Evaluation of the effect of site substitution of Pr doping in the lithium garnet system Li$_5$La$_3$Nb$_2$O$_{12}$†

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Li ion conducting garnets have been attracting considerable interest for use as the electrolyte in all solid-state batteries, due to their high ionic conductivity and wide electrochemical stability window. Consequently, there have been a number of doping studies aimed at optimising the conductivity, focusing on both doping in Li$_5$La$_2$Zr$_2$O$_{12}$ and Li$_5$La$_3$(Nb/Ta)$_2$O$_{12}$ systems. In this paper, we report a detailed study of Pr doping in Li$_5$La$_3$Nb$_2$O$_{12}$, and show that this is a rare example of an ambivalent site dopant, being able to be doped onto either the La or Nb site. Interestingly the resultant Pr oxidation state is determined by the site substitution, with oxidation states of 3+ for the La site, and 4+ for the Nb site. While the conductivity is essentially unchanged for the La site substitution, Pr$^{3+}$ substitution on the Nb site leads to a large increase in the conductivity associated with the increase in Li content (Li$_{5-x}$La$_3$Nb$_{2-x}$Pr$_x$O$_{12}$) up to 0.56 mS cm$^{-1}$ (at 50 °C) for $x = 0.8$. Overall, this work highlights the flexibility of these garnet materials to doping, and suggests that further consideration of site substitution be considered for other dopants.

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partially occupies the interstitial octahedral sites 48 h and 96 g, in a disordered fashion. This gives a disordered Li sublattice and a migration pathway which leads to high ionic conductivity via the Li\(^{+}\) charge carrier, which is thought to follow the hopping mechanism of 24 d → 96 h → 48 g → 96 h → 24 d, as determined by high temperature neutron diffraction studies.\(^{23}\)

Of the wide variety of garnet systems, particular attention has been afforded to Li\(_{2}\)La\(_{2}\)Zr\(_{2}\)O\(_{12}\) (LLZO). This stoichiometric system is tetragonal at room temperature, with comparatively low conductivity, and changes to a cubic cell at around 750 °C; this temperature can be reduced to 350 °C by doping at the Zr site with Ce, leading to an increase in conductivity.\(^{24}\) Stabilisation of the cubic cell at room temperature (c-LLZO) requires a reduction of the lithium content, often using Al or Ga substitution at the Li site.\(^{16,25,26}\) Dopants at the Zr site (e.g. Nb, Ti\(^{27,28}\)) also can stabilise c-LLZO.

Although c-LLZO has been reported with conductivities >10\(^{-4}\) S cm\(^{-1}\), these often require complex methodologies and/or equipment, such as field assisted sintering, which presents a barrier to commercial scalability.\(^{16,29,30}\) Consequently, the majority of c-LLZO doping strategies lead to conductivities ~10\(^{-3}\) S cm\(^{-1}\), or lower, and are suboptimal compared with current Li\(_{x}\) liquid electrolytes.\(^{31-38}\) Therefore, it is of interest to investigate alternative doping strategies of other lithium garnet systems, such as Li\(_{5}\)La\(_{3}\)Nb\(_{2}\)O\(_{12}\) (LLNO). This system was the first to show fast Li-ion conductivity, and outside of garnet systems, such as Li\(_{5}\)La\(_{3}\)Nb\(_{2}\)O\(_{12}\) (Pr\(^{3+}\)). We note that a range of high Pr contents: it has been shown to occur for garnet samples at lower temperatures.\(^{1,39,40}\) However, of the prior reports of doping into the LLNO system, many show room temperature conductivities of ~10\(^{-4}\) S cm\(^{-1}\) and are thus similar to c-LLZO.\(^{13,41}\) Therefore, further doping studies on the LLNO system are warranted. Herein we report an examination of Pr doping in this system. Pr was chosen because of its ability to adopt different oxidation states (3\(^{+}\), 4\(^{+}\)), and so potential, based on size considerations, to dope onto either the Nb or the La site according to the following formula Li\(_{5}\)La\(_{3-x}\)Nb\(_{2-x}\)Pr\(_{x}\)O\(_{12}\) (Pr\(^{3+}\)) and Li\(_{1-x}\)La\(_{3-x}\)Pr\(_{x}\)Nb\(_{2}\)O\(_{12}\) (Pr\(^{4+}\)). We confirm this ambi-site substitutional ability of Pr, and illustrate in particular that Pr doping on the Nb site leads to samples with high Li ion conductivity.

