

Optimum Li-site Vacancy in Garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte

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Abstract: Precisely modulating the lithium vacancy concentration is critical for maximizing the ionic conductivity of garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid electrolytes. However, conventional high-temperature synthesis inevitably introduces parasitic impurities (e.g., Al^{3+} from alumina crucibles), which profoundly perturb the intrinsic defect chemistry. Consequently, the fundamental structure-property relationship between lithium vacancies and ionic transport remains obscured. To unveil the genuine ion-transport mechanism, we employ a strictly contamination-free sintering strategy. By integrating a tailored microstructural model to decouple morphological interferences such as grain size and boundary effects, we systematically investigate the crystallographic evolution and transport kinetics in a series of Nb^{5+} -doped LLZO (0.2–0.7 per formula unit, pfu). Our findings unambiguously demonstrate that within a pristine, impurity-free lattice, the room-temperature ionic conductivity peaks at an optimal lithium vacancy concentration of exactly 0.45 pfu. This work not only identifies the intrinsic vacancy metric required for ultrafast ion transport in lithium garnets but also establishes a rigorous crystallographic foundation for the rational design of high-performance solid electrolytes.

Key words: garnet-type solid electrolyte; lithium vacancy concentration; Nb doping; transport kinetics

Driven by intrinsic safety and exceptionally high theoretical energy density, solid-state lithium batteries (SSBs) represent a leading paradigm for next-generation energy storage^[1]. Among solid electrolyte candidates, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is exceptionally promising due to its robust chemical stability against lithium metal and broad electrochemical window^[2–3]. However, pristine LLZO adopts a tetragonal phase at room temperature, which severely restricts its ionic conductivity^[4]. To stabilize the highly conductive cubic phase and unlock the three-dimensional (3D) Li^+ transport network, aliovalent doping is essential to engineer an optimal concentration of lithium vacancies^[5]. Because vacancy concentration fundamentally governs long-range charge-carrier kinetics, precisely pinpointing this optimal metric is prerequisite to maximizing the electrochemical performance of LLZO.

Current structural engineering predominantly relies on cationic substitution at the Li or Zr sites. However, Li-site doping (e.g., Al^{3+} [6] or Ga^{3+} [7]) faces profound fundamental and synthetic constraints. Physically, foreign cations occupying Li sites inevitably induce steric hindrance (lattice blocking)^[8–9], and strong competitive electrostatic interactions^[10] which impede Li^+ mobility. Synthetically, these dopants readily provoke the segregation of insulating secondary phases at grain boundaries during high-temperature densification^[11–12], making it extremely challenging to accurately quantify the effective vacancy concentration incorporated within the bulk lattice. In contrast, substituting Zr sites with high-valence cations (e.g., Nb^{5+} [13] or Ta^{5+} [14]) inherently avoids direct occupation of Li pathways. By precluding phase segregation and external impurity interference, the Zr-site doping system provides an ideal,

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pristine physical model to unambiguously elucidate the intrinsic relationship between lithium vacancy concentration and ionic conductivity in LLZO.

Despite extensive investigations into Zr-site doping, a profound discrepancy persists between theoretical predictions and experimental observations regarding the optimal Li^+ vacancy concentration. Density functional theory (DFT) and lattice dynamics computations suggest that as the vacancy concentration approaches 0.5 pfu, the carrier population and 3D transport network reach an ideal percolation balance^[15], theoretically maximizing ionic flux. Conversely, classical experimental studies frequently report optimal Nb or Ta doping levels plateauing at 0.25 pfu^[16] or 0.5 pfu^[17-18]. This inconsistency originates primarily from historical synthesis protocols. To facilitate densification or accommodate crucible constraints, high-temperature sintering conventionally employed alumina crucibles or deliberate additions of Al_2O_3 ^[19] or MgO ^[20] as sintering aids. These impurity cations (Al^{3+} , Mg^{2+}) spontaneously diffuse into the LLZO lattice, consuming intrinsic lithium ions or occupying critical vacancy sites. Consequently, the "nominal" doping levels in prior literature severely deviate from the actual defect chemistry, masking the genuine optimum vacancy concentration.

To bridge this theoretical-experimental divide, this study systematically investigates the intrinsic relationship between lithium vacancy concentration and ionic transport in a series of Nb-doped LLZO (0.2–0.7 pfu). To achieve this, we implement a strictly impurity-free regime by employing an alumina-free synthesis environment coupled with precise lithium compensation, thereby eliminating external contamination pathways. Furthermore, we construct tailored microstructural control models to successfully decouple morphological artifacts—such as grain size and boundary resistance—from intrinsic lattice transport behavior. By deploying this rigorous methodological framework, the present work aims to systematically evaluate the crystallographic evolution and bulk kinetics across varying defect concentrations, with the ultimate objective of identifying the genuine defect threshold required to kinetically optimize the 3D long-range lithium-ion transport network.

1 Experimental

1.1 Powder synthesis and green pellet fabrication

The solid-state electrolytes were synthesized *via* a conventional high-temperature solid-state reaction approach^[21]. Lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, analytical grade, with a 1% excess to compensate for high-temperature volatilization loss), lanthanum oxide (La_2O_3 , 99.95%), zirconium dioxide (ZrO_2 , analytical grade, 99.99%), and niobium pentoxide (Nb_2O_5 , 99.9%) were utilized as the starting precursors. These raw materials were precisely weighed according to the stoichiometric ratio of the target products, $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Nb}_x\text{O}_{12}$ ($x=0.2-0.7$). For brevity, compositions with varying Nb doping concentrations are hereafter denoted as "LLZN_xO".

The precursor mixture was placed into a planetary ball mill and dry-milled at a rotational speed of 165 r/min for 3 h in polyurethane (PU) tank. After passing through a 20-mesh sieve, 100 g of the blended powder was loaded into a magnesium oxide (MgO) crucible and calcined at 850 °C for 6 h to facilitate the initial phase transition. The as-calcined powder was subsequently sieved through an 80-mesh (180 μm) screen and hermetically sealed in reagent bottles. To further refine the particle size and enhance the sintering activity of the precursors, a secondary ball-milling step was performed at 150 r/min for 3 h in PU tank. Finally, after sieving through a 200-mesh screen, precisely 1 g of the resultant powder (Fig. S1) was transferred into a mold with an internal diameter of 12 mm and dry-pressed under a load of 3 tons (equivalent to an applied pressure of 265 MPa) to yield the green bodies (Fig. S2) for subsequent sintering (S1).

1.2 Ceramic sintering process

The densification of the ceramic specimens was carried out in a muffle furnace. To ensure consistency in experimental conditions and suppress lithium volatilization, six identical green bodies with the same composition were stacked in parallel and placed within a MgO crucible^[22] (dimensions: $\phi 27\text{ mm}\times 25\text{ mm}$). Notably, samples across all eight compositions were sintered simultaneously in a single furnace run. This study systematically evaluated the influence of heat treatment protocols on ceramic densification by designing seven distinct sintering schedules: holding at 1220, 1240, 1260, and 1280 °C for 20 min, and holding at 1300, 1320, and 1340 °C for 10 min. The heating rate for all programs was strictly controlled at 5 °C $\cdot\text{min}^{-1}$. Following the high-temperature sintering and subsequent cooling, two specimens were randomly selected from the six parallel samples in each group for downstream

phase analysis and electrochemical characterization.

To decouple grain boundary effects, an abnormal grain growth (AGG) control group ($>100\ \mu\text{m}$ grains) was prepared using composition-tailored rapid-sintering protocols to accommodate the varying thermodynamic barriers of different Nb-doping levels. To suppress lithium volatilization at elevated temperatures, specimens were sintered in sealed MgO crucibles bedded with identical sacrificial mother powder. At a $5\ ^\circ\text{C}\cdot\text{min}^{-1}$ heating rate, the applied peak temperatures and dwell time were: $1240\ ^\circ\text{C}/20\ \text{min}$ ($\text{LLZN}_{0.2}\text{O}$), $1260\ ^\circ\text{C}/20\ \text{min}$ ($\text{LLZN}_{0.3}\text{O}$), $1280\ ^\circ\text{C}/20\ \text{min}$ ($\text{LLZN}_{0.35}\text{O}$), $1300\ ^\circ\text{C}/10\ \text{min}$ ($\text{LLZN}_{0.4-0.5}\text{O}$), $1340\ ^\circ\text{C}/10\ \text{min}$ ($\text{LLZN}_{0.6}\text{O}$), and $1360\ ^\circ\text{C}/20\ \text{min}$ ($\text{LLZN}_{0.7}\text{O}$).

