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X-ray Pair Distribution Function Analysis, Electrical and Electrochemical Properties of Cerium Doped Li$_5$La$_3$Nb$_2$O$_{12}$ Garnet Solid-State Electrolyte

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Abstract

Garnet solid state electrolytes have been considered as potential candidates to enable next generation all solid state batteries (ASSBs). To facilitate the practical application of ASSBs, a high room temperature ionic conductivity and a low interfacial resistance between solid state electrolyte and electrodes are essential. In this work, we report a study of cerium doped Li$_5$La$_3$Nb$_2$O$_{12}$ through X-ray pair distribution function analysis, impedance spectroscopy and electrochemical testing. The successful cerium incorporation was confirmed by both X-ray diffraction refinement and X-ray pair distribution function analysis, showing the formation of an extensive solid solution. The local bond distances for Ce and Nb on the octahedral site were determined using X-ray pair distribution function analysis, illustrating the longer bond distances around Ce. This Ce doping strategy was shown to give a significant enhancement in conductivity (1.4 x 10$^{-4}$ S cm$^{-1}$ for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$, which represents one of the highest conductivities for a garnet with less than 6 Li) as well as a dramatically deceased in interfacial resistance (488 $\Omega$ cm$^2$ for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$). In order to demonstrate the potential of this doped system for use in ASSBs, the long term cycling of a Li//garnet//Li symmetric cell over 380 h has been demonstrated.
Introduction

State-of-the-art lithium ion batteries (LIBs) have dominated the energy storage market for more than 2 decades because of their long cycle life and high energy and power density over other battery systems\textsuperscript{1-3}. Nowadays, the increasing demand in developing electrical vehicles (EVs) not only need higher energy density, but more importantly, require improved safety properties\textsuperscript{4}. The flammable organic solvent in LIBs can trigger safety issues, and so makes it a non-ideal system for EVs. Instead, all-solid-state batteries (ASSBs) using a non-flammable inorganic solid-state electrolyte are considered to be a promising candidate to address the safety issues for future EVs\textsuperscript{5}.

Garnet lithium ion conductors have attracted increasing interest in the last decade due to their relatively good electrochemical stability against Li metal/cathode materials, and high lithium ionic conductivity at room temperature compared to other solid state electrolyte materials\textsuperscript{6-8}. The ideal garnet framework has the chemical formula $A_3B_2C_3O_{12}$, where $A$, $B$ and $C$ ions are located at eight, six and four oxygen coordinated sites, respectively. $La_3M_2Li_5O_{12}$ ($M = Nb, Ta$), was the first fast Li\textsuperscript{+} ion conducting garnet reported by Thangadurai et al. in 2003\textsuperscript{9}. Detailed studies have revealed that the lithium content and the distribution of lithium in the structure are key to the diffusion pathway and resulting lithium ion conductivity in garnet materials\textsuperscript{10, 11}. Li\textsuperscript{+} ions occupy both 24d tetragonal and 96h/48g octahedral Wyckoff sites in cubic $Li_5La_3Nb_2O_{12}$, with lithium ions shifting from 24d tetragonal sites to 96h/48g
octahedral sites as a function of increasing lithium content to reduce the lithium-lithium interaction strain\textsuperscript{6, 7}. The maximum lithium content in the structure was found to be 7, leading to compositions such as Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}, which adopts tetragonal symmetry with lithium ions ordering in three fully occupied tetrahedral 8a and octahedral 16f and 32g sites; this Li ordering reduces its ionic conductivity\textsuperscript{12-14}. The highly conductive cubic phase can be stabilised through the creation of lithium vacancies, and the optimum conductivity is found for lithium contents of 6.4 – 6.6 per garnet formula unit\textsuperscript{15-25}.

In addition, to facilitate the practical application of ASSBs, issues such as high interfacial resistances between electrode and electrolyte, and the lithium dendrite penetration problem within solid state electrolytes have attracted much attention in recent years\textsuperscript{26-29}. The interfacial impedance between the garnet and electrode mainly comes from the poor contact in association with microscopic voids and grain boundaries of garnet, as well as an insulating Li\textsubscript{2}CO\textsubscript{3} surface layer formed in air initiated by the proton/lithium exchange at the surface\textsuperscript{30-33}. The ionic transport was reported to be limited by the grain boundaries, which are heavily affected by the segregation of dopants and Li\textsuperscript{34}. Mechanical polishing, carbon annealing or acid treatment were reported to remove this unwanted surface layer\textsuperscript{35, 36}. Besides, metal or non-metal coating on garnet pellets and consequently lithium alloying effects have also been used to minimise the interfacial resistance between lithium metal and garnet, and to reduce the dendrite growth\textsuperscript{37-40}. Despite the potential for short-circuiting from
electronic conduction, a mixed ion/electron-conductive interface was demonstrated to beneficial for Li dendrite suppression\textsuperscript{41, 42}. Another common strategy in this field is to utilise polymer – ceramic composite electrolytes, which combine good wetting properties of polymer electrolyte with the high ionic conductivity of ceramic electrolytes, forming a uniform interfacial contact with decreased interfacial resistance\textsuperscript{43-45}.