### Methods

#### Synthesis

Li\(_{1-x}\)La\(_{3-x}\)Nb\(_{2-x}\)Pr\(_{x}\)O\(_{12}\) garnets were prepared via the solid-state route from stoichiometric quantities of Li\(_{2}\)CO\(_{3}\), La\(_{2}\)O\(_{3}\), Nb\(_{2}\)O\(_{5}\) and Pr\(_{2}\)O\(_{3}\) under air. A 40% molar excess of lithium was added to compensate for lithium loss during high temperature sintering. All powders were ball milled for 1 h (500 rpm) and heated to 950 °C (16 hours). Impure phases (x > 0.25) were subsequently ball milled with a 20% lithium mol excess and heated to 950 °C (12 hours). Samples where x ≥ 0.8 were synthesised in a dry room with a dewpoint between −45 °C to −64 °C (the elimination of humidity was found to be necessary to prepare good quality samples for these high Pr contents: it is known that moisture can be an issue in the synthesis of Li garnet systems).\(^{42-44}\)

Li\(_{5}\)La\(_{3-x}\)Pr\(_{x}\)Nb\(_{2}\)O\(_{12}\) was also prepared via the solid-state route in either air or 5%H\(_{2}\)/N\(_{2}\). Samples were heated to 950 °C for 16 hours, cooled to room temperature and reheated to 950 °C for 16 hours. After synthesis, all samples were stored in an argon glove box.

#### Characterisation

Samples were characterised by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu K\(_{\alpha}\) radiation. Cell parameters were determined from Rietveld refinement using GSAS II software.\(^{45}\) In order to evaluate the Pr oxidation states X-ray absorption near edge spectroscopy (XANES) data were recorded at Diamond Light Source on beamline B18 and data interpreted via the Athena/Aartemis software.\(^{46}\) Scanning electron microscopy (SEM) was performed using a TM4000plus SEM, with elemental compositions evaluated by the corresponding AZtecOne EDX attachment. The Pr–LLNO garnet powders were placed on carbon tape, attached to the SEM stub and evaluated at 15 kV in back scattered electron mode.

#### Impedance spectroscopy

Pellets for conductivity measurements were prepared as follows: 10 mm diameter pellets were uniaxially hot pressed with an atlas heating platen to ca. 3 tonnes at 300 °C and, subsequently, heated to 1000–1050 °C for 12 hours under dry N\(_{2}\) to densify the SSE membrane. During N\(_{2}\) treatment sacrificial powders were used to protect pellets from Li loss and to prevent Al contamination from the Al\(_{2}\)O\(_{3}\) crucible. Pellets were then polished, painted with gold electrodes and heated to 800 °C for 1 hour in air to cure the Au paste. The pellets were then quenched from 700 °C to limit any H\(^{+}\)/Li\(^{+}\) on cooling, as has been shown to occur for garnet samples at lower temperatures in air.\(^{26,47}\) A.C. impedance spectroscopy data were collected during heating over a temperature range of 50 °C to 250 °C (with 16 measurements taken), using a Hewlett Packard 4192A instrument. Data for the most conductive phases (~10\(^{-4}\) S cm\(^{-1}\)) were also measured at room temperature. All measurements were conducted in air.

### Results and discussion

#### Praseodymium doping on the Nb Site: Li\(_{5}\)La\(_{3}\)Nb\(_{2-x}\)Pr\(_{x}\)O\(_{12}\)

The powder XRD patterns for Li\(_{5}\)La\(_{3}\)Nb\(_{2-x}\)Pr\(_{x}\)O\(_{12}\) (0 ≤ x ≤ 1) are shown in Fig. 1, illustrating pure garnet samples across the range. All patterns could be indexed based on a cubic garnet with space group Ia\(_{3d}\) (no. 230).\(^{22,39,40}\) Phases where x > 0.25 initially demonstrated Pr\(_{2}\)O\(_{3}\) and La\(_{2}\)O\(_{3}\) impurity phases which were overcome by addition of 20% excess lithium and reheating. Phases where x > 0.8 showed decreased conductivity (see later), hence the synthesis method was not undertaken past x = 1. The colour of the samples became increasingly yellow as a function of Pr content, which is attributed to the presence of...
Pr⁴⁺, which is commonly believed to be responsible for the colour in the yellow pigment Pr–ZrSiO₄ (although some debate persists behind the chemistry of Pr–ZrSiO₄).⁴⁸⁻⁵⁰

Rietveld refinements, based on the structural model from Cussenᵉ⁹ showed a linear increase in lattice parameters with increasing Pr content (Fig. 2 and Table 1), in agreement with Vegard’s law and so confirming the solid solution range. This increase is due to the larger ionic radius of Pr⁴⁺ compared to Nb⁵⁺. The refined Pr occupancies on the Nb site were similar to the expected stoichiometric ratio across the series, however, did deviate slightly from the ideal ratio as the Pr content increased, see Table 1.

