archimedes method.

The purity and crystal structure of the samples were characterized by powder X-ray diffraction with a Cu $K\alpha$ source ($\lambda = 1.54 \text{ \AA}$). The XRD pattern of the LLZTO powder is consistent with the cubic garnet structure with space group $Ia\bar{3}d$, as previously reported [12]. No impurity phases were detected in the diffraction pattern. Rietveld refinement was performed to determine the lattice constant, yielding $a = 12.918(3) \text{ \AA}$, in excellent agreement with the previously reported value of $12.921 \text{ \AA}$ [120]. The reliability parameter of the refinement was $R_{\text{wp}} = 7.94\%$, confirming the quality of the structural model.

The crystal structure of LLZTO is illustrated schematically. LLZTO adopts the cubic garnet framework in which two types of lithium sites, tetrahedral (24d) and octahedral (96h), form a three-dimensional network within a rigid scaffold built from octahedral $\text{Zr/Ta}-\text{O}_6$ and dodecahedral $\text{La}-\text{O}_8$ coordination polyhedra. It is this three-

dimensionally connected lithium sublattice that provides the pathways for fast lithium-ion conduction, while the partial occupancy of the lithium sites in the cubic phase, stabilized by Ta^{5+} doping, creates the vacancies necessary for facile ion migration [30, 121, 122].

The microstructure of the cold-pressed LLZTO pellet was investigated by SEM on a fracture surface. The average grain size was determined to be approximately $8\text{ }\mu\text{m}$. Energy-dispersive X-ray spectroscopy (EDS) mapping confirmed a uniform distribution of La, Zr, and Ta elements throughout the sample. The EDS analysis yielded an atomic ratio of La:Zr:Ta close to the designed stoichiometric ratio of 3.0:1.5:0.5, confirming the homogeneous incorporation of the Ta^{5+} dopant.

The cold-pressed pellet (sample #1) had a porosity (Φ) of 18%, as determined from the ratio of the measured density to the theoretical density of $\rho_{\text{th}} = 5428\text{ kg m}^{-3}$ obtained from the XRD refinement. A second sample prepared by spark plasma sintering (SPS, sample #2) was also used for comparison. As discussed in the following section, porosity has a significant effect on the measured thermal conductivity, which must be corrected to obtain the intrinsic solid thermal conductivity.

4.3 Thermal Property Measurements and Analysis

The specific heat of LLZTO was measured by two complementary techniques: the PPMS (see Section 2.3.1) from 2 K to 276 K, and a Netzsch 404 DSC (see Section 2.3.3) with a sapphire standard from 308 K to 964 K. Both datasets exhibit a consistent and continuous trend with no first-order phase transition observed within the measured temperature range. This is consistent with previous studies showing that sufficient Ta-doping in LLZO stabilizes the cubic phase at room temperature and prevents the tetragonal-to-cubic phase transition [121, 122]. The measured room-temperature specific heat is $C_p = 0.55(1)\text{ J g}^{-1}\text{ K}^{-1}$.

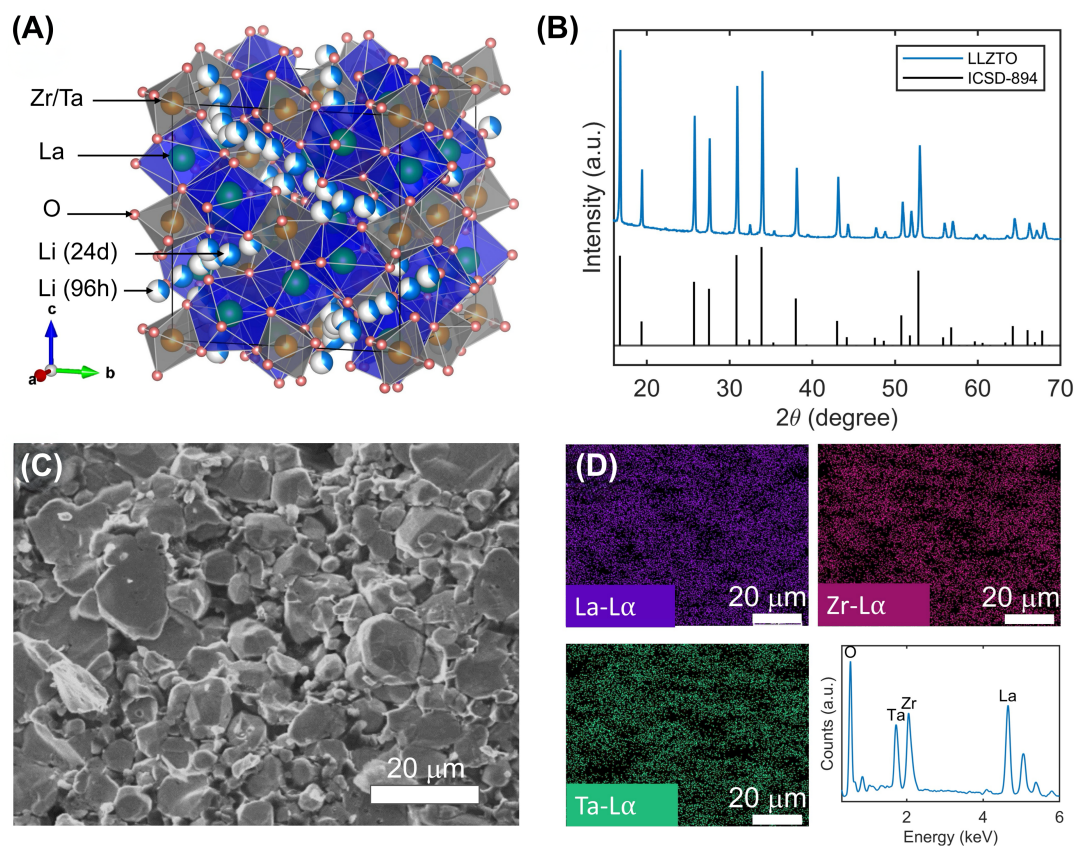


Figure 4.1: Phase and microstructure of LLZTO polycrystals. (A) Cubic LLZTO crystal structure. (B) Rietveld refinement of XRD pattern ($R_{wp} = 7.94\%$). (C) SEM image of fracture surface. (D) EDS elemental mapping showing La, Zr, and Ta distribution.

The low-temperature specific heat data can be fitted to the Debye model:

$$C_p(T) = \frac{12\pi^4 k_B N}{5\rho V} \left(\frac{T}{\theta_D} \right)^3 + \beta T, \quad (4.1)$$

where k_B is the Boltzmann constant, θ_D is the Debye temperature, N/V is the atomic density of the system (estimated as $8.7 \times 10^{28} \text{ m}^{-3}$), ρ is the theoretical density (5428 kg m^{-3}), and β is the coefficient of any electronic contribution to specific heat. The fitting yields a Debye temperature of $\theta_D = 479(1) \text{ K}$, close to the previously reported value of 526 K for $\text{Li}_{6.45}\text{Al}_{0.05}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ [13].

The bulk sound velocity (v_b) is related to the Debye temperature through:

$$\theta_D^3 = \frac{k_B}{\hbar} \left(\frac{6\pi^2 N}{V} \right)^{1/3} v_b, \quad (4.2)$$

where $\hbar$ is the reduced Planck constant. The corresponding bulk sound velocity is calculated as $v_b = 3627(10) \text{ m s}^{-1}$, which agrees reasonably well with the previously reported result of 3953 m s^{-1} for $\text{Li}_{6.45}\text{Al}_{0.05}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ [13] calculated from measured mechanical properties [119]. The room-temperature physical properties of LLZTO polycrystals are summarized in Table 4.1.

Table 4.1: Room-temperature physical properties of LLZTO polycrystals.

κ ($\text{W m}^{-1} \text{ K}^{-1}$)	κ_s ($\text{W m}^{-1} \text{ K}^{-1}$)	C_p ($\text{J g}^{-1} \text{ K}^{-1}$)	θ_D (K)	v_b (km s^{-1})	α_l (10^{-5} K^{-1})	γ
1.2 ± 0.2	1.6 ± 0.3	0.55 ± 0.01	479 ± 1	3.63 ± 0.01	1.59 ± 0.01	1.63 ± 0.04

The thermal conductivity of the cold-pressed LLZTO (sample #1) was measured using the PPMS TTO (see Section 2.3.1) from 5 K to 300 K and by a Netzsch LFA 457 (see Section 2.3.4) from 300 K to 824 K . For the high-temperature measurements, the thermal conductivity was calculated using $\kappa = \rho \alpha C_p$, where α is the thermal diffusivity.

The measured thermal conductivity exhibits several notable features. At low temperatures, the thermal conductivity increases with temperature as the phonon population grows. A peak emerges at approximately 50 K, arising from the competition between increasing phonon population (which raises κ) and increasing phonon–phonon scattering (which lowers κ). Above 200 K, the thermal conductivity shows a remarkably weak temperature dependence, a hallmark of glass-like thermal transport behavior that is commonly observed in materials with complex crystal structures and significant atomic disorder [69].

The room-temperature value of $\kappa = 1.2(2) \text{ W m}^{-1} \text{ K}^{-1}$ is consistent with the reported data for $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ [3] and $\text{Li}_{6.45}\text{Al}_{0.05}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$ [13]. The slightly smaller value of our sample compared to these literature reports can be attributed to its higher porosity. This finding is significant because it suggests that the thermal conductivity of LLZO is nearly independent of the specific chemical substitution employed to stabilize the cubic phase, whether Ta^{5+} , Al^{3+} , or a combination thereof.

It is noteworthy that the temperature dependence of our measured thermal conductivity differs from that reported by Cheng *et al.* [3] for $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$, which exhibits a decrease of thermal conductivity with reduced temperature below 300 K. This discrepancy can be attributed to the different preparation methods used, which result in varying defect concentrations and grain sizes. The monotonic decrease of thermal conductivity with decreasing temperature is commonly observed in highly disordered materials or materials with very small grain sizes [70, 123], where extrinsic scattering dominates over the entire temperature range and no peak emerges.

To obtain the intrinsic thermal conductivity of the solid material, the effect of porosity must be corrected. We employ the Maxwell–Eucken relation introduced in Chapter 2 (Equation 2.6), where κ_s is the solid thermal conductivity, κ_p is the pore thermal conductivity, and Φ is the porosity (18% for the cold-pressed pellet). Since the measurements were conducted under ultra-high vacuum, $\kappa_p = 0$. The resulting porosity-corrected solid thermal

conductivity is $\kappa_s = 1.6(3) \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. The solid thermal conductivity values for both the cold-pressed (sample #1) and SPS (sample #2) samples show good agreement after porosity correction, confirming the validity of this approach.

We further evaluated the minimum thermal conductivity ($\kappa_{\min}$) using the Cahill model summarized in Chapter 2 (Equation 2.7) [69]. This model is formulated upon the Einstein model to compute the minimum lattice thermal conductivity of highly disordered solids. In this model, thermal transport is characterized by the random walk of energy among localized oscillators with varying frequencies, with the primary energy transfer occurring between nearest neighbors. The calculated $\kappa_{\min}$ for LLZTO is $1.07 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. The fact that the porosity-corrected solid thermal conductivity κ_s approaches this calculated minimum value suggests that the phonon mean free path in LLZTO is on the order of atomic spacing at high temperatures, a characteristic of glass-like thermal transport that reflects the strong phonon scattering inherent in the complex garnet crystal structure.

At temperatures significantly lower than θ_D , thermal transport is predominantly governed by acoustic phonons. In this low-temperature regime, the phonon mean free path (ℓ) can be extracted from the measured thermal conductivity using the Debye approximation summarized in Chapter 2 (Equation 2.8) [70]. The phonon mean free path increases with decreasing temperature as phonon–phonon scattering weakens, reaching approximately 500 nm at 5 K. This value is significantly smaller than the measured average grain size of 8 μm , indicating that phonon scattering at grain boundaries is not the dominant mechanism limiting thermal transport at low temperatures. Instead, the primary scattering appears to occur at inhomogeneities or defects within the crystal lattice, consistent with the findings of Neises *et al.* [13] who observed that the thermal conductivity of LLZO is independent of grain size. As the temperature increases, the phonon mean free path decreases due to enhanced phonon–phonon and phonon–defect scattering, reaching a value of approximately 5 nm around 50 K.

These findings provide a quantitative picture of phonon transport in polycrystalline LLZTO. The low thermal conductivity, its weak temperature dependence above 200 K, and the approach to the minimum thermal conductivity all point to the intrinsically strong phonon scattering in the garnet lattice. However, the polycrystalline nature of these samples, with their grain boundaries, porosity, and processing-dependent defects, obscures whether these characteristics are truly intrinsic to the LLZTO lattice or artifacts of the microstructure. This question was addressed in Chapter 3, where we demonstrated that the low, glass-like thermal conductivity persists even in the absence of grain boundaries.

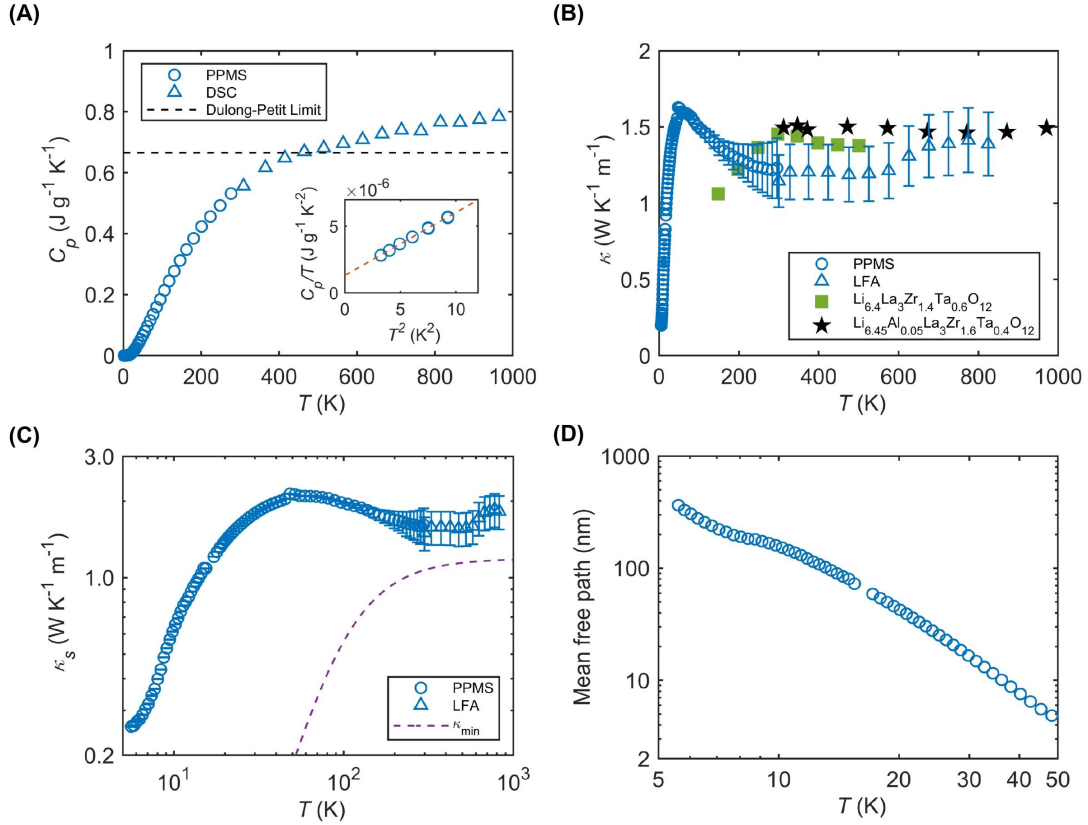


Figure 4.2: Thermal properties and transport analysis of LLZTO polycrystals. (A) Specific heat by PPMS and DSC with low-temperature C_p/T plot. (B) Thermal conductivity by PPMS and LFA with literature comparison. (C) Porosity-corrected thermal conductivity with minimum thermal conductivity limit. (D) Average phonon mean free path.