Ce\textsuperscript{3+} or Ce\textsuperscript{4+} incorporation on La\textsuperscript{3+} site in Li\textsubscript{7}La\textsubscript{3}Zr(Hf)\textsubscript{2}O\textsubscript{12} has been previously studied albeit showing limited solid solution range for this site substitution, before the detection of impurity phases\textsuperscript{46, 47}. In contrast, we showed in a previous study, that there was a greater degree of Ce\textsuperscript{4+} substitution possible on the Zr\textsuperscript{4+} site in Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12} leading to a reduction in the tetragonal distortion, which consequently increased the ionic conductivity, although due to the stoichiometric Li content in this system, the room temperature conductivity was just below the value of 10\textsuperscript{-4} Scm\textsuperscript{-1}, which is considered the minimum for applications\textsuperscript{48}. In this paper, the possibility to replace Ce\textsuperscript{4+} on the Nb\textsuperscript{5+} site in Li\textsubscript{5}La\textsubscript{3}Nb\textsubscript{2}O\textsubscript{12} with the creation of excess Li\textsuperscript{+} as the charge compensation mechanism has been examined for the first time, aiming to enhance the overall conductivity for these Ce doped garnets, in addition to providing the beneficial decrease in the interfacial impedance previously reported for Ce-doped Li\textsubscript{7}La\textsubscript{3}Zr\textsubscript{2}O\textsubscript{12}. We investigate effects on the local structure, electrical and electrochemical properties of Ce-doped Li\textsubscript{5}La\textsubscript{3}Nb\textsubscript{2}O\textsubscript{12} through combined X-ray pair distribution function analysis, impedance spectroscopy and
electrochemical testing.

**Experimental**

**Synthesis**

\[ \text{Li}_2\text{CO}_3 \ (99.9\%, \text{Alfa Aesar}), \text{CeO}_2 \ (99.9\%, \text{Acros}), \text{La}_2\text{O}_3 \ (99.9\%, \text{Sigma Aldrich}) \text{ and } \text{Nb}_2\text{O}_5 \ (99\%, \text{Sigma Aldrich}) \text{ were used as starting materials.} \]

\[ \text{Li}_2\text{CO}_3 \text{ was dried at } 180 \ ^\circ\text{C while } \text{La}_2\text{O}_3 \text{ and } \text{Nb}_2\text{O}_5 \text{ were dried at } 900 \ ^\circ\text{C before use.} \]

\[ \text{Samples of } \text{Li}_{5+x}\text{La}_3\text{Nb}_{2-x}\text{Ce}_x\text{O}_{12} \text{ with } x = 0, 0.25, 0.5, 0.75 \text{ and } 1 \text{ were prepared from intimately ground stoichiometric amounts of starting reagents which were heated initially to } 650 \ ^\circ\text{C for 12 hours at a rate of } 5 \ ^\circ\text{C} \text{ min}^{-1}. \]

\[ 10-15\% \text{ excess } \text{Li}_2\text{CO}_3 \text{ was then added to the precursor and the powder milled for 30 minutes using a Pulverisette 5 planetary ball mill. The mixture was pressed into a pellet and heated to } 950-1000 \ ^\circ\text{C for 12 hours at a rate of } 5 \ ^\circ\text{C} \text{ min}^{-1} \text{ to form the final product.} \]

**Characterisation**

A Bruker D8 X-ray diffractometer (XRD) with a CuK\(\alpha\) radiation and linear position sensitive detector was used to collect X-ray diffraction data. Patterns were recorded over the 2\(\theta\) range 15° to 80° with a 0.02° step size. Structural refinement was carried out with the GSAS suite of Rietveld refinement software using the XRD data\textsuperscript{49}.

Scanning electron microscopy (SEM, HITACHI TM4000plus) was employed to assess the microstructure. Bulk samples were polished and thermally etched at 90% of the sintering temperature for 0.5 h. The distribution of elements was
probed with an energy dispersive X-ray spectroscopy (EDX) detector.

Pellets (9.8 mm diameter) were pressed and sintered at 1000 - 1050 °C for 4 hours (ramp rate of 5 °C min⁻¹) in a dry room to limit H⁺/Li⁺ exchange and prevent the decomposition of samples for impedance measurements. Mother powder was used to cover the pellets to prevent the Li loss and reduce reaction with the Al₂O₃ crucible. Au paste was painted on both sides of pellet and heated at 850 °C for 1 hour in air. Impedance data were collected with a HP 4192 analyser over the frequency range from 1 to 10⁷ Hz with 100 mV ac amplitude.

**Cell assembly and electrochemical test**

For the cell tests, a Li₅.₇₅La₃Zr₁.₂₅Ce₀.₇₅O₁₂ pellet (2 mm thickness) was sintered at 1000 °C for 12h in a dry room. The Li//Li₅.₇₅La₃Zr₁.₂₅Ce₀.₇₅O₁₂//Li symmetric cell was hot pressed at 175 °C for 1 hour and assembled using a Swagelok cell in an Argon filled glove box. Electrochemical impedance spectroscopy (EIS) was performed over the frequency range from 0.1 to 10⁷ Hz (100 mV ac applied potential) with a Solatron 1260 analyser. The Li plating/stripping performance was evaluated using a Bio-logic SP50 cell tester.

**Pair Distribution Function data collection**

Total scattering data were collected at the I15-1 XPDF beamline at Diamond Light Source, UK. Powdered samples were loaded into borosilicate capillaries (1.5 mm OD, 1.17 mm ID) and spun perpendicular to the beam during data collection to improve powder averaging. Scattering data were collected at an X-ray energy of 76.69 keV using a Perkin Elmer XRD 4343 CT area detector.
placed ~200 mm from the sample. The 2-D data were corrected for polarization and flat-field, then integrated to 1-D using the DAWN package prior to processed the scattering range $0.7 \ \text{Å}^{-1} \leq Q \leq 25 \ \text{Å}^{-1}$ into PDFs using the GudrunX package$^{50, 51}$. A modified Lorch Function ($\Delta_1 = 0.05 \ \text{Å}$) was applied to suppress spurious low-$r$ features$^{52}$.