1.3 Phase analysis and performance evaluation

The phase compositions of both the calcined powders and the sintered ceramic specimens were determined using a powder X-ray diffractometer (XRD, Rigaku Ultima IV) equipped with Ni-filtered Cu K α radiation ($\lambda=1.542\ \text{\AA}$). All measurements were conducted at room temperature over a 2θ scanning range of 10° to 60° with a scan rate of $8(^\circ)\cdot\text{min}^{-1}$. Prior to analysis, the ceramic specimens were respectively extracted and thoroughly ground into fine powders using an agate mortar.

The bulk density of the ceramic pellets was measured at room temperature using the Archimedes method with ethanol as the immersion medium (employing a Mettler-Toledo density measurement kit). The relative density was then calculated as the ratio of the measured bulk density to the theoretical density. Furthermore, the cross-sectional micro-morphology of the ceramic specimens was observed and characterized using a scanning electron microscope (SEM, TESCAN MIRA 3).

The ionic conductivity of the samples was evaluated *via* electrochemical impedance spectroscopy (EIS) using a Toyo LN-Z2-HF impedance analyzer. The measurements were performed over a frequency range from 100 MHz to 1 Hz, with an applied AC perturbation voltage of 20 mV. Prior to the test, silver layers were sputtered onto both parallel surfaces of the specimens to serve as lithium-ion blocking electrodes. The ionic conductivity ($\sigma\ (\text{S}\cdot\text{cm}^{-1})$) was calculated according to the equation $\sigma=L/(R\times S)$, where L (cm) is the thickness of the ceramic pellet, R (Ω) represents the total resistance of the LLZO ceramic, and S (cm^2) denotes the contact area of the blocking electrodes.

To probe the local coordination environments and

mobility of the lithium ions, ^7Li solid-state nuclear magnetic resonance (NMR) spectroscopy was performed under magic-angle spinning (MAS) conditions. The spectral data were collected utilizing a 400 MHz JEOL ECZ400R spectrometer outfitted with a dedicated MAS probe. During the measurements, the samples were subjected to a constant rotation rate of 10 kHz at a strictly controlled temperature of $25\ ^\circ\text{C}$. For the precise calibration of the ^7Li chemical shifts, crystalline lithium chloride (LiCl) was employed as the external zero reference (0 ppm).

2 Results and Discussion

2.1 Phase evolution

Fig. 1 presents the XRD patterns of the Nb-doped LLZO powders and corresponding bulk ceramics. The powder XRD results clearly reveal that below a lithium vacancy concentration of 0.4 pfu (specifically, 0.2–0.35 pfu), the calcined powders exhibit a biphasic mixture of cubic and tetragonal phases. Notably, the Nb=0.2 sample displays pronounced peak splitting at $2\theta\approx 27^\circ$, and characteristic tetragonal reflections persist even at 0.35 pfu. These observations unambiguously demonstrate that an intrinsic vacancy concentration of 0.25 pfu is insufficient to fully stabilize the pure cubic phase, directly contradicting prevailing claims in early literature^[16]. The ostensible pure-phase formation historically reported originates primarily from systematic synthesis artifacts rather than intrinsic defect chemistry. Specifically, prolonged thermal exposure in conventional corundum crucibles drives the spontaneous infiltration of Al^{3+} into the LLZO lattice^[23], uncontrollably generating extraneous lithium vacancies. Concurrently, excessive sintering temperatures and protracted dwell time exacerbate intrinsic lithium volatilization^[24], causing actual vacancy concentrations to severely exceed their predetermined nominal values.

Further structural analysis of the rapidly sintered ceramics reveals significantly narrowed full width at half maximum (FWHM) compared to their powder counterparts, indicating substantially enhanced crystallinity. Crucially, the phase constitution of the bulk ceramics faithfully inherits that of the precursor powders: the mixed-phase state robustly persists for vacancy concentrations <0.4 pfu. Furthermore, trace residual La_2O_3 does not perturb the high-temperature phase evolution of the host lattice, aligning with previous reports^[25]. Ultimately, based on this strictly contamination-free

model, we definitively establish that a minimum intrinsic lithium vacancy concentration ≥ 0.4 pfu is the absolute thermodynamic prerequisite to stabilize the pure cubic LLZO structure.

2.2 Compositional verification and micro-morphology

To establish a robust compositional foundation for subsequent property analyses, the as-sintered Nb-LLZO ceramics were evaluated *via* inductively coupled plasma optical emission spectroscopy (ICP-OES). As detailed in Table 1, the measured elemental stoichiometries across all eight compositions align precisely with their nominal targets. This high degree of compositional fidelity definitively rules out extraneous impurity infiltration and severe elemental volatilization during synthesis, thereby ensuring the absolute reliability of our subsequent lithium vacancy quantifications.

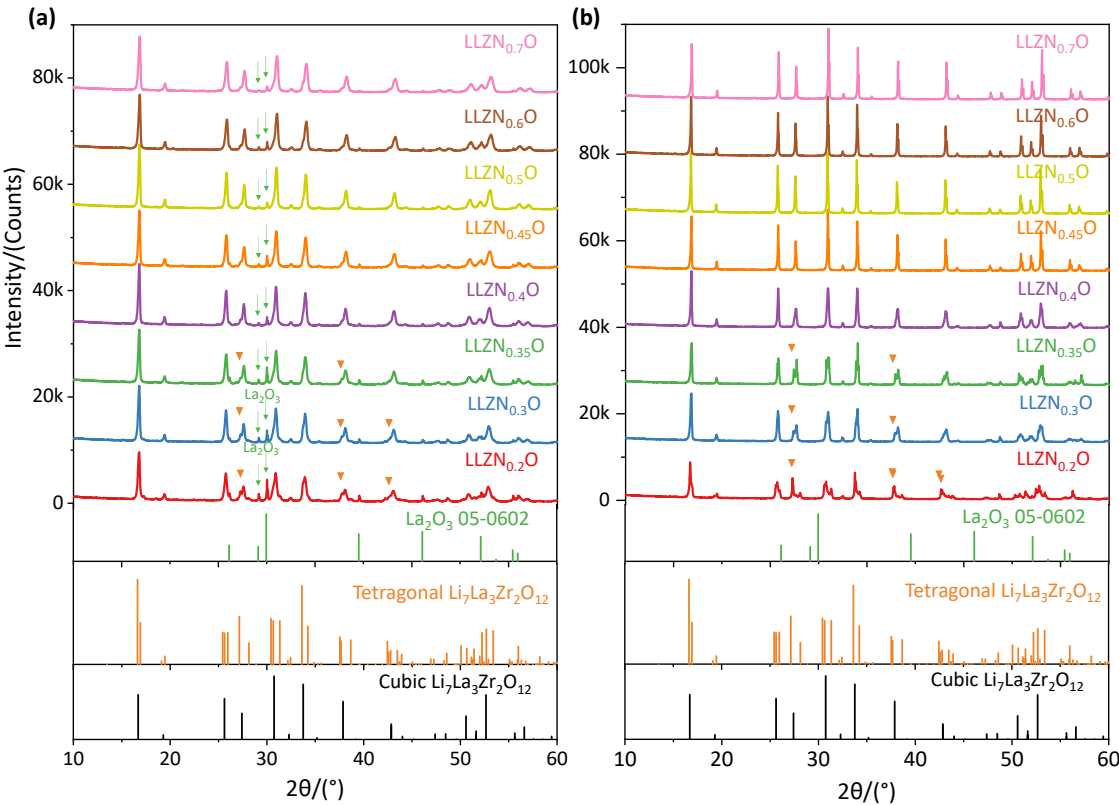


Fig. 1 XRD patterns of the Nb-LLZO

(a) Calcined powders; (b) Sintered ceramics

Table 1 ICP-OES of Nb-LLZO ceramics

Doping Amount of Nb/pfu	Li	La	Zr	Nb
0.20	7.92	3.00	1.85	0.21
0.30	7.91	3.00	1.82	0.29
0.35	8.00	3.00	1.77	0.34
0.40	7.44	3.00	1.66	0.37
0.45	7.66	3.00	1.65	0.43
0.50	7.74	3.00	1.55	0.46
0.60	7.75	3.00	1.47	0.57
0.70	7.41	3.00	1.31	0.65

Beyond compositional purity, microstructural morphology-specifically grain size-critically dictates the

macroscopic ion transport in garnet electrolytes^[26-28].

