Dual Substitution Strategy to Enhance Li⁺ Ionic Conductivity in Li₇La₃Zr₂O₁₂ Solid Electrolyte

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Supporting Information

ABSTRACT: Solid state electrolytes could address the current safety concerns of lithium-ion batteries as well as provide higher electrochemical stability and energy density. Among solid electrolyte contenders, garnet-structured Li₇La₃Zr₂O₁₂ appears as a particularly promising material owing to its wide electrochemical stability window; however, its ionic conductivity remains an order of magnitude below that of ubiquitous liquid electrolytes. Here, we present an innovative dual substitution strategy developed to enhance Li-ion mobility in garnet-structured solid electrolytes. A first dopant cation, Ga³⁺, is introduced on the Li sites to stabilize the fast-conducting cubic phase. Simultaneously, a second cation, Sc³⁺, is used to partially populate the Zr sites, which consequently increases the concentration of Li ions by charge compensation. This aliovalent dual substitution strategy allows fine-tuning of the number of charge carriers in the cubic Li₄.65Ga₀.15La₃Zr₁.9Sc₀.1O₁₂ according to the resulting stoichiometry, Li₇−₃ₓGaₓLa₃Zr₂−₃Sc₂O₁₂. The coexistence of Ga and Sc cations in the garnet structure is confirmed by a set of simulation and experimental techniques: DFT calculations, XRD, ICP, SEM, STEM, EDS, solid state NMR, and EIS. This thorough characterization highlights a particular cationic distribution in Li₆.65Ga₀.15La₃Zr₁.9Sc₀.1O₁₂, with preferential Ga³⁺ occupation of tetrahedral Li二十四 sites over the distorted octahedral Li九十二 sites. ⁷Li NMR reveals a heterogeneous distribution of Li charge carriers with distinct mobilities. This unique Li local structure has a beneficial effect on the transport properties of the garnet, enhancing the ionic conductivity and lowering the activation energy, with values of 1.8 × 10⁻³ Sc m⁻¹ at 300 K and 0.29 eV in the temperature range of 180 to 340 K, respectively.

INTRODUCTION

Safety issues related to Li-ion batteries have become of general concern and are currently limiting their further development for powering larger scale devices such as electric vehicles or aircraft.³⁻⁴ The replacement of flammable and toxic organic liquid electrolytes with inorganic solid electrolytes will offer a tremendous increase in safety, preventing thermal runaway in case of battery failure.⁴ Additionally, it will also boost the energy density of the cell as inorganic electrolytes may be combined with high voltage cathodes unlike liquid electrolytes—and with Li metal anodes. Among the most suitable inorganic solid electrolyte candidates, Li₇La₃Zr₂O₁₂ has become a strong contender over the years.⁶ Not only does this garnet compound present a good Li⁺ conductivity,⁶⁻⁸ it is also stable over a wide electrochemical window⁹⁻¹⁰ and provides more stable interfaces with cathode materials,¹⁰ which are key advantages over other promising inorganic electrolytes, such as superionic sulfides. In addition, garnets have higher structural/chemical stability in an air atmosphere than superionic sulfides.⁶⁻⁸ Li₇La₃Zr₂O₁₂ (LLZ) crystallizes in two polymorphs: a poorly conducting tetragonal phase I₄₁/acd (142) at room temper-
at and a highly conductive cubic phase \( \text{Ia}3\bar{d} \) (230) obtained at high temperature (>1273 K).\(^{11}\) \( \text{Al}^{3+} \) diffusion from the \( \text{Al}_2\text{O}_3 \) crucible to the garnet structure during thermal treatment has been proven to stabilize the metastable cubic phase\(^{12}\) via disordering of the \( \text{Li}^+ \) distribution over the available sites (tetrahedral \( \text{Li}_{x}^{3+} \) octahedral \( \text{Li}_{y}^{3+} \) and distorted octahedral \( \text{Li}_{z}^{9+} \)), the latter obtained by off-centering the cation in \( \text{Li}_{z}^{9+} \). As a way to induce crystallization into a cubic system, various substitution strategies, resulting in the creation of \( \text{Li} \) vacancies, have been studied in recent years.\(^6\) Intentional substitution on substitution strategies, resulting in the creation of \( \text{Li} \) vacancies, various reported by our team and others.\(^{14,15}\) The high mobility of \( \text{Li}^+ \) for a substitution level of 0.02 mol per formula unit, i.e., \( \text{Ga}^3+ \) per supercell on a \( \text{Li}^+ \) site (\( \text{Li}_{53}\text{Ga}1\text{La}24\text{Zr}16\text{O}96 \), following the occupancy in garnets\(^{16,20}\) and other solids.\(^{27}\) Molecular dynamics (MD) simulations, reported by Jalem et al.\(^6\) on \( \text{Ga} \) substituted LLZ using interatomic potentials predict a very high ionic conductivity, close to \( 6 \times 10^{-6} \) S cm\(^{-1} \) for tetragonal and cubic phases, respectively.\(^{6,14,15}\) To date, the best ionic conductivity has been achieved for \( \text{Li} \) substitution by \( \text{Ga} \), with a total ionic conductivity (\( \sigma \)) of 1.3 \( \times 10^{-3} \) S cm\(^{-1} \) for \( \text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}2\text{O}12 \) and \( \text{Li}_{6.46}\text{Ga}_{0.22}\text{La}_{3}\text{Zr}2\text{O}12 \) as previously reported by our team and others.\(^{14,15}\) The high mobility of \( \text{Li}^+ \) in \( \text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}2\text{O}12 \) can be ascribed to the preferential occupancy of \( \text{Ga}^3+ \) in the tetrahedral \( \text{Li}_{x}^{3+} \) sites, inducing \( \text{Li} \) vacancies and thus increasing the ratio of \( \text{Li}_{y}^{3+}/\text{Li}_{z}^{9+} \).\(^{14}\)

