ISSN (Online) 2395-2717

International Journal of Engineering Research in Electrical and Electronic Engineering (IJEREEE)

Volume 13, Issue 02, February 2026

Optimizing Garnet Type LLZO Electrolytes Through Solid-State Processing for Solid State Batteries

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Abstract*— All Solid-State Batteries (ASSBs) offer significant advantages for electric vehicle and grid storage applications including enhanced safety and higher energy density compared to conventional lithium-ion batteries. Garnet-type Lithium Lanthanum Zirconium Oxide, LLZO, ($Li_7La_3Zr_2O_{12}$) is a ceramic oxide solid electrolyte candidate due to its wide electrochemical stability window (>5 V), chemical compatibility with lithium metal, and mechanical rigidity. However, processing-related microstructural variations often introduce additional grain boundary resistance, which reduces ionic transport through the material affecting the net ionic conductivity of the electrolyte. The current work systematically investigates the influence of solid-state synthesis processes on the morphology and ionic conductivity of cubic LLZO. A modified synthesis route incorporating optimized wet ball milling and subsequent thermal treatment was conducted to improve chemical reactivity, phase stabilization, densification. X-ray diffraction (XRD) pattern confirmed the formation of cubic garnet phase of LLZO. Microstructural analysis revealed particle size reduction following ball milling, indicating effective mechanical refinement and improved powder homogeneity prior to pelletization. Electrochemical Impedance Spectroscopy (EIS), in the frequency range of 0.1 Hz–1 MHz, enabled analysis of bulk and grain boundary resistance through Nyquist plots. These findings highlight the importance of synthesis process in modifying the structural and electrochemical properties of LLZO electrolyte. They also correlate the processing–structure–transport relationships and provide practical insight for integrating LLZO electrolytes into scalable, high performance solid-state battery systems for energy storage applications.

Index Terms*— All-solid-state batteries, high-energy-density storage, lithium metal batteries, processing optimization, solid-state electrolytes.

I. INTRODUCTION

The increasing global demand for safer and higher energy density energy storage systems has accelerated research into advanced battery technologies for electric vehicle (EV) and grid-scale storage applications. Conventional lithium-ion batteries (LIBs) employ organic liquid electrolytes that are flammable and thermally unstable, posing safety risks under abusive conditions such as overcharging, short-circuiting, and mechanical damage [1]. Furthermore, the use of liquid electrolytes limits the practical implementation of lithium metal anodes due to dendritic lithium growth and unstable solid electrolyte interphase (SEI) formation, which compromise cycle life and safety [2], [3].

In this context, all solid-state batteries (ASSBs) have emerged as a promising energy storage technology. By replacing flammable liquid electrolytes with solid ionic conductors, ASSBs offer improved thermal stability, enhanced safety margins, and the possibility of pairing high capacity lithium metal anodes with high voltage cathodes [4], [5]. The solid electrolyte plays a central role in enabling these advantages, as it must simultaneously provide high ionic conductivity, wide electrochemical stability, mechanical robustness, and chemical compatibility with electrode materials [6].

Among the various classes of solid electrolytes investigated including sulfides, polymers, NASICON-type oxides, and perovskites, garnet-type lithium lanthanum zirconium oxide ($Li_7La_3Zr_2O_{12}$, LLZO) has attracted significant attention [7]. First reported as a fast lithium-ion conductor in 2007 [8], LLZO exhibits a three-dimensional lithium conduction network and demonstrates favourable chemical stability against lithium metal compared to many other oxide electrolytes. The electrochemical stability window of LLZO extends beyond 5 V versus Li/Li^+, making it compatible with high voltage cathode materials [9].

LLZO exists in tetragonal and cubic phases, with the cubic phase exhibiting significantly higher ionic conductivity due to increased lithium disorder and enhanced vacancy mobility

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[10]. Stabilization of the cubic phase at room temperature typically requires controlled processing conditions and/or aliovalent doping strategies to modify lithium site occupancy and promote structural disorder [11], [12]. The ionic conductivity of stabilized cubic LLZO can reach values on the order of 10^{-4} to 10^{-3} $S \cdot cm^{-1}$ at ambient temperature, making it one of the most promising oxides based solid electrolytes [13].