To decouple morphological artifacts from intrinsic vacancy-driven conductivity, we engineered microstructural control groups with distinctly varied grain boundaries (Fig. S3 and Fig. S4). Cross-sectional SEM (Fig. 2) reveals that the conventional grain-sized group (without abnormal grain growth, AGG) exhibits near-theoretical densification with intimate intergranular contact and negligible voiding across all Nb doping levels. This confirms that these baseline specimens possess the high-quality structural framework prerequisite for reliable electrochemical evaluation.

In stark contrast, the tailored AGG control group features massively enlarged grains ($>100\ \mu\text{m}$) across the

fracture surfaces. High-magnification analysis confirms these ultra-large grains possess pristine transgranular facets and clean boundaries, entirely devoid of secondary phase precipitation or elemental segregation. The fundamental physical rationale for engineering this ultra-large-grain architecture is to construct a macroscopic framework with extended long-range continuity, thereby drastically minimizing grain boundary quantity and its associated interfacial impedance fluctuations^[29]. By imposing these stringent geometrical constraints, we successfully isolate the physical perturbations of grain boundaries, enabling an unambiguous evaluation of the intrinsic transport dynamics governed strictly by the lattice vacancy concentration.

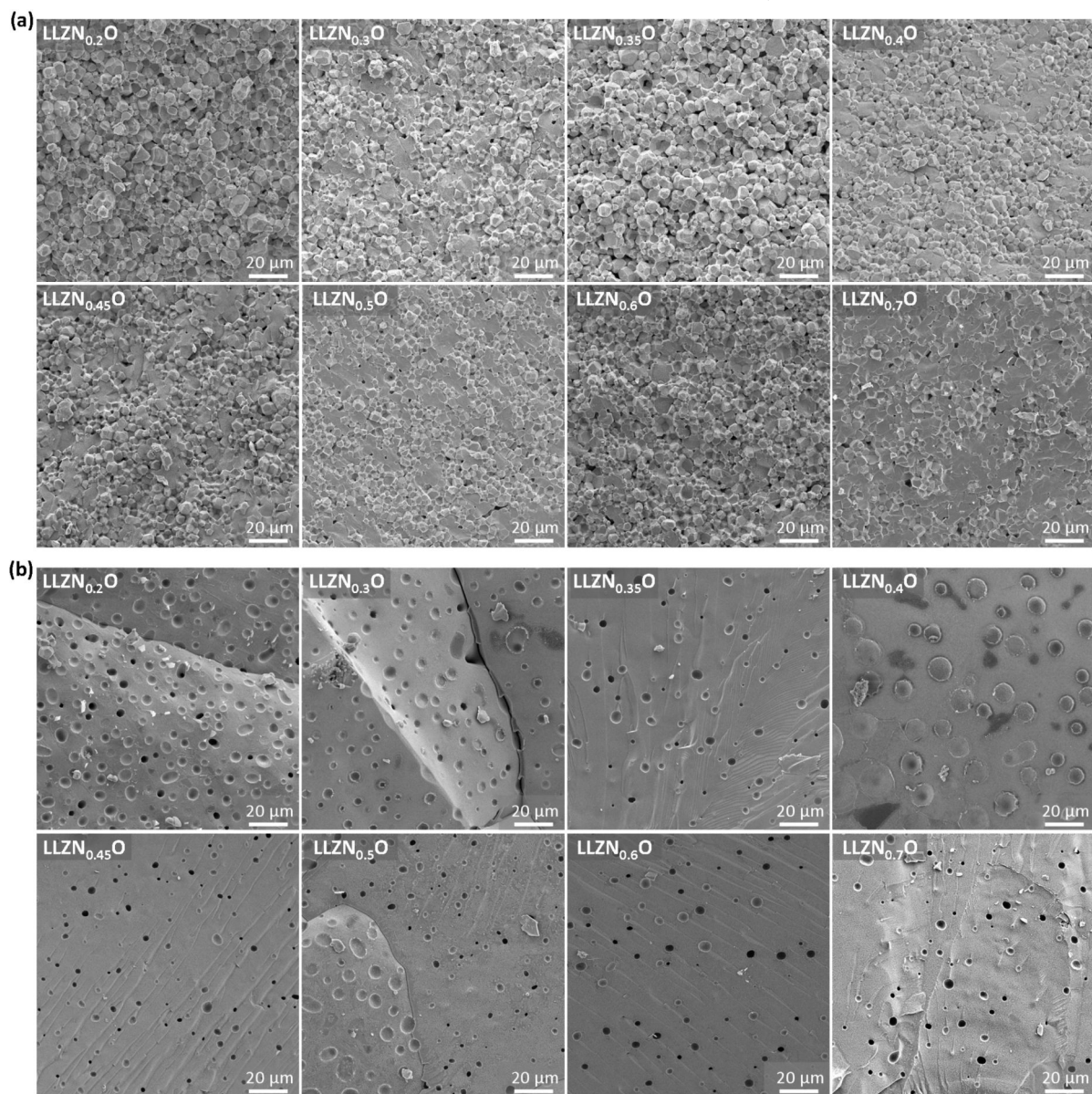


Fig. 2 Cross-sectional SEM images of Nb-LLZO ceramics with various lithium vacancy concentrations
(a) Sample group with regular uniform grains; (b) Control group exhibiting abnormal grain growth (AGG)

2.3 Relative density and ion transport performance

Fig. 3(a) and Table S1 illustrate the relative density of the Nb-LLZO ceramics as a function of lithium vacancy concentration. Across all evaluated groups, the relative density positively correlates with vacancy concentration up to 0.4 pfu, beyond which it plateaus at approximately 95%. Universally, all specimens achieve relative densities exceeding 92%. This confirms that the rapid sintering protocol successfully yields highly dense ceramic frameworks with intimate intergranular bonding, effectively eliminating porosity-induced artifacts in subsequent electrochemical evaluations.

Fig. 3(b) plots the room-temperature ionic conductivity against lithium vacancy concentration. The conductivity exhibits a characteristic volcano-shaped dependence on the vacancy metric: it initially ascends, peaks sharply at exactly 0.45 pfu ($\sim 1 \text{ mS}\cdot\text{cm}^{-1}$), and subsequently deteriorates with further vacancy introduction. Crucially, this volcano-shaped trend is highly reproducible across all four morphological and thermal control groups. Compositions adjacent to the peak (0.4 and 0.5 pfu) also maintain robust conductivities exceeding $0.8 \text{ mS}\cdot\text{cm}^{-1}$. This stringent reproducibility reinforces 0.45 pfu as the intrinsic, configurationally optimal vacancy concentration for maximizing long-range Li^+ transport.

The macroscopic conductivity trends are structurally corroborated by normalized EIS spectra (Fig. 3(c-f)). The corresponding Nyquist plots uniformly display a single depressed semicircle at high frequencies—arising from the overlapping relaxation time constants of the bulk and grain boundaries at room temperature—and a low-frequency diffusional tail. The high-frequency intercept with the real axis (cut-off frequency), which positively correlates with the intrinsic Li^+ migration rate^[30], definitively confirms the kinetic superiority of the $\text{LLZN}_{0.45}\text{O}$ sample. Across all experimental groups, the 0.45 pfu composition consistently exhibits the highest cut-off frequency and minimum total impedance. The 0.4 and 0.5 pfu samples present highly superimposable impedance contours with cut-off frequencies maintained near $\sim 1 \text{ MHz}$. Conversely, compositions with lower vacancy concentrations ($\leq 0.35 \text{ pfu}$) display significantly augmented impedance. This is primarily governed by the retention of the ion-blocking tetragonal phase. As the Nb concentration increases toward 0.4 pfu, the progressive elimination of this sluggish phase mechanistically drives the initial surge in ionic conductivity.