In order to try to confirm the Pr oxidation state, X-ray absorption near edge spectroscopy (XANES) data were collected for the Li₅.₅La₃Nb₂.₅Pr₀.₅O₁₂ systems. However, the La L₂ edge of La (~5897 eV) interfered with the Pr L₃ edge (~5968 eV) to some degree. Nevertheless, when compared to the Pr⁴⁺ and Pr⁴⁺ reference (Pr₂O₃ and BaPrO₃ respectively), the peaks are qualitatively characteristic of Pr⁴⁺, see Fig. 3. These data show a peak at 5973 eV with a shoulder at 5980 eV, which closely matches the Pr⁴⁺ (BaPrO₃) reference (Fig. 3) and can be assigned to Pr⁴⁺. Further support for the assignment of Pr⁴⁺ in the Li₅.₅La₃Nb₂.₅Pr₀.₅O₁₂ samples is provided by comparison with Pr₀.₅Ce₀.₅O₂, a Pr⁴⁺ reference used elsewhere,⁵²,⁵³ which shows peaks at 5970 and 5980 eV.

Therefore, considering the XRD, XANES and refinement data, there is compelling evidence that Pr⁴⁺ has been doped into the LLNO structure at the Nb site [16a].

SEM and EDX
SEM and EDX on a singular grain of Li₅.₅La₃Nb₂.₅Pr₀.₅O₁₂ demonstrated uniform Pr presence (in the expected stoichiometric ratio) when compared to La, Nb and O. However, for Pr (x) contents ≥0.5 Al contamination from the Al₂O₃ crucible became increasingly apparent (Fig. 4).

Praseodymium doping on the La site (Pr⁴⁺): Li₅.₅La₃₋ₓPrₓNb₂O₁₂
The successful synthesis of Li₅.₅La₃₋ₓPrₓNb₂O₁₂ garnets in air was limited to samples in the range 0 ≤ x ≤ 1. In contrast synthesis under 5%H₂/N₂ permitted a complete solid solution range for the replacement of La with Pr, 0 ≤ x ≤ 3. Both XRD patterns for air prepared samples (0 ≤ x ≤ 1) and 5%H₂ prepared samples (0 ≤ x ≤ 3) could be indexed on a cubic garnet cell with space group Ia₃d (no. 230);²²,³⁹,⁴⁰ see Fig. 5 and 8 respectively. In some cases, particularly for the air-based synthesis, a small amount of Li₅NbO₄ impurity was observed marked in the respective figures (also see ES†).

### Table 1 Pellet and conductivity data in addition to lattice parameters for Li₅.₅La₃Nb₂.₅Pr₀.₅O₁₂ samples which were uniaxially hot pressed. The Arrhenius plot x = 1 was not linear, hence no activation energy available