4.4 Thermal Expansion and Grüneisen Parameter

The thermal expansion coefficient is a fundamental thermophysical property that connects the lattice dynamics to the macroscopic dimensional changes of a material under temperature variation. For solid-state battery applications, knowledge of the thermal expansion coefficient is essential for assessing the thermomechanical compatibility between the electrolyte and adjacent battery components. Mismatches in thermal expansion between the solid electrolyte and electrode materials can generate interfacial stresses during thermal cycling or during the co-sintering processes used to fabricate dense battery cells [119].

To determine the thermal expansion coefficient of LLZTO, we performed high-temperature XRD measurements from 323 K to 523 K. The sample remained stable throughout this temperature range, with no phase transitions observed, consistent with the stabilization of the cubic garnet phase by Ta⁵⁺ doping. The lattice constant a of LLZTO increases monotonically with temperature. We note that the a values for LLZTO lie between those reported for Li₆La₃ZrTaO₁₂ [94] and undoped Li₇La₃Zr₂O₁₂ [109], reflecting the intermediate composition.

The temperature dependence of the lattice constant was fitted by a second-order polynomial [124]:

$$a(T) = a_0 + a_1T + a_2T^2, \quad (4.3)$$

where a_0 , a_1 , and a_2 are fitting parameters. The obtained fitting results are $a_0 = 12.90 \text{ \AA}$, $a_1 = 5.814 \times 10^{-6} \text{ \AA K}^{-1}$, and $a_2 = 3.327 \times 10^{-7} \text{ \AA K}^{-2}$.

According to the definition of the linear thermal expansion coefficient, $\alpha_l \equiv \frac{1}{a} \frac{da}{dT}$, the temperature dependence can be calculated as:

$$\alpha_l(T) = \frac{a_1 + 2a_2T}{a_0 + a_1T + a_2T^2}. \quad (4.4)$$

The linear thermal expansion coefficient of LLZTO increases nearly linearly with temperature from $\alpha_l = (1.71 \pm 0.01) \times 10^{-5} \text{ K}^{-1}$ at 323 K to $(2.72 \pm 0.01) \times 10^{-5} \text{ K}^{-1}$ at 523 K. The α_l near 300 K is similar to the result for $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$ [94], while the reported α_l of undoped LLZO is approximately 18% smaller [109]. Furthermore, our LLZTO sample demonstrates a similar temperature dependence of α_l as $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$, while the α_l of undoped LLZO has a much weaker temperature dependence. Compared to other garnets [125], LLZTO exhibits a thermal expansion coefficient approximately twice as large, indicating unusually large lattice expansion in this solid electrolyte.

The volumetric thermal expansion coefficient (α_V) of LLZTO, which adopts a cubic crystal structure, can be estimated as $\alpha_V = 3\alpha_l$, leading to a value of $(4.77 \pm 0.03) \times 10^{-5} \text{ K}^{-1}$ at 300 K.

One powerful method to assess phonon anharmonicity, the degree to which the interatomic potential deviates from the harmonic approximation, is through the Grüneisen parameter. The thermodynamic Grüneisen parameter relates the thermal expansion, bulk modulus, and heat capacity [126]:

$$\gamma = \frac{\alpha_V B_S}{C_V \rho}, \quad (4.5)$$

where B_S is the adiabatic bulk modulus and C_V is the specific heat at constant volume. The adiabatic bulk modulus was reported as $B_S = 96.0(14) \text{ GPa}$ for LLZO [119]. The C_V of LLZTO was calculated from the measured C_p using the standard thermodynamic relationship [127] and the reported compressibility of LLZO [128], yielding $C_V = 0.52(1) \text{ J g}^{-1} \text{ K}^{-1}$. Using the theoretical density of $\rho = 5.428 \text{ g cm}^{-3}$ determined from the XRD refinement, the calculated Grüneisen parameter is $\gamma = 1.63 \pm 0.04$ at 300 K.

This value is close to the reported Grüneisen parameter of 1.56–1.65 for Nb-doped LLZO [129], providing independent confirmation. To place this value in context, we compare it with other ionic conductors: $\gamma = 0.77$ for Cu_2Se [130] and $\gamma = 1.2$ for

$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [131]. The relatively large Grüneisen parameter of LLZTO indicates strong phonon anharmonicity, that is, a pronounced deviation of the interatomic potential from the simple harmonic form. This strong anharmonicity enhances phonon–phonon scattering, which is one of the primary mechanisms responsible for the low thermal conductivity observed in Section 4.3.

The connection between ionic conductivity and lattice anharmonicity is a subject of growing interest in the solid-state ionics community. It has been found that some superionic conductors also exhibit low thermal conductivity, which is attributed to large phonon anharmonicity [85, 132]. The mobile lithium ions in the garnet lattice may contribute to this anharmonicity by creating a disordered, partially occupied sublattice that breaks the translational symmetry of the lithium network. As shown in Chapter 3, mode-resolved Grüneisen parameter calculations from DFT reveal that the anharmonicity is particularly pronounced for phonon modes near 6 meV, where the lithium-ion vibrational contribution is anomalously enhanced. In order to better understand the phonon properties and the origin of the low thermal conductivity in LLZTO, further research involving phonon dispersion measurements and first-principles calculations on single crystals was performed, as discussed in Chapter 3.

4.5 Effect of Aging on Thermal Conductivity

Garnet-type LLZO and its doped variants are known to be chemically unstable against moisture [133–135]. When exposed to ambient air, lithium ions in LLZTO can be ex-

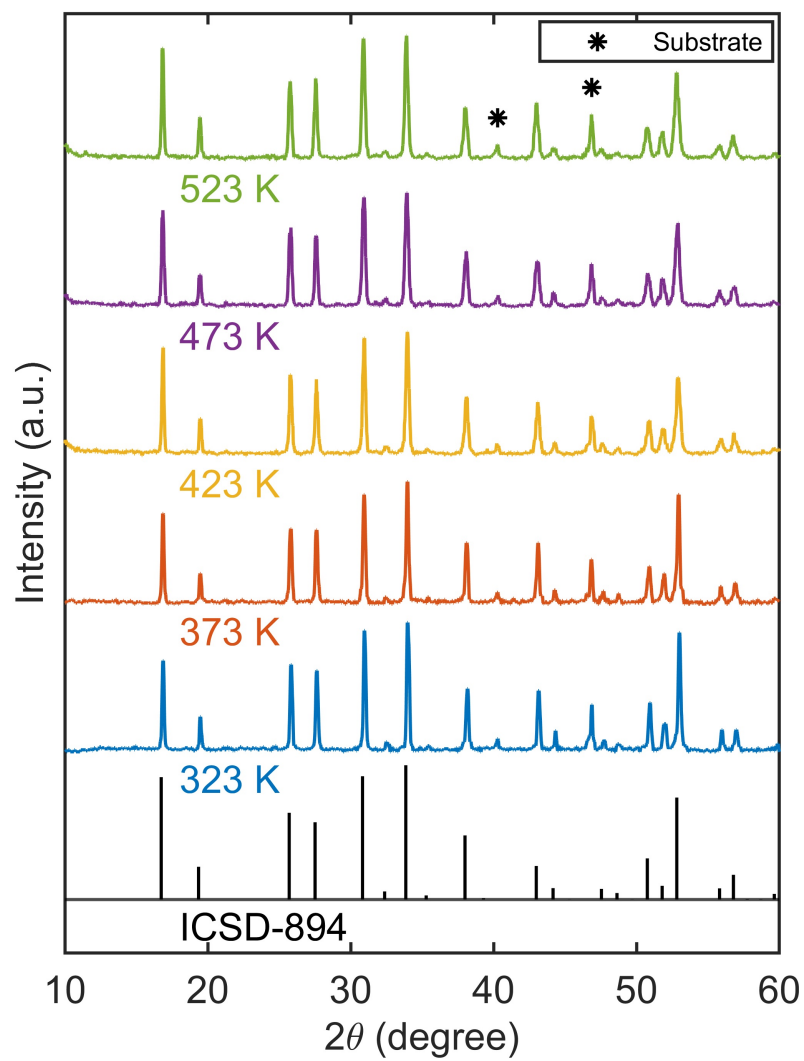


Figure 4.3: High-temperature XRD patterns of LLZTO. XRD patterns measured from 323 K to 523 K, showing no phase transition.

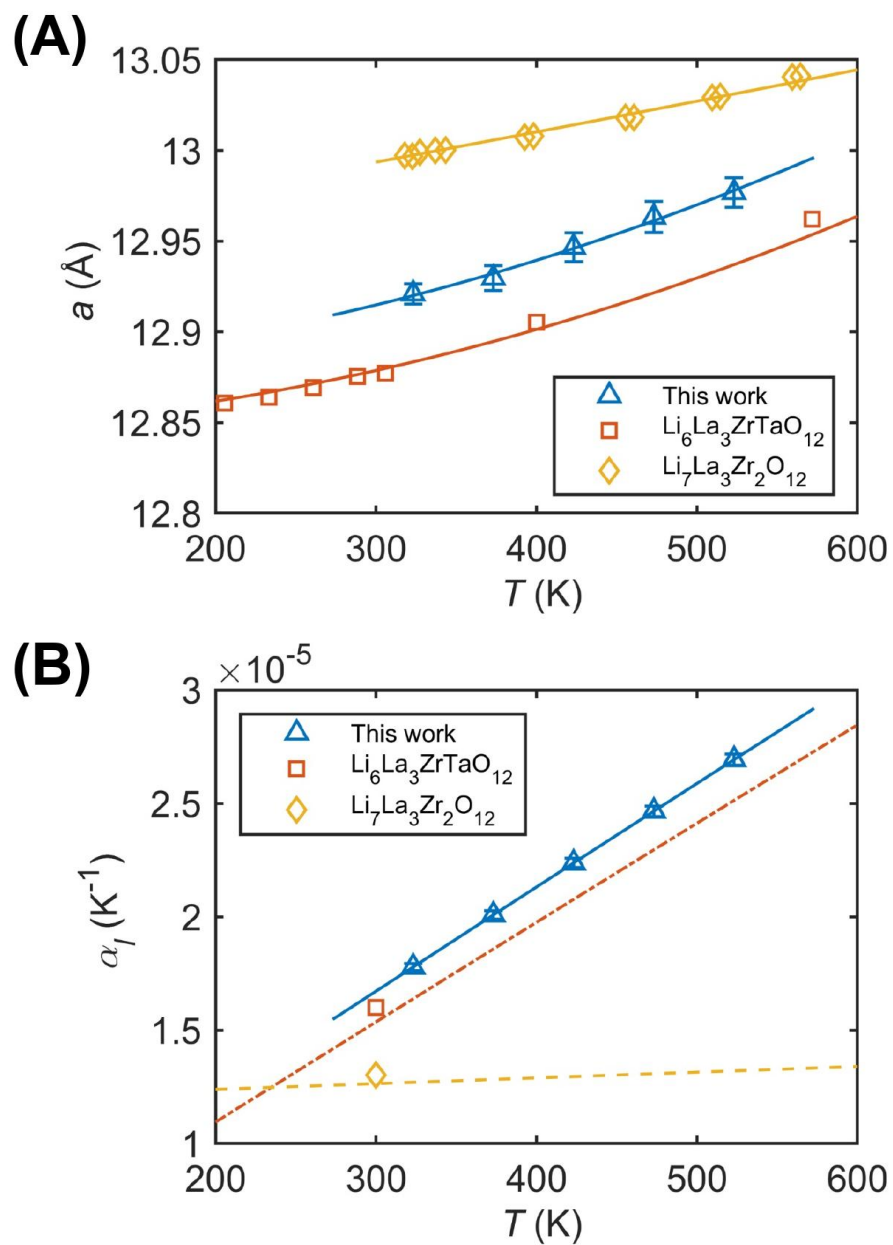
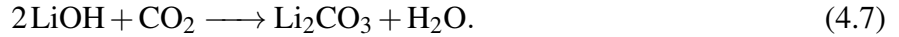
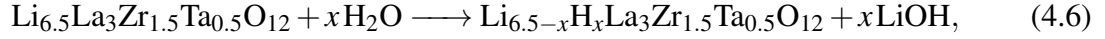


Figure 4.4: Lattice expansion and thermal expansion coefficient of LLZTO. (A) Lattice constant vs temperature with literature comparison. (B) Linear thermal expansion coefficient vs literature values.

changed with protons from atmospheric water vapor, leading to the formation of insulating surface layers. The detailed reactions proceed as follows:



The net effect is that lithium is extracted from the garnet lattice and converted to Li_2CO_3 on the grain surfaces, with concurrent insertion of protons into the lithium sites. This process is well known to degrade the ionic conductivity of LLZO by increasing the interfacial resistance and reducing the lithium-ion concentration in the bulk [135, 136]. However, prior to our study, the effect of this aging process on the thermal transport properties remained unexplored, a significant gap, given the importance of thermal management in aged battery cells.

To investigate the aging effect, LLZTO samples were aged in air for approximately one year. As shown in Figure 4.5(a), the XRD pattern of the aged sample clearly shows the presence of Li_2CO_3 as a secondary phase, confirming that the aging reactions described by Equations 4.6 and 4.7 have proceeded to a significant extent. The Raman spectrum presented in Figure 4.5(b) provides complementary information: all Raman peaks below 800 cm^{-1} are associated with LLZTO, while a sharp peak at 1090 cm^{-1} can be attributed to the presence of Li_2CO_3 . The markedly different peak widths, sharp for Li_2CO_3 and broad for LLZTO, reflect the difference in crystallinity between the two phases. In a well-ordered crystalline material, the vibrational modes are restricted to specific frequencies dictated by the crystal symmetry, producing sharp Raman peaks. In contrast, the broader peaks from LLZTO indicate the presence of disorder in the garnet lattice, consistent with the partially occupied and disordered lithium sublattice.