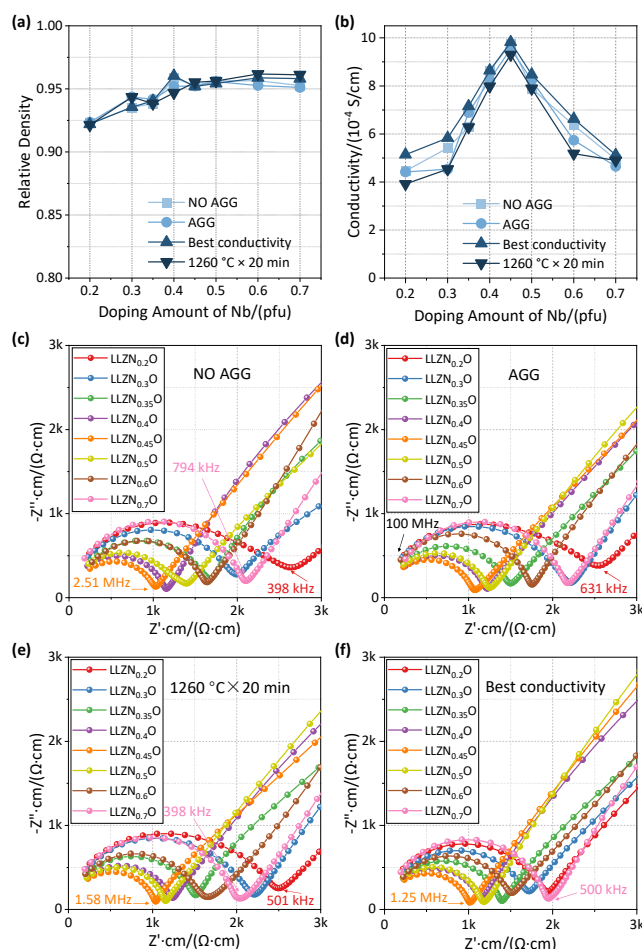


Fig. 3 Characterization of relative density and ionic transport properties of Nb-LLZO ceramics

Evolution of (a) relative density and (b) room-temperature ionic conductivity as a function of Nb doping level; Normalized EIS spectra recorded at a controlled environmental temperature of 30°C for four representative sample sets: (c) regular uniform grain group, (d) group with abnormal grain growth (AGG), (e) constant sintering group ($1260^\circ\text{C}\times 20 \text{ min}$), and (f) optimized conductivity group

To meticulously decouple the polarization dynamics, the distribution of relaxation times (DRT) technique^[31-32] was applied at a cryogenic temperature of -60°C (Fig. 4(a) and Fig. S5). For heavily doped compositions ($\text{LLZN}_{0.6-0.7}\text{O}$), prominent grain relaxation peaks (D_g) emerge within the time constant range of 10^{-6} to 10^{-5} s . These intensified peaks denote substantial kinetic barriers to bulk Li^+ conduction. Crystallographically, excessive doping introduces a surplus of lithium vacancies, which over-expands the inter-lithium spacing. This reduction in effective carrier density, coupled with diminished Coulombic repulsive driving forces, severely impedes concerted Li^+ migration along the primary $96h \leftrightarrow 24d \leftrightarrow 96h$ pathways within the cubic framework.

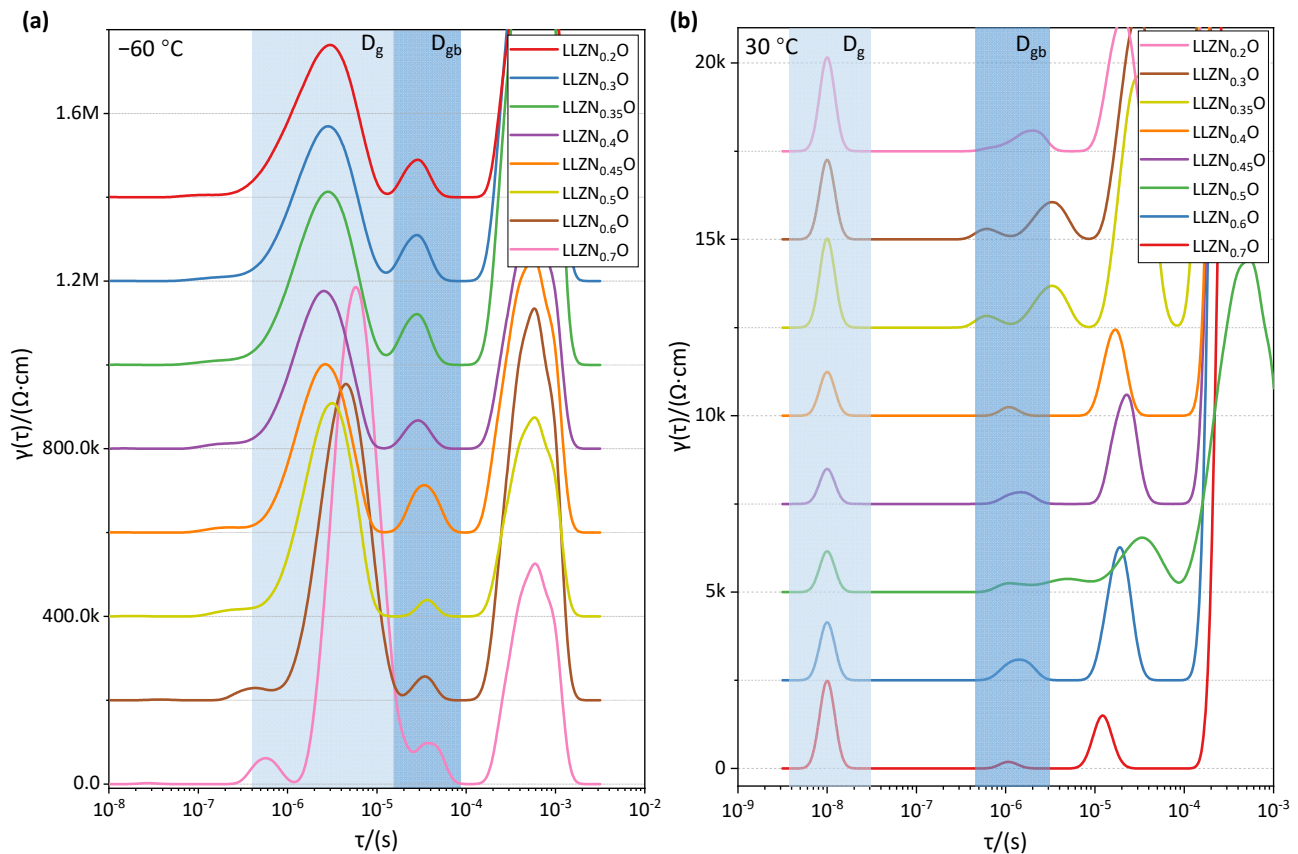


Fig. 4 DRT analysis of electrochemical processes in the optimized conductivity group of Nb-LLZO ceramics
DRT spectra as a function of Nb doping level at (a) cryogenic temperature ($-60\text{ }^{\circ}\text{C}$) and (b) room temperature ($30\text{ }^{\circ}\text{C}$)

At $30\text{ }^{\circ}\text{C}$, kinetic behaviors diverge distinctly across the phase boundaries (Fig. 4(b)). Constrained by the high transport barriers of the tetragonal phase, the D_g peak intensities for low-vacancy compositions (LLZ-N_xO ($x=0.20-0.35$)) surge to approximately twice those of the optimal group (LLZN_xO ($x=0.40-0.50$)). Concurrently, the over-doped Nb=0.6 composition also exhibits a markedly intensified bulk relaxation peak. Crucially, across both cryogenic ($-60\text{ }^{\circ}\text{C}$) and room-temperature ($30\text{ }^{\circ}\text{C}$) regimes, grain boundary characteristic peaks (D_{gb}) remain entirely absent for all investigated samples. This explicitly corroborates our microstructural design, confirming that macroscopic impedance in this high-purity system is overwhelmingly governed by intrinsic bulk (grain) transport rather than interfacial barriers.

To elucidate the thermodynamic characteristics of ion transport, Fig. 5(a, b) displays the temperature-dependent impedance spectra of the optimal LLZN_{0.45}O composition from -60 to $20\text{ }^{\circ}\text{C}$. With increasing temperature, the cut-off frequency governing bulk relaxation shifts distinctly to higher frequencies, confirming a highly thermally activated ion migration process. Arrhenius plots constructed from the sub-ambient conductivity data (-60 to $0\text{ }^{\circ}\text{C}$) exhibit exceptional linearity

across all eight compositions (Adj. $R^2>0.9999$), verifying adherence to a single thermally activated conduction mechanism within this regime. As illustrated in Fig. 5(c, d), the intrinsic activation energy (E_a) increases monotonically with lithium vacancy concentration (Table S2). Consequently, depleting the occupied Li⁺ states systematically elevates the macroscopic energy barrier for ion hopping (Table S3). This thermodynamic behavior highlights the fundamental physics of concerted migration within the garnet framework: high Li⁺ occupancy leverages strong inter-ionic Coulombic repulsion to facilitate low-energy, concerted multi-ion hopping. Conversely, excessive vacancies not only dilute the effective carrier density but also dampen this synergistic Coulombic driving force, ultimately manifesting as a progressively higher activation barrier.