| Hot pressed samples | Pellet density (g cm⁻³) | Refined density (g cm⁻³) | Relative density (%) | Lattice parameters (Å) | Pr fractional site occupancies on the Nb site | Conductivity (50 °C) (S cm⁻¹) | Activation energy (eV) |
|---------------------|-------------------------|-------------------------|----------------------|------------------------|--------------------------------------------|-------------------------------|------------------------|
| LLNO reference      | —                       | 5.259                   | —                    | 12.7943                | ~ × 10⁻⁶                                    | 4.3 × 10⁻⁶                  | 0.32                   |
| LLNO                | 4.52                    | 5.248                   | 86                   | 12.7880(3)             | 0.0649                                    | 5.6 × 10⁻⁵                  | 0.28                   |
| x = 0.1             | 4.32                    | 5.284                   | 82                   | 12.8066(3)             | 0.1265                                    | 7.3 × 10⁻⁵                  | 0.32                   |
| x = 0.25            | 4.50                    | 5.300                   | 85                   | 12.8410(4)             | 0.2568                                    | 1.6 × 10⁻⁴                  | 0.29                   |
| x = 0.5             | 4.33                    | 5.321                   | 81                   | 12.9048(3)             | 0.3876                                    | 3.4 × 10⁻⁴                  | 0.37                   |
| x = 0.75            | 4.72                    | 5.361                   | 88                   | 12.9527(3)             | 0.4179                                    | 5.6 × 10⁻⁴                  | 0.36                   |
| x = 0.8             | 4.53                    | 5.358                   | 85                   | 12.9741(5)             | ~                           |                               |                       |
| x = 1               | 3.50                    | 5.366                   | 65                   | 13.0269(4)             | 0.5160                                    | 1.9 × 10⁻⁴                  | —                      |
Li$_{5.5}$La$_3$Nb$_{1.5}$Pr$_{0.5}$O$_{12}$ samples prepared in air demonstrated an increasingly straw yellow/brown colour, which was distinctly different from the colour of the Li$_{5.5}$La$_3$Nb$_{1.5}$Pr$_{0.5}$O$_{12}$ samples discussed earlier. Cell parameters determined from Rietveld refinement indicated the expected decrease with increasing Pr content (due to the smaller size of Pr$^{3+}$ versus La$^{3+}$) (Fig. 6) and

Li$_{3-x}$La$_3$Pr$_x$Nb$_2$O$_{12}$ samples prepared in air demonstrated an increasingly straw yellow/brown colour, which was distinctly different from the colour of the Li$_{5.5}$La$_3$Nb$_{1.5}$Pr$_{0.5}$O$_{12}$ samples discussed earlier. Cell parameters determined from Rietveld refinement indicated the expected decrease with increasing Pr content (due to the smaller size of Pr$^{3+}$ versus La$^{3+}$) (Fig. 6) and

![Fig. 3 XANES spectrum for Li$_{5.5}$La$_3$Nb$_{1.5}$Pr$_{0.5}$O$_{12}$ compared to BaPrO$_3$ (Pr$^{4+}$) reference.](image1)

![Fig. 5 The powder XRD patterns for Li$_{3-x}$La$_3$Pr$_x$Nb$_2$O$_{12}$ (0 ≤ x ≤ 1.5) synthesised in air. Phase pure samples are shown up to x = 1, but all show garnet type symmetry. Li$_3$NbO$_4$ impurity marked by arrow. See ESI† for expanded XRD pattern.](image2)

![Fig. 4 SEM image and EDX map of elemental distribution in Li$_{5.5}$La$_3$Nb$_{1.5}$Pr$_{0.5}$O$_{12}$. Scale bar at 10 μm in all images.](image3)
were similar to the results for equivalent Li$_{5}$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$ phases synthesised under 5%H$_2$ (discussed below). The presence of the Li$_3$NbO$_4$ impurity in the air synthesised samples may suggest Nb site vacancies in the LLNO structure which have been filled by Pr$^{4+}$, which could account for the yellow powder colour. It could also be the case that the Pr$^{4+}$ is located on the La site. Therefore, these data suggest that there may be some partitioning of the Pr over both sites however, more work is needed to confirm whether this is so and to what extent.

In order to confirm the oxidation state of Pr in these samples, XANES data were collected on both $x = 0.5$ and 1, however, as outlined previously, in all cases the La L2 edge interfered somewhat with the Pr L3 edge. Nevertheless, the

![Fig. 6 Cell parameters vs. Pr content for air-based synthesis of Li$_{5}$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$.](image)

![Fig. 7 (a) XANES spectra for Li$_{5}$La$_{2.5}$Pr$_{0.5}$Nb$_2$O$_{12}$ (air synthesised) compared to the Pr$_2$O$_3$ (Pr$^{3+}$) reference. (b) XANES spectra for Li$_{5}$La$_{2}$Pr$_1$Nb$_2$O$_{12}$ (air synthesised) compared to the Pr$_2$O$_3$ (Pr$^{3+}$) reference.](image)

![Fig. 8 The powder XRD patterns of Li$_{5}$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$ (0 ≤ $x$ ≤ 3) prepared in a reducing atmosphere (5%H$_2$). Phase pure samples with garnet type symmetry were obtained for all. For the small Li$_3$NbO$_3$ impurity see ESI† for expanded XRD pattern.](image)