In addition to its favourable electrochemical properties, LLZO possesses relatively high mechanical modulus compared to polymer and sulfide electrolytes. This mechanical rigidity is considered beneficial in suppressing lithium dendrite propagation, as it increases resistance to dendrite penetration across the electrolyte thickness [14]. However, despite these advantages, the practical electrochemical performance of LLZO is strongly influenced by processing conditions and microstructural features.

Solid-state synthesis routes often introduce microstructural irregularities such as broad particle size distributions, incomplete phase formation, residual secondary phases, and grain boundary irregularities [15]. Lithium volatilization or loss during high temperature calcination and sintering further complicates phase stability and compositional control, potentially leading to formation of impurity phases and increased interfacial resistance [16]. In polycrystalline LLZO, grain boundary resistance can constitute a significant fraction of total impedance, thereby limiting effective ionic conductivity [17]. Consequently, microstructural optimization, particularly particle refinement, homogeneous mixing, and controlled densification are critical for achieving improved transport properties.

Mechanical processing techniques such as ball milling play a vital role in enhancing powder homogeneity, reducing diffusion distances, and promoting uniform phase formation during calcination [18]. Optimized milling conditions can improve particle packing behaviour and influence sintering kinetics, ultimately affecting grain growth and grain boundary characteristics. Therefore, understanding the relationship between processing parameters, powder morphology, and ionic transport is essential for advancing LLZO toward practical ASSB integration.

In the present work, garnet type LLZO was synthesized using a modified solid-state route incorporating optimized wet ball milling and controlled thermal treatment. Structural and morphological evolution of the powder before and after milling was systematically analysed, and the electrochemical performance of sintered pellets was evaluated using impedance spectroscopy. This work focuses on understanding how solid-state processing influences phase formation, powder homogeneity, and grain boundary characteristics in LLZO, and how these factors collectively govern its ionic conductivity and electrochemical performance in solid-state battery applications.

II. EXPERIMENTAL

A. Materials and Synthesis

Cubic garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte was synthesized using a conventional solid-state reaction route. Lithium carbonate (Li_2CO_3), lanthanum oxide (La_2O_3), and zirconium dioxide (ZrO_2), all of analytical grade purity (≥99%), were used as starting precursors and procured from commercial suppliers.

Prior to weighing, La_2O_3 was preheated at 900 °C for 2 h to remove absorbed moisture and surface hydroxides due to its hygroscopic nature. The precursor powders were then weighed in stoichiometric proportions corresponding to the $Li_7La_3Zr_2O_{12}$ composition. A slight excess (10%) of lithium source was incorporated to compensate for lithium volatilization during high-temperature processing. All handling was performed with care to minimize atmospheric moisture exposure and prevent surface Li_2CO_3 formation.

The weighed powders were mixed using planetary ball milling for 10.5 h at 420 rpm to ensure uniform compositional mixing. The milling media used is ethanol. Ball milling enhances interparticle contact, reduces diffusion distance during calcination, and promotes homogeneous phase formation. After milling, the slurry was dried at 100 °C for 10 h to remove residual solvent.

The dried powder was calcined in a muffle furnace at 950 °C for 10 h in air. Calcination promotes decomposition of lithium carbonate and initiates solid-state reaction between lanthanum and zirconium oxides, leading to formation of the garnet LLZO phase. The calcined powder was then reground to break agglomerates and improve packing uniformity.

The powder was compacted into circular pellets using a hydraulic press under uniaxial pressure of approximately 200–300 MPa. Pellet thickness and diameter were maintained uniformly to enable accurate conductivity calculations. The compaction step was performed to shape the material for densification and electrochemical testing.

The compacted pellets were sintered at 650 °C for 20 h in air. High temperature sintering promotes grain growth, neck formation, and densification while reducing porosity. Since ionic conductivity in LLZO is strongly influenced by grain connectivity and grain boundary resistance, optimization of sintering time and temperature was critical. Measures were taken to minimize lithium loss during sintering. After completion of the dwell period, the furnace was allowed to cool naturally to room temperature.

The final sintered pellets exhibited good mechanical rigidity and structural integrity suitable for structural and electrochemical characterization.