DFT calculations were performed using a periodic model and the semilocal Perdew–Burke–Ernzerhof (PBE) functional\(^{11}\) as implemented in the Vienna Ab Initio Simulation Package (VASP, version 5.4.1).\(^{22,23}\) The inner electrons were replaced by PBE-based projector augmented wave potentials,\(^{22,24}\) whereas \( \text{Li} \) (1s, 2s), \( \text{La} \) (5s, 5p, 6s, 6d), \( \text{Zr} \) (4s, 4p, 5s, 4d), \( \text{O} \) (2s, 2p), \( \text{Ga} \) (4s, 3d, 4p), and \( \text{Sc} \) (3s, 3p, 4s, 4d) valence electrons were expanded in plane-waves with a cutoff energy of 520 eV. We used the 8-formula-unit (\( \text{Li}_{24}\text{La}24\text{Zr}16\text{O}96 \)) conventional supercell, with cubic symmetry group \( \text{Ia}3\bar{d} \) (230). The equilibrium lattice parameters of the cell were fixed to the experimental values reported in the ICSD (CC: 422259) by Awaka et al.\(^{25} \) (\( a = b = c = 12.9827 \) Å and \( \alpha = \beta = \gamma = 90^\circ \)), whereas the internal atomic positions were allowed to relax with a residual force threshold of 0.02 eV Å\(^{-1} \). We considered a 2 × 2 × 2 Monkhorst–Pack \( k \)-point mesh. These computational settings guarantee a tight convergence in total energies (better than 10 meV per formula unit) and equilibrium distances (better than 0.02 Å). \( \text{Ga} \) substituted LLZ was modeled by placing one \( \text{Ga}^3+ \) per supercell on a \( \text{Li}^+ \) site (\( \text{Li}_{53}\text{Ga}1\text{La}24\text{Zr}16\text{O}96 \)), following the site preference of \( \text{Ga}^3+ \) in LLZ computed by Miara et al. using DFT,\(^{20} \) therefore evaluating two configurations, one with \( \text{Ga}^3+ \) in tetrahedral \( \text{Li}_{x}^{3+} \) and the second one with \( \text{Ga}^3+ \) in octahedral \( \text{Li}_{y}^{3+} \). In the case of the dual substituted system, we replaced one \( \text{Zr} \) atom per supercell by one \( \text{Sc} \) atom in the presence of one \( \text{Ga}^3+ \) again on a \( \text{Li}^+ \) site (\( \text{Li}_{53}\text{Ga}_{x}\text{La}_{y}\text{Zr}_{1-x}\text{Sc}_{y}\text{O}_{96} \) with 0.125 mol of \( \text{Sc} \) ). We considered all 32 possible arrangements of \( \text{Ga}^3+ \) and \( \text{Sc}^3+ \) within the supercell, involving the 16 different \( \text{Zr}^4+ \) sites, with \( \text{Ga}^3+ \) either in a tetrahedral \( \text{Li}_{x}^{3+} \) or octahedral \( \text{Li}_{y}^{3+} \) site. Notice that the disordered nature of \( \text{Li}^+ \) sites in the pristine and doped cubic garnet structures results in a very large number of possible \( \text{Li}^+ \) and \( \text{Li} \) vacancy arrangements within the \( \text{Li} \) sublattice. Therefore, we applied a screening procedure by first computing the electrostatic energy using formal charges and the Ewald summation.\(^{26} \) In order to improve the efficiency in the sampling of low-energy states, we considered only atomic arrangements with no \( \text{Li} = \text{Li} \) pairs at distances lower than 1 Å. We evaluated a total of 200 000 random \( \text{Li} \) arrangements, with no restriction in the partial occupancies of tetrahedral and octahedral sites. We then computed the energies of the 10–20 lowest electrostatic energy structures using DFT. In the dual substituted system, we applied this procedure for each of the 32 \( \text{Ga}^3+–\text{Sc}^3+ \) configurations. Similar two-step screening procedures have recently been applied to account for disordered \( \text{Li} \) site occupancy in garnet.\(^{16,20} \) and other solids.\(^{27}\)