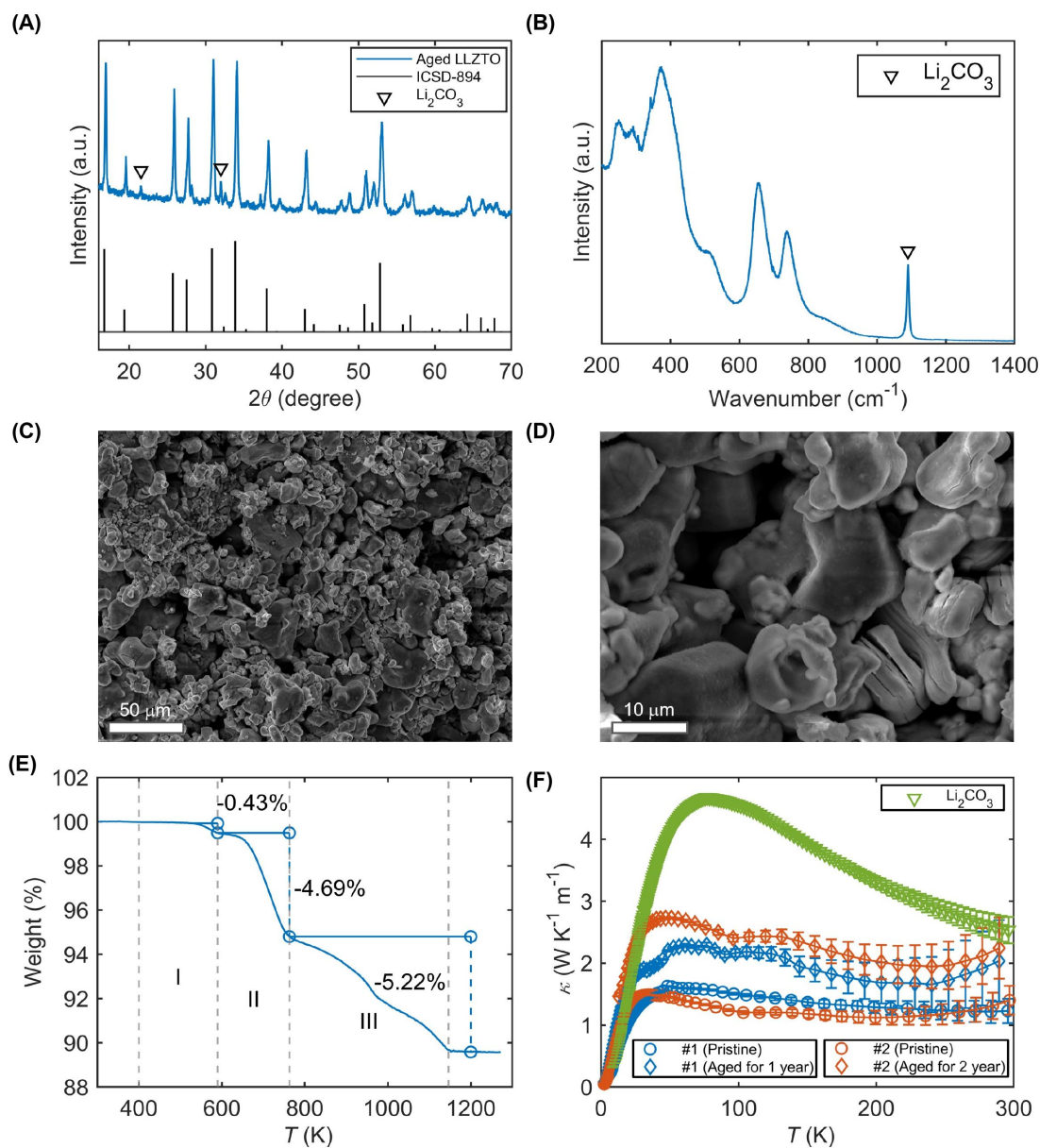


Figure 4.5: Aging characterization of LLZTO after air exposure. (A) XRD pattern showing Li_2CO_3 formation. (B) Raman spectrum. (C,D) SEM images of cracked grains and roughened surfaces. (E) EDS analysis in selected regions. (F) TGA analysis of the aged sample.

SEM imaging presented in Figures 4.5(c) and (d) reveals significant microstructural changes in the aged samples. The grain size shows a broad distribution, ranging from approximately 2 μm to 40 μm . Rough layers have formed on the surfaces of some grains, indicating that the grain surfaces have reacted with atmospheric moisture, as reported in previous studies [137]. More notably, some grains exhibit large cracks, which can be attributed to the volume change accompanying the Li^+/H^+ exchange reaction. As shown in Figure 4.5(e), EDS analysis reveals that the cracked grains are severely deficient in Ta and Zr ($\text{La}:\text{Zr}:\text{Ta} = 3.0:0.03:0.01$), while intact grains retain the expected stoichiometry ($\text{La}:\text{Zr}:\text{Ta} = 3.0:1.37:0.65$). While previous reports had suggested that the aging reaction occurs primarily at the grain surface, with the garnet structure preserved in the interior [137], our results demonstrate that the reaction can also penetrate deep into the grains, leading to grain fracture.

Thermogravimetric analysis (TGA) under N_2 gas flow, presented in Figure 4.5(f), confirmed at least three weight loss steps: step I due to evaporation of adsorbed surface water at about 523 K; step II related to the release of H^+ as H_2O around 673 K to 723 K; and step III attributed to the decomposition of Li_2CO_3 and release of CO_2 in the range 823 K to 973 K [134]. The weight loss from step II was used to quantify the extent of Li^+/H^+ exchange, yielding the composition $\text{Li}_{2.05}\text{H}_{4.45}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ for the aged sample, indicating that nearly 70% of the lithium has been replaced by protons.

The most striking and counterintuitive finding of the aging study is the effect on thermal conductivity. The aged LLZTO samples exhibit an *enhanced* thermal conductivity compared to the pristine samples across nearly the entire measured temperature range. At room temperature, the thermal conductivity of the aged samples is increased by 70–80%. This result is surprising because the microstructural observations, rough surface layers, intragranular cracks, and compositional inhomogeneity, would be expected to *increase* phonon scattering and thereby *reduce* the thermal conductivity.

Two mechanisms can explain this unexpected enhancement. First, and most importantly, the aged samples contain a significant amount of Li_2CO_3 , which has a higher thermal conductivity than LLZTO. To verify this, we measured the thermal conductivity of a cold-pressed Li_2CO_3 pellet and obtained a room-temperature value of $2.5 \text{ W m}^{-1} \text{ K}^{-1}$, approximately twice that of pristine LLZTO. The Li_2CO_3 exhibits higher thermal conductivity than LLZTO over the entire measured temperature range from 20 K to 300 K. Therefore, the presence of Li_2CO_3 as a secondary phase in the aged samples provides a higher-conductivity pathway for heat transport, increasing the effective thermal conductivity of the composite.

Second, the enhanced thermal conductivity could be partially attributed to a reduction in thermal boundary resistance in the aged samples. Thermal boundary resistance arises from phonon scattering at interfaces between grains. When this resistance is reduced, phonons can propagate more freely across grain boundaries, increasing the effective thermal conductivity. Because Li_2CO_3 typically forms on the surface of garnet grains [137], the high crystallinity of Li_2CO_3 may enhance the phonon transmission coefficient across grain boundaries by providing a structurally ordered interfacial layer. Similar enhancement of thermal transport by insertion of an interfacial layer has been reported in other material systems [138]. To quantify this effect, we estimated the thermal boundary resistance using the model developed by Nan and Birringer [139], obtaining the values summarized in Table 4.2. The calculation used the single-crystal LLZTO thermal conductivity as the grain thermal conductivity and treated the grains as randomly oriented ellipsoidal crystallites, following the supporting analysis of Ref. [5]. The significantly reduced thermal boundary resistance in the aged sample supports the hypothesis that the Li_2CO_3 interlayer facilitates phonon transport across grain boundaries.

Table 4.2: Thermal boundary resistance of pristine and aged LLZTO. Thermal boundary resistance estimated using Nan-Birringner effective-medium model at 290 K.

Sample	Thermal boundary resistance ($\text{m}^2 \text{K W}^{-1}$)
Pristine LLZTO	9.2×10^{-4}
Aged LLZTO sample #1	5.5×10^{-4}

These findings have important practical implications for thermal management in garnet-based solid-state batteries. While aging degrades the ionic conductivity of LLZO-based electrolytes, the simultaneous increase in electrolyte thermal conductivity creates a complex tradeoff: the formation of Li_2CO_3 impedes ion transport but can facilitate heat transport within the electrolyte pellet. Cell-level heat dissipation, however, will also depend on architecture, interfaces, and contact resistances. For battery design, these results highlight the need to consider the coupled evolution of ionic and thermal transport properties over the battery lifetime, rather than treating them independently.

4.6 Summary

This chapter presented a comprehensive investigation of the thermal properties and lattice anharmonicity of polycrystalline LLZTO garnet solid electrolyte [5]. The thermal conductivity of polycrystalline LLZTO was measured over a wide temperature range from 5 K to 824 K. A peak emerges at approximately 50 K, followed by a remarkably weak temperature dependence above 200 K. The room-temperature thermal conductivity is $\kappa = 1.2(2) \text{ W m}^{-1} \text{ K}^{-1}$, and the porosity-corrected solid thermal conductivity of $\kappa_s = 1.6(3) \text{ W m}^{-1} \text{ K}^{-1}$ approaches the calculated minimum thermal conductivity of $\kappa_{\min} = 1.07 \text{ W m}^{-1} \text{ K}^{-1}$.

The average phonon mean free path, calculated from the low-temperature thermal conductivity using a Debye model, reaches approximately 500 nm at 5 K, well below the aver-

age grain size of 8 μm . This indicates that grain-boundary scattering is not the primary mechanism limiting thermal transport; rather, scattering at lattice defects and inhomogeneities dominates. High-temperature XRD measurements from 323 K to 523 K yield a linear thermal expansion coefficient of $\alpha_l = (1.71 \pm 0.01) \times 10^{-5} \text{ K}^{-1}$ at 323 K, increasing to $(2.72 \pm 0.01) \times 10^{-5} \text{ K}^{-1}$ at 523 K. This thermal expansion coefficient is larger than the reported value for undoped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [109] and approximately twice that of conventional garnet minerals [125].

Together with the measured specific heat, thermal expansion coefficient, and the reported bulk modulus [119], the Grüneisen parameter is determined to be $\gamma = 1.63 \pm 0.04$ at 300 K. This relatively large value indicates strong phonon anharmonicity in LLZTO, consistent with the low thermal conductivity and suggesting that the disordered lithium sublattice contributes significantly to the anharmonic character of the lattice vibrations. Aged LLZTO samples exposed to ambient air for one year show an enhanced thermal conductivity of 70–80% at room temperature compared to pristine samples. This counterintuitive increase is attributed to the formation of Li_2CO_3 ($\kappa = 2.5 \text{ W m}^{-1} \text{ K}^{-1}$), which has approximately twice the thermal conductivity of pristine LLZTO, and to the reduced thermal boundary resistance in the aged samples.

These results provide a broad thermal characterization of LLZTO over a wide temperature range and establish key baseline properties for thermal management in garnet-based solid-state batteries. The finding that the thermal conductivity approaches the amorphous limit and that the Grüneisen parameter indicates strong anharmonicity raises fundamental questions about the origin of these properties, specifically whether they are intrinsic to the LLZTO lattice or influenced by the polycrystalline microstructure. Together with the single-crystal measurements and lattice-dynamics analysis presented in Chapter 3, these polycrystalline results show that low, glass-like thermal conductivity is intrinsic to the

LLZTO lattice while also being modified by microstructure, aging chemistry, and thermal-boundary effects.

Chapter 5

Glass-Like Thermal Transport and Diffuson Contribution to Heat Conduction in Perovskite $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$

5.1 Introduction

The preceding chapters of this dissertation have focused on the thermal transport properties of garnet-type LLZTO, first in single crystals (Chapter 3) and then in polycrystalline and aged samples (Chapter 4). Those investigations established that LLZTO exhibits intrinsically low, glass-like thermal conductivity, with diffuson-mediated heat transport playing a significant role alongside conventional propagon transport. A natural question that arises from those findings is whether such behavior is unique to the garnet crystal structure or whether it represents a more general feature of oxide-based solid electrolytes. To address this question, we now turn to the perovskite family and investigate the thermal transport properties of perovskite LSHT [7].

Perovskite-type $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) is one well-studied oxide-based solid electrolytes, owing to its high bulk lithium-ion conductivity, which can reach up to $10^{-3} \text{ S cm}^{-1}$ at room temperature [35, 140]. LLTO also offers excellent thermal stability, good mechanical strength, and low electronic conductivity, making it attractive for safe and durable solid-state battery applications. Despite these advantages, LLTO suffers from poor chemical stability against lithium metal, which limits its compatibility with lithium metal anodes, and exhibits high grain boundary resistance, which significantly reduces its overall ionic conductivity to about $2 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature [140]. To address these issues, researchers have developed multiple modified perovskite compositions, including

($\text{Li}_{0.45}\text{La}_{0.85}\text{ScO}_3$ [141], $\text{Li}_{2x-y}\text{Sr}_{1-x-y}\text{La}_y\text{TiO}_3$ [142], and $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Ta}_{3/4}\text{Zr}_{1/4}\text{O}_3$ (LSTZ) [143]. Building on LSTZ, substitution of Zr with Hf led to the optimized composition LSHT, which achieves a high ionic conductivity of $3.8 \times 10^{-4} \text{ S cm}^{-1}$ and a low activation energy of 0.36 eV [144].

While considerable progress has been made in understanding the electrochemical properties of LSHT, its thermal properties remain largely unexplored. As discussed throughout this dissertation, thermal management is critical in battery systems to mitigate temperature gradients, enhance operational safety, and ensure long-term reliability [23]. Inadequate heat dissipation can result in localized overheating and thermal runaway, which compromises both safety and performance [145]. The importance of thermal transport in solid electrolytes has been increasingly recognized in recent years [1, 3, 5, 6], as demonstrated by the results presented in Chapters 3 and 4 for the garnet system. Therefore, a detailed understanding of the thermal behavior of perovskite solid electrolytes like LSHT is essential for the rational design of next-generation ASSBs.

In this chapter, we investigate the specific heat (C_p) and thermal conductivity (κ) of LSHT over a broad temperature range. We find that LSHT exhibits glass-like thermal transport with a low κ of $1.7(5) \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, comparable to some amorphous materials yet distinct from typical crystalline perovskites. This thermal behavior can be attributed to the combination of boundary scattering, structural disorder, and vacancy-driven phonon scattering. Using a two-channel model analysis, we show that diffusions contribute approximately 34% of the total thermal conductivity at room temperature, indicating that diffuson-mediated transport plays a significant role in the thermal transport of LSHT, much as it does in LLZTO (Chapter 3). These results extend the thermal transport framework developed for garnets in the preceding chapters to the perovskite LSHT and provide important insights for thermal management in ASSBs.

5.2 Sample Preparation and Characterization

Polycrystalline LSHT samples were prepared as pellets using a conventional solid-state synthesis route, following the procedure reported by Huang *et al.* [144]. The resulting pellets were characterized by X-ray diffraction to confirm the crystal structure and by SEM with energy-dispersive X-ray spectroscopy (EDS) to assess the microstructure and composition.