B. Characterization

Scanning Electron Microscopy (SEM) was performed on the precursor powders both before and after ball milling to evaluate morphological changes, particle size refinement, and the degree of agglomeration induced by mechanical

ISSN (Online) 2395-2717

International Journal of Engineering Research in Electrical and Electronic Engineering (IJEREEE)

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processing.

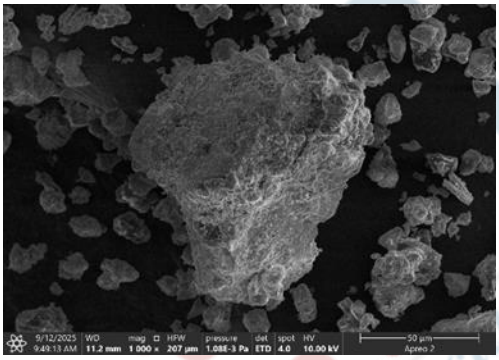
Phase identification and structural verification were carried out using X-ray Diffraction (XRD) analysis. This technique was employed to confirm crystallization of the garnet-type LLZO structure and to verify phase purity following thermal processing.

Electrochemical characterization was performed using a CH Electrochemical Workstation through Electrochemical Impedance Spectroscopy (EIS). Impedance spectra were obtained in the form of Nyquist plots

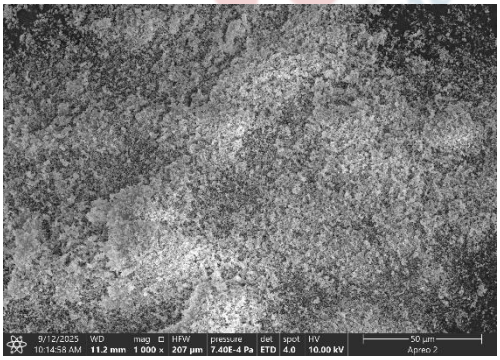
III. RESULTS & DISCUSSIONS

A. Scanning Electron Microscope

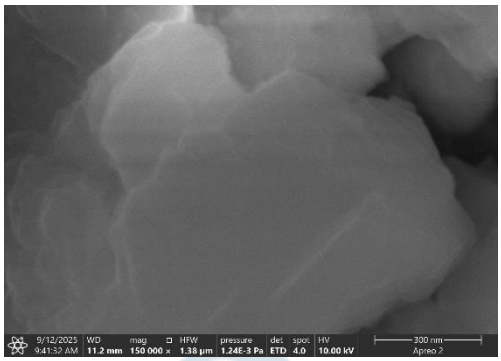
Scanning Electron Microscopy (SEM) images of the as-calcined LLZO powder and ball-milled LLZO are presented in Figure 1. The micrographs clearly demonstrate a significant reduction in particle size after ball milling. Figures 1(a) and 1(c) show the as-calcined powders, where particle sizes are observed to be as large as ~100 µm. In contrast, Figures 1(b) and 1(d) illustrate the ball-milled LLZO, where the particle size is reduced to below 300 nm. This substantial refinement in particle size can be attributed to the high-energy impact and shear forces during the ball milling process, consistent with reports by Zheng et al [19], who observed similar size reduction behaviour induced by mechanical milling during processing.



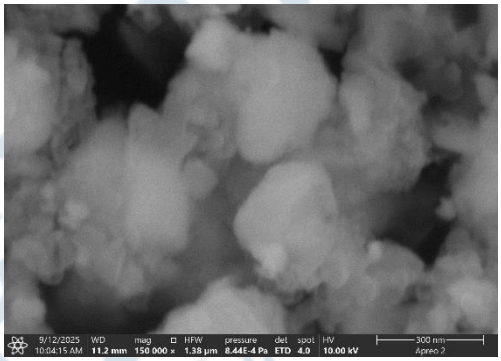
(A)



(B)



(C)



(D)

Fig.1.

Scanning Electron Microscope images of the As Calcined powders and Ball Milled Powders: (A) As calcined LLZO powders and (B) ball milled powder at 1000 magnification, (C) As calcined powder LLZO powder and (D) ball milled powder at 150,000 magnification.