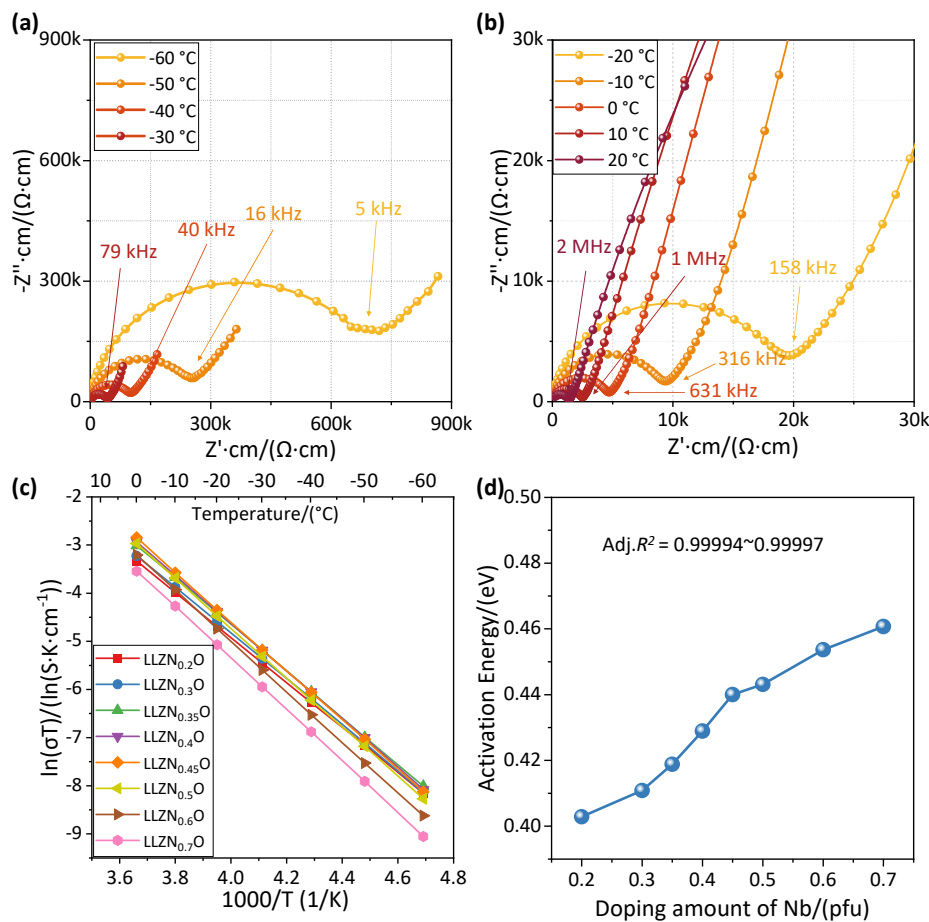


Fig. 5 Ion transport kinetics of Nb-LLZO ceramics

(a, b) Temperature-dependent impedance spectra and corresponding cut-off frequencies for the optimized composition ($x=0.45$) from -60 to 20 °C; (c) Arrhenius plots and (d) extracted activation energies (E_a) for Nb-LLZO ceramics with various lithium vacancy concentrations

2.4 Crystallographic and microscopic transport mechanisms

To elucidate the crystallographic origins governing the divergent electrochemical behaviors, Rietveld structural refinement was performed on the powder XRD data of the sintered ceramics (Fig. S6). In the ideal LLZO lattice, $[\text{ZrO}_6]$ octahedra share vertices with adjacent tetrahedra to form a rigid 3D skeletal framework, harboring mobile Li^+ within its interstitial sites. Geometrically, the Zr-O bond length dictates the octahedral volume, which directly scales with the macroscopic lattice parameters. Expanding this unit-cell framework enlarges the free volume of the Li^+ transport channels, effectively alleviating steric bottlenecks along long-range migration pathways. This structural dilation substantially lowers the energy barrier for Li^+ hopping, fundamentally enhancing ionic conductivity. However, because the dopant Nb^{5+} possesses a smaller ionic radius than the host Zr^{4+} , heavy doping inevitably induces localized contraction of the $(\text{Nb/Zr})\text{-O}$ bonds.

This localized distortion triggers a reduction in octahedral volume and a consequent shrinkage of the overall lattice parameters (Fig. 6(a, b)). This pronounced structural contraction mechanistically explains the deterioration of ionic conductivity observed in the heavily over-doped regime.

Furthermore, the sluggish room-temperature kinetics inherent to the tetragonal phase are microscopically corroborated by ^7Li solid-state nuclear magnetic resonance (NMR) spectroscopy (Fig. 6(c)). In NMR spectra, the full width at half maximum (FWHM) of the resonance peak is inversely proportional to the Li^+ hopping frequency, serving as a robust probe for local ionic mobility^[33-34]. The three low-doping, tetragonal-rich compositions exhibit resonance peaks significantly broader than those of the pure cubic samples. Crucially, as the tetragonal phase fraction progressively diminishes, the FWHM of the ^7Li NMR signals narrows monotonically. This local-environment spectroscopic evidence definitively confirms the severe spatial confinement exerted

by the tetragonal lattice on long-range Li^+ migration. These microscopic findings provide elegant structural

validation for the macroscopic impedance and conductivity trends established previously.

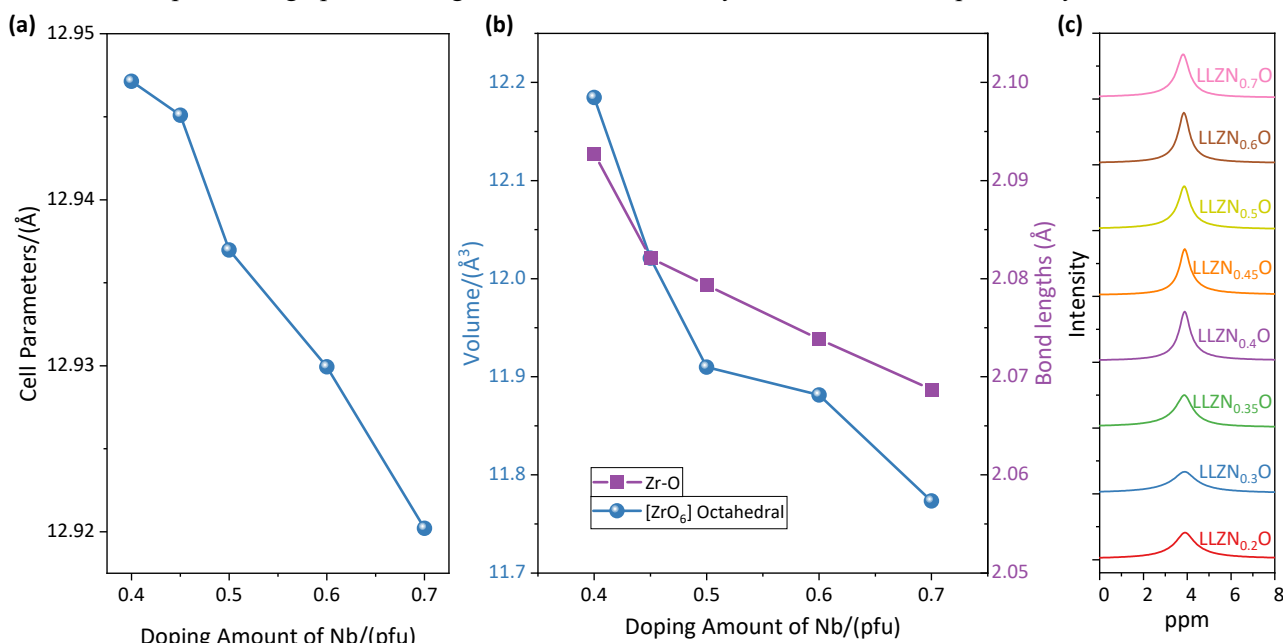


Fig. 6 Microscopic transport mechanism analysis based on structural refinement and NMR characterization

(a) Evolution of lattice parameters and (b) corresponding Zr–O bond lengths and $[\text{ZrO}_6]$ octahedral volumes as a function of Nb doping concentration; (c) ^7Li solid-state NMR spectra