In this paper, a novel dual substitution approach is presented where partial substitution of \( \text{Li}^+ \) by \( \text{Ga}^3+ \) combined to partial substitution of \( \text{Zr}^4+ \) by \( \text{Sc}^3+ \) gives access to \( \text{Li} \) compositions with \( n_{Li} > 6.55 \) while maintaining the cubic structure of LLZ. This strategy has the potential to enhance the ionic conductivity in LLZ. The presence of \( \text{Ga} \) ensures crystallization in the cubic phase by disordering the \( \text{Li} \) network over \( \text{Li}_{x}^{3+} \) and \( \text{Li}_{y}^{3+} \) sites via \( \text{Li}_{z}^{9+} \) occupation by \( \text{Ga}^3+ \), while the substitution of \( \text{Zr}^4+ \) by a lower valence cation opens a window for fine-tuning of the number of charge carriers according to the resulting formula: \( \text{Li}_{7-x-y}\text{Ga}_{x}\text{La}_{y}\text{Zr}_{2-x-y}\text{Sc}_{x}\text{O}_{12} \). Substitution of \( \text{Zr}^4+ \) by \( \text{Sc}^3+ \) is proposed, instead of \( \text{Y}^3+ \) as previously reported in single substituted LLZ.\(^{17,18} \) \( \text{Sc}^3+ \) provides a better ionic radius match with \( \text{Zr}^4+ \) (ionic radius for an octahedral coordination of 0.72, 0.75, and 0.90 Å for \( \text{Zr}^4+ \), \( \text{Sc}^3+ \), and \( \text{Y}^3+ \), respectively),\(^{19} \) ensuring smaller structural distortions in the vicinity of \( \text{Sc}^3+ \) compared to \( \text{Y}^3+ \). Additionally, density functional theory (DFT) calculations predict a lower defect energy for scandium over yttrium for the \( \text{Zr} \) site, yttrium being more prone to be found on the \( \text{La} \) site.\(^{20} \) Here, we investigated the effect of dual substitution by \( \text{Ga} \) and \( \text{Sc} \) on the crystal structure, microstructure, local cationic distribution, and ionic conductivity of \( \text{Li}_{7-x-y}\text{Ga}_{x}\text{La}_{y}\text{Zr}_{2-x-y}\text{Sc}_{x}\text{O}_{12} \) with different substitution levels (\( x = 0.15 \) and \( y = 0.10, 0.15, 0.20 \)). The present study highlights the reasons behind the ionic conductivity enhancement in such dual substituted LLZ garnets, offering new design rules for the development of high-conducting ceramic electrolytes.
water was added to the reagents mixture, with a citric acid to cation ratio of 4:1. After dissolution, the solution was dehydrated on a hot plate, and the resulting gel was then annealed at 873 K for 12 h to decompose the organic components. The resulting powder was ground and heated to 1073 K for 12 h under a dry O₂ atmosphere (H₂O content < 1 ppm). After this thermal treatment, the calcined powder was quickly transferred to an argon-filled glovebox (H₂O content < 0.1 ppm and O₂ content < 0.6 ppm) for further grinding. The powder was then pressed at 2 tons into pellets with a 1/4 in. diameter. The pellets were buried in their mother powder and sintered at 1473 K for 6 h under dry O₂ atmosphere (H₂O content < 1 ppm). After the final thermal treatment, the pellets were quickly transferred to an argon-filled glovebox (H₂O content < 0.1 ppm and O₂ content < 0.6 ppm). Both thermal treatments were performed in Al₂O₃ crucibles. After sintering, the pellets were polished to a mirror-like finish with silicon carbide polishing disks of successively smaller grit down to P4000. Their geometrical dimensions and weight were measured to estimate the relative density of the samples based on a theoretical density of 5.11 g cm⁻³.

X-ray diffraction (XRD) was performed after grinding the pellets in an argon-filled glovebox with an air-protected sample holder with a Be window. A Bruker-D8 diffractometer using a Cu source with Kα1 and Kα2 (accelerating voltage of 30 kV and current of 50 mA) was used in the Bragg–Brentano geometry; the data were collected for 2Θ angles from 15 to 80° with a 0.02° step size. Refinements of the spectra and lattice parameter calculation were performed using the WinPlotr/FullProf packages.²⁻⁹ The peak shape was described by a pseudo-Voigt function and the background level was modeled using a polynomial function.

Elemental analysis was performed using a Horiba Ultima2 inductively coupled plasma optical emission spectrometer (ICP-OES) after digestion of the samples in ultrapure HNO₃ acid (30% concentration, trace metal grade, Fischer Scientific) via a microwave treatment (400 W, 463 K, 1 h) and subsequent dilution in deionized water (Millipore, registering 13.1 MΩcm at 298 K).

The microstructure of the pellet cross section was analyzed by scanning electron microscopy (SEM) using a FEI Quanta 200 FEG operated at a voltage of 30 kV. Elemental composition of local areas was acquired using energy dispersive X-ray spectroscopy (EDS). The pellets were gently broken in an argon-filled glovebox and quickly transferred to the SEM chamber to minimize air exposure. To reveal the grain shape and boundaries, a thermal etching was performed on the broken pellets after fine polishing of the cross section. The pellet pieces were taken to 1423 K for 10 min followed by quenching; the procedure was achieved under an Ar atmosphere. EDS analysis was also performed in scanning transmission electron microscopy (STEM) mode by applying a FEI G2 TEM, operated at 200 kV. Pieces of the pellets were thoroughly ground under an argon atmosphere in order to analyze single particles. Some powder was then mixed with ethanol, and a drop of the solution was deposited on top of the carbon film supported by the copper grid. The grid was then heated at 473 K for 5 min to evaporate the ethanol.

All magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded with a Bruker Avance III 500 MHz (11.7 T) spectrometer working at Larmor frequencies of 500.24, 194.41, 152.56, 130.35, and 121.52 MHz for ¹H, Li, ⁷¹Ga, ⁵²Al, and ⁴⁵Sc, respectively. Rotors with a diameter of 1.3 mm were packed inside a glovebox with air-unexposed powdered samples. The MAS frequency was set to 50 kHz in all cases. ¹Li, ⁷¹Ga, ⁵²Al, and ⁴⁵Sc spectra were referenced to 0.1 M LiCl, Ga(NO₃)₃, Al(NO₃)₃, and Sc(NO₃)₃ solutions, respectively, and ¹H shifts were referenced to a bulk water sample resonating at 4.8 ppm. The noneffective π/2 pulse durations were 4.0, 2.5, 1.3, 1.3, and 1.5 μs for ¹H, ¹Li, ⁷¹Ga, ⁵²Al, and ⁴⁵Sc, respectively. π¹H echo experiments were carried out, and the magnetization observed in empty rotor measurements was subtracted from the sample measurements in order to suppress background signals. Single pulse experiments were performed for the other nuclei. Recycle times of 3, 35, 1, 1, and 7 s for ¹H, ¹Li, ⁷¹Ga, ⁵²Al, and ⁴⁵Sc along with 16, 16, 149.136, 7712, and 5120 scans accumulated, respectively. The DMFIT²⁰ software was used to reconstruct and simulate the spectra.