**Results and discussion**

**Phase formation**

Stoichiometric $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (LLNO) can be indexed with an $Ia\overline{3}d$ cubic cell. In Kroger - Vink notation, the relationship for substitution of $\text{Nb}^{5+}$ by $\text{Ce}^{4+}$ is as follows:

$$[\text{Ce}_N\text{Nb}] = [\text{Li}_i]$$

As shown in figure 1a, XRD patterns of Ce-doped $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ with formulae $\text{Li}_{5+x}\text{La}_3\text{Nb}_{2-x}\text{Ce}_x\text{O}_{12}$ show peak shifts to lower $2\theta$ angle with increasing Ce content, without the detection of any impurity phases up to $x = 0.75$. The cell parameter was shown to obey Vegard’s law, increasing linearly as a function of $x$ (figure 1b), which further confirms the successful incorporation of Ce into the structure due to the larger radius of $\text{Ce}^{4+}$ to that of $\text{Nb}^{5+}$ (0.87 and 0.64 ionic radius for $\text{Ce}^{4+}$ and $\text{Nb}^{5+}$ respectively in 6 oxygen coordinated octahedral sites).

$\text{Li}_2\text{La}_2\text{CeO}_6$ and $\text{CeO}_2$ impurity phases were detected for compositions with $x = 1$, which is consistent with the leveling off of the cell parameter increase; from these data, a solid solution limitation around $x = 0.85$ is estimated. As shown in figure 2, EDX mapping of $\text{Li}_{5.75}\text{La}_3\text{Nb}_{1.25}\text{Ce}_{0.75}\text{O}_{12}$ shows a homogeneous
distribution of La, Nb, Ce and O within the sample.

XRD data of Li$_5$La$_3$Nb$_2$O$_{12}$ and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ were used to carry out structure refinement in order to confirm the incorporation of Ce on the Nb site. The $U_{iso}$ parameters of all atoms were initially set to a typical value of 0.1 Å. It was not possible to refine the Li positions and occupancies due to the poor sensitivity of Li with X-rays in the presence of heavier elements; Li positions were not refined and Li occupancies for the doped samples were scaled up from published occupancies of the undoped phase to ensure that the charge-neutrality of the resulting structure. First the scale factor, background (6 terms of shifted Chebyshev function) and lattice parameters were refined. Then, peak profile parameters and 2θ zero error were refined before fixing them at the converged value. Finally, the atomic coordinates of O1, $U_{iso}$ of La1, Nb1 were refined in sequence followed by refining together in the last step. Final refined parameters for Li$_5$La$_3$Nb$_2$O$_{12}$ are summarised in table 1.

A similar structure refinement for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ was performed. In this case, a constraint of the same atomic coordinates, the same $U_{iso}$ and full occupancy between Nb1 and Ce1 was made initially. This refinement gave site occupancies of 0.61(1) for Nb1 and 0.39(1) for Ce1 which is consistent with expected composition within 2 esds. Final refined parameters for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ are shown in table 2. Selected bond lengths for both Li$_5$La$_3$Nb$_2$O$_{12}$ and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ are shown in table 3. The data show that all Nb1/Ce1 – O1 bonds expand in the Ce doped sample (bond distance =
2.138 Å) compared to undoped LLNO (bond distance = 2.020 Å), consistent with the larger size of Ce$^{4+}$ versus Nb$^{5+}$.

Pair Distribution Function (PDF)

X-ray PDF data for undoped Li$_5$La$_3$Nb$_2$O$_{12}$ and Ce-doped Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ are shown in figure 4. The peaks in the low-r region of the PDF were assigned based on simulations of the partial PDFs of the undoped structure using the computer program PDFgui (figure S1)$^{53}$. The single Nb–O peak at ~1.94 Å in undoped LLNO develops a shoulder at high-r with doping, which increases in intensity concurrent with Ce content. Gaussian peaks were fit to the observed PDF data using the computer program TOPAS (figure S2) allowing for the extraction of the local structure bond lengths given in Table 4$^{54}$. In contrast to the long-range average bond length from Rietveld refinement which calculates a single average Nb, Ce–O bond length which increases from 2.020(8) Å to 2.138(6) Å on doping, the local structure information provided by the PDF allows us to separate the contributions of the individual bond distances. These results show that the Nb–O bond remains constant at ~1.94 Å, while the Ce–O bond length of 2.16 Å can be extracted for the doped samples, which is consistent with the increase expected on moving to the larger Ce$^{4+}$ ion on simple ionic radii arguments.

Figure 5 shows the PDF data with the r axis for the doped samples normalised to the lattice parameter of the undoped LLNO; this normalisation highlights changes upon doping beyond simple expansion of the lattice. At low-r (figure
peaks around 5.9 Å due to the second La–La and Nb,Ce–Nb,Ce coordination shell contract relative to the normalised lattice parameter, but the rest of the features remain unchanged. Neutron PDF data would be required to determine the full impact of doping on the Li and O environments (previous neutron PDF study shows lithium atoms within either tetrahedral or octahedral sites prefer to stay at the off-center positions in the undoped Li$_5$La$_3$Nb$_2$O$_{12.55}$). However, it is clear that doping introduces more disorder into the system, evidenced by broader peaks at high $r$ (figure 5b); this additional disorder is expected due to the significantly different sizes of Nb and Ce, and the additional lithium which requires occupation of more varied coordination environments.

**Conductivity Measurement**

The morphology of undoped and cerium doped Li$_5$La$_3$Nb$_2$O$_{12}$ are shown in figure 6. The relative density of garnet pellets increased as a function of Ce content (51.2% for Li$_5$La$_3$Nb$_2$O$_{12}$ and 75.1% for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$). A typical dataset of Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ impedance spectroscopy is shown in figure 7. From the $Z^*$ complex plane (figure 7a), a non-ideal semicircle was observed at higher frequency while a sharp spike is seen at lower frequency. To fit the circuit, a resistor $R_1$ and a constant phase element (CPE) CPE1 in parallel were used to simulate the high frequency semicircle. Another CPE2 which is in series with the $R_1$/CPE1 in the circuit was utilised to interpret the low frequency spike.

