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Synthesis and characterization of LLZTO solid electrolyte via the solid-state ball-milling method

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ABSTRACT

The rapid advancement of electronic devices and energy storage systems demands the development of safe, durable, and high-performance battery components. One of the key challenges in this field is replacing flammable liquid electrolytes with more stable and reliable inorganic solid electrolytes. Among various candidates, garnet-type lithium lanthanum zirconium tantalum oxide $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) has emerged as a promising material due to its excellent chemical stability and high ionic conductivity. In this study, we present the synthesis and characterization of LLZTO solid electrolyte prepared using the solid-state ball-milling method. The as-prepared LLZTO exhibited a well-defined grain structure with particle sizes ranging from 3 to 5 micrometers. Electrochemical analysis revealed an ionic conductivity on the order of 10^{-5} S·cm^{-1} at room temperature, demonstrating its potential for application in solid-state lithium-ion batteries. These findings contribute to the ongoing efforts to develop safer and more efficient energy storage solutions, paving the way for next-generation battery technologies.

Keywords: solid electrolyte, LLZTO, ionic conductivity, garnet-type, X-ray diffraction, SEM.

1. Introduction

In recent years, Li-ion batteries have gained increasing importance due to the rapid advancement of electronic devices and electric vehicles [1,2]. Consequently, researchers are actively working to develop safer battery components. Current Li-ion batteries rely on flammable organic liquid electrolytes, posing significant safety concerns. Therefore, replacing these hazardous liquids with solid electrolytes is a crucial research focus to enhance battery safety and stability [3].

Among solid electrolytes, ceramic electrolytes are considered promising alternatives to liquid electrolytes and are being widely explored for their advantages in battery technology [4]. Ceramic electrolytes are known for their high ionic conductivity and excellent thermal and chemical stability, making them attractive candidates for solid-state lithium-ion batteries (SSLIBs). Unlike liquid electrolytes, which are prone to leakage, flammability, and dendrite growth, ceramic electrolytes provide a robust and stable framework for lithium-ion transport [5,6]. There are two main types of ceramic solid electrolytes: sulfides and oxides. Sulfide electrolytes exhibit high ionic conductivity, reaching 10^{-3} to 10^{-2} S·cm^{-1} [7]. However, they suffer from poor chemical compatibility with the lithium anode and are unstable under ambient conditions [8]. Unlike sulfide-based electrolytes, oxide-type ceramic electrolytes, particularly garnet-type LLZTO, exhibit stability in air and good compatibility with anode materials. Due to its high ionic conductivity, excellent chemical stability, and strong resistance to temperature fluctuations, LLZTO is considered one of the most promising electrolytes for all-solid-state batteries [9–11].

The cubic phase of $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ is particularly promising for next-generation batteries due to its high reliability and energy density. This is primarily attributed to its impressive lithium-ion conductivity (~10^{-3}–10^{-4} S/cm at room temperature), excellent chemical stability in contact with metallic lithium, and broad electrochemical stability relative to the Li^+/Li pair [12]. The ordered lithium-ion

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arrangement in the cubic phase facilitates efficient ion mobility, enabling rapid charge transfer. The incorporation of tantalum (Ta) into the structure further enhances ionic conductivity by reducing defect concentration in the crystal lattice. Additionally, Ta helps stabilize the cubic phase, ensuring consistent conductive properties even under varying temperatures and external conditions [12,13].

Nowadays there are a lot of methods for preparation LLZTO nanoparticles, such as solid-state reaction, sol-gel synthesis, molten salt method, and high-energy ball milling [14–16]. Each method has its own advantages and challenges, influencing the particle size, phase purity, and ionic conductivity of LLZTO nanoparticles. Wet chemical methods, such as sol-gel techniques, coprecipitation routes, and polymer combustion, enable homogeneous mixing of precursors at the molecular or atomic level, leading to the production of finer LLZTO particles at lower calcination temperatures [17,18]. However, the classical solid-state reaction (SSR) method remains the most commonly used synthesis route for preparing such ceramics [19].

This study aims to synthesize LLZTO ceramic nanoparticles using the solid-state ball-milling method and to investigate their physical and chemical properties. We present a simple and efficient approach for the large-scale production of nanoscale LLZTO with enhanced ionic conductivity.

2. Experimental part

2.1. Materials

Li_2CO_3 (99.00%), La_2O_3 (99.99%), ZrO_2 (99.00%), and Ta_2O_5 (99.00%) were purchased from Sigma-Aldrich and used as received without further purification.