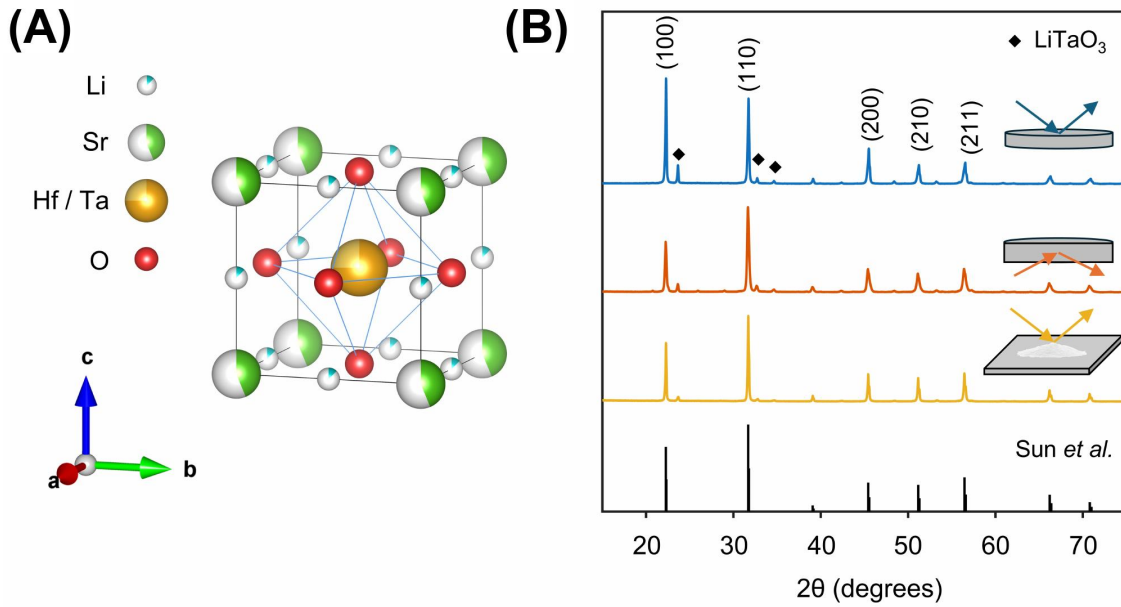


Figure 5.1: Crystal structure and XRD patterns of LSHT. (A) Cubic perovskite structure with $Pm\bar{3}m$ symmetry showing Li, Sr, and B-site (Hf/Ta) positions. (B) XRD patterns from different pellet orientations with calculated comparison.

Figure 5.1a shows the crystal structure of LSHT, which adopts the cubic perovskite structure with $Pm\bar{3}m$ symmetry. In this perovskite structure, Li ions occupy the midpoints of the cube edges, Sr ions occupy the A-sites, while Hf and Ta ions are located at the B-sites, each surrounded by oxygen octahedra. The perovskite framework is important because it supports efficient Li-ion migration, contributing to both high ionic conductivity and stability [144]. Recent structural analysis [36] indicates that the Li crystallographic

sites might be the cause of ionic mobility. Specifically, Li ions are found at the (24k) site near the unit cell edge, whereas oxygen atoms deviate from typical face-centered locations. This configuration forms a "zig-zag" migration pathway for Li ions, rather than a straight path. The zig-zag pathway may facilitate Li transport by providing accessible vacancies, although ordering effects at low temperatures could reduce conductivity.

The XRD patterns of LSHT pellets measured along different orientations are shown in Figure 5.1b. The dominant diffraction peaks are indexed to the cubic perovskite structure, confirming the successful formation of the LSHT phase. The lattice parameter was refined to be 3.98 Å, consistent with previous reports on LSHT [36, 144]. A minor LiTaO₃ impurity phase was detected, similar to a previous study [36]. The XRD patterns also reveal a discernible texture effect in the LSHT pellets, with the (100) plane being the most preferred orientation on the press surface and the (211) plane being the preferred orientation on the cross-section surface. The orientation factors along the (100) direction were calculated as 0.13 for the press surface sample, while the (211) direction has an orientation factor of 0.05 for the cross-section surface sample. These values indicate a moderate degree of crystallographic alignment in the LSHT pellets, which, as will be discussed in Section 5.4, gives rise to anisotropic thermal conductivity.

SEM images of LSHT, shown in Figure 5.2a and b, reveal a dense, homogeneous microstructure with an average grain size of approximately 3 μm. The grains are tightly packed with well-defined intergranular connectivity and minimal porosity. Some layer-like structures are visible in the high-magnification image (Figure 5.2b), which may play a role in anisotropic thermal transport, as discussed in Section 5.4. The EDS spectrum (Figure 5.2c) shows peaks corresponding to O, Ta, Hf, and Sr, with measured atomic percentages of 68%, 15%, 5%, and 12%, respectively, in good agreement with the expected stoichiometric composition. EDS elemental mapping (Figure 5.2d) further confirms a uni-

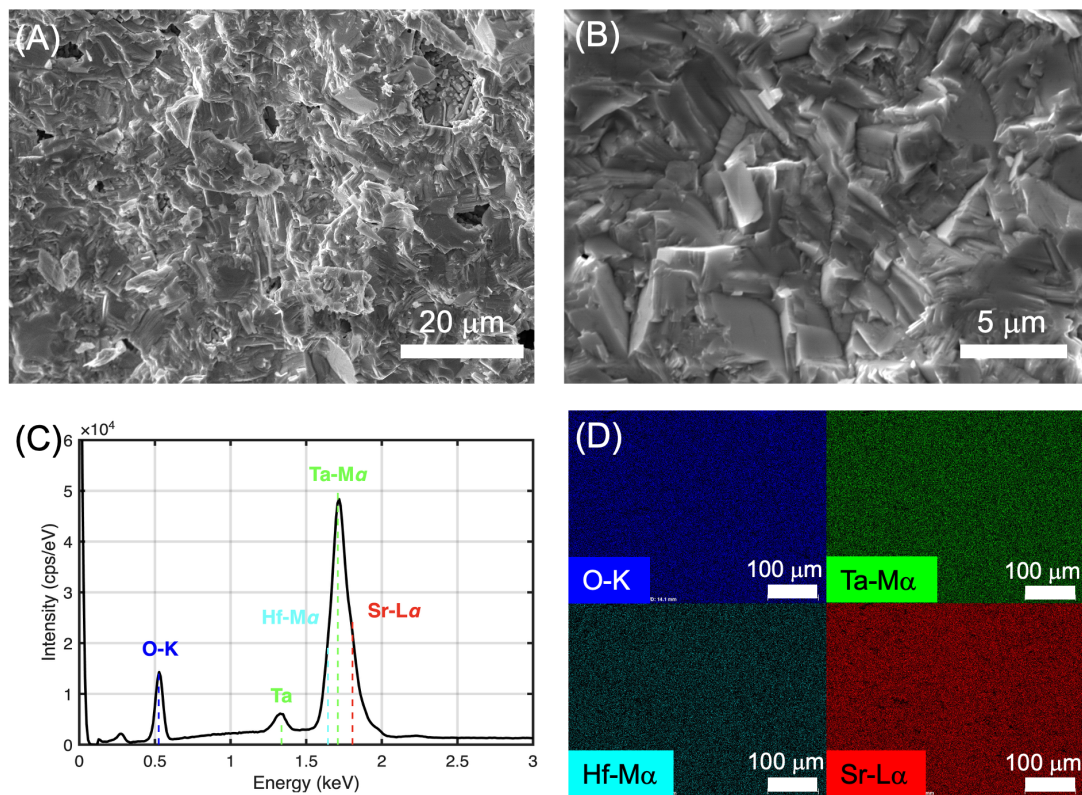


Figure 5.2: SEM micrographs and EDS analysis of LSHT. (A) Low-magnification SEM showing fracture surface. (B) High-magnification view revealing grain structure. (C) EDS spectrum for O, Ta, Hf, and Sr. (D) Elemental distribution maps of all constituent elements.

form distribution of all elements throughout the sample, with no evidence of compositional segregation.

Compared to the LLZTO polycrystals studied in Chapter 4, the LSHT samples exhibit a finer microstructure, with cubic grain shapes and a smaller average grain size of 3 μm versus 8 μm for LLZTO. This smaller grain size, combined with the structural disorder inherent to the perovskite lattice, will have important consequences for the thermal transport behavior, as discussed in the following sections.

5.3 Specific Heat

The temperature-dependent specific heat (C_p) of LSHT was measured using two complementary techniques: the PPMS (see Section 2.3.1) for low temperatures and DSC (see Section 2.3.3) for high temperatures. The results are presented in Figure 5.3.

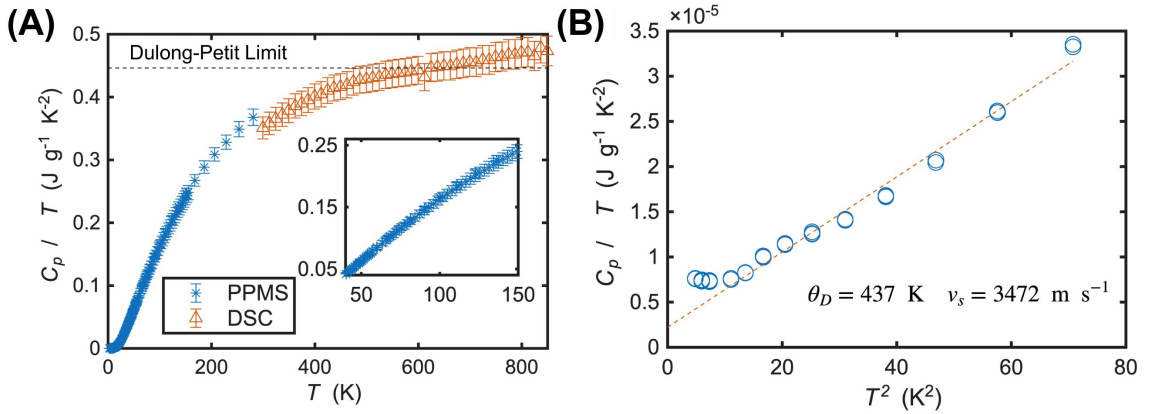


Figure 5.3: Temperature-dependent specific heat of LSHT. (A) Specific heat from PPMS and DSC showing approach to Dulong-Petit limit. (B) Low-temperature C_p/T vs T^2 plot fitted to extract Debye temperature.

As shown in Figure 5.3a, the specific heat increases monotonically with temperature and converges toward the Dulong-Petit limit [146] of $0.45 \text{ J g}^{-1} \text{K}^{-1}$ at high temperatures, indicative of classical lattice vibrations dominating thermal energy storage at elevated tem-

peratures. No discontinuities or anomalies suggestive of typical first-order phase transitions were observed in the specific heat data.

The low-temperature behavior of the specific heat provides access to the Debye temperature (θ_D), which is a fundamental parameter governing the phonon spectrum of the material. Figure 5.3b shows a linear dependence of C_p/T against T^2 at low temperatures, which can be fitted with the Debye model [147]. The fitting procedure is analogous to that employed for LLZTO in Chapter 4 (Equation 4.1). The resulting Debye temperature is:

$$\theta_D = 437(7) \text{ K.} \quad (5.1)$$

Using the obtained Debye temperature, the average sound velocity (v_s) was calculated through the standard Debye relation:

$$v_s = \frac{\theta_D}{\hbar} \left(\frac{k_B}{(6\pi^2 N/V)^{1/3}} \right), \quad (5.2)$$

where $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and N/V is the atomic number density. The resulting sound velocity is $v_s = 3472(55) \text{ m s}^{-1}$.

It is instructive to compare these values with those obtained for LLZTO in Chapter 4. The Debye temperature of LSHT (437(7) K) is somewhat lower than that of LLZTO (479(1) K), reflecting differences in atomic masses, bonding strengths, and crystal structure between the perovskite and garnet frameworks. Similarly, the sound velocity of LSHT (3472(55) m s^{-1}) is slightly lower than that of LLZTO (3627(10) m s^{-1}). Despite these differences, both materials share Debye temperatures and sound velocities in the same general range, which is characteristic of oxide lithium-ion conductors [6]. These similar phonon energy scales set the stage for comparable thermal transport behavior, as will be demonstrated in the following section.

5.4 Thermal Conductivity

The thermal conductivity of LSHT was measured along different directions using the PPMS TTO (see Section 2.3.1) at low temperatures and by LFA (see Section 2.3.4) at high temperatures. The results are presented in Figure 5.4 alongside reference data for single-crystal KTaO_3 (KTO) [148] and amorphous SiO_2 [149].

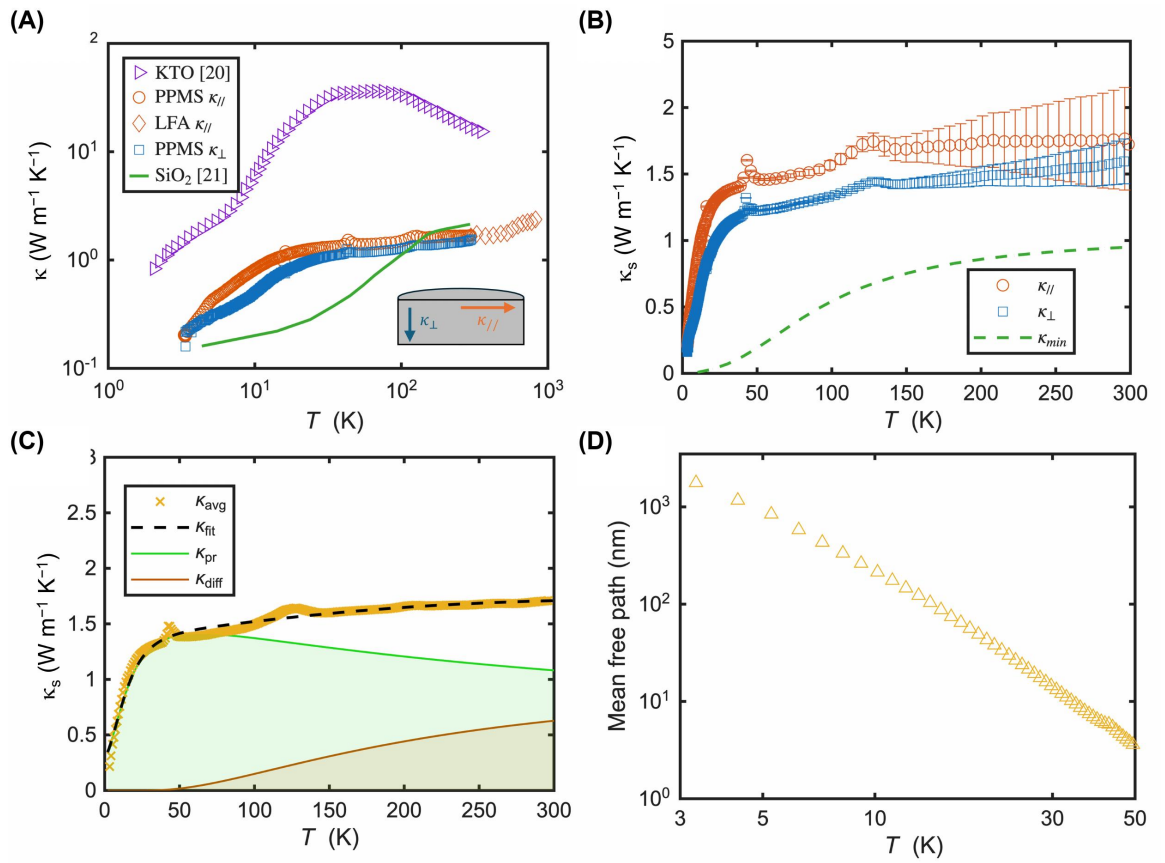


Figure 5.4: Temperature-dependent thermal conductivity of LSHT. (A) Thermal conductivity in in-plane and cross-plane directions with KTO and amorphous SiO_2 comparison. (B) Porosity-corrected thermal conductivity with minimum thermal conductivity limit. (C) Two-channel decomposition into propagon and diffuson contributions. (D) Phonon mean free path.