The corresponding spectroscopic $C'$ plot (figure 7b) shows a higher frequency
plateau with a capacitance of 8.2 pF cm\(^{-1}\) with an associated permittivity of 91 (calculated from \(\varepsilon'\) = \(C/\varepsilon_0\), where \(\varepsilon_0\) is the permittivity of free space with a value of 8.854 x 10\(^{-14}\) F cm\(^{-1}\)), which is a typical value for the bulk response\(^{56}\). In addition, a low frequency plateau with a capacitance of 3 \(\mu\)F cm\(^{-1}\) was observed, which is due to the double layer effect at the sample – electrode interface; hence consistent with \(\text{Li}^+\) ion conduction.

The spectroscopic \(Y'\) plot (figure 7c) shows a frequency-independent plateau at intermediate frequency, which is associated with the bulk conductivity. A dispersion at lower frequency was seen due to the blockage of lithium ions at the sample – electrode interface. At higher frequency, a curvature was detected related to the Jonscher's power law\(^{57}\).

The Arrhenius plot (figure 8) shows the bulk conductivities of undoped and Ce-doped LLNO. Conductivities increased with increasing cerium content in agreement with more excess lithium in the structure. The maximum conductivity was found in Li\(_{5.75}\)La\(_3\)Nb\(_{1.25}\)Ce\(_{0.75}\)O\(_{12}\) sample, which reached a value of 1.4 x 10\(^{-4}\) S cm\(^{-1}\) at 25 °C and is ~ two orders more than that of LLNO, and represents one of the highest conductivities for a garnet with less than 6 Li. The activation energy also decreased from 0.41(1) eV for Li\(_5\)La\(_3\)Nb\(_2\)O\(_{12}\) to 0.35(1) eV for Li\(_{5.75}\)La\(_3\)Nb\(_{1.25}\)Ce\(_{0.75}\)O\(_{12}\). This decrease in activation energy may be indicative of an opening of the bottleneck for Li migration between sites, due to the increase in cell size through Ce doping.

Electrochemical Properties

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The electrochemical impedance spectroscopy of the Li//Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$/Li cell is shown in figure 9a. For circuit fitting, a parallel R1 and CPE1 representing a bulk semicircle in series with another parallel R2 and CPE2 related to the interfacial semicircle were used. A significant interfacial resistance decrease from 3802 Ω cm$^2$ for Li$_5$La$_3$Nb$_2$O$_{12}$ to 488 Ω cm$^2$ for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ was observed (figure S3), which is consistent with our previous work on Ce doped Li$_7$La$_3$Zr$_2$O$_{12}$, and represents a reduced interfacial resistance attributed to the formation of a mixed valence Ce$^{4+}$/Ce$^{3+}$ product at the electrode/lithium interface$^{48}$. Long-term cycling properties of the Li//Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$/Li cell at 55 °C are shown in figure 9b. A voltage plateau with a voltage overpotential of 251 mV at 50 μA cm$^{-2}$ current density was observed; the long-term cycling stability over 380 h was shown.

Conclusion

Cerium was successfully doped into the Li$_5$La$_3$Nb$_2$O$_{12}$ garnet structure through a conventional solid-state method. The lattice parameter increased linearly as a function of composition to $x \sim 0.85$, indicating the formation of an extensive solid solution range. XRD PDF analysis confirmed the incorporation of cerium, allowing the separate Nb/Ce-O bond distances to be determined, and thus illustrating the longer bond distances for Ce on the octahedral site to those of Nb. The conductivity increased by two orders of Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ compared to that of Li$_5$La$_3$Nb$_2$O$_{12}$ with a reduction in the activation energies for
Ce-doped samples. The interfacial resistance also dramatically decreased to 488 $\Omega \text{cm}^2$ for $\text{Li}_{5.75}\text{La}_3\text{Nb}_{1.25}\text{Ce}_{0.75}\text{O}_{12}$, demonstrating that cerium doping benefits the interfacial issue. The long-term cycling stability of a Li//garnet//Li symmetric cell over 380 h was demonstrated, thus illustrating the potential of this Ce doped garnet system. Further studies are required to characterise the formation and possible change of the interlayer between garnet and lithium metal.

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References

1. Tarascon, J.-M.; Armand, M., Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature*. **2001**, *414*, (6861), 359-367.
2. Bruce, P. G.; Scrosati, B.; Tarascon, J. M., Nanomaterials for Rechargeable Lithium Batteries. *Angew. Chem. Int. Ed.* **2008**, *47*, (16), 2930-2946.
3. Goodenough, J. B.; Park, K. S., The Li-Ion Rechargeable Battery: a Perspective. *J. Am. Chem. Soc.* **2013**, *135*, (4), 1167-1176.
4. Larcher, D.; Tarascon, J. M., Towards Greener and More Sustainable...
Batteries for Electrical Energy Storage. *Nature Chem.* 2015, 7, (1), 19-29.

5. Zhao, N.; Khokhar, W.; Bi, Z.; Shi, C.; Guo, X.; Fan, L.-Z.; Nan, C.-W., Solid Garnet Batteries. *Joule*. 2019, 3, (5), 1190-1199.

6. Thangadurai, V.; Narayanan, S.; Pinzaru, D., Garnet-Type Solid-State Fast Li Ion Conductors for Li Batteries: Critical Review. *Chem. Soc. Rev.* 2014, 43, (13), 4714-4727.

7. Ramakumar, S.; Deviannapoorani, C.; Dhivya, L.; Shankar, L. S.; Murugan, R., Lithium Garnets: Synthesis, Structure, Li$^+$ Conductivity, Li$^+$ Dynamics and Applications. *Prog. Mater. Sci.* 2017, 88, 325-411.