2.2. Characterization

The structure of LLZTO before and after sintering was analyzed using X-ray diffraction (XRD) with a Rigaku SmartLAB system, equipped with a Cu X-ray tube and a D-Text detector. Data were collected over a 2θ range of 10–70° with a step size of 0.06°.

The grain size and morphology of the LLZTO powder and pellet were examined using scanning electron microscopy (FESEM, Auriga Crossbeam 540). To enhance electronic conductivity, a 5 nm gold coating was applied to the powder surfaces using an automatic Q150T atomizer, as electrolyte materials are electronic insulators.

The ionic conductivity was measured via electrochemical impedance spectroscopy (EIS) using a Metrohm AutoLab 204 potentiostat/galvanostat over a frequency range of 1 Hz to 1 MHz. The ionic conductivity of electrolyte pellets was determined using the equation $\sigma = d/RS$ where σ represents the ionic conductivity, d is the pellet thickness, R is the resistance, and S is the pellet area.

2.3. Preparation of solid electrolyte

The cubic-phase LLZTO powder was synthesized using the traditional solid-state method. Stoichiometric amounts of Li_2CO_3 (99.00%, preheated at 120 °C for 12 h), La_2O_3 (99.99%, preheated at 900 °C for 12 h), ZrO_2 (99.00%), and Ta_2O_5 (99.00%) were accurately weighed and ball-milled together. To compensate for lithium loss during calcination, an excess of 15 wt.% Li_2CO_3 was added [20]. The precursor materials were ball-milled using zirconia balls (0.5 mm and 0.2 mm in diameter) with isopropanol as a dispersant at 400 rpm for 6 hours. The slurry was then dried at 80 °C for 1 hour. The resulting powder was calcined in a closed crucible within a muffle furnace at 900 °C for 6 h, followed by natural cooling to room temperature. The synthesis process is illustrated in Fig. 1.

An uniaxial hydraulic press was employed to form the material into tablets at a pressure of 3–5 bar. These tablets were then sintered in a muffle furnace at 1100 °C for 15 hours. To prevent sticking to the alumina crucible, the tablets were covered with mother powder during the sintering process. No additional lithium source was added to either the granules or the starting powder. To minimize lithium loss during sintering, the crucible was sealed with a lid.

3. Results and discussion

In the synthesis of LLZTO, tantalum – a pentavalent element – is commonly used to substitute Zr^{4+} in the garnet-type LLZ structure, promoting the stabilization of the cubic phase and enhancing lithium-ion conductivity. Ta^{5+} doping leads to the formation of additional lithium vacancies, which increases structural disorder and stabilizes the highly conductive cubic phase. LLZTO solid electrolytes have been synthesized via various methods, including solid-state, sol–gel and methods including different thermal treatment conditions. As a result, the composition exhibiting the highest ionic conductivity varies depending on the synthesis approach [21–23] .

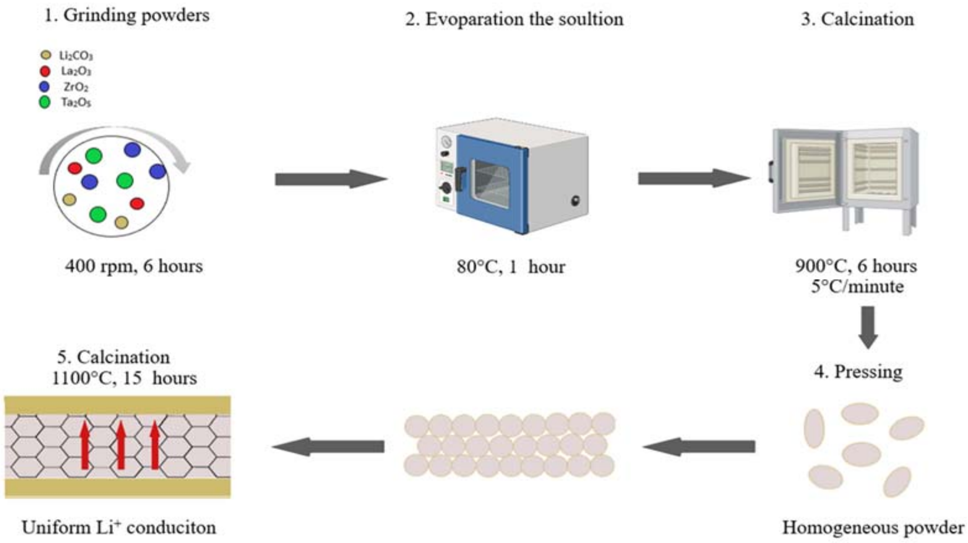

Fig. 1. General illustrative scheme for obtaining LLZTO solid electrolytes.