In comparison with KTaO_3 and amorphous SiO_2 , as shown in Figure 5.4a, LSHT exhibits a remarkably lower thermal conductivity than KTO across the entire temperature

range, despite sharing the same perovskite crystal structure. In fact, the thermal conductivity of LSHT is comparable to that of amorphous SiO_2 , a material that lacks long-range crystalline order. This pronounced reduction in κ relative to the prototypical crystalline perovskite KTO can be attributed to several factors. First, the increased boundary scattering in the polycrystalline sample, with an average grain size of only $3\text{ }\mu\text{m}$, suppresses the thermal conductivity by limiting the phonon mean free path at low temperatures. Second, the doping of multiple cations (Li, Sr, Hf, and Ta) into the perovskite lattice introduces substantial atomic mass and force-constant disorder, which strengthens phonon scattering and suppresses thermal transport. Third, the significant concentration of Li vacancies intrinsic to the LSHT structure further enhances phonon scattering by introducing additional mass and bonding disorder. Recent structural analysis [36] suggests a higher concentration of Li vacancies than previously assumed, which, while necessary to facilitate high ionic conductivity, also promotes low, glass-like thermal conductivity [3]. In addition to these factors, strong phonon anharmonicity, previously identified in other complex solid electrolytes [1, 5, 6], likely plays a key role in limiting κ in LSHT. Anharmonicity increases phonon-phonon scattering rates, particularly at elevated temperatures, further reducing the mean free path and impeding heat transport. Together, these effects result in the low glass-like thermal conductivity of LSHT.

Some qualitative similarities with LLZTO were noted in earlier chapters, where complex crystal structure, atomic disorder, and anharmonicity contributed to glass-like transport; however, material-specific differences mean such comparisons should be made cautiously. The observation of glass-like behavior in a perovskite system motivates broader, careful comparisons across oxide-based solid electrolytes.

To examine anisotropic thermal conductivity, the thermal conductivity of LSHT was corrected for porosity to obtain the solid thermal conductivity (κ_s), using the Maxwell–Eucken relation introduced in Chapter 2 (Equation 2.6). As shown in Fig-

ure 5.4b, anisotropic thermal conductivity is clearly manifested in the LSHT samples, with the in-plane component ($\kappa_{\parallel}$) consistently exceeding the cross-plane component ($\kappa_{\perp}$). This anisotropy can be rationalized by the crystallographic texture revealed by the XRD analysis described in Section 5.2. The ratio of $\kappa_{\parallel}$ to $\kappa_{\perp}$ is about 1.2:1 at 100 K, consistent with the moderate texture observed by XRD. It has been reported that even for cubic crystal structures, crystallographic orientation can cause anisotropy in the thermal conductivity [150]. The preferred crystallographic orientation and possible alignment of grains during densification contribute to anisotropic phonon transport [151]. Additionally, the layer-like microstructure observed in the SEM images (Figure 5.2b) may further enhance the anisotropic behavior by introducing direction-dependent grain boundaries and interfaces that scatter phonons.

The dashed line in Figure 5.4b indicates the estimated minimum thermal conductivity ($\kappa_{\min}$) based on the Cahill model [69], calculated using the approach summarized in Chapter 2 (Equation 2.7). The fact that the measured solid thermal conductivity of LSHT approaches but does not fall below $\kappa_{\min}$ confirms that LSHT operates near the lower limit of thermal transport for a crystalline material, consistent with the glass-like behavior observed in other solid electrolytes [1, 6].

To evaluate the average thermal conductivity and its temperature dependence while accounting for the texture effect, we calculated the average solid thermal conductivity (κ_{avg}), as shown in Figure 5.4c. The obtained room-temperature value is:

$$\kappa_{\text{avg}} = 1.7(5) \text{ W m}^{-1} \text{ K}^{-1}. \quad (5.3)$$

The temperature dependence of κ_{avg} shows a weak increase with increasing temperature. This behavior is common in amorphous materials [152] but is unusual for crystalline materials, which typically exhibit an apparent κ peak at intermediate temperatures followed by

a $1/T$ decline. The weak temperature dependence is consistent with the glass-like thermal transport behavior observed in materials with complex or highly defective crystal structures [6, 103].

Two minor anomalies appear in the low-temperature regime near 40 K and 130 K. However, comparison with the specific heat data indicates that these features are not associated with typical phase transitions. Possible explanations may involve Li-ion activation processes or a broadened, smeared phase transition. Further investigation is needed to fully understand their origins.

Finally, the average phonon mean free path (MFP) of LSHT at low temperatures was calculated based on the Debye–Callaway model [70], using the approach summarized in Chapter 2 (Equation 2.8). As shown in Figure 5.4d, the MFP exhibits a steep decrease from approximately $2\text{ }\mu\text{m}$ at 3 K to approximately 4 nm at 50 K. This rapid reduction with increasing temperature highlights the strong temperature dependence of phonon scattering processes in LSHT. The upper limit of the MFP is comparable to the average grain size of $3\text{ }\mu\text{m}$ determined by SEM, as expected at low temperatures where phonon scattering is dominated by grain boundaries. This can be contrasted with LLZTO in Chapter 4, where the phonon MFP reached approximately 500 nm at 5 K, slightly below the average grain size of $8\text{ }\mu\text{m}$.

5.5 Two-Channel Model Analysis

To elucidate the underlying thermal transport mechanisms in LSHT, we applied the analytical two-channel model developed by Bernges *et al.* [14], following the same framework employed for LLZTO in Chapter 3 (Section 3.5) and summarized in Chapter 2 (Equations 2.9–2.13). In this framework, the thermal conductivity is decomposed into contribu-

tions from two distinct channels: propagons and diffusons [57], where κ_{pr} is the contribution from propagons and κ_{diff} is the contribution from diffusons.

Propagons are phonons with well-defined group velocities under the harmonic approximation, behaving independently in a gas-like manner. Their contribution to thermal conductivity follows the conventional kinetic theory description, with a characteristic peak at low temperatures arising from the competition between increasing specific heat and decreasing phonon MFP. On the other hand, diffusons mediate thermal transport through coupling between different phonon modes that are close in energy and momentum, which would be independent under the harmonic assumption. This mechanism becomes prominent in complex or disordered crystals where anharmonicity and structural complexity hinder propagons [1]. As discussed in Chapter 3, the boundary between propagon and diffuson regimes is defined by the Ioffe-Regel limit, above which the concept of a phonon as a propagating wave packet breaks down.

The results of the two-channel model fitting are shown in Figure 5.4c. The propagon component (κ_{pr}) exhibits a peak near 58 K, arising from the competition between the increasing specific heat at low temperatures and the reduction of the phonon MFP due to enhanced phonon scattering at higher temperatures. The peak temperature of 58 K in LSHT falls within the range reported for other solid electrolytes, such as LLZTO (22 K) [6] and $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (NZP) (45 K) [1]. In contrast to the propagon contribution, the diffuson component (κ_{diff}) increases monotonically with temperature due to enhanced mode coupling in the disordered structure. As more high-energy phonon modes become thermally populated, the probability of energy transfer between adjacent modes increases, leading to a growing diffuson contribution. At room temperature, diffusons contribute approximately 34% of the total solid thermal conductivity (Table 5.1). The detailed fit coefficients (initial guesses and final fitted values) for the analytical two-channel model are listed in Table 5.2. Definitions of the model parameters and the fitting procedure are given in Chapter 2 (Equa-

Table 5.1: Summary of measured and fit parameters for LSHT. Summary of measured values and key two-channel fit results for LSHT.

Parameter	Value	Notes
Debye temperature θ_D	437(7) K	from low-T C_p fit (Eq. 5.1)
Average sound velocity v_s	3472(55) m s ⁻¹	Debye relation (Eq. 5.2)
Average thermal conductivity κ_{avg} (RT)	1.7(5) W m ⁻¹ K ⁻¹	porosity-corrected
Propagon peak temperature $T_{\text{pr,peak}}$	58 K	from two-channel fit
Diffuson fraction (RT)	34%	from two-channel fit
Average grain size	3 μm	SEM (Figure 5.2)

tions 2.9, 2.11, 2.14, 2.13). The fit returned $C_1 = 0.1047$, $C_2 = 0.5907$, $A = 0.0014$, and $P = 1.0000$ (units and conventions follow Bernges *et al.* [14]). Notably, the parameter P reached unity within fitting tolerance. This substantial diffuson parameter, P , indicates that

Table 5.2: Two-channel model fitting for LSHT: initial guesses and final fits. Initial guesses and final fitted values for the two-channel model parameters for LSHT. Units follow conventions in Bernges *et al.* [14].

Parameter	Unit	Initial Guess	Final Fit
C_1	$10^{-16} \text{ s K}^{-1}$	0.1	0.1047
C_2	10^{-40} s^3	0.1	0.5907
A	unitless	0.1	0.0014
P	unitless	0.5	1.0000

diffuson-mediated transport plays a significant role in the thermal conductivity of LSHT, similar to the behavior observed in other ionic conductors, including LLZTO [6], NZP [1], and NaSbS₂ [153]. The interplay between the decreasing κ_{pr} and the increasing κ_{diff} results in the overall weak temperature dependence of κ observed in LSHT. This cancellation mechanism is the same one identified for LLZTO in Chapter 3: as temperature increases, the propagon contribution declines due to intensifying Umklapp scattering, while the diffuson contribution grows as more modes participate in incoherent energy transfer. The near-cancellation of these opposing trends produces the characteristic plateau in total ther-

mal conductivity above approximately 100 K, which is the hallmark of glass-like thermal transport behavior in crystalline materials. For context, previous LLZTO studies reported diffuson fractions of roughly 30% in single crystals and up to 50% in polycrystalline samples, but differences in grain size, texture, and measurement conditions make direct numerical comparisons uncertain. The 34% diffuson contribution found for polycrystalline LSHT lies within this broad range, reflecting its polycrystalline nature and moderate structural disorder. Observing substantial diffuson contributions across different oxide families suggests that structural complexity, multi-site cation disorder, and high vacancy concentrations—features that benefit ionic conductivity—can also promote strong phonon scattering and mode coupling, although direct confirmation in LSHT will require further first-principles and spectroscopic investigation.

5.6 Summary

In this chapter, we investigated the thermal properties of the perovskite-type lithium-ion conductor LSHT [7]. The specific heat was measured over a broad temperature range, yielding a Debye temperature of $\theta_D = 437(7)\text{ K}$ and a sound velocity of $v_s = 3472(55)\text{ ms}^{-1}$. Both values are comparable to those obtained for LLZTO in Chapter 4 ($\theta_D = 479(1)\text{ K}$, $v_b = 3627(10)\text{ ms}^{-1}$), indicating similar phonon energy scales across garnet and perovskite solid electrolytes.

The thermal conductivity of LSHT was measured to be $\kappa_{\text{avg}} = 1.7(5)\text{ W m}^{-1}\text{ K}^{-1}$ at room temperature, exhibiting glass-like thermal transport behavior comparable to amorphous materials. This value is dramatically lower than that of the prototypical perovskite KTaO_3 and approaches the calculated minimum thermal conductivity, consistent with the behavior observed for LLZTO. The LSHT pellets exhibit moderate crystallographic texture, resulting in anisotropic thermal conductivity with $\kappa_{\parallel}/\kappa_{\perp} \approx 1.2$ at 100 K. This

anisotropy is attributed to the preferred crystallographic orientation and the layer-like microstructure observed by SEM.

The phonon mean free path decreases steeply from approximately 2 μm at 3 K to approximately 4 nm at 50 K. The upper limit is comparable to the average grain size of 3 μm , consistent with grain-boundary-dominated scattering at low temperatures. Two-channel model analysis indicates that diffusons contribute approximately 34% of the solid thermal conductivity at room temperature. The interplay between the decreasing propagon contribution and the increasing diffuson contribution produces the observed weak temperature dependence of κ , which is the signature of glass-like thermal transport.

These results extend the thermal transport framework established for garnet-type LLZTO in Chapters 3 and 4 to a newly emerged perovskite electrolyte. The observation of glass-like thermal conductivity with substantial diffuson contributions in both the garnet and perovskite crystal structures suggests that this behavior is a recurring feature among the oxide solid electrolytes studied here, while the microscopic balance remains material dependent. The structural features that promote high ionic conductivity, including multi-site cation disorder, high vacancy concentrations, and complex unit cells, simultaneously create the conditions for strong phonon scattering and diffuson-mediated heat transport. These findings underscore the importance of considering thermal transport in the design of ASSBs and provide essential data for thermal management strategies. In the following chapter, we extend our investigation to the NASICON family of solid electrolytes, completing our survey of thermal transport across the three major oxide solid electrolyte structural families.

Chapter 6

Thermal Transport and Lattice Anharmonicity in

$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$

6.1 Introduction

The preceding chapters of this dissertation have established that several solid electrolytes, including garnet LLZTO (Chapters 3 and 4) and perovskite LSHT (Chapter 5), exhibit remarkably low, glass-like thermal conductivity. For full chemical formulas, see Chapter 1. In these systems, the room-temperature thermal conductivity approaches the calculated amorphous limit, the phonon mean free path can collapse toward interatomic length scales, and two-channel analysis for LLZTO and LSHT indicates a crossover from ideal phonon gas (propagon) transport toward diffuson-mediated heat transfer above approximately 200 K. Rather than treating this behavior as a cross-family curiosity, the present chapter asks how thermal transport evolves within a single framework as lattice anharmonicity changes from composition to composition. To address that question, we now turn to a third major family of solid electrolytes: the Na super ionic conductor (NaSICON) framework. In this chapter we focus on one representative composition, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP), as a case study within the broader NaSICON family that contains many compositions and doping schemes.

The NaSICON family is often represented by the formula $\text{NaZr}_2(\text{PO}_4)_3$ (NZP), with NZSP sitting in one of the doping schemes: $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$). The NaSICON family has been one of the most intensively studied classes of sodium-ion solid electrolytes since its introduction by Hong [32] and subsequent development by Goodenough

and co-workers [33]. The NaSICON framework offers a rigid three-dimensional network of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra, creating interconnected channels that facilitate fast Na^+ transport. Among the numerous NaSICON compositions, the prototypical NZP and its derivatives (e.g., NZSP) have been widely studied for sodium-ion conduction. Compositions in this family have exhibited bulk ionic conductivities exceeding 1 mS cm^{-1} in many cases [34, 154–157]. Specifically doped compositions are often chemically and electrochemically robust in ambient conditions and against metallic Na, making them attractive candidates for practical solid-state sodium-ion batteries [158–163]. Recent studies of NZP-family compositions have advanced understanding of Na^+ transport, highlighting mechanisms such as correlated Na^+ migration and, in some reports, polaron-assisted transport that can enhance ionic mobility [164, 165].