8. Samson, A. J.; Hofstetter, K.; Bag, S.; Thangadurai, V., A Bird's-Eye View of Li-Stuffed Garnet-Type Li$_7$La$_3$Zr$_2$O$_{12}$ Ceramic Electrolytes for Advanced All-Solid-State Li Batteries. *Energy Environ. Sci.* 2019, 12, (10), 2957-2975.

9. Thangadurai, V.; Kaack, H.; Weppner, W., Novel Fast Lithium Ion Conduction in Garnet-Type Li$_5$La$_3$M$_2$O$_{12}$ (M = Nb, Ta). *J. Am. Ceram. Soc.* 2003, 86, (3), 437-440.

10. Cussen, E. J., The Structure of Lithium Garnets: Cation Disorder and Clustering in a New Family of Fast Li$^+$ Conductors. *Chem. Commun.* 2006, (4), 412-413.

11. Cussen, E. J., Structure and Ionic Conductivity in Lithium Garnets. *J. Mater. Chem.* 2010, 20, (25), 5167-5173.

12. Percival, J.; Kendrick, E.; Smith, R. I.; Slater, P. R., Cation Ordering in Li Containing Garnets: Synthesis and Structural Characterisation of the
Tetragonal System, Li$_7$La$_3$Sn$_2$O$_{12}$. *Dalton Trans.* 2009, (26), 5177-5181.

13. Awaka, J.; Kijima, N.; Hayakawa, H.; Akimoto, J., Synthesis and Structure Analysis of Tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ with the Garnet-Related Type Structure. *J. Solid State Chem.* 2009, 182, (8), 2046-2052.

14. Awaka, J.; Kijima, N.; Kataoka, K.; Hayakawa, H.; Ohshima, K.-i.; Akimoto, J., Neutron Powder Diffraction Study of Tetragonal Li$_7$La$_3$Hf$_2$O$_{12}$ with the Garnet-related Type Structure. *J. Solid State Chem.* 2010, 183, (1), 180-185.

15. Thangadurai, V.; Weppner, W., Li$_6$Al$_2$Ta$_2$O$_{12}$ (A = Sr, Ba): Novel Garnet-Like Oxides for Fast Lithium Ion Conduction. *Adv. Funct. Mater.* 2005, 15, (1), 107-112.

16. Murugan, R.; Thangadurai, V.; Weppner, W., Fast Lithium Ion Conduction in Garnet-Type Li$_7$La$_3$Zr$_2$O$_{12}$. *Angew. Chem. Int. Ed.* 2007, 46, (41), 7778-7781.

17. Ohta, S.; Kobayashi, T.; Asaoka, T., High Lithium Ionic Conductivity in the Garnet-Type Oxide Li$_{7-x}$La$_3$(Zr$_{2-x}$, Nb$_x$)O$_{12}$ (x=0-2). *J. Power Sources.* 2011, 196, (6), 3342-3345.

18. Howard, M. A.; Clemens, O.; Kendrick, E.; Knight, K. S.; Apperley, D. C.; Anderson, P. A.; Slater, P. R., Effect of Ga Incorporation on the Structure and Li Ion Conductivity of La$_3$Zr$_2$Li$_7$O$_{12}$. *Dalton Trans.* 2012, 41, (39), 12048-12053.

19. Howard, M. A.; Clemens, O.; Knight, K. S.; Anderson, P. A.; Hafiz, S.; Panchmatia, P. M.; Slater, P. R., Synthesis, Conductivity and Structural Aspects of Nd$_3$Zr$_2$Li$_{7-3x}$Al$_x$O$_{12}$. *J. Mater. Chem. A.* 2013, 1, (44), 14013-14022.

20. El Shinawi, H.; Janek, J., Stabilization of Cubic Lithium-Stuffed Garnets of
the Type “Li$_7$La$_3$Zr$_2$O$_{12}$” by Addition of Gallium. *J. Power Sources.* 2013, 225, 13-19.

21. Miara, L. J.; Richards, W. D.; Wang, Y. E.; Ceder, G., First-Principles Studies on Cation Dopants and Electrolyte/Cathode Interphases for Lithium Garnets. *Chem. Mater.* 2015, 27, (11), 4040-4047.

22. Yeandel, S. R.; Chapman, B. J.; Slater, P. R.; Goddard, P., Structure and Lithium-Ion Dynamics in Fluoride-Doped Cubic Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) Garnet for Li Solid-State Battery Applications. *J. Phys. Chem. C* 2018, 122, (49), 27811-27819.

23. Squires, A. G.; Scanlon, D. O.; Morgan, B. J., Native Defects and Their Doping Response in the Lithium Solid Electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$. *Chem. Mater.* 2019, 32, (5), 1876-1886.

24. Dong, B.; Driscoll, L. L.; Stockham, M. P.; Kendrick, E.; Slater, P. R., Low Temperature Synthesis of Garnet Solid State Electrolytes: Implications on Aluminium Incorporation in Li$_7$La$_3$Zr$_2$O$_{12}$. *Solid State Ionics* 2020, 350, 115317.

25. Stockham, M. P.; Dong, B.; Ding, Y.; Li, Y.; Slater, P. R., Evaluation of the effect of site substitution of Pr doping in the lithium garnet system Li$_5$La$_3$Nb$_2$O$_{12}$. *Dalton Trans.* 2020, 49, (30), 10349-10359.

26. Park, K.; Yu, B.-C.; Jung, J.-W.; Li, Y.; Zhou, W.; Gao, H.; Son, S.; Goodenough, J. B., Electrochemical Nature of the Cathode Interface for a Solid-State Lithium-Ion Battery: Interface between LiCoO$_2$ and Garnet- Li$_7$La$_3$Zr$_2$O$_{12}$. *Chem. Mater.* 2016, 28, (21), 8051-8059.
27. Pesci, Federico M.; Brugge, R. H.; Hekselman, A. K. O.; Cavallaro, A.; Chater, R. J.; Aguadero, A., Elucidating the Role of Dopants in the Critical Current Density for Dendrite Formation in Garnet Electrolytes. *J. Mater. Chem. A* 2018, 6, (40), 19817-19827.