In this study pure garnet-structured LLZTO particles were successfully synthesized using the solid-state ball-milling method. The density of the tablets was determined by measuring their weight and physical dimensions, a common and effective method for evaluating LLZTO ceramics, which achieved a relative density of 90–93%. After the final sintering, obtained tablets, with varying tantalum content, changed color from white to light yellow (Fig. 2a). This color shift is attributed to the high amount of tantalum in the composition.

To monitor phase formation, X-ray diffraction (XRD) analysis was performed using a MiniFlex Benchtop Powder X-ray Diffractometer, scanning the 2θ range from 10° to 70° with a step size of 0.02°. The XRD results for the LLZTO powders matched the standard data reported in the literature for the cubic garnet phase $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, confirming the successful synthesis of the desired cubic phase [24] (Fig. 2b). The starred peak at 27° is attributed to Li_2CO_3 impurities present after synthesis [13,25], which disappear after sintering at 1100 °C. Li_2CO_3 forms as a result of the reaction between Li_2CO_3 (or other lithium precursors) and ZrO_2 when lithium volatilizes or is insufficiently compensated. The XRD analysis confirmed the formation of a single-phase cubic garnet structure after sintering, in agreement with the literature, and the disappearance of secondary impurity peaks after thermal treatment validated the phase purity of the synthesized samples. This is significant, as the cubic phase is known to support higher lithium-ion conductivity than the tetragonal counterpart.

Additionally, cross-sectional analysis using Scanning Electron Microscopy (SEM, ZEISS Crossbeam 540) revealed densely packed particles composed of

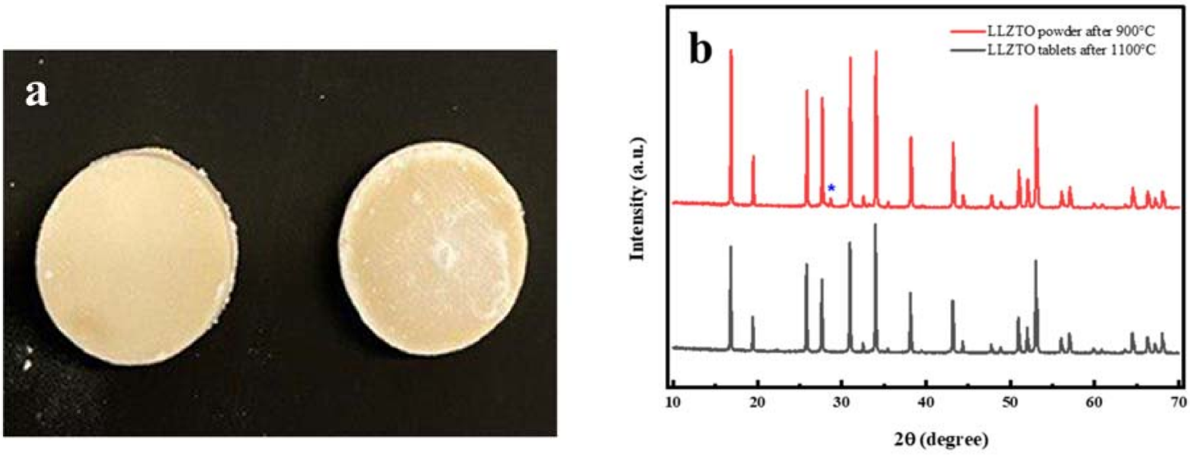

Fig. 2 (a) – photographs of LLZTO tablets before and after sintering at 1100 °C, (b) – XRD-pattern of LLZTO particles.