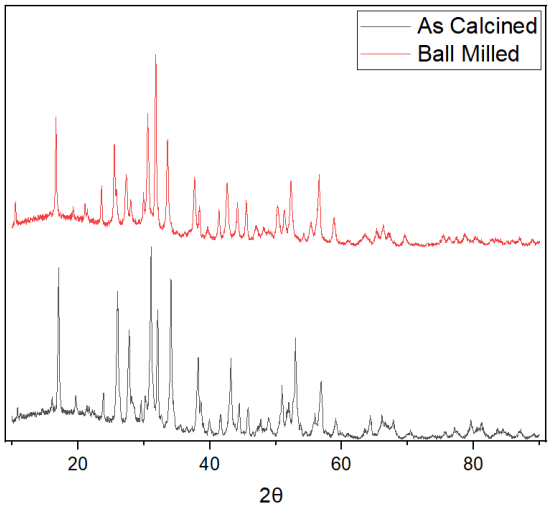
B. X-ray Diffraction

The X-ray Diffraction (XRD) patterns of the as-calcined and ball-milled LLZO powders are presented in Figure 3. The diffraction peaks of both samples correspond to the characteristic reflections of garnet-type $Li_7La_3Zr_2O_{12}$, confirming phase retention after mechanical processing [20]. However, noticeable differences in peak intensity and width are observed following ball milling. The as-calcined LLZO exhibits sharp, high-intensity diffraction peaks and indicating high crystallinity. In contrast, the ball-milled sample shows a clear reduction in peak intensity accompanied by significant peak broadening. Peak broadening is typically associated with crystallite size refinement and the introduction of lattice strain, both of which arise from the repeated high-energy impacts during the ball milling process. The reduction in peak height further suggests a partial loss of long-range structural order, indicating decreased crystallinity due to mechanical processing [21].

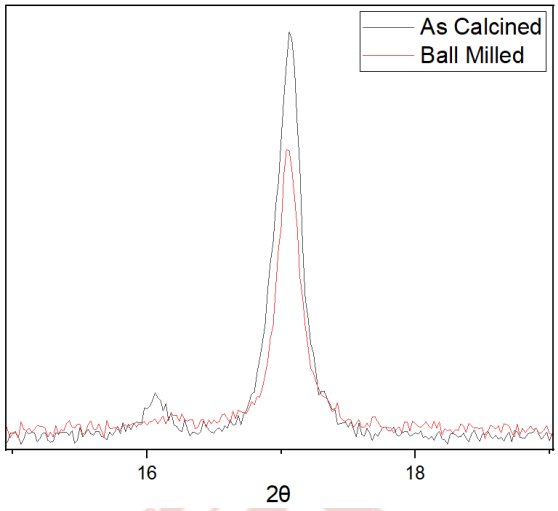
ISSN (Online) 2395-2717

International Journal of Engineering Research in Electrical and Electronic Engineering (IJEREEE)

Volume 13, Issue 02, February 2026



(A)



(B)

Fig. 2.

X-ray Diffraction: (A) Comparative diffractograms of as-calcined and ball-milled powders indicating phase purity and retention of the cubic structure; (B) Magnified view of a diffraction peak illustrating significant peak shortening and broadening.

A closer examination of the diffraction peak near $2\theta \approx 17°$ reveals a distinct difference between the two samples. The as-calcined LLZO exhibits a sharp and well-defined peak at 17.02°, characteristic of a highly crystalline lattice. In contrast, the corresponding peak in the ball-milled sample appears broader and less intense, reflecting reduced crystallite size and increased lattice distortion. Additionally, using the Debye-Scherrer formula,

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos(\theta)} \quad [1]$$

Where, K = dimensionless shape factor

λ = X-ray wavelength

β= Full-width half maxima

θ= Bragg angle

Based on this calculation, the average crystallite size decreased by 6% after processing. This decrease in grain size is directly correlated with the observed peak broadening and reduction in peak intensity.

C. Impedance Test

The ionic transport properties of the LLZO pellets were investigated using Electrochemical Impedance Spectroscopy (EIS) across a frequency range of 0.01 Hz to 3×10^6 Hz. The resulting Nyquist plot, shown in Figure 3(A), exhibits a semicircular arc in the high-to-intermediate frequency regions, followed by a characteristic low-frequency tail. This multi-component response is typical of polycrystalline solid-state electrolytes, where different physical processes occur at varying time constants [22][23][24].