28. Canepa, P.; Dawson, J. A.; Sai Gautam, G.; Statham, J. M.; Parker, S. C.; Islam, M. S., Particle Morphology and Lithium Segregation to Surfaces of the Li₇La₃Zr₂O₁₂ Solid Electrolyte. *Chem. Mater.* 2018, 30, (9), 3019-3027.

29. Philipp, M.; Gadermaier, B.; Posch, P.; Hanzu, I.; Ganschow, S.; Meven, M.; Rettenwander, D.; Redhammer, G. J.; Wilkening, H. M. R., The Electronic Conductivity of Single Crystalline Ga-Stabilized Cubic Li₇La₃Zr₂O₁₂: A Technologically Relevant Parameter for All-Solid-State Batteries. *Adv. Mater. Interfaces* 2020, 2000450.

30. Galven, C.; Fourquet, J.-L.; Crosnier-Lopez, M.-P.; Le Berre, F. o., Instability of the Lithium Garnet Li₇La₃Sn₂O₁₂: Li⁺/H⁺ Exchange and Structural Study. *Chem. Mater.* 2011, 23, (7), 1892-1900.

31. Larraz, G.; Orera, A.; Sanjuán, M. L., Cubic Phases of Garnet-Type Li₇La₃Zr₂O₁₂: the Role of Hydration. *J. Mater. Chem. A* 2013, 1, (37), 11419-11428.

32. Truong, L.; Howard, M.; Clemens, O.; Knight, K. S.; Slater, P. R.; Thangadurai, V., Facile Proton Conduction in H⁺/Li⁺ Ion-Exchanged Garnet-Type Fast Li-Ion Conducting Li₅La₃Nb₂O₁₂. *J. Mater. Chem. A* 2013, 1, (43), 13469-13475.
33. Brugge, R. H.; Hekselman, A. K. O.; Cavallaro, A.; Pesci, F. M.; Chater, R. J.; Kilner, J. A.; Aguadero, A., Garnet Electrolytes for Solid State Batteries: Visualization of Moisture-Induced Chemical Degradation and Revealing Its Impact on the Li-Ion Dynamics. *Chem. Mater.* **2018**, *30*, (11), 3704-3713.

34. Pesci, F. M.; Bertei, A.; Brugge, R. H.; Emge, S. P.; Hekselman, A. K. O.; Marbella, L. E.; Grey, C. P.; Aguadero, A., Establishing Ultralow Activation Energies for Lithium Transport in Garnet Electrolytes. *ACS Appl. Mater. Interfaces* **2020**, *12*, (29), 32806-32816.

35. Li, Y.; Chen, X.; Dolocan, A.; Cui, Z.; Xin, S.; Xue, L.; Xu, H.; Park, K.; Goodenough, J. B., Garnet Electrolyte with an Ultralow Interfacial Resistance for Li-Metal Batteries. *J. Am. Chem. Soc.* **2018**, *140*, (20), 6448-6455.

36. Ruan, Y.; Lu, Y.; Huang, X.; Su, J.; Sun, C.; Jin, J.; Wen, Z., Acid Induced Conversion Towards a Robust and Lithiophilic Interface for Li–Li$_7$La$_3$Zr$_2$O$_{12}$ Solid-State Batteries. *J. Mater. Chem. A.* **2019**, *7*, (24), 14565-14574.

37. Han, X.; Gong, Y.; Fu, K. K.; He, X.; Hitz, G. T.; Dai, J.; Pearse, A.; Liu, B.; Wang, H.; Rubloff, G.; Mo, Y.; Thangadurai, V.; Wachsman, E. D.; Hu, L., Negating Interfacial Impedance in Garnet-Based Solid-State Li Metal Batteries. *Nat. Mater.* **2017**, *16*, (5), 572-579.

38. Fu, K.; Gong, Y.; Hitz, G. T.; McOwen, D. W.; Li, Y.; Xu, S.; Wen, Y.; Zhang, L.; Wang, C.; Pastel, G.; Dai, J.; Liu, B.; Xie, H.; Yao, Y.; Wachsman, E. D.; Hu, L., Three-Dimensional Bilayer Garnet Solid Electrolyte Based High Energy
Density Lithium Metal–Sulfur Batteries. *Energy Environ. Sci.* **2017**, **10**, (7), 1568-1575.

39. Dai, J.; Yang, C.; Wang, C.; Pastel, G.; Hu, L., Interface Engineering for Garnet-Based Solid-State Lithium-Metal Batteries: Materials, Structures, and Characterization. *Adv. Mater.* **2018**, **30**, (48), 1802068.

40. Fu, J.; Yu, P.; Zhang, N.; Ren, G.; Zheng, S.; Huang, W.; Long, X.; Li, H.; Liu, X., In situ Formation of a Bifunctional Interlayer Enabled by a Conversion Reaction to Initiatively Prevent Lithium Dendrites in a Garnet Solid Electrolyte. *Energy Environ. Sci.* **2019**, **12**, (4), 1404-1412.

41. Song, Y.; Yang, L.; Tao, L.; Zhao, Q.; Wang, Z.; Cui, Y.; Liu, H.; Lin, Y.; Pan, F., Probing into the Origin of an Electronic Conductivity Surge in a Garnet Solid-State Electrolyte. *J. Mater. Chem. A.* **2019**, **7**, (40), 22898-22902.

42. Gao, J.; Zhu, J.X.; Li, X.L.; Li, J.P.; Guo, X.X.; Li, H.; Zhou, W.D., Rational Design of Mixed Electronic-Ionic ConductingTi-Doping Li$_7$La$_3$Zr$_2$O$_{12}$ for Lithium Dendrites Suppression. *Adv. Funct. Mater.* **2020**, **11**, (1), 2001918.