Thermal management is essential in battery systems to maintain operational safety and long-term performance [24, 145]. Inadequate thermal regulation can lead to thermal runaway, posing serious safety risks, while non-uniform temperature distributions accelerate localized degradation, resulting in capacity fading and reduced overall efficiency. As demonstrated for LLZTO in Chapters 3 and 4, and for LSHT in Chapter 5, the intrinsically low thermal conductivities of solid electrolytes make them potential thermal bottlenecks in all-solid-state battery architectures. Understanding whether this behavior extends to the NaSICON family is therefore critical for informed thermal design of sodium-ion cells.

While the electrochemical properties of the specific NZSP composition have been extensively studied, its thermal behavior remains less well understood, particularly at low temperatures. One recent study by Rohde *et al.* [166] reported the thermal conductivity data for NZSP above room temperature, focusing primarily on compositional variations and doping effects. However, a comprehensive measurement of thermal conductivity across the full temperature range has been lacking. In comparison, related NaSICON-type compounds, such as pristine NZP and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ (NZS), have been characterized both be-

low and above 300 K by Böger *et al.* [1]. At low temperatures, NZS exhibits a much lower thermal conductivity than NZP, a difference attributed to varying anharmonicity related to Na ions. The Na(2) site in NZS was identified as the primary cause of the stronger anharmonicity by Böger *et al.* [1]. Above approximately 200 K, both NZP and NZS exhibit low and nearly temperature-independent thermal conductivities, a behavior that deviates from conventional phonon-gas models. This anomalous behavior has been rationalized in the literature by invoking diffuson-mediated heat transport [55, 57], wherein energy is exchanged between vibrational modes that would otherwise be independent under the conventional phonon-gas model. Diffusons typically emerge in amorphous or strongly scattered crystalline materials characterized by short phonon lifetimes, strong phonon scattering, and suppressed harmonic phonon transport [58, 59, 167]. For NZSP, the plateau-like thermal conductivity and short mean free paths are therefore interpreted as signatures consistent with non-phonon-gas, diffuson-like heat transport. Previous work on related NaSICON end members (NZP and NZS) has applied explicit two-channel decompositions and fitting using calculated vibrational DOS to separate propagon and diffuson contributions [1]; however, the present chapter does not perform that fitting because a reliable phonon DOS for NZSP is not available.

In this chapter, we present a systematic investigation of the thermal properties of NZSP across a wide temperature range [8]. Specific heat and thermal conductivity measurements were performed from cryogenic to high temperatures, enabling a comprehensive understanding of phonon transport behavior in NZSP. By elucidating the intrinsic thermal transport mechanisms and quantifying the lattice anharmonicity through the Grüneisen parameter, this study extends the cross-family comparison initiated in the garnet and perovskite chapters to the NaSICON family and tests which thermal-transport features recur across structurally distinct oxide SEs.

6.2 Sample Preparation and Characterization

Polycrystalline NZSP samples were synthesized by a solid-state reaction method. Stoichiometric amounts of precursors Na_2CO_3 (with a 10% excess to compensate for Na loss during sintering), ZrO_2 , SiO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed with an appropriate amount of ethanol, ball-milled for 6 h, and then dried overnight at 80°C . The resulting material was manually ground into a fine white powder and pressed into pellets. The pellets were sintered following a two-stage heating procedure: first heated at a rate of 5°Cmin^{-1} to 950°C , followed by further sintering at 1150°C for 12 h in air at a heating rate of 1°Cmin^{-1} .

After synthesis, phase characterization shows that at room temperature, NZSP adopts a monoclinic structure with space group $C2/c$, as illustrated in Figure 6.1a. The crystal structure comprises a robust three-dimensional framework of corner-sharing ZrO_6 octahedra and SiO_4/PO_4 tetrahedra, creating interconnected channels that facilitate Na^+ ion transport. Na^+ ions reside within these channels, occupying interstitial sites that contribute to the high ionic conductivity. It is noted that NZSP lies near a structural phase boundary at room temperature and transforms into a rhombohedral phase (space group $R\bar{3}c$) above approximately 400 K [166, 168–171], as shown in Figure 6.1b. This structural evolution is noteworthy because it contrasts with the behavior of the garnet LLZTO system studied in Chapters 4 and 3, where Ta^{5+} doping stabilizes the cubic phase over the entire temperature range, and with the perovskite LSHT system of Chapter 5, which maintains a single perovskite phase.

To confirm the phase purity and structural integrity of the synthesized NZSP, Rietveld refinement of the X-ray diffraction pattern was performed using GSAS-II software, with a previously reported structural model [172] as the initial input. The refinement results, depicted in Figure 6.1c, affirm the formation of the monoclinic NaSICON-type phase with space group $C2/c$ at room temperature. The obtained lattice parameters are $a = 1.5635\text{ nm}$,

$b = 0.9051 \text{ nm}$, $c = 0.9205 \text{ nm}$, $\alpha = \gamma = 90.00^\circ$, and $\beta = 123.75^\circ$. The refinement yielded a chi-square (χ^2) value of 4.8 and a weighted profile R-factor (R_{wp}) of 7.7%, indicating a satisfactory fit between the observed and calculated patterns. Notably, minor reflections corresponding to a secondary ZrO_2 phase were detected and accounted for in the refinement model, with a calculated weight fraction of 8%. The presence of ZrO_2 impurities in NZSP materials has been previously reported [170, 173–175] and is often attributed to the evaporation of Na and P precursors during synthesis and the high thermodynamic stability of ZrO_2 [170].

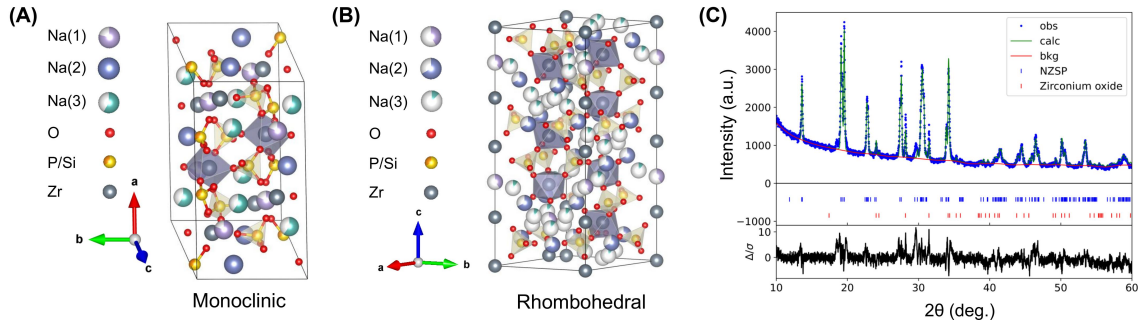


Figure 6.1: Crystal structure and XRD refinement of NZSP. (A) Monoclinic crystal structure at room temperature with ZrO_6 octahedra and SiO_4/PO_4 tetrahedra framework. (B) Rhombohedral crystal structure at elevated temperatures. (C) Rietveld refinement of XRD pattern with NZSP and ZrO_2 phases marked.

The microstructure of the synthesized NZSP pellet was characterized using SEM and energy-dispersive X-ray spectroscopy (EDS). SEM imaging of the fractured surface (Figure 6.2a) reveals a dense microstructure composed of well-sintered grains with minimal residual porosity. The theoretical density of NZSP, calculated based on the XRD refinement, is 3.254 g cm^{-3} . In comparison, the measured bulk density obtained using the Archimedes method is 3.10 g cm^{-3} , corresponding to a porosity of 5%, which is consistent with the visual assessment of microstructural compactness. A high-magnification SEM image (Figure 6.2b) reveals the presence of two types of grains: large cubic grains with a size of about $5 \mu\text{m}$ and small submicron grains. The estimated average grain size is ap-

proximately 0.7 μm . This bimodal grain size distribution is consistent with prior reports on NZSP ceramics [176]. A previous study attributed the large deviation in grain size to the presence of intergranular liquid or amorphous phases during the sintering process [177]. EDS analysis (Figure 6.2c) confirms the presence of Na, Zr, Si, P, and O elements, aligning with the expected stoichiometry of NZSP. Furthermore, elemental mapping (Figure 6.2d) demonstrates a relatively homogeneous distribution of these elements across the analyzed region, indicating uniform chemical composition.

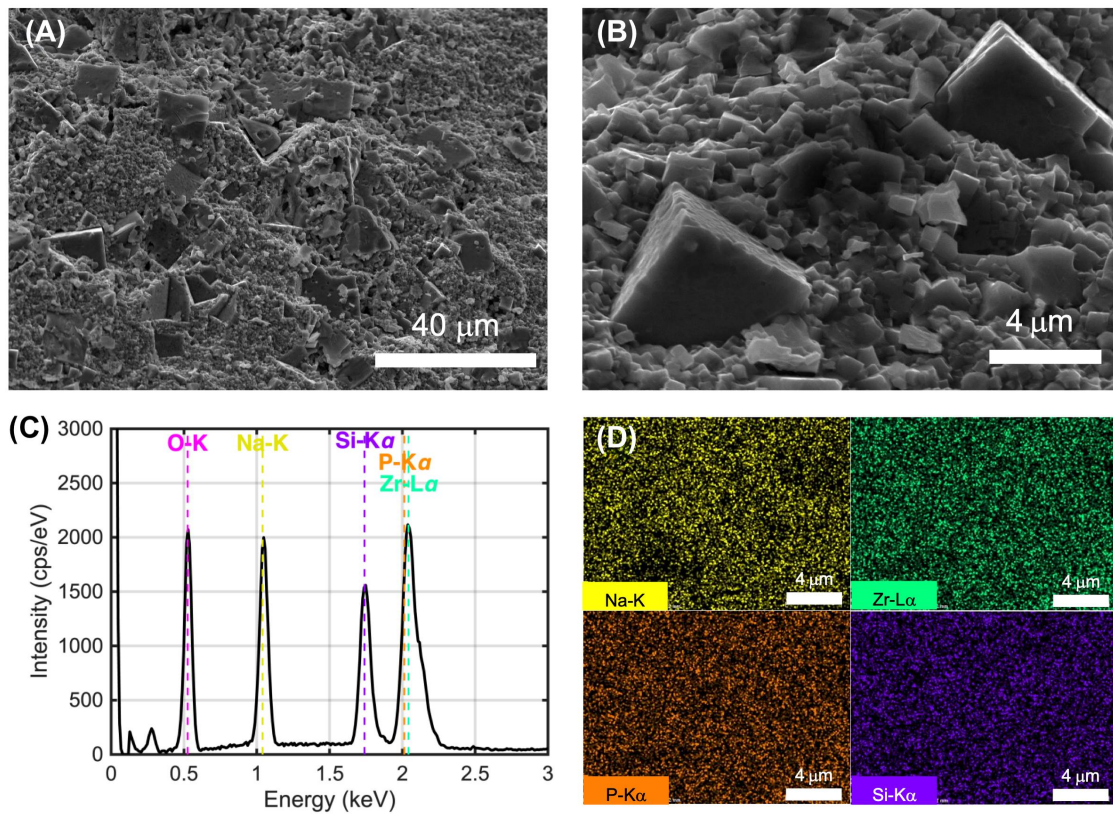


Figure 6.2: SEM and EDS characterization of NZSP. (A) SEM image of fractured pellet surface showing dense microstructure. (B) High-magnification SEM showing bimodal grain size distribution. (C) EDS spectrum confirming Na, Zr, Si, P, and O elements. (D) Elemental mapping showing homogeneous distribution.

6.3 Specific Heat and Debye Temperature

The temperature-dependent specific heat (C_p) of NZSP was measured using two complementary techniques: the PPMS (see Section 2.3.1) from 2 K to 300 K, and a DSC; (see Section 2.3.3) from 300 K to 775 K. As shown in Figure 6.3a, the measured C_p data from both techniques exhibit good continuity at 300 K, validating the consistency of the measurements. A pronounced peak in C_p is observed at approximately 422 K, corresponding to the monoclinic-to-rhombohedral structural phase transition. For comparison, literature data reported by Rohde *et al.* [166] are included and show good agreement with our results.

The Dulong-Petit limit [146, 178] was calculated to be $0.941 \text{ J g}^{-1} \text{ K}^{-1}$. At high temperatures, the measured C_p approaches this classical limit, as expected. This behavior parallels our observations for LLZTO (Chapter 4), where the specific heat likewise approaches the Dulong-Petit value at elevated temperatures, confirming that all lattice degrees of freedom are thermally excited.

To extract the Debye temperature, the low-temperature C_p data were analyzed. Figure 6.3b presents C_p/T as a function of T^2 , which follows a linear behavior as expected from the Debye model. The data were fitted using the following relation:

$$C_p(T) = \frac{12\pi^4 k_B N}{5\rho V} \left(\frac{T}{\theta_D} \right)^3 + \lambda T, \quad (6.1)$$

where k_B is the Boltzmann constant, N/V is the number density, θ_D is the Debye temperature, and λT represents the electronic contribution, which is negligible for insulating oxides like NZSP. The fit yields a Debye temperature of approximately 370 K.

Using the obtained Debye temperature, the average sound velocity v_s was calculated based on:

$$v_s = \left(6\pi^2 \frac{N}{V} \right)^{-1/3} \frac{k_B}{\hbar} \theta_D, \quad (6.2)$$

where $\hbar$ is the reduced Planck constant. The estimated average sound velocity is approximately 2962 m s^{-1} . This value is notably lower than that found in stiffer oxide ceramics such as garnet LLZTO, where $v_s = 3627 \text{ m s}^{-1}$ was measured in Chapter 4 [5], suggesting a relatively soft lattice in NZSP. The lower Debye temperature and sound velocity of NZSP compared to LLZTO are consistent with the generally weaker bonding in the NaSICON framework, where the open-channel architecture that facilitates fast Na^+ conduction also reduces the overall lattice stiffness. A similar trend was observed for the perovskite LSHT in Chapter 5, where the lattice softness was linked to the large, partially occupied A-site sublattice. Across all three families, garnet, perovskite, and NaSICON, the low sound velocities reflect the fundamental tradeoff between ionic mobility and lattice rigidity: the structural features that enable fast ion transport simultaneously soften the lattice and suppress thermal transport.