3 Conclusion

By employing a strictly contamination-free rapid sintering regime-eliminating both extrinsic alumina impurities and intrinsic lithium volatilization, we decoupled the morphological and crystallographic contributions to ion transport. Consequently, the intrinsic relationship between lithium vacancy concentration and ionic conductivity in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) was unambiguously established. Contrary to historical consensus, an intrinsic vacancy concentration of 0.25 pfu is fundamentally insufficient to stabilize the pure cubic phase; rather, a minimum threshold of ≥ 0.4 pfu is the absolute thermodynamic prerequisite. Upon excluding grain boundary artifacts, the room-temperature ionic conductivity exhibits a distinct volcano-shaped dependence on vacancy concentration, peaking precisely at 0.45 pfu ($\sim 1 \text{ mS}\cdot\text{cm}^{-1}$). This definitive finding resolves long-standing empirical discrepancies. Structural and kinetic analyses reveal that in the low-vacancy regime (< 0.4 pfu), transport is severely restricted by the retention of the tetragonal phase, whose tortuous conduction topology and rigid lattice confinement induce sluggish bulk kinetics. Conversely, the precipitous decline in conductivity beyond 0.45 pfu stems from profound intrinsic lattice distortion rather than interfacial blocking. High concentrations of smaller Nb^{5+} dopants

trigger localized (Nb/Zr)–O bond contraction, reducing the $[\text{ZrO}_6]$ octahedral volume and narrowing the spatial bottleneck for Li^+ hopping. Coupled with the dilution of effective carrier density and the loss of concerted multi-ion driving forces, this structural shrinkage imposes massive bulk activation barriers. Ultimately, this work clarifies the historical controversy surrounding the optimal vacancy metric in LLZO, establishes a comprehensive mechanistic framework for ultrafast ion conduction, and provides rigorous crystallographic guidelines for the rational design of high-performance solid-state electrolytes.

Supporting Materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20260225>.

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石榴石型 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ 固态电解质的最优锂空位浓度

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摘要: 精准调控锂空位浓度对于最大化石榴石型 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) 固态电解质的离子电导率至关重要。然而, 传统的高温合成方法不可避免地会引入寄生杂质(如来自氧化铝坩埚的 Al^{3+}), 从而极大地扰乱其本征的缺陷化学。因此, 锂空位与离子传输之间的基础构效关系一直未能得到明确的阐释。为了揭示真实的离子传输机制, 本研究采用了一种严格无污染的烧结策略, 通过引入定制的微观结构模型以解耦晶粒尺寸和晶界效应等形貌干扰, 系统研究了一系列 Nb^{5+} 掺杂(掺杂量为 0.2~0.7 pfu) LLZO 的结晶学演变与传输动力学。研究结果明确表明, 在纯净、无杂质的晶格中, 当锂空位浓度处于 0.45 pfu 的最优值时, 室温离子电导率达到峰值。这项工作不仅确定了锂石榴石中实现超快离子传输所需的本征空位指标, 也为设计高性能固态电解质奠定了严谨的晶体学基础。

关键词: 石榴石固态电解质; 锂空位浓度; Nb 掺杂; 迁移动力学

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Supporting Materials

Optimum Li-site Vacancy in Garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte

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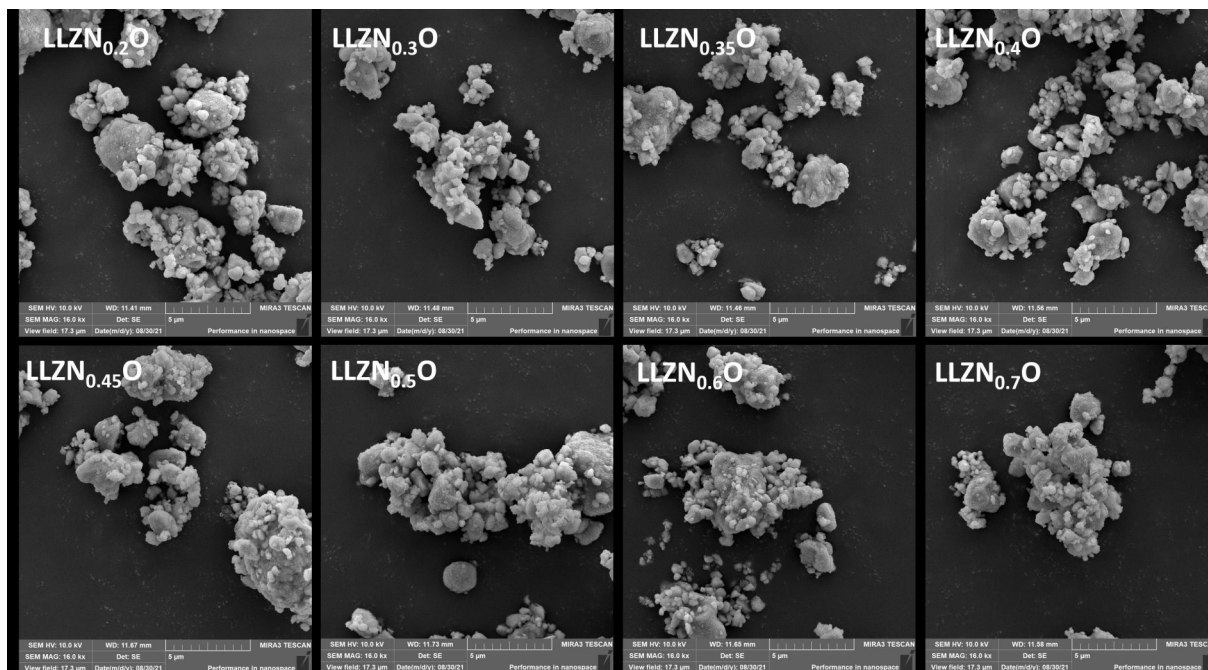


Fig. S1 Micromorphologies of Nb-LLZO precursor powders after calcination at 850 °C and subsequent ball milling. Particle size distribution and surface features of the samples with eight different lithium vacancy concentrations.

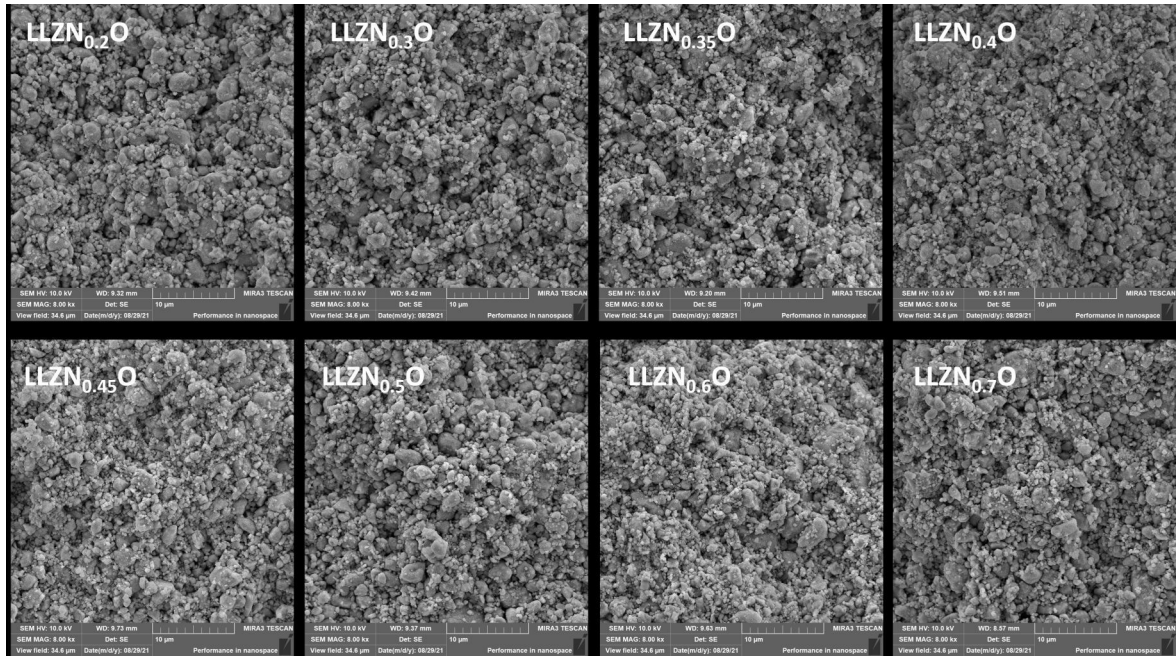


Fig. S2 Cross-sectional SEM images of Nb-LLZO green pellets with various lithium vacancy concentrations

Table S1 Physical parameters of Nb-LLZO ceramics with various lithium vacancy concentrations before and after sintering including mass, geometric dimensions, density, mass loss, and shrinkage