43. Zhou, W.; Wang, Z.; Pu, Y.; Li, Y.; Xin, S.; Li, X.; Chen, J.; Goodenough, J. B., Double-Layer Polymer Electrolyte for High-Voltage All-Solid-State Rechargeable Batteries. *Adv. Mater.* **2019**, **31**, (4), 1805574.

44. Huang, Z.; Pang, W.; Liang, P.; Jin, Z.; Grundish, N.; Li, Y.; Wang, C.-A., A Dopamine Modified Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$/PEO Solid-state Electrolyte: Enhanced Thermal and Electrochemical Properties. *J. Mater. Chem. A.* **2019**, **7**, (27), 16425-16436.
45. Chi, S.-S.; Liu, Y.; Zhao, N.; Guo, X.; Nan, C.-W.; Fan, L.-Z., Solid Polymer Electrolyte Soft Interface Layer with 3D Lithium Anode for All-Solid-State Lithium Batteries. *Energy Storage Mater.* **2019**, **17**, 309-316.

46. Rangasamy, E.; Wolfenstine, J.; Allen, J.; Sakamoto, J., The Effect of 24c-Site (A) Cation Substitution on the Tetragonal–Cubic Phase Transition in Li$_{7-x}$La$_3$A$_x$Zr$_2$O$_{12}$ Garnet-Based Ceramic Electrolyte. *J. Power Sources.* **2013**, **230**, 261-266.

47. Trofimov, A. A.; Li, C.; Brinkman, K. S.; Jacobsohn, L. G., Luminescence Investigation of Ce Incorporation in Garnet-Type Li$_7$La$_3$Zr$_2$O$_{12}$. *Opt. Mater.* **2017**, **68**, 7-10.

48. Dong, B.; Yeandel, S. R.; Goddard, P.; Slater, P. R., Combined Experimental and Computational Study of Ce-Doped La$_3$Zr$_2$Li$_7$O$_{12}$ Garnet Solid-State Electrolyte. *Chem. Mater.* **2019**, **32**, (1), 215-223.

49. Toby, B. H., EXPGUI, a Graphical User Interface for GSAS. *J. Appl. Crystallogr.* **2001**, **34**, (2), 210-213.

50. Soper, A. K., Programs for Correcting Raw Neutron and X-Ray Diffraction Data to Differential Scattering Cross Section. *Technical Report RAL-TR-2011-013; Rutherford Appleton Laboratory.* **2011**.

51. Filik, J.; Ashton, A. W.; Chang, P. C. Y.; Chater, P. A.; Day, S. J.; Drakopoulos, M.; Gerring, M. W.; Hart, M. L.; Magdysyuk, O. V.; Michalik, S.; Smith, A.; Tang, C. C.; Terrill, N. J.; Wharmby, M. T.; Wilhelm, H., Processing Two-Dimensional X-Ray Diffraction and Small-Angle Scattering Data in DAWN
2. J. Appl. Crystallogr. 2017, 50, (Pt 3), 959-966.

52. Soper, A. K.; Barney, E. R., On the Use of Modification Functions When Fourier Transforming Total Scattering Data. J. Appl. Crystallogr. 2012, 45, (6), 1314-1317.

53. Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Bozin, E. S.; Bloch, J.; Proffen, T.; Billinge, S. J., PDFfit2 and PDFgui: Computer Programs for Studying Nanostructure in Crystals. J. Phys. Condens. Matter. 2007, 19, (33), 335219.

54. Coelho, A. A., TOPAS and TOPAS-Academic: an Optimization Program Integrating Computer Algebra and Crystallographic Objects Written in C++. J. Appl. Crystallogr. 2018, 51, (1), 210-218.

55. Wang, Y.; Klenk, M.; Page, K.; Lai, W., Local Structure and Dynamics of Lithium Garnet Ionic Conductors: A Model Material Li₅La₃Ta₂O₁₂. Chem. Mater. 2014, 26, (19), 5613-5624.

56. Irvine, J. T. S.; Sinclair, D. C.; West, A. R., Electroceramics: Characterization by Impedance Spectroscopy. Adv. Mater. 1990, 2, (3), 132-138.

57. Dong, B.; Yan, J.; Walkley, B.; Inglis, K. K.; Blanc, F.; Hull, S.; West, A. R., Synthesis and Characterisation of the New Oxyfluoride Li⁺ Ion Conductor, Li₅SiO₄F. Solid State Ionics. 2018, 327, 64-70.
Captions of figures and tables

Figure 1. (a) XRD patterns of Li$_{5+x}$La$_3$Nb$_{2-x}$Ce$_x$O$_{12}$: x = 0, 0.25, 0.5, 0.75, 1. Triangle and rectangle labels represent CeO$_2$ and La$_2$CeLi$_2$O$_6$ respectively. (b) Variation of lattice parameter, a, and volume, V, of Li$_{5+x}$La$_3$Nb$_{2-x}$Ce$_x$O$_{12}$ with composition x.

Figure 2. EDX elemental mapping of Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$.

Figure 3. Observed, calculated and difference profiles from Rietveld refinement for (a) Li$_5$La$_3$Nb$_2$O$_{12}$ and (b) Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ using XRD data.

Figure 4. Pair distribution function data for Li$_5$La$_3$Nb$_2$O$_{12}$ (black), Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ (green) and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ (red) focusing in the low-r region.

Figure 5. Pair distribution function data for Li$_5$La$_3$Nb$_2$O$_{12}$ (black), Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ (green) and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ (red), with the r axis normalized to the lattice parameter of Li$_5$La$_3$Nb$_2$O$_{12}$.

Figure 6. SEM images of (a) Li$_5$La$_3$Nb$_2$O$_{12}$, (b) Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ and (c) Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ pellets.