In order to measure the ionic conductivity of the samples, the finely polished pellets with a thickness of 1 mm were assembled in CR2032 coin cells using two Li metal electrodes under an argon atmosphere. Electrochemical impedance spectroscopy (EIS) was performed on the cells using a Solartron 1260A Impedance Analyzer and Z-plot software with a frequency range of 10 MHz to 1 Hz and a signal amplitude of 50 mV. The EIS spectra were normalized using the surface area and thickness of each pellet and fitted to an equivalent circuit (Supporting Information Figure S10) using the Z-view software. To determine the activation energy of each sample, EIS measurements were performed over a temperature range of 180 to 340 K using a physical property management system (PPMS) and the CR2032 coin cells with Li electrodes. The ionic conductivity of each sample over the temperature range was plotted versus 1/T in order to extract the activation energy, Eₜ, according to the following equation:

\[ \sigma T = A \exp(-E_\tau / RT) \]

### RESULTS AND DISCUSSION

The dual substitution strategy reported here can be described by the following crystal-chemistry (defect) reactions, using Kröger–Vink notations:

\[
\text{Ga}_2\text{O}_3 + \text{Li}_2\text{O} \rightarrow 2\text{Ga}^{3+} + 3\text{O}^{2-} + 4\text{V}_{\text{Li}}^0
\]

(2)

\[
\text{Sc}_2\text{O}_3 + \text{Li}_2\text{O} + 2\text{V}_{\text{Li}}^0 \rightarrow 2\text{Sc}^{3+} + 2\text{Li}^{+} + 7\text{O}^{2-} + 2\text{V}_{\text{Li}}^0
\]

(3)

With an overall resulting reaction of

\[
\text{Ga}_2\text{O}_3 + \text{Sc}_2\text{O}_3 + \text{Li}_2\text{O} \rightarrow 2\text{Ga}^{3+} + 2\text{Sc}^{3+} + 2\text{Li}^{+} + 7\text{O}^{2-} + 2\text{V}_{\text{Li}}^0
\]

(4)

where Ga⁴⁺ indicates a Ga³⁺ at a Li¹⁺ site with an effective charge of +2, Sc³⁺ indicates a Sc⁵⁺ at a Zr⁴⁺ site with an effective charge of −1, Li⁺ indicates a Li¹⁺ at a Li⁻ site with a neutral charge, O²⁻ is an O at the O site with a neutral charge, and \( V_{\text{Li}}^0 \) represents a vacancy at a Li¹⁺ site with an effective charge of −1. In Li₃₋₄ₓGaₓScₓLa₂₄Zr₁₆O₉₆, the substitution of x moles of Ga³⁺ on Li¹⁺ sites leads to the creation of 2x moles of Li⁻ vacancies, which helps disordering the Li population over Li₄₋₃ₓGaₓScₓO₉₆ sites but decreases the number of moles of Li by 3x. Simultaneously, substitution of y moles of Zr⁴⁺ by Sc⁵⁺ allows fine-tuning of the number of Li¹⁺ charge carriers by an incorporation of y moles of Li¹⁺.

We first used DFT calculations to investigate the effect of the proposed dual substitution strategy on the garnet structure. In the (Sc-free) supercell Li₃₋₄ₓGaₓLa₂₄Zr₁₆O₉₆ (\( n_{\text{Ga-per-formula-unit}} = 0.125 \)), the DFT results indicate that Ga ions in tetrahedral Li₄₋₃ₓGaₓO₉₆ sites are 161 meV per formula unit more stable than Ga in Li₄₋₃ₓGaₓScₓO₉₆ in agreement with our previous experimental results.¹⁴ The additional partial substitution of Zr by Sc leads to 32 possible arrangements of Ga and Sc in the supercell Li₃₋₄ₓGaₓLa₂₄Zr₁₅Sc₁O₉₆ (\( n_{\text{Sc-per-formula-unit}} = 0.125 \) and \( n_{\text{Sc-per-formula-unit}} = 0.125 \)). The ground state crystal structure shows the presence of Sc on Zr sites and Ga on Li₄₋₃ₓGaₓO₉₆ sites (Figure 1a). The relative stability of other computed structures is represented as a function of the Ga⁻ Sc distance in Figure 1b. Our results clearly indicate a preference of Ga³⁺ in tetrahedral Li₄₋₃ₓGaₓO₉₆ sites, with the first Ga in the Li₄₋₃ₓGaₓO₉₆ site appearing 139 meV per formula unit higher in energy than the ground state. This energy difference is 22 meV per formula unit lower than the one found in the case of Sc-free supercells. This suggests that the dual substituted system shows a slightly larger tendency toward Ga populating Li₄₋₃ₓGaₓO₉₆ sites than the Sc-free
Figure 1. DFT simulations of dual substituted LLZ garnet. (a) Polyhedral representation of the lowest energy Li54Ga1La24Zr15Sc1O96 unit cell with Li, Ga, La, Zr, Sc, and O ions shown in yellow, orange, green, blue, turquoise, and red, respectively. (b) Relative energy E, of the unit cell Li54Ga1La24Zr15Sc1O96 with Ga in Li24 octahedral sites (turquoise data points) and with Ga in Li48Sc1 octahedral sites (red data points), as a function of Ga–Sc distance (d_{Ga-Sc}). Each point corresponds to a DFT calculation of a Ga–Sc configuration with a given Li+ arrangement. The turquoise (red) dotted line indicates the ground-state configuration for Ga in Li24 (Li48Sc1). All energies are referenced to the total energy of the ground state for Ga in Li24. The light blue band highlights Ga in Li24 structures at different Ga–Sc distances with relative energies within a range of less than 15 meV per formula unit compared to the ground state.