![Fig. 9 Cell parameters vs. Pr content for 5%H$_2$ based synthesis of Li$_{5}$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$.](image)
XANES spectra of the $\text{Li}_3\text{La}_{2.5}\text{Pr}_{0.5}\text{Nb}_2\text{O}_{12}$ phase, which was prepared in air, do demonstrate characteristics of the Pr$^{4+}$ reference (which would be consistent with presence of Pr$^{4+}$ on either the Nb or La site), such as the peak broadness and the shoulder noted at 5982 eV, however the main peak appears to be positioned in line with the Pr$_2$O$_3$ reference at 5969 eV, consistent with mainly La site substitution, see Fig. 7a. However, the XANES spectra of the higher Pr content phase, $\text{Li}_3\text{La}_3\text{Pr}_1\text{Nb}_2\text{O}_{12}$, possesses only an absorption peak which is consistent with the Pr$^{3+}$ reference at 5970 eV, Fig. 7b. Therefore, these spectra are somewhat contradictory but indicate, potentially, the presence of Pr in different oxidation states for $x = 0.5$, but not when $x = 1$ where only Pr$^{3+}$ is seen.

The colours of the 5%H$_2$ synthesised garnets were increasingly vibrant green as the Pr content was increased, which indicates the presence of Pr$^{3+}$. Cell parameters determined from Rietveld refinement show a linear decrease with increasing Pr content, consistent with the smaller ionic radius of Pr$^{3+}$ compared to La$^{3+}$, see Fig. 9. Despite the interference from the La L2 edge, the XANES data for these garnets are somewhat clearer than those derived from the $\text{Li}_{5-x}\text{La}_3\text{Nb}_{2-x}\text{Pr}_x\text{O}_{12}$ phases (Fig. 10a and b). The 5%H$_2$ prepared samples show a clear correlation with the Pr$^{3+}$ reference (Pr$_2$O$_3$) in terms of peak intensity and characteristics, in both $x = 0.5$ and 1. Each phase has a strong absorption peak noted at 5970 eV, characteristic of Pr$^{3+}$, which matches both the Pr$_2$O$_3$ reference and other Pr$^{3+}$ references used elsewhere. When the Pr content is increased to $x = 1$, only increased absorbance occurs, as expected, but the peak characteristics remain unchanged. Hence, the characterisation data support the conclusion that only Pr$^{3+}$ is present, and the different characteristics of the $x = 0.5$ phase prepared in air are unique to the synthesis method, as seen in the XANES data.

The XANES and XRD data for the H$_2$ synthesised samples therefore support the conclusion that Pr$^{3+}$ has successfully been doped into the LLNO structure at the La site (24c).

**SEM and EDX**

SEM/EDX data for $\text{Li}_3\text{La}_{3-x}\text{Pr}_x\text{Nb}_2\text{O}_{12}$ garnets, synthesised in air or H$_2$, showed uniform elemental distribution throughout the analysed grains, and have similar grain characteristics, see Fig. 11 and 12 respectively. The data for both air and H$_2$ synthesised samples demonstrated Pr and La present in the expected ratio. Hence EDX data supports the stoichiometric incorporation. However, the air synthesised samples did show some aluminium contamination, see Fig. 11, attributed to a reaction with the Al$_2$O$_3$ crucible.

**Conductivity data for Nb site substitution:**

$\text{Li}_{5-x}\text{La}_3\text{Nb}_{2-x}\text{Pr}_x\text{O}_{12}$

Lithium ion conductivity was evaluated via impedance spectroscopy (a typical Nyquist impedance plot is shown in Fig. 13). A single non ideal semicircle was observed. A resistor, $R_1$, in parallel with a constant phase element, CPE1, were used to fit the semicircle, and an inductor, $L_1$, in series with $R_1$/CPE1 was used to account for the inductance effect due to the limitations of the HP impedance spectroscopy equipment. A characteristic spike relative to the semi-circle is present in all plots. This is attributed to a sample – electrode double layer effect. This spike represents the Li-ion transfer resistance between the garnet electrolyte and the Au electrode and corresponds to the capacitive behaviour of the gold electrodes which block Li-ion diffusion. As the semi-circle and tail were obtained in high and low frequency regions respectively it can be considered that conduction is primarily ionic in nature.31