Figure 7. Impedance data of Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$. (a) Complex Z* plot (b) Spectroscopic plot of C' (c) Spectroscopic plot of Y'

Figure 8. Arrhenius conductivity plot for Ce-doped Li$_5$La$_3$Nb$_2$O$_{12}$

Figure 9. (a) Electrochemical impedance spectroscopy of Li/Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$/Li cell. (b) Stripping/Plating properties of
Li/Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$/Li cell at 55 °C.

Table 1 Refined structural parameters for Li$_5$La$_3$Nb$_2$O$_{12}$ using XRD data.

Table 2 Refined structural parameters for Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ using XRD data.

Table 3 Bond lengths for Nb1(Ce1) – O of Li$_5$La$_3$Nb$_2$O$_{12}$ and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ from refinement results.

Table 4 Bond lengths for Nb–O, Ce–O, La–O, La–Nb,Ce, La–La of Li$_5$La$_3$Nb$_2$O$_{12}$, Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ and Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ from X-ray PDF data.
Figure 1

(a) X-ray diffraction patterns for Li$_{5+x}$La$_3$Nb$_{2-x}$Ce$_x$O$_{12}$ with different Ce contents: x = 0, 0.25, 0.50, 0.75, and 1.00.

(b) Plot showing the variation of lattice parameters (a and V) with the Li content (x) for Li$_{5+x}$La$_3$Nb$_{2-x}$Ce$_x$O$_{12}$. The solid line represents a linear fit for the data points.
Figure 2
Figure 3

(a) and (b) show X-ray diffraction patterns for different phases. The patterns compare observed (I(obs)) and calculated (I(cal)) intensities, along with background (I(bac)) and observed minus calculated intensities (Obs - Cal). The reference phase (ref-phase) is also indicated. The 2 Theta (Degree) range is from 20 to 80 degrees.
Figure 5
Figure 6
Figure 7

(a) Nyquist plot showing experimental and fitted data.

(b) Bode plot showing the log of the magnitude of the impedance as a function of log frequency.

(c) Bode phase plot showing the phase angle as a function of log frequency.
Figure 9

(a) A plot showing experimental and fitted data for $-Z'' \times 10^{-3}$ against $Z' \times 10^{-3}$ in $\Omega \text{cm}^2$.

(b) A graph illustrating voltage (V) over time (h) with different current densities (12.5, 25, and 50 $\mu\text{A cm}^{-2}$).
| Atom | x     | y     | z     | Multi. | Occupancy | \( \mu_{\text{iso}} \times 100 \) (Å²) |
|------|-------|-------|-------|--------|-----------|-----------------|
| La1  | 0.125 | 0     | 0.25  | 24     | 1         | 0.6(1)          |
| Nb1  | 0     | 0     | 0     | 16     | 1         | 0.2(1)          |
| O1   | 0.2844(5) | 0.1044(6) | 0.1996(6) | 96   | 1         | 0.7(3)          |
| Li1  | 0.25  | 0.875 | 0     | 24     | 0.836     | 0.1             |
| Li2  | 0.125 | 0.6798| 0.5702| 48     | 0.110     | 0.1             |
| Li3  | 0.095 | 0.6818| 0.5778| 96     | 0.152     | 0.1             |

\( a = 12.7949(1) \) Å, \( V = 2094.67(4) \) Å³

\( \chi^2 = 5.266 \), \( R_{wp} = 11.49\% \), \( R_p = 9.13\% \)
Table 2

| Atom | x    | y    | z     | Multi. | Occupancy | $u_{iso} \times 100$ (Å²) |
|------|------|------|-------|--------|-----------|----------------------------|
| La1  | 0.125| 0    | 0.25  | 24     | 1         | 0.1                        |
| Nb1  | 0    | 0    | 0     | 16     | 0.61(1)   | 0.1                        |
| Ce1  | 0    | 0    | 0     | 16     | 0.39(1)   | 0.1                        |
| O1   | 0.2874(4) | 0.0980(5) | 0.1984(5) | 96 | 1 | 1.2(3) |
| Li1  | 0.25 | 0.875| 0     | 24     | 0.961     | 0.1                        |
| Li2  | 0.125| 0.6798| 0.5702| 48 | 0.127     | 0.1                        |
| Li3  | 0.095| 0.6818| 0.5778| 96 | 0.175     | 0.1                        |

$a = 12.9761(1)$Å, $V = 2184.90(7)$ Å³

$\chi^2 = 2.823$, $R_{wp} = 8.18$, $R_p = 6.69\%$
Table 3

| Composition            | Bond                | Length (Å) |
|------------------------|---------------------|------------|
| Li₅La₃Nb₂O₁₂           | Nb1-O1 (x6)         | 2.020(8)   |
| Li₅.₇₅La₃Nb₁.₂₅Ce₀.₇₅O₁₂ | Nb1/Ce1-O1 (x6)    | 2.138(6)   |
| Bond      | Li$_5$La$_3$Nb$_2$O$_{12}$ | Li$_{5.5}$La$_3$Nb$_{1.5}$Ce$_{0.5}$O$_{12}$ | Li$_{5.75}$La$_3$Nb$_{1.25}$Ce$_{0.75}$O$_{12}$ |
|-----------|---------------------------|---------------------------------------------|-------------------------------------------------|
| Nb–O      | 1.93(3) Å                 | 1.95(2) Å                                  | 1.94(2) Å                                       |
| Ce–O      | -                         | 2.16(4) Å                                  | 2.16(2) Å                                       |
| La–O      | 2.474(5) Å                | 2.475(7) Å                                 | 2.476(7) Å                                      |
| La–Nb,Ce  | 3.531(1) Å                | 3.572(1) Å                                 | 3.591(1) Å                                      |
| La–La     | 3.904(1) Å                | 3.929(1) Å                                 | 3.942(2) Å                                      |