The semicircle, occurring at the highest frequencies, is attributed to the total resistance (Bulk and grain boundary resistance, $R_b + R_{gb}$), which is analysed using an equivalent circuit described by equation 2.

$$R_b||CPE_b + CPE_{int} \quad [2]$$

Where, R_b is bulk resistance, CPE_b is the capacitance of the electrolyte and CPE_{int} is the capacitance of the electrode-pellet, respectively. Figure 3(B) represents the Nyquist plot for the fitted model using the equivalent circuit.

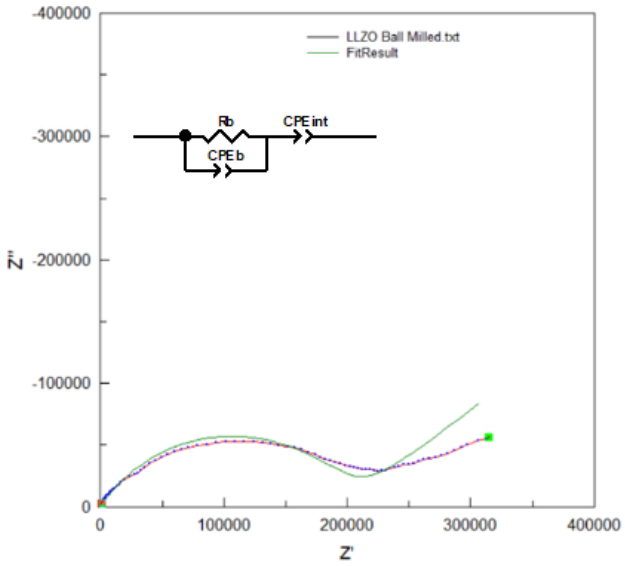


Fig. 3.

Nyquist plot of the ball-milled LLZO powder illustrating the experimental data (black) and the modeled fit (green). The inset displays the equivalent circuit.

IV. CONCLUSIONS

This work investigated the influence of solid-state processing on the structural and electrochemical behaviour of garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolytes. Emphasis was placed on correlating mechanical homogenization, thermal treatment, and microstructural evolution with ionic transport characteristics.

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Mechanical refinement through wet ball milling significantly improved powder uniformity and reduced particle agglomeration, facilitating more effective solid-state reaction during calcination. Structural analysis confirmed the formation of the desired garnet phase, while morphological observations revealed enhanced homogeneity in the processed powders. These microstructural improvements contributed to improved packing behaviour and densification during sintering.

Electrochemical impedance analysis of the sintered pellets demonstrated that ionic transport in LLZO is strongly governed by grain boundary characteristics and microstructural integrity. The study highlights that even in oxide-based solid electrolytes with intrinsically high bulk conductivity, processing-induced heterogeneities can substantially influence total resistance.

Overall, the results underscore the critical role of controlled powder processing in governing phase stability and transport behaviour in LLZO. Establishing this processing–structure–transport linkage provides a foundation for rational optimization of garnet electrolytes aimed at reliable and scalable integration into advanced all-solid-state battery systems.

Future investigations may focus on targeted grain boundary engineering and lithium stoichiometry control to further enhance room-temperature ionic conductivity and interfacial stability.

V. ACKNOWLEDGEMENTS

The authors gratefully acknowledge CHRIST (DEEMED TO BE UNIVERSITY), School of Engineering & Technology, Kengeri, for providing the academic framework and institutional support necessary for carrying out this research work. The authors sincerely thank the Centre of Excellence in Frontier Materials Research for financial assistance, laboratory infrastructure, and access to characterization facilities that were essential for the successful execution of this study.

The authors also acknowledge the Department of Electrical and Electronics Engineering, CHRIST (DEEMED TO BE UNIVERSITY) for facilitating this work as part of the undergraduate thesis requirements and for fostering an interdisciplinary research environment conducive to advanced materials research.

The guidance, technical discussions, and continuous academic support provided by the supervising faculty members, who are co-authors of this work, are also formally recognized and appreciated.

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