Geometrical density measurements of the sintered pellets indicate high density for all three compositions with 93%, 93%, and 94% for LGLZ_{Sc10}, LGLZ_{Sc15}, and LGLZ_{Sc20}, respectively. In agreement, cross-sectional SEM imaging shows only a limited number of pores remaining in the pellets (Figure 3a, b). The porosity represents 2 to 3% of the observed areas with a mean diameter of 3 to 4 μm. Thermal etching of the sample with LGLZ_{Sc15} reveals the presence of a wide array of grain sizes ranging from ~5 to ~70 μm (Figure 3c). Backscattering imaging of the three cross-sections (Supporting Information Figure S2) discloses the presence of a secondary phase containing lighter elements (due to its darker contrast), its ratio increasing with Sc content. This could correspond to the small amount of LiScO2 observed by XRD.

The stoichiometry of the dual substituted garnet samples was confirmed by using a combination of analytical techniques: ICP, SEM-EDS, and STEM-EDS (Table 1).

ICP characterization of the overall sample composition indicated a Zr/La ratio slightly higher than expected, while the ratios of Ga/La and Sc/La are those expected. Only a small amount of Al is detected, indicating minor contamination during thermal treatment of the samples in Al2O3 crucibles,12,30 the Al/La ratio being well below the one required for cubic stabilization of the garnet by Al (0.068).31

The chemical composition of local regions of the pellets was analyzed by SEM-EDS. The metal ratio values shown in Table 1 are extracted from averaging over several locations of the LGLZ_{Sc} region. These analyses confirm that the LGLZ_{Sc} regions contain the expected amount of Ga for all samples. The Sc content linearly increases with the substitution level in the garnet region (with y = 0.07, 0.08, and 0.09 for LGLZ_{Sc10}, LGLZ_{Sc15}, and LGLZ_{Sc20}, respectively). This value is slightly below the total amount of Sc measured by ICP (y = 0.09, 0.12, and 0.18 for LGLZ_{Sc10}, LGLZ_{Sc15}, and LGLZ_{Sc20}, respectively). The Zr concentration in the garnet region is also lower than expected for all samples. The missing Sc and Zr cations are both encountered in the secondary phase (Supporting Information Figure S3 and Table S1), which would be best described as Zr substituted LiScO2. This phase probably acts both as a reaction intermediate and as a sintering aid during thermal treatment of the garnet and would explain the high density of the obtained pellets.

Finally, single-particle STEM-EDS measurements were also performed on LGLZ_{Sc20} and confirmed the presence of both Ga and Sc within the LGLZ_{Sc} grains (Table 1, Figure 3d, and Supporting Information Figure S4). Only a trace amount of Al was detected, suggesting its segregation at the grain boundary, and thus not affecting the stoichiometry of the dual substituted garnet. STEM-EDS analysis on a grain of the secondary phase confirms its previous assignment to a Zr substituted LiScO2 phase (Supporting Information Table S1 and Figure S4).

Next, a thorough solid state NMR study has been carried out on the dual substituted garnets (LGLZ_{Sc10} and LGLZ_{Sc20}) to identify the local cationic distribution and to assess the local Li+ mobility. All samples were carefully handled in a glovebox to avoid Li+−H+ exchange (protonation), as confirmed by the absence of peaks in 1H NMR (Supporting Information Figure S5).

71Ga NMR of LGLZ_{Sc10} shows the presence of a single Ga resonance with a distinctive second order quadrupolar broadening (Figure 4a). This resonance is reminiscent of the one observed in single substituted Li4.65Ga0.15La2Zr2O12,16 and can therefore be assigned to Ga2+ in tetrahedral Li24 sites. The
same resonance appears in LGLZ_Sc20, though a second signal is also observed at 240 ppm, which shift and line shape can be ascribed to Ga cations with a distorted octahedral Li96h environment as reported in analogous garnet materials.32,33 Therefore, it can be concluded that, at low Sc content (y = 0.10), the preferred atomic sites for Ga3+ are the tetrahedral Li24d sites and, at higher Sc content (y = 0.20), Ga3+ can also populate the distorted octahedral Li96h sites.

The 45Sc NMR spectra of LGLZ_Sc10 and LGLZ_Sc20 are very similar, with a higher signal intensity for the latter in agreement with the sample composition (Figure 4b). Spectral deconvolution allowed the identification of two Sc signals (Supporting Information Figure S6): a main signal is observed at 140 ppm with a weaker contribution at about 120 ppm. The resonance at 140 ppm falls in the range of expected shifts for 6-coordinated Sc cations (100−160 ppm).34 On the one hand, substitution of octahedral Zr4+ by Sc3+ in BaZr1−yScyO3 led to a similar 45Sc signal with a shift of 140 ppm.35 On the other hand, LiScO2 presents a comparable line shape but with a chemical shift value of 148 ppm,34 slightly higher than the one of the observed species. However, substitution of Sc3+ by Zr4+ in LiScO2 could lead to a slight decrease of its chemical shift, as observed in the BaZr1−yScyO3 series,35 in which case it would be difficult to separate its contribution from that of Sc in the LLZ phase. The quadrupolar constant of the resonance observed at 140 ppm is small, indicating a highly symmetric octahedral distribution of cations in the surroundings of Sc3+. It reveals minimal geometrical distortion related to the partial substitution of Zr4+ by Sc3+ as expected from the low strain owing to similar ionic radii between the two cations (0.72 and 0.75 for Zr4+ and Sc3+, respectively, in octahedral environment).19 The weak resonance observed at 120 ppm is reminiscent of Sc2O334−36 and could result from a trace amount of undissolved Sc precursor reagent during solution mixing, below the detection limit of XRD. Prior dissolution of Sc2O3 via acid digestion could facilitate homogenization of the initial solution in future work.