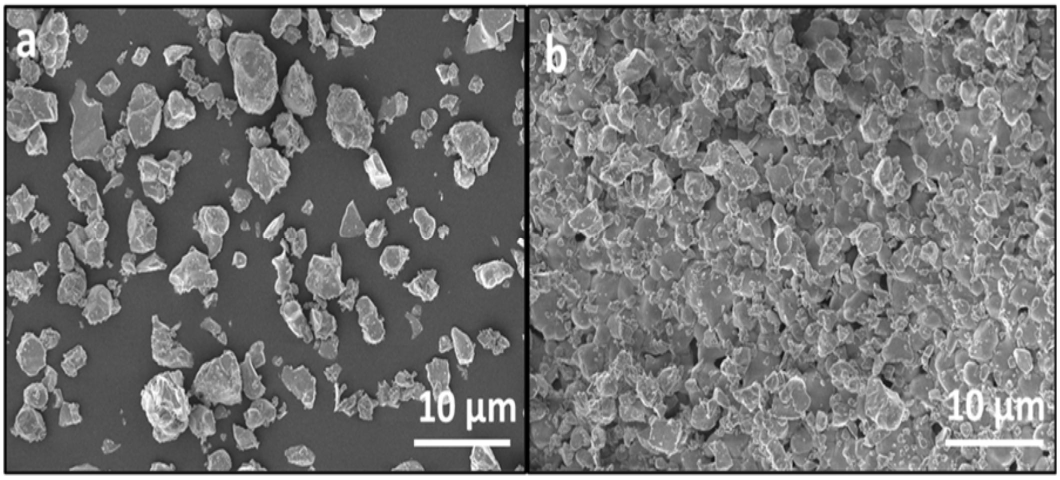

Fig. 3. SEM-patterns of LLZTO particles: (a) – SEM image of LLZTO powders, (b) – SEM analysis of LLZTO tablet.

crystals measuring 3–5 micrometers in size (Fig. 3a, b). The SEM images revealed densely packed particles with a grain size distribution of 3–5 µm, which is consistent with typical microstructures achieved through conventional solid-state routes [26]. However, some porosity remained, which is likely responsible for the slightly lower ionic conductivity observed (9.2×10^{-5} S/cm). Han et al. reported that pore formation can be minimized by sintering pellets in an oxygen atmosphere, resulting in dense LLZTO structures with a significantly higher ionic conductivity of 6.18×10^{-4} S·cm^{-1} [14]. Furthermore, Shu et al. explored the effect of substituting O^{2-} sites with Cl^{-} anions in LLZTO garnet electrolytes, achieving an ionic conductivity of 4.21×10^{-6} S·cm^{-1} [27].

LLZTO solid electrolytes typically exhibit ionic conductivity values in the range of ~10^{-3} to 10^{-4} S/cm at room temperature [24]. Impedance spectroscopy results (Fig. 4) displayed a characteristic semicircular Nyquist plot, indicating bulk and grain boundary contributions to the total resistance. The ionic conductivity of the synthesized LLZTO solid electrolyte was measured to be 9.2×10^{-5} S/cm. Comparable results were reported by Hongqi et al., who synthesized various compositions of $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (x = 0.2–1.0) via solid-state reaction and found that the composition with x = 0.6 achieved an ionic conductivity of 3.25×10^{-5} S·cm^{-1}, which is in good agreement with our findings [22].

In another study, Liu et al. investigated LLZTO ceramics fabricated via pressureless sintering at 1230 °C in air. The composition sintered at this temperature exhibited the highest total ionic conductivity of 6.01×10^{-4} S·cm^{-1} at room temperature [30]. Lee et al. synthesized and characterized LLZTO powders and pellets with a garnet-type cubic structure using the sol-gel method [29]. While their materials demonstrated relatively high ionic conductivity (0.21 mS/cm), the process involved toxic organic solvents such as 2-methoxyethanol and 1-propanol, raising safety and environmental concerns.

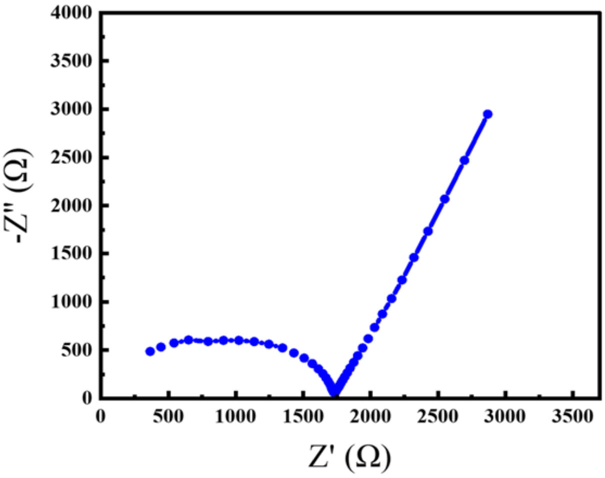

Fig. 4. Electrochemical impedance spectrum of LLZTO pellet (sample with area 0.785 cm^2 and 0.125 cm thickness).