Parameter	LLZN _{0.2} O	LLZN _{0.3} O	LLZN _{0.35} O	LLZN _{0.4} O	LLZN _{0.45} O	LLZN _{0.5} O	LLZN _{0.6} O	LLZN _{0.7} O
Green pellet								
Weight/g	1.00693	0.99394	1.03081	0.98119	1.02223	1.04278	1.05294	1.02627
Diameter/mm	12.07	12.03	12.06	12.04	12.03	12.03	12.03	12.04
Thickness/mm	2.88	2.63	2.72	2.6	2.71	2.81	2.77	2.73
Geometric density/(g·cm ⁻³)	3.25636	3.32662	3.31929	3.31633	3.32031	3.26652	3.34598	3.30352
Ceramic								
Weight/g	1.01457	0.9368	0.97643	0.92705	0.96078	0.98015	0.99336	0.96632
Diameter/mm	10.45	10.42	10.38	10.35	10.29	10.24	10.29	10.22
Thickness/mm	2.49	2.31	2.41	2.3	2.38	2.42	2.41	2.37
Geometric density/(g·cm ⁻³)	4.75073	4.75565	4.78784	4.79076	4.8543	4.91799	4.95643	4.97028
Weight loss/%	5.40404	5.74884	5.27546	5.51779	6.01137	6.00606	5.65844	5.84154
Shrinkage radial	13.42171	13.38321	13.93035	14.03654	14.46384	14.87947	14.46384	15.11628
Shrinkage portrait	13.54167	12.1673	11.39706	11.53846	12.17712	13.879	12.99639	13.18681

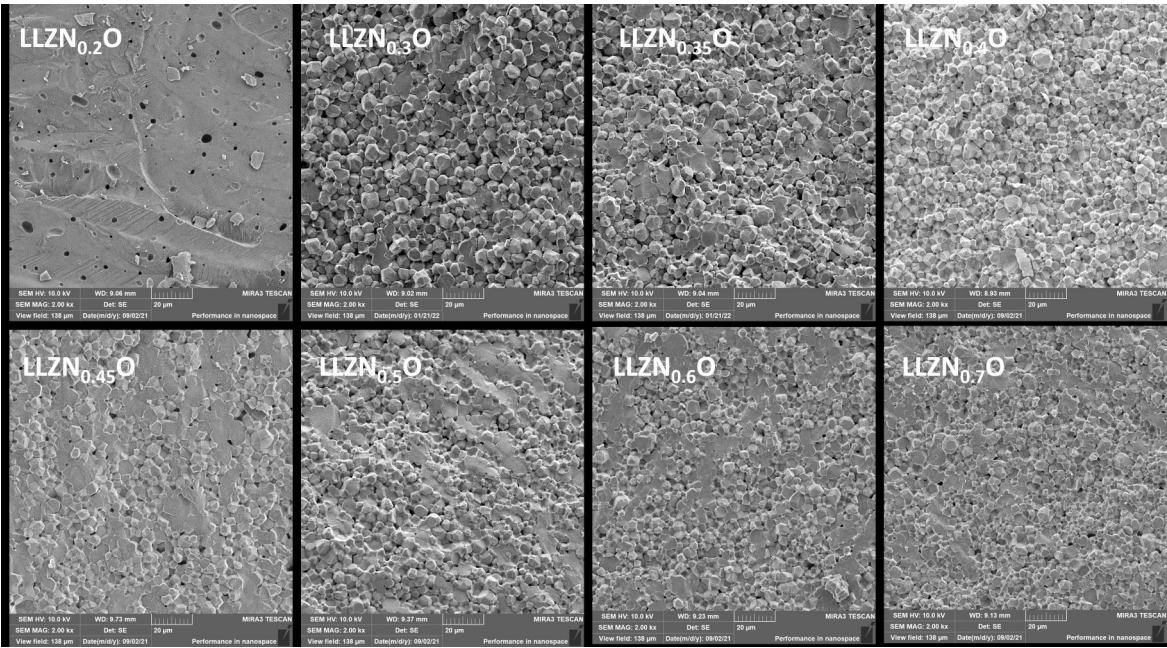


Fig. S3 Cross-sectional SEM images of Nb-LLZO ceramics with various lithium vacancy concentrations
All sintered at 1260 °C for 20 min

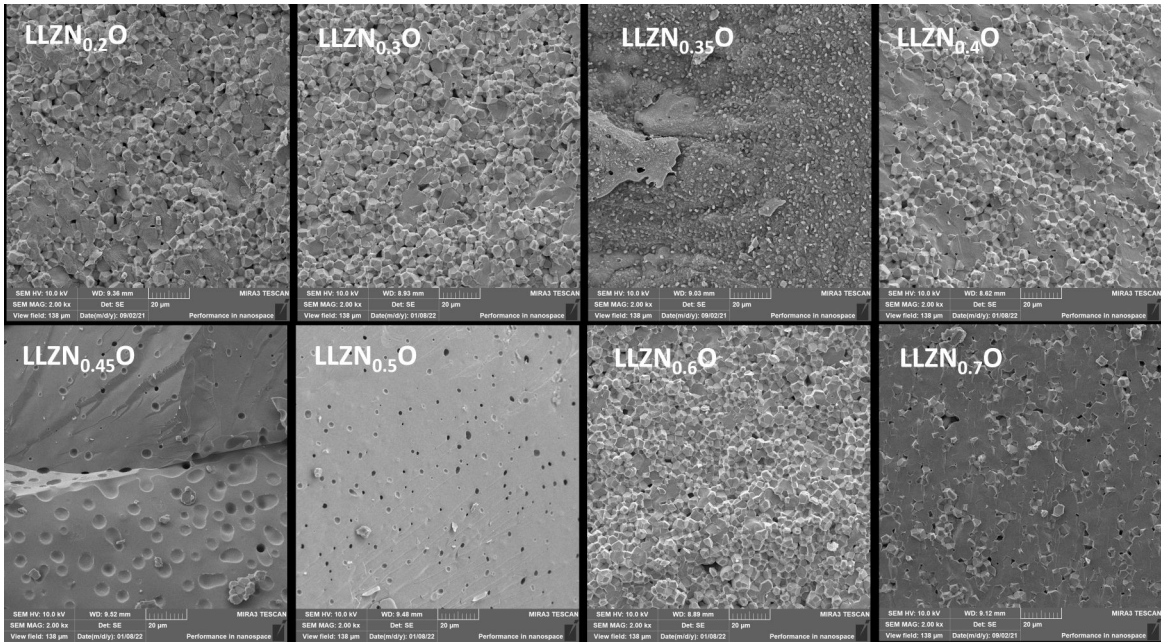


Fig. S4 Cross-sectional SEM images of Nb-LLZO ceramics with eight different lithium vacancy concentrations, each at its respective state of maximum ionic conductivity

Table S2 Comprehensive summary of the physical and electrochemical properties for the eight Nb-LLZO ceramic compositions

Detailed evolution of room-temperature ionic conductivity, relative density, and activation energy as a function of lithium vacancy concentration

Doping Amount of Nb /pfu	Sample Status	$\sigma(25\text{ }^{\circ}\text{C})$ /($\times 10^{-4}, \text{S}\cdot\text{cm}^{-1}$)	Relative density	E_a/eV
0.2	No AGG	4.46049	92.27%	0.40287
	AGG	4.4212	92.36%	
	Best conductivity	5.14189	92.21%	
	1260 $^{\circ}\text{C}\times 20\text{ min}$	3.91971	92.15%	
0.3	No AGG	5.41506	93.53%	0.41084
	AGG	4.53306	94.36%	
	Best conductivity	5.83411	93.56%	
	1260 $^{\circ}\text{C}\times 20\text{ min}$	4.53306	94.36%	
0.35	No AGG	6.28427	93.84%	0.41884
	AGG	6.89147	94.18%	
	Best conductivity	7.15369	94.05%	
	1260 $^{\circ}\text{C}\times 20\text{ min}$	6.28427	93.84%	
0.4	No AGG	8.63646	95.87%	0.42893
	AGG	8.25602	95.20%	
	Best conductivity	8.63822	96.04%	
	1260 $^{\circ}\text{C}\times 20\text{min}$	7.9779	94.69%	
0.45	No AGG	9.76145	95.27%	0.44003
	AGG	9.54286	95.23%	
	Best conductivity	9.82279	95.20%	