27Al NMR of the dual substituted samples shows two resonances, at 62 and 78 ppm (Supporting Information Figure S7). On the basis of prior studies12,37−40 they are respectively

Figure 2. XRD characterization of the dual substituted garnet Li6.55+yGa0.15La3Zr2−yScyO12. (a) Rietveld refinement for y = 0.10. The asterisk denotes contribution from the sample holder, and the bars in black and red below the profile represent the Bragg peak positions associated with the cubic garnet phase and traces LiScO2, respectively. (b) Details of the (422) reflection showing the peak shift upon Sc substitution. (c) Change of the cubic lattice parameter, a, upon Sc substitution (the error bars are smaller than the points).
The observed differences in the Li local structure are expected to influence the transport properties of the dual substituted garnets. To evaluate the Li-ion dynamics at the local scale, we performed saturation recovery experiments (Supporting Information Figure S9). A multiexponential behavior in the Li spin–lattice relaxation times ($T_1$) for the dual substituted samples further reveals the presence of a heterogeneous distribution of Li environments (Table 2 and Supporting Information Figure S9). Fitting of the relaxation curves indicates the existence of a Li population with a $T_1$ value lower (< 0.20 s) than in single substituted $Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$ (0.38 s) garnet. This difference could suggest faster Li hopping rates for part of the Li population in the dual substituted samples, although quantification of the individual activation energies by longitudinal relaxation measurements requires a complete NMR spin–lattice relaxation study with temperature and frequency-dependent measurement of the spin–lattice relaxation rates in the laboratory and rotating frames.

Solid state NMR gives valuable information on the Li-ion dynamics, but only on a local scale. Thus, to evaluate the effect of the dual substitution strategy on the macroscopic transport properties, electrochemical impedance spectroscopy (EIS) measurements were performed at various temperatures. Nyquist plots (Figure 5a) of dual substituted LGLZ pellets recorded at 300 K show two semicircles, the one at high frequency being representative of the total ionic conductivity (bulk + grain boundary) of the pellet and the one at low frequency arising from the interfacial resistance between the pellet and the Li electrodes. The total ionic conductivity at 300 K (Figure 5b) is calculated for each composition by fitting the Nyquist plots with a circuit model previously described (Supporting Information Figure S10) and taking into consideration the pellet dimensions. As a result of the dual substitution, the ionic conductivity increases from 1.1(1) $\times 10^{-3}$ S cm$^{-1}$ for the Sc-free sample to an optimal value of 1.8 $\times 10^{-3}$ S cm$^{-1}$ for LGLZ$_{S c10}$ ($Li_{6.55}Ga_{0.15}La_3Zr_5Sc_{10}O_{12}$), proving the beneficial effect of the Sc and representing a new maximum for garnet electrolytes: $1.8 \times 10^{-3}$ S cm$^{-1}$ at 300 K. This conductivity value is in the range of the one predicted by Matsui et al. for a cubic Li$_2$La$_3$Zr$_2$O$_{12}$ based on extrapolation of their high temperature

**Table 1. Expected Chemical Composition and Experimental Metal Ratios of the As-Prepared Samples Determined by ICP, SEM-EDS, and STEM-EDS Techniques**

<table>
<thead>
<tr>
<th>composition</th>
<th>Zr/La</th>
<th>Ga/La</th>
<th>Sc/La</th>
<th>Al/La</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected</td>
<td>0.633</td>
<td>0.050</td>
<td>0.033</td>
<td>0.000</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.617</td>
<td>0.050</td>
<td>0.050</td>
<td>0.000</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.600</td>
<td>0.050</td>
<td>0.067</td>
<td>0.000</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>0.674(2)</td>
<td>0.053(6)</td>
<td>0.031(0)</td>
<td>0.010(1)</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.678(47)</td>
<td>0.050(2)</td>
<td>0.039(2)</td>
<td>0.032(2)</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.704(9)</td>
<td>0.060(3)</td>
<td>0.060(1)</td>
<td>0.007(2)</td>
</tr>
<tr>
<td>STEM-EDS</td>
<td>0.49(9)</td>
<td>0.055(3)</td>
<td>0.024(2)</td>
<td>0.09(1)</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.47(7)</td>
<td>0.061(5)</td>
<td>0.026(3)</td>
<td>0.089(1)</td>
</tr>
<tr>
<td>L$\text{Ga}<em>{6.55}$Ga$</em>{0.15}$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>0.45(6)</td>
<td>0.062(4)</td>
<td>0.029(1)</td>
<td>0.053(6)</td>
</tr>
</tbody>
</table>

*The given errors are experimental for ICP and statistical for SEM-EDS and STEM-EDS results.*
The ionic conductivity enhancement observed for the dual substituted \(\text{Li}_{6.65}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{1.90}\text{Sc}_{0.10}\text{O}_{12}\) cannot be associated with a possible Al contamination, as Al substituted \(\text{Li}_{6.65}\text{Zr}_{1.90}\text{O}_{12}\) garnets typically show much lower ionic conductivities, with \(\sigma \approx \leq 5 \times 10^{-4}\) S cm\(^{-1}\).\(^{3,31}\) It is possible that the higher ionic conductivity of \(\text{LGLZ}_{\text{Sc}10}\) arises from higher densification of the pellet; a similar effect has been reported in \(\text{Li}_{6.32}\text{La}_{3}\text{Nb}_{2.2}\text{Sc}_{0.15}\text{O}_{12}\) on Sc substitution.\(^{46}\) It could also be related to the presence of the Zr substituted LiScO\(_2\) secondary phase, known to offer some (limited) ionic conductivity.\(^{47}\)