The relatively low conductivity in this work may be attributed to several factors: incomplete densification (as the density reached only 93%), residual porosity acting as scattering centers for Li$^+$ ions, and possible lithium loss during high-temperature sintering, despite the addition of excess Li_2CO_3. Although a 15 wt.% excess of Li_2CO_3 was added to compensate for lithium loss, lithium evaporation at high temperatures remains a significant challenge and can lead to secondary phase formation or structural vacancies that adversely affect ion transport [24,25].

4. Conclusion

In conclusion, cubic-phase LLZTO particles were successfully synthesized using a conventional solid-state method. Dense electrolyte pellets were prepared at 900 °C. The synthesized LLZTO, with an average particle size of 3–5 µm and a relative density of 93%, exhibits a total lithium-ion conductivity of 9.2×10^{-5} $S\cdot cm^{-1}$ at room temperature. These findings confirm that the solid-state ball-milling method is one of the effective approaches for obtaining pure LLZTO.

Comparatively, while wet chemical methods such as sol-gel or polymer combustion offer improved particle homogeneity and lower processing temperatures, they often involve complex precursor chemistries and scalability limitations. The solid-state ball-milling method used here, despite its known drawbacks in achieving nanoscale homogeneity, remains advantageous due to its simplicity, cost-effectiveness, and compatibility with large-scale production. Thus, the current work serves as a foundation for further optimization of LLZTO fabrication via solid-state routes, potentially including hybrid techniques that combine mechanochemical activation with reactive sintering to boost performance.

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Синтез и характеристика твердого электролита LLZTO методом твердотельного шарового измельчения

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АННОТАЦИЯ

Быстрое развитие электронных устройств и систем хранения энергии требует разработки безопасных, долговечных и высокопроизводительных компонентов аккумуляторов. Одной из ключевых задач в этой области является замена легковоспламеняющихся жидких электролитов более стабильными и надежными неорганическими твердыми электролитами. Среди различных кандидатов литий-лантан-цирконий-танталовый оксид гранатового типа (LLZTO) является многообещающим материалом, благодаря своей превосходной химической стабильности и высокой ионной проводимости. В этом исследовании рассматриваются синтез и характеристики твердого электролита LLZTO, полученного с использованием метода твердотельной шаровой мельницы. Готовый электролит LLZTO продемонстрировал четко определенную структуру зерна с размером частиц от 3 до 5 микрометров. Электрохимический анализ выявил ионную проводимость порядка 10^{-5} См·см$^{-1}$ при комнатной температуре, что демонстрирует его потенциал для применения в твердотельных литий-ионных аккумуляторах. Полученные результаты способствуют развитию более безопасных и эффективных технологий хранения энергии, открывая путь к аккумуляторным системам нового поколения.

Ключевые слова: твердый электролит, LLZTO, ионная проводимость, гранатовый тип, рентгеновская дифракция, СЭМ.

LLZTO қатты электролитін қатты шарлы ұнтақтау әдісімен синтездеу және оның сипаттамасы

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АҢДАТПА

Электрондық құрылғылар мен энергия сақтау жүйелерінің жылдам дамуы қауіпсіз, берік және жоғары өнімді батарея компоненттерін әзірлеуді талап етеді. Бұл саладағы негізгі мәселелердің бірі жанғыш сұйық электролиттерді тұрақты және сенімді бейорганикалық қатты электролиттермен ауыстыру болып табылады. Әртүрлі кандидаттар арасында гранат типті литий лантан цирконий тантал оксиді (LLZTO) тамаша химиялық тұрақтылығы мен жоғары иондық өткізгіштігінің арқасында перспективалы материал ретінде пайда болды. Бұл зерттеуде біз қатты күйдегі шарикті фрезерлік әдіспен дайындалған LLZTO қатты электролитінің синтезі мен сипаттамасын ұсынамыз. Дайындалған LLZTO бөлшектердің өлшемдері 3-тен 5 микрометрге дейін болатын жақсы анықталған дән құрылымын көрсетті. Электрохимиялық талдау бөлме температурасында 10^{-5} S·cm^{-1} тәртібінде иондық өткізгіштігін анықтады, бұл оның қатты күйдегі литий-ионды батареяларда қолдану мүмкіндігін көрсетті. Бұл нәтижелер энергияны қауіпсіз және тиімдірек сақтау шешімдерін әзірлеу бойынша үздіксіз күш-жігерге септігін тигізіп, келесі ұрпақ батарея технологияларына жол ашады.

Түйінді сөздер: қатты электролит, LLZTO, иондық өткізгіштік, гранат түрі, рентгендік дифракция, СЭМ.

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