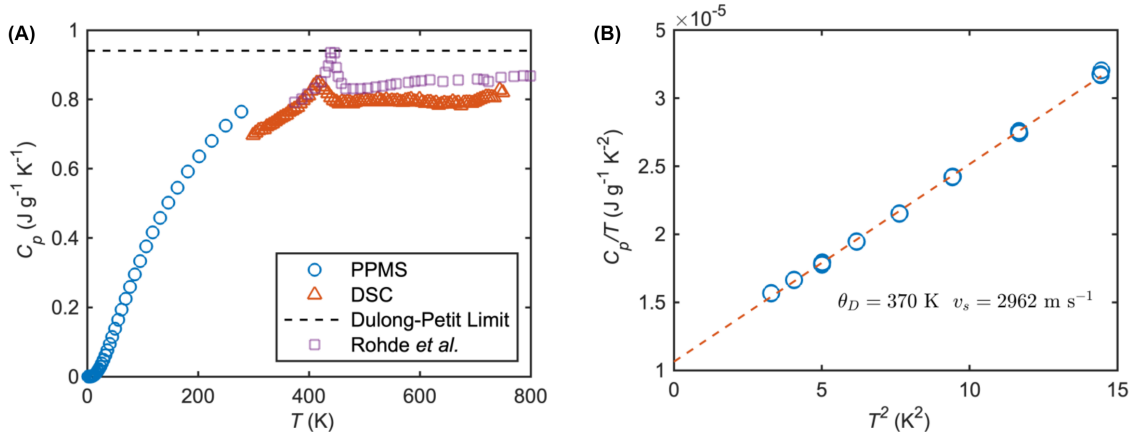


Figure 6.3: Temperature-dependent specific heat of NZSP. (A) Specific heat by PPMS and DSC with Dulong-Petit limit and phase transition peak near 422 K. (B) Low-temperature C_p/T vs T^2 plot fitted to extract Debye temperature and sound velocity.

6.4 Thermal Conductivity

The measured temperature-dependent thermal conductivity of NZSP is presented in Figure 6.4a, combining data obtained from PPMS and LFA (see Section 2.3.4) measurements. Low-temperature thermal conductivity was measured using the PPMS TTO (four-probe method; see Section 2.3.1), while high-temperature thermal diffusivity (α) was measured from 300 K to 775 K using a Netzsch LFA 457 (see Section 2.3.4). The high-temperature thermal conductivity was calculated using:

$$\kappa = \alpha \rho C_p, \quad (6.3)$$

where ρ is the bulk density and C_p is the specific heat measured by DSC.

A pronounced peak in κ is observed near 95 K, which is characteristic of crystalline materials where phonon transport is initially governed by boundary and defect scattering at very low temperatures and then limited by phonon-phonon Umklapp processes as temperature increases. Above the peak, the thermal conductivity decreases and transitions into a regime of weak temperature dependence, which is consistent with prior observations in NaSICON-type materials [166]. For comparison, the literature data for the parent compounds NZP and NZS from Böger *et al.* [1] are also included in Figure 6.4a. The peak position of NZSP lies between those of NZP and NZS, reflecting the influence of compositional tuning in the $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$ series.

The room-temperature thermal conductivity of NZSP was measured to be $\kappa = 1.01(6) \text{ W m}^{-1} \text{ K}^{-1}$, as summarized in Table 6.1 along with other physical properties. This value is notably low, comparable to that of certain glass-like materials [3, 70, 179, 180]. The overall thermal conductivity profile of NZSP, with its low-temperature peak followed by a plateau approaching the amorphous limit, is strikingly

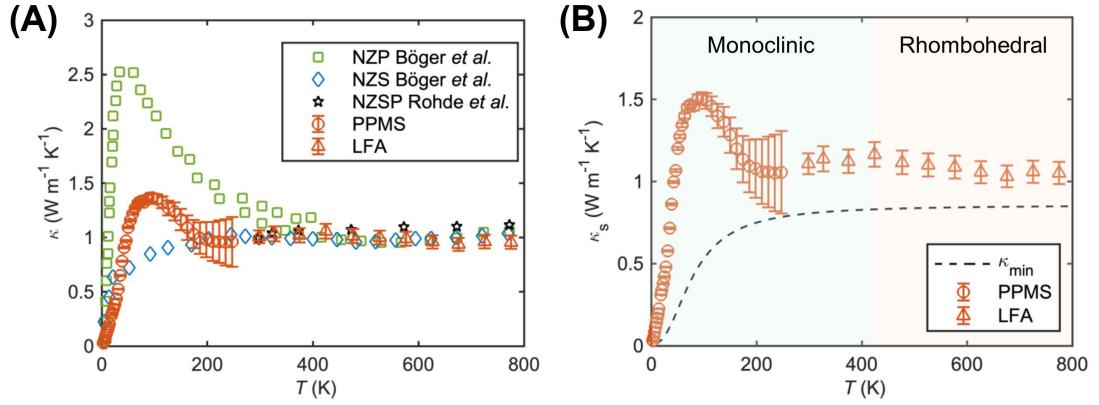


Figure 6.4: Temperature-dependent thermal conductivity of NZSP. (A) Thermal conductivity measured by PPMS and LFA (see Section 2.3.4) with literature data for NZSP, NZP, and NZS. (B) Porosity-corrected thermal conductivity with Cahill minimum thermal conductivity limit.

similar to the behavior observed in LLZTO (Chapter 4, where the peak appeared at approximately 50 K) and in LSHT (Chapter 5). Although the peak temperatures and absolute magnitudes differ, reflecting the distinct lattice dynamics of each system, the qualitative behavior is identical across all three solid electrolyte families.

Table 6.1: Room-temperature physical properties of NZSP.

Sample	κ (W m ⁻¹ K ⁻¹)	κ_s (W m ⁻¹ K ⁻¹)	C_p (J g ⁻¹ K ⁻¹)	θ_D (K)	v_s (km s ⁻¹)	γ
NZSP	1.01 ± 0.06	1.11 ± 0.06	0.70 ± 0.02	370	2.96	0.70

To account for microstructural effects and extract the intrinsic solid thermal conductivity, κ_s was obtained by correcting for the 5% porosity using the Maxwell-Eucken model [181–183]. This correction procedure follows the general approach summarized in Chapter 2 (Equation 2.6), where pores are treated as a dispersed phase of zero thermal conductivity within the solid matrix. Figure 6.4b presents the temperature dependence of κ_s , which remains largely unaffected by the monoclinic-to-rhombohedral structural phase transition near 422 K. This insensitivity is consistent with prior reports identifying the

phase transition as a slight shear distortion [164] rather than a reconstructive transformation that would significantly alter the phonon spectrum. At 300 K, κ_s is approximately $1.11(6) \text{ W m}^{-1} \text{ K}^{-1}$.

The ZrO_2 impurity phase identified in the XRD refinement (Section 6.2) has a reported thermal conductivity of approximately 1.5 to $3.0 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [184, 185], which is comparable to κ_s of NZSP. Given its relatively small weight fraction of approximately 8%, the presence of ZrO_2 has a negligible impact on the measured thermal properties. Moreover, ZrO_2 is a common impurity in NaSICON solid electrolytes [170, 173–175], allowing for a fair comparison across different NaSICON compositions.

The minimum thermal conductivity ($\kappa_{\min}$) of NZSP was calculated using the Cahill model summarized in Chapter 2 (Equation 2.7) [69, 147]. This model, formulated based on the Einstein model, describes the minimum lattice thermal conductivity of highly disordered solids. In this model, thermal transport is described by the random walk of energy among localized oscillators with varying frequencies, with the primary energy transfer occurring between nearest neighbors. The obtained $\kappa_{\min}$ is $0.82 \text{ W m}^{-1} \text{ K}^{-1}$, shown as the dashed line in Figure 6.4b.

The proximity between κ_s and $\kappa_{\min}$ at room temperature is significant: the porosity-corrected thermal conductivity is only about 35% above the theoretical amorphous floor. This suggests that the phonon mean free path in NZSP is approaching the same order of magnitude as the atomic spacing at high temperatures, precisely the same conclusion reached for LLZTO in Chapter 4, where $\kappa_s/\kappa_{\min} \approx 1.5$, and for LSHT in Chapter 5. The consistency of this ratio across three structurally distinct solid electrolyte families provides strong evidence that approaching the amorphous limit is a generic feature of fast-ion-conducting ceramics.

At elevated temperatures, both the measured thermal conductivity and the estimated minimum thermal conductivity approach constant values, resulting in a pronounced ther-

mal conductivity plateau. This trend signifies a substantial suppression of heat transport by gas-like traditional phonons (propagons), a hallmark of strong anharmonic scattering. In this regime, thermal transport is increasingly dominated by a secondary mechanism: diffuson-mediated energy transfer, arising from mode coupling between vibrational states of similar energies. Such behavior is characteristic of disordered crystals and complex lattices with pronounced lattice anharmonicity [58, 59, 103, 167]. The emergence of diffuson-mediated transport in NZSP mirrors the conclusions drawn for LSHT in Chapter 5, where a two-channel model analysis explicitly decomposed the thermal conductivity into propagon and diffuson contributions. Together, these observations across the garnet, perovskite, and NaSICON families indicate that propagon-diffuson crossover is not an anomaly of a single system, but a recurring feature in several complex oxide SEs with partially occupied mobile-ion sublattices.

Compared to other families of solid electrolytes, NZSP exhibits a moderate thermal conductivity that reflects its unique structural and bonding characteristics. As shown in Figure 6.5, NZSP's room-temperature thermal conductivity (approximately $1.1 \text{ W m}^{-1} \text{ K}^{-1}$) is lower than that of other oxide-based solid electrolytes such as $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP, approximately $2.2 \text{ W m}^{-1} \text{ K}^{-1}$) [3] and LLZTO (approximately $1.6 \text{ W m}^{-1} \text{ K}^{-1}$) [5], but significantly higher than that of sulfide and halide electrolytes, which typically fall below $0.7 \text{ W m}^{-1} \text{ K}^{-1}$. The intermediate position of NZSP within the oxide electrolyte landscape can be understood from its structural characteristics: the open-channel NaSICON framework, while providing excellent ionic conductivity, also creates a less rigid lattice compared to the three-dimensionally connected garnet structure. However, the oxide bonding in the NaSICON framework still provides substantially stronger interatomic interactions than those found in sulfide or halide electrolytes, explaining why NZSP's thermal conductivity exceeds that of these softer material classes.

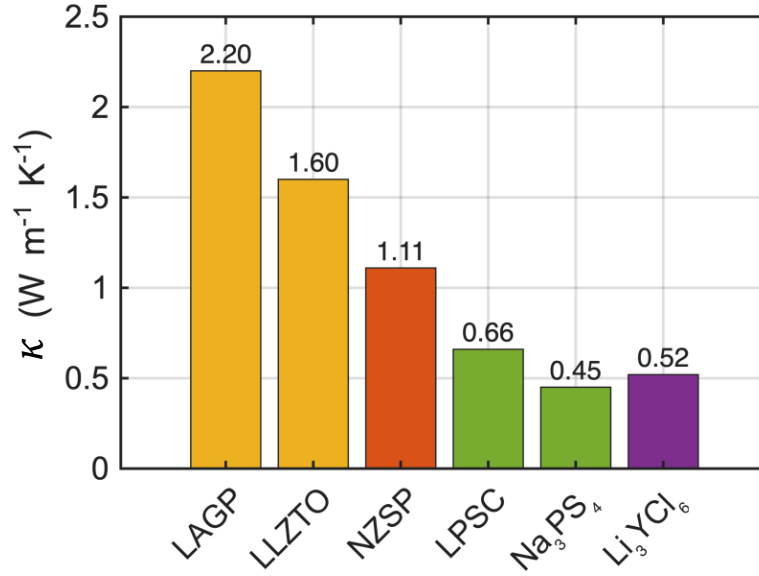


Figure 6.5: Room-temperature thermal conductivity comparison. Room-temperature thermal conductivity of NZSP compared with oxide, sulfide, and halide solid electrolytes. Data from Cheng *et al.* and Wang *et al.* citations.

To gain further insight into the microscopic phonon scattering mechanisms, the temperature-dependent average phonon mean free path (L) of NZSP was estimated using the Debye approximation summarized in Chapter 2 (Equation 2.8) [70].

The results, presented in Figure 6.6, reveal the characteristic temperature dependence expected for a crystalline material with significant extrinsic scattering. At low temperatures (approximately 3 K), the calculated L approaches 400 nm, which is in good agreement with the sub-micron grain size observed by SEM (Section 6.2). This agreement suggests that grain boundary scattering is the dominant phonon scattering mechanism at the lowest temperatures, consistent with the relatively small average grain size of 0.7 μm in our NZSP sample. This situation differs from the LLZTO polycrystals of Chapter 4, where the low-temperature phonon mean free path of approximately 500 nm was well below the much larger average grain size of 8 μm , indicating that defect scattering rather than grain boundary scattering was the limiting mechanism.

With increasing temperature, L drops sharply, falling below 3 nm by 50 K. This rapid reduction and overall low value of L reflect the enhanced phonon-defect and phonon-phonon scattering with increasing temperature. At room temperature, the phonon mean free path is on the order of interatomic spacing, confirming the glass-like character of thermal transport in this regime, a finding that echoes the results for LLZTO and LSHT in earlier chapters of this dissertation.

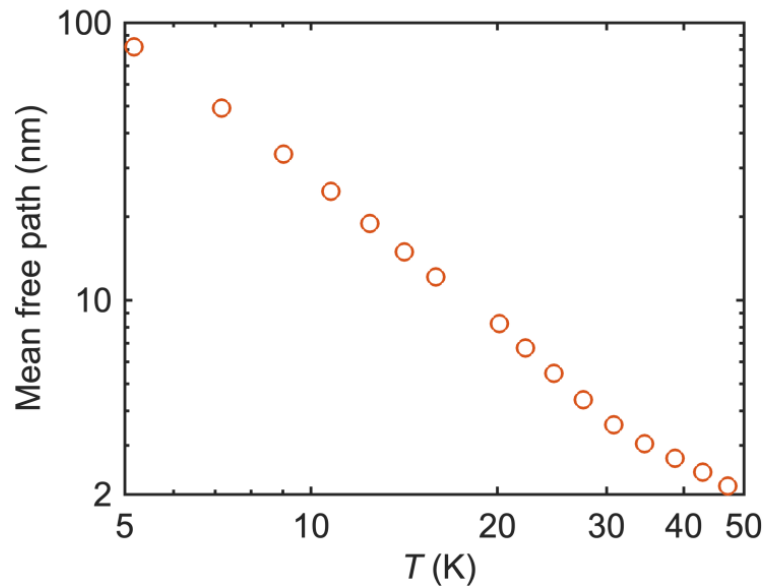


Figure 6.6: Phonon mean free path of NZSP. Temperature-dependent average phonon mean free path from Debye model showing grain-boundary scattering at low temperature and approach to interatomic spacing at room temperature.

6.5 Lattice Anharmonicity

As established in the garnet (Chapter 4) and perovskite (Chapter 5) investigations, the Grüneisen parameter (γ) provides a powerful metric for quantifying the degree of lattice anharmonicity, the extent to which the interatomic potential deviates from the harmonic

approximation. Following the same thermodynamic approach used in Section 4.4, the Grüneisen parameter for NZSP was calculated using [124, 186]:

$$\gamma = \frac{\alpha_V B_S}{C_V \rho}, \quad (6.4)$$

where B_S is the adiabatic bulk modulus, α_V is the volumetric thermal expansion coefficient, C_V is the specific heat at constant volume (approximated by C_p at 300 K due to the limited compressibility of solids), and ρ is the theoretical density.

The volumetric thermal expansion coefficient of NZSP was calculated to be $\alpha_V = 1.82 \times 10^{-5} \text{ K}^{-1}$ based on previously reported linear thermal expansion coefficients [187]. The adiabatic bulk modulus was reported as $B_S = 87.7 \text{ GPa}$ for NZSP [188, 189]. The specific heat measured in this work is $C_p = 0.70(2) \text{ J g}^{-1} \text{ K}^{-1}$ at 300 K from DSC. Using the theoretical density of 3.254 g cm^{-3} determined from the XRD refinement, the calculated Grüneisen parameter for NZSP is $\gamma = 0.70$.