However, the previous hypotheses cannot stand as the sole explanations for the ionic conductivity enhancement. Indeed, analysis of the Li populations by \(^7\text{Li}\) NMR in the dual substituted samples highlights clear differences compared to the Sc-free sample. While all samples host a Li population with a relaxation time in the range of 0.38(2) s, the dual substituted samples accommodate a second population of Li\(^+\) with a shorter relaxation time—of 0.16(1) s—hinting toward the presence of Li\(^+\) with faster local motion. It is also associated with a decrease in activation energy observed for \(\text{LGLZ}_{\text{Sc}10}\) and \(\text{LGLZ}_{\text{Sc}15}\) (0.29 eV versus 0.31 eV for LGLZ), the activation energy reflecting on local energy barriers for Li-ion migration. Nevertheless, faster local motion is not necessarily correlated to faster long-range mobility as local cationic distribution may influence the long-range diffusion. This hypothesis could explain the decrease of ionic conductivity observed upon further Sc substitution in \(\text{LGLZ}_{\text{Sc}15}\) and \(\text{LGLZ}_{\text{Sc}20}\), the latter showing some occupation of Ga\(^{3+}\) in the octahedral Li sites, as opposed to the preferential occupation of the tetrahedral Li sites at lower Sc content (\(y = 0.10\)).

The proposed dual substitution strategy, \(\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{1.90}\text{Sc}_{0.20}\text{O}_{12}\), leads to a very particular cationic distribution. For low substitution levels, Ga\(^{3+}\) is found in the tetrahedral Li\(_{24}\)d sites, as suggested by our DFT calculations. The smaller ionic radius of Ga\(^{3+}\) makes it a preferential occupant of the Li\(_{24}\)d sites over Li\(_{96}\)h sites (0.47 and 0.59 Å for Ga\(^{3+}\) and Li\(^+\), respectively, in a tetrahedral coordination).\(^{19}\) The addition of Sc leads to a larger number of local environments for Li\(^+\), which increases the local disorder surrounding the charge carrier and therefore its local mobility. For high Sc contents (\(y = 0.20\)), the amount of Ga in tetrahedral Li\(_{24}\)d decreases slightly and is compensated by the presence of some Ga\(^{3+}\) on the distorted octahedral Li\(_{96}\)h sites. This occupation of the Li\(_{96}\)h sites appears to have a negative impact on the long-range Li\(^+\) mobility.

Overall, the limited occupation of Li\(_{96}\)h sites by cations other than Li\(^+\) combined with the presence of a larger distribution of Li environments could explain the better performances of the dual substituted sample \(\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{1.90}\text{Sc}_{0.20}\text{O}_{12}\) over the single substituted \(\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{1.90}\text{O}_{12}\). These findings support the prior hypothesis from Thompson et al.,\(^{35}\) which stated that a further increase in ionic conductivity could be expected for \(n_{\text{Li}} > 6.5\), not by generally increasing the concentration of Li\(^+\) in the garnet but by selectively increasing the ratio of \(n_{\text{Li}}/n_{\text{Al}}\).

It is worth noting that Ga site occupancy in our samples (this study and our previous work\(^{34}\)) is different from other reported studies.\(^{32,33}\) At low substitution levels, we observe Ga in Li\(_{24}\)d sites (1.7 \(\times 10^{-3}\) S cm\(^{-1}\)). A further increase in Sc content leads to a decrease in ionic conductivity with 1.0(2) and 0.5(1) \(\times 10^{-3}\) S cm\(^{-1}\) for \(\text{LGLZ}_{\text{Sc}15}\) and \(\text{LGLZ}_{\text{Sc}20}\), respectively.

In accordance to the ionic conductivity enhancement, the activation energy \(E_a\) extracted from the Arrhenius plots (Figure 5c) decreases in the dual substituted garnets. \(E_a\) lowers from 0.31 for the Sc-free sample to 0.29 eV for \(y = 0.10\) in \(\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{1.90}\text{Sc}_{0.10}\text{O}_{12}\) (Figure 5d). The same minimum is observed for \(y = 0.15\) before increasing back to 0.31 eV for \(y = 0.20\). Therefore, the fastest ionic conductivity observed for \(y = 0.10\) is combined with the lowest activation energy, representing the optimal Sc content to achieve faster ion transport in these dual substituted garnets.

Table 2. \(T_1\) Relaxation Times for \(^7\text{Li}\) Extracted from Saturation Recovery Experiments (Supporting Information Figure S9) of \(\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_{3}\text{Zr}_{0.20}\text{Sc}_{0.10}\text{O}_{12}\)

<table>
<thead>
<tr>
<th>(y)</th>
<th>(T_1) (s)</th>
<th>(\text{component})</th>
<th>(\text{contribution}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.38</td>
<td>A</td>
<td>100</td>
</tr>
<tr>
<td>0.10</td>
<td>0.36</td>
<td>A</td>
<td>50</td>
</tr>
<tr>
<td>0.20</td>
<td>0.15</td>
<td>B</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>50</td>
</tr>
</tbody>
</table>

\(\sigma \approx \leq 5 \times 10^{-4}\) S cm\(^{-1}\). This dependence of \(n_{\text{Li}}/n_{\text{Al}}\) on Sc content is further explained by the \(\text{Li}_{24}\)d sites' occupation being related to the presence of Ga\(^{3+}\) in the Li\(_{96}\)h sites, as suggested by our DFT calculations. The smaller ionic radius of Ga\(^{3+}\) makes it a preferential occupant of the Li\(_{24}\)d sites over Li\(_{96}\)h sites (0.47 and 0.59 Å for Ga\(^{3+}\) and Li\(^+\), respectively, in a tetrahedral coordination).\(^{19}\) The addition of Sc leads to a larger number of local environments for Li\(^+\), which increases the local disorder surrounding the charge carrier and therefore its local mobility. For high Sc contents (\(y = 0.20\)), the amount of Ga in tetrahedral Li\(_{24}\)d decreases slightly and is compensated by the presence of some Ga\(^{3+}\) on the distorted octahedral Li\(_{96}\)h sites. This occupation of the Li\(_{96}\)h sites appears to have a negative impact on the long-range Li\(^+\) mobility.