	1260 °C×20 min	9.29823	95.53%	
0.5	No AGG	7.8948	95.63%	0.44312
	AGG	8.24012	95.58%	
	Best conductivity	8.47594	95.43%	
	1260 °C×20 min	7.8948	95.63%	
0.6	No AGG	6.36279	95.66%	0.45367
	AGG	5.73874	95.27%	
	Best Conductivity	6.62897	95.88%	
	1260 °C×20 min	5.18087	96.19%	
0.7	No AGG	4.94644	95.27%	0.46073
	AGG	4.65569	95.12%	
	Best Conductivity	5.12546	95.81%	
	1260 °C×20 min	4.89817	96.13%	

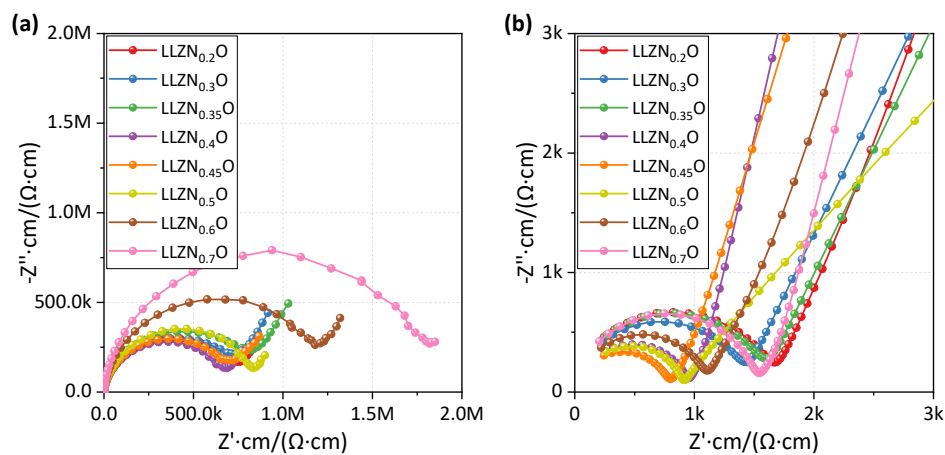


Fig. S5 Normalized EIS spectra of Nb-LLZO ceramics with various lithium vacancy concentrations at (a) -60 and (b) 30 °C

Table S3 Summary of ionic conductivities for Nb-LLZO ceramics with eight different lithium vacancy concentrations from -60 to 110 $^{\circ}\text{C}$

Temperature / $^{\circ}\text{C}$	σ / $(\times 10^{-4}, \text{S}\cdot\text{cm}^{-1})$							
	LLZN _{0.2} O	LLZN _{0.3} O	LLZN _{0.35} O	LLZN _{0.4} O	LLZN _{0.45} O	LLZN _{0.5} O	LLZN _{0.6} O	LLZN _{0.7} O
-60	0.013439	0.013643	0.015606	0.014551	0.01	0.011991	0.08451	0.005484
-50	0.035038	0.036477	0.041185	0.040737	0.039485	0.034056	0.02406	0.0165
-40	0.080808	0.087961	0.101595	0.100857	0.099996	0.0848872	0.062743	0.044138
-30	0.176289	0.193431	0.230938	0.229923	0.231484	0.202347	0.15318	0.107537
-20	0.362652	0.402027	0.485296	0.494784	0.509379	0.449156	0.34539	0.247676
-10	0.706493	0.790605	0.970078	1.007665	1.066166	0.953055	0.748612	0.532421
0	1.311038	1.45603	1.803396	1.946384	2.134367	1.881533	1.481177	1.057806
10	2.287869	2.567053	3.201157	3.540016	3.999016	3.543812	2.793285	2.022572
20	3.852415	4.430829	5.568068	6.236217	7.277042	6.343698	5.177881	3.671054
30	5.996538	6.970231	9.250049	10.50304	12.531645	10.951198	9.003058	6.466682
40	9.863578	11.69428	14.889745	17.1455	20.688617	18.032719	14.86674	10.984291
50	15.144596	17.99289	22.77648	27.00215	32.639081	28.312286	24.29051	17.709819
60	22.454334	27.03843	34.0544	41.58033	50.158911	42.964829	37.23216	27.588102

70	32.212338	39.79888	51.27766	61.41285	73.017985	63.97469	55.53651	41.379911
80	45.548599	56.6469	74.358277	88.1348	102.958777	91.919652	79.88348	60.323926
90	62.128774	79.25522	102.784957	121.5335	137.577551	126.195462	109.6173	84.560501
100	82.858876	109.0803	140.138264	163.6651	187.589136	166.60626	145.5776	115.248521
110	108.928209	144.5939	195.269556	215.1808	242.313929	216.3424	174.5266	153.869036

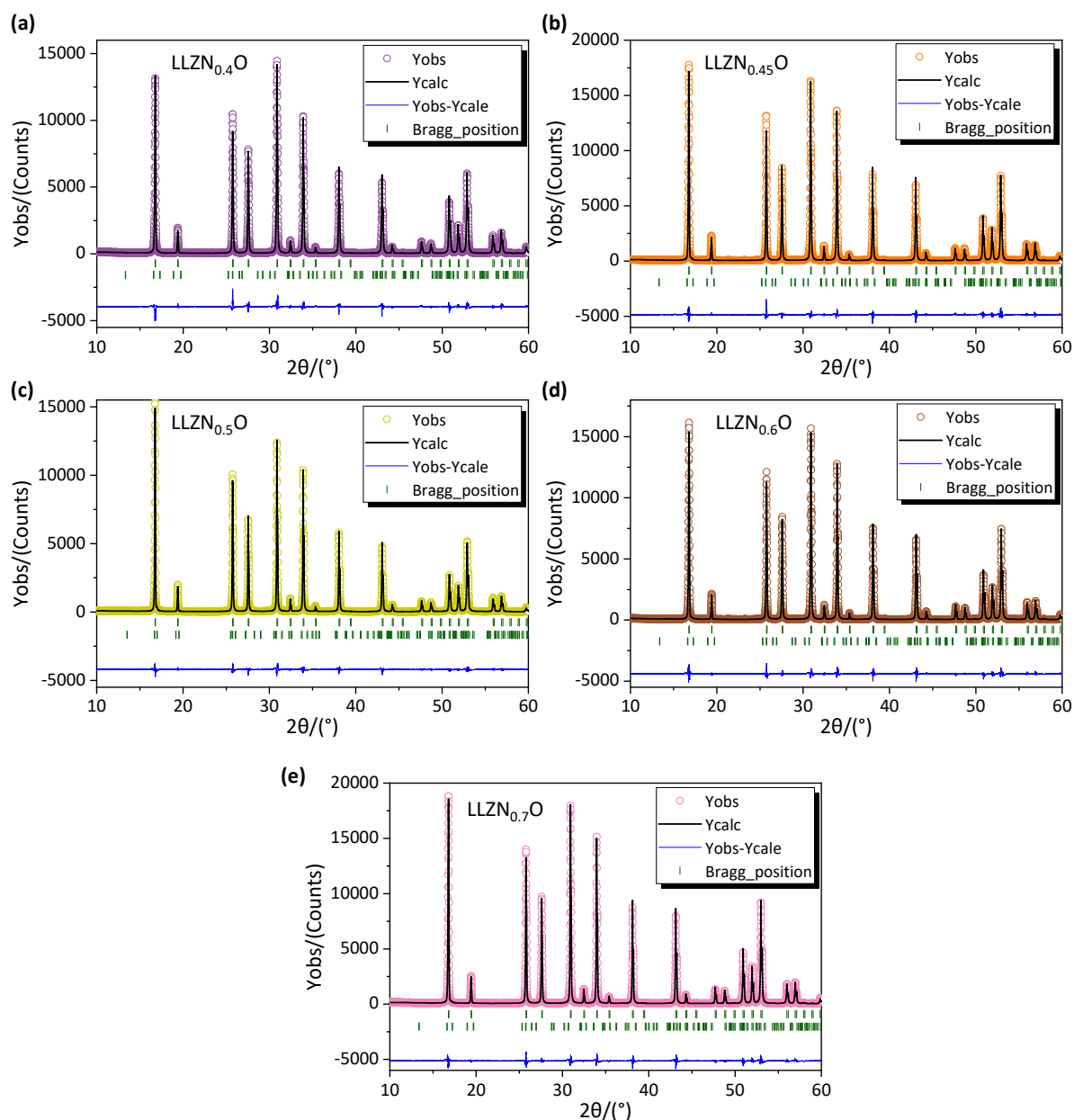


Fig. S6 Rietveld refined XRD patterns of Nb-LLZO ceramics with various Nb doping concentrations