This value of $\gamma = 0.70$ is markedly lower than the $\gamma = 1.63$ determined for LLZTO in Chapter 4, indicating that the NaSICON lattice exhibits significantly weaker anharmonicity than the garnet lattice. The lower Grüneisen parameter of NZSP is consistent with its lower thermal expansion coefficient and the generally more rigid oxygen-framework bonding in the NaSICON structure compared to the garnet framework. Interestingly, despite the lower anharmonicity, NZSP still exhibits a thermal conductivity that approaches the amorphous limit. This apparent paradox can be resolved by recognizing that the low thermal conductivity in NZSP arises from a combination of anharmonic phonon scattering and the inherently low sound velocity of the NaSICON framework, both the strength of scattering and the baseline transport capacity contribute to the final thermal conductivity.

In comparison with NZP and NZS, Figure 6.7a presents the average Grüneisen parameters for NZSP, NZP, and NZS [1], demonstrating a progressive increase in lattice an-

harmonicity across the $\text{Na}_{1+x}\text{Zr}_2\text{P}_x\text{Si}_{3-x}\text{O}_{12}$ series. NZP exhibits the lowest γ , while NZS shows the highest, with NZSP positioned in between. This trend suggests enhanced phonon anharmonicity as the composition evolves from phosphate-rich to silicate-rich frameworks. The systematic variation of γ within a single structural family provides a particularly clean test of the relationship between anharmonicity and thermal transport, because the crystal topology remains fixed while only the chemical composition and sodium content change.

Figure 6.7b shows the thermal conductivity measured at 120 K plotted against the inverse square of the corresponding Grüneisen parameter ($1/\gamma^2$). The correlation between $1/\gamma^2$ and κ has been established in previous studies [50, 51, 54, 190]: within the relaxation-time approximation, the Umklapp phonon-phonon scattering rate scales as γ^2 , so that $\kappa \propto 1/\gamma^2$ when other parameters are held constant. In the NaSICON compounds, a monotonic relationship is indeed observed, where higher thermal conductivity is associated with lower anharmonicity. NZSP again appears as an intermediate case, reinforcing its position between NZP and NZS in terms of both thermal transport behavior and anharmonic character.

It is worth noting that our samples were sintered under conditions similar to those used in prior studies [1, 166], suggesting comparable grain sizes and enabling a consistent basis for comparison. This internal consistency within the NaSICON family strengthens the conclusion that the observed differences in thermal conductivity arise from intrinsic differences in lattice anharmonicity rather than from extrinsic microstructural effects.

The intermediate anharmonicity observed in NZSP can be attributed to its unique sodium site distribution, providing a microscopic origin for the macroscopic Grüneisen parameter. According to Böger *et al.* [1], the elevated anharmonicity in NZS stems primarily from the occupancy of the Na(2) sites with loose bonding, which induce large atomic displacements and enhance low-frequency phonon scattering. NZP, by contrast,

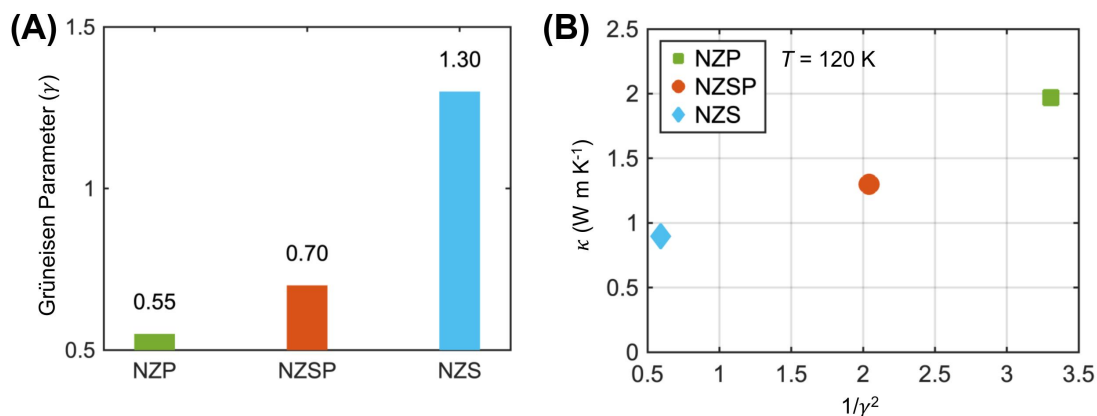


Figure 6.7: Grüneisen parameters and anharmonicity-thermal-conductivity correlation. (A) Average Grüneisen parameters for NZP, NZSP, and NZS showing progressive anharmonicity increase. (B) Correlation between thermal conductivity at 120 K and inverse-square Grüneisen parameter ($1/\gamma^2$).

lacks Na(2) site occupation entirely, resulting in a more rigid sodium sublattice and reduced anharmonicity.

In the rhombohedral phase accessible to NZSP at elevated temperatures, the Na sites align structurally with those in NZS and NZP, with Na(1), Na(2), and Na(3) exhibiting respective occupancies of approximately 0.4, 0.7, and 0.1, as previously reported [168]. The partial occupancy of 0.7 for the Na(2) site in NZSP thus offers a plausible explanation for its intermediate Grüneisen parameter and associated thermal transport behavior. Compared to NZS, where the Na(2) site is more fully occupied and contributes more strongly to anharmonicity, NZSP's partial Na(2) occupation results in a moderate degree of lattice disorder and phonon scattering, sufficient to bring the thermal conductivity near the amorphous limit, but not as extreme as in the fully silicate-substituted end member.

This Na-site-occupancy mechanism bears a strong conceptual resemblance to the role of the disordered lithium sublattice in garnet LLZTO (Chapter 3), where mode-resolved Grüneisen parameter calculations revealed that the anharmonicity is concentrated in phonon modes associated with the partially occupied Li sites. In both families, it is the

mobile-ion sublattice, with its partial site occupancy and loosely bonded ions, that drives the anharmonicity responsible for the low thermal conductivity. The perovskite LSHT system of Chapter 5 extends this picture to a third structural family, where the A-site disorder serves an analogous function. Taken together, these observations across garnet, perovskite, and NaSICON systems support a more limited hypothesis: partial mobile-ion site occupancy is one important structural factor that can enhance anharmonicity and suppress thermal transport, but it should be considered alongside material-specific bonding, mass disorder, microstructure, and phonon-spectrum complexity.

6.6 Summary

This chapter presented a systematic investigation of the thermal properties and lattice anharmonicity of NZSP, a NaSICON-type solid electrolyte, across a broad temperature range [8]. Specific heat measurements from 2 K to 775 K yield a Debye temperature of 370 K and an average sound velocity of 2962 m s^{-1} , indicating a relatively soft lattice compared with garnet LLZTO ($\theta_D = 479 \text{ K}$, $v_s = 3627 \text{ m s}^{-1}$). The specific-heat anomaly at 422 K marks the monoclinic-to-rhombohedral structural phase transition.

The thermal conductivity of NZSP exhibits a pronounced phonon peak at approximately 95 K, followed by plateau-like behavior above approximately 200 K, where the thermal conductivity approaches the amorphous limit. At room temperature, the measured thermal conductivity is $\kappa = 1.01(6) \text{ W m}^{-1} \text{ K}^{-1}$, and the porosity-corrected solid thermal conductivity of $\kappa_s = 1.11(6) \text{ W m}^{-1} \text{ K}^{-1}$ is only about 35% above the calculated minimum value of $\kappa_{\min} = 0.82 \text{ W m}^{-1} \text{ K}^{-1}$. The thermal conductivity remains largely unaffected by the structural phase transition, suggesting that strong phonon scattering and vibrational disorder dominate the heat transport over the measured temperature range. Consistent with this picture, the average phonon mean free path calculated from the Debye model reaches ap-

proximately 400 nm at 3 K, comparable to the sub-micron grain size, but collapses to below 3 nm above 50 K, approaching interatomic distances.

Comparison with structurally related NaSICON compounds, NZP and NZS, shows that NZSP has an intermediate Grüneisen parameter of $\gamma = 0.70$ and an intermediate degree of lattice anharmonicity. The monotonic correlation between $1/\gamma^2$ and κ at 120 K confirms that anharmonicity governs the thermal-transport differences among these NaSICON compositions. The intermediate behavior of NZSP can be attributed to the partial occupancy of the Na(2) site, approximately 0.7, which induces moderate lattice disorder and phonon scattering. These results highlight the critical role of mobile-ion sublattice configuration and anharmonicity in governing heat conduction in complex solid electrolytes.

These NaSICON results strengthen the broader dissertation theme that low thermal conductivity is common among fast-ion oxides, but the microscopic balance of harmonic transport, anharmonic scattering, and possible diffuson contributions depends strongly on the lattice dynamics of each material. Within NaSICON specifically, the comparison among NZP, NZSP, and NZS provides a clean in-family test of how composition and sodium-site occupancy tune anharmonicity and thermal transport. At the same time, the LLZTO, LSHT, and NZSP chapters together show that different oxide frameworks can arrive at similarly low thermal conductivity through different combinations of lattice softness, disorder, and phonon scattering. This has important implications for the thermal design of all-solid-state batteries: many candidate electrolytes are likely to serve as thermal bottlenecks, and battery thermal management strategies must account for both intrinsic lattice dynamics and material-specific microstructure and interfaces.

Chapter 7

Conclusion and Future Work

This dissertation investigated thermal transport and lattice dynamics in oxide solid electrolytes for all-solid-state batteries, with a central focus on how the structural features that enable fast ion conduction also influence heat transport. Across three major electrolyte families, garnet LLZTO, perovskite LSHT, and NaSICON NZSP, the results show that several crystalline oxide solid electrolytes exhibit low, glass-like thermal conductivity, while the microscopic balance of mechanisms remains material dependent.

The key findings are summarized as follows.

First, single-crystal garnet measurements show quantitatively that the intrinsic lattice of $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ has a low room-temperature thermal conductivity ($\kappa = 1.59(33) \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K). INS directly measures phonon excitations and confirms clear acoustic phonon dispersion in LLZTO, while DFT calculations reproduce the measured INS intensity and identify dense optical modes, an acoustic–optical avoided crossing near 7 meV, and mode-resolved Grüneisen peaks near 6 meV. QENS finds local Li hopping with $\tau \approx 2.1 \text{ ps}$ and $d \approx 1.3 \text{ Å}$, and a two-channel propagon–diffuson model reproduces the weak temperature dependence with a sizable diffuson fraction ($\sim 30\%$ at room temperature). These results collectively demonstrate that the glass-like thermal transport is intrinsic and arises from complex phonon avoided crossings, strong anharmonicity, mobile-ion dynamics, and diffuson contributions.

Second, the polycrystalline garnet studied in Chapter 4 exhibits a phonon peak near 50 K, weak temperature dependence above 200 K, and a measured room-temperature thermal conductivity of $\kappa = 1.2(2) \text{ W m}^{-1} \text{ K}^{-1}$ (porosity-corrected $\kappa_s \approx 1.6(3) \text{ W m}^{-1} \text{ K}^{-1}$), with an average Grüneisen parameter $\gamma \approx 1.63$ indicating strong anharmonicity; aging in

air produces surface Li_2CO_3 and raises the apparent κ by roughly 75%, underscoring how surface chemistry and microstructure alter measured heat transport compared with intrinsic single-crystal behavior.

Third, the perovskite LSHT system emerges as a new oxide solid electrolyte with anomalous thermal transport behavior fundamentally distinct from typical perovskites. LSHT exhibits low thermal conductivity ($1.7(5) \text{ W m}^{-1} \text{ K}^{-1}$) with clear signatures of non-phonon-gas transport, comparable to amorphous materials despite its crystalline structure. Two-channel analysis reveals that diffusons contribute approximately 34% of room-temperature heat conduction, establishing that mixed propagon-diffuson transport is not unique to garnets. This outcome is particularly significant because perovskites and garnets differ substantially in crystal topology, cation coordination, and ion migration pathways, suggesting that abnormal thermal transport in fast-ion conductors might share roots with structural features that promote ion mobility.

Lastly, the NaSICON NZSP system adds an especially clear in-family comparison. NZSP exhibits low thermal conductivity, high-temperature plateau-like behavior, and short phonon mean free paths approaching interatomic length scales. Its intermediate Grüneisen parameter within the NZP–NZSP–NZS composition series shows how sodium-site occupancy and structural features tune lattice anharmonicity and thermal transport within a single structural family. The observed trend between anharmonicity and thermal conductivity in related NaSICON compositions suggests a correlation that merits further investigation.

Taken together, these results support a more cautious central conclusion of this dissertation: *Low, glass-like thermal conductivity is a recurring feature among oxide solid electrolytes studied here. Strong anharmonicity, mobile-ion disorder, complex phonon dispersion, and diffuson-mediated heat-transport channels each affect heat transport in their own ways, with different significance in garnet, perovskite, and NaSICON systems.*

This conclusion has direct implications for battery thermal management. Many solid electrolytes have similarly low thermal conductivity, which can be a critical factor in thermal management of all-solid-state cells. Electrolyte selection and interface design must therefore be guided not only by ionic conductivity and electrochemical stability, but also by thermal transport properties and their evolution during operation and aging.

Looking forward, several research directions follow directly from the findings of this dissertation. A first priority is to expand cross-family measurements without assuming a universal mechanism in advance. Applying the same thermal-conductivity, heat-capacity, elastic-property, and lattice-dynamics workflow to emerging oxide, sulfide, halide electrolytes or even some cathode materials would clarify which signatures affecting thermal transport are broadly recurring and which are specific to individual structures or chemistries. A second direction is phonon-mode-resolved characterization of thermal transport. Further neutron and X-ray inelastic scattering studies, combined with temperature-dependent lattice-dynamics calculations, can quantify which vibrational modes dominate thermal resistance in each electrolyte family. Such investigations could also explain how the same lattice dynamics enable fast ion conduction. This direction is especially relevant because it could provide insights into how structural features enable high ionic conductivity and help create guidelines for designing new solid electrolytes. A third direction is interface-aware thermal transport. Real battery architectures involve complex interfaces, residual porosity, secondary phases, and processing-dependent grain structures. The LLZTO polycrystal and aging results show that microstructure and surface chemistry can change thermal transport in ways that are not captured by intrinsic single-crystal measurements alone. Extending current models to include interfacial thermal resistance and chemically evolving boundaries is therefore essential for connecting intrinsic materials physics to cell-level thermal behavior.

In summary, this dissertation compares thermal transport in three oxide solid-electrolyte families and shows that glass-like heat conduction is not limited to a single garnet composition. Thus, thermal transport provides not only a practical materials parameter for battery design, but also a sensitive probe of the lattice dynamics and mobile-ion disorder that underlie fast-ion conduction. By linking lattice dynamics, anharmonicity, and transport across garnet, perovskite, and NaSICON systems while preserving their material-specific differences, this work advances both fundamental understanding and practical thermal design principles for next-generation solid-state batteries.

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