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It is worth noting that Ga site occupancy in our samples (this study and our previous work\(^{34}\)) is different from other reported studies.\(^{32,33}\) At low substitution levels, we observe Ga in Li\(_{24}\)d sites (1.7 \(\times 10^{-3}\) S cm\(^{-1}\)). A further increase in Sc content leads to a decrease in ionic conductivity with 1.0(2) and 0.5(1) \(\times 10^{-3}\) S cm\(^{-1}\) for \(\text{LGLZ}_{\text{Sc}15}\) and \(\text{LGLZ}_{\text{Sc}20}\), respectively.
preferentially, with Li96h occupation on further substitution, while other studies found Ga to systematically occupy Li96h even at a low Ga substitution level. Those discrepancies could be related to the sample preparation and/or the sample composition. In the present study, the as-prepared garnets are synthesized in an ultradry atmosphere (O2 flow with < 1 ppm of H2O for calcination and sintering steps and material handling performed in an argon glovebox), while other works processed the samples in air. The latter processing is often characterized by a poorly connected network of small grains (≈ 10 μm), which typically leads to lower ionic conductivity and higher activation energy. Unfortunately, impedance measurements were not performed in those studies, and direct comparison of ionic conductivity based on cationic distribution cannot be proposed. In such a case, sample preparation in a dry atmosphere should be considered as it would allow further comparison as well as leading to higher conductivity. Additionally, a smaller amount of substitution could possibly favor occupancy of Li24d sites by Al3+ and/or Ga3+ over Li96h sites based on the smaller ionic radii of Al3+ and Ga3+ compared to Li+. This hypothesis is corroborated by the latest contribution of Rettenwander et al., where neutron powder diffraction and single crystal diffraction of Li6.4Al0.2−xGaxLa3Zr2O12 compositions did not show Al or Ga occupancy of Li96h sites and led to a conductivity of 1 × 10−3 S cm−1 at 295 K for x = 0.15: Li6.4Al0.15La3Zr2.85Sc0.15O12.

The proposed dual substitution of Li-La3Zr2O12, in which 0.15 mol Ga3+ occupies the Li24d sites while 0.10 mol Sc3+ occupies the Zr sites leading to Li6.65Ga0.05Ga0.15Sc0.10O12, offers new opportunities for fine-tuning the charge carrier concentration as well as the Li local structure in garnet electrolytes. The accurate control of the crystal chemistry achieved in these materials is possibly the key to enhancing the ionic conductivity, which is of great importance for enabling their practical application in solid state batteries. This strategy could be extrapolated to other inorganic conductors, contributing to the progress toward the design of superionic electrolytes with optimal transport properties.

### CONCLUSION

A dual substitution strategy, Li6.55+yGa0.15La3Zr2−yScyO12, is proposed to investigate the ionic conductivity of cubic garnets with nLi > 6.55, the Ga substitution aimed at stabilizing the cubic crystal structure and the incorporation of Sc at increasing the number of charge carriers. The dual substitution scheme results in a complex cationic distribution with a unique Li local structure. DFT calculations predict a clear preference for Ga occupation of the tetrahedral Li24d sites, which is experimentally confirmed by 71Ga NMR for low Sc substitution level (y = 0.10). The presence of Sc increases the disorder of the Li network at the local scale (i.e., broader distribution of chemical environments), which causes an enhancement of the local mobility of part of the Li population. Further Sc substitution leads to Ga occupation of octahedral Li96h sites, which suppresses the ionic conductivity via possible obstruction of the Li percolation network. Therefore, the existence of a Li+ population with higher local mobility seems to be related to a Li-only occupation of Li96h sites to promote Li+ long-range diffusion. These conditions are met in the targeted composition Li6.45Ga0.15La3Zr1.90Sc0.10O12, leading to the highest ionic conductivity observed for the garnets so far, with 1.8 × 10−3 S cm−1 at 300 K.
The crystal chemistry concepts and the thorough characterization carried out in this study highlight the complex interconnection between substitution scheme, cationic distribution, Li local environments, and transport properties in garnet-structured electrolytes. Analogous dual substitution strategies will be of interest for other Li-ion conductors, as well as Na-ion conductors, allowing access to the new compositions with higher ionic mobility. The possibility of fine-tuning the mobile ion concentration and/or local structure is expected to have a great impact not only on the field of batteries but also on electrochromics and solid oxide fuel cells.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b05369.

Rietveld refinements, microstructures, EDS analysis, and fitting of the EIS spectra for LGLZ_Sc10, LGLZ_Sc15, and LGLZ_Sc20, STEM analysis of LGLZ_Sc20 and 1H NMR, 27Al NMR, 45Sc and 7Li spectral deconvolution, and Li T1 relaxation time analysis for LGLZ_Sc 10 and LGLZ_Sc20 (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Spotnitz, R.; Franklin, J. Abuse behavior of high-power, lithium-ion cells. J. Power Sources 2003, 113, 81–100.


(23) Kresse, G.; Marsman, M.; Furthmüller, J. Vienna Ab-initio Simulation Package, Version 5.4.1; Computational Materials Physics, University of Vienna: Vienna. www.vasp.at/.