The ionic conductivity of the $\text{Li}_{5-x}\text{La}_3\text{Nb}_{2-x}\text{Pr}_x\text{O}_{12}$ samples increased in line with increased Pr and hence lithium content (Fig. 14). The highest ionic conductivity of $5.6 \times 10^{-4}$ S cm$^{-1}$ at 50 °C was observed for $x = 0.8$, with a measured conductivity of $4.1 \times 10^{-4}$ S cm$^{-1}$ at 21 °C. See Table 1 and Fig. 14. These

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**Fig. 10** (a) XANES spectra for $\text{Li}_3\text{La}_{2.5}\text{Pr}_{0.5}\text{Nb}_2\text{O}_{12}$ (5%H$_2$) compared to the Pr$_2$O$_3$ (Pr$^{3+}$) reference. (b) XANES spectrum for $\text{Li}_3\text{La}_2\text{Pr}_1\text{Nb}_2\text{O}_{12}$ (5%H$_2$) compared to the Pr$_2$O$_3$ (Pr$^{3+}$) reference.
conductivity values represent some of the highest ever reported for garnets with Li content <6 per formula unit.

Higher content Pr phases ($x > 0.75$) were, however, prone to degradation during the high temperature densification treatment under N$_2$, resulting in small Pr$_2$O$_3$, La$_2$O$_3$, and PrNb$_2$O$_{14}$ impurities. In particular the XRD patterns for the $x = 1$ sample after N$_2$ sintering showed a more severe phase degradation. This degradation most likely accounts for the low relative pellet density of this sample and the resultant lower conductivity associated with this phase, as well as the non-linear temperature dependence of the Arrhenius plot, see Table 1 and ESI.$^\dagger$ Consequently, further studies of samples with higher Pr contents, $x > 1$, were not performed (see ESI$^\dagger$ for comparative XRD patterns before and after sintering treatments).

The activation energies for all samples (Fig. 14) ranged between $0.24-0.38$ eV, which are similar to reports for other garnets, see Table 1.$^{51,54}$

Conductivity data for La site substitution: Li$_3$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$

All samples where Pr was doped on the La site showed similar conductivities to LLNO consistent with no change in Li content for this series. A typical Nyquist plot is displayed in Fig. 15a and b for air-based and H$_2$ synthesis respectively. These plots were fitted to two R/CPE components, representative of overlapping bulk and grain boundary resistance.

It was noted earlier that in the air synthesis samples, there may be some Pr$^{4+}$ partitioning onto the Nb$^{5+}$ site in the air synthesised Li$_3$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$ samples. The corresponding H$_2$ synthesised sample, where only La site substitution is believed to occur, showed no Al contamination.

![SEM images and EDX map of elemental distribution in Li$_3$La$_2$Pr$_1$Nb$_2$O$_{12}$ (air). The presence of Al in this air synthesised sample is attributed to partial substitution onto the Li site. Al incorporation is often apparent in higher lithium content systems, and so this may support the postulation that there is some Pr$^{4+}$ partitioning onto the Nb$^{5+}$ site in the air synthesised Li$_3$La$_{3-x}$Pr$_x$Nb$_2$O$_{12}$ samples. The corresponding H$_2$ synthesised sample, where only La site substitution is believed to occur, showed no Al contamination.](image-url)

Fig. 11
Fig. 12  SEM images and EDX map of elemental distribution in Li$_5$La$_{1.5}$Pr$_{1.5}$Nb$_2$O$_{12}$ (H$_2$). Since there is no increased Li content for Pr$^{3+}$ doping on the La$^{3+}$ site, therefore there is a decreased chance of Al exchange, hence no contamination from the alumina crucible is present.

Fig. 13  Nyquist impedance plot for Li$_{5.75}$La$_3$Nb$_{1.25}$Pr$_{0.75}$O$_{12}$ at 30 °C which was fit the equivalent circuit in the top left.

Fig. 14  Arrhenius plots for Li$_{5-x}$La$_3$Nb$_{2-x}$Pr$_x$O$_{12}$ ($x = 0.1–0.8$) samples which were hot pressed prior to sintering under N$_2$. 
The H₂ synthesised samples showed similar conductivities for all samples, with a small peak in the conductivity of the series \(1.7 \times 10^{-5} \text{ S cm}^{-1}\) (50 °C) for \(x = 0.5\), see Fig. 17 for Arrhenius plots. Activation energies fall within the 0.3–0.4 eV range, hence are similar to reports for other garnets, see Table 3.51,54

Samples with Pr doping at the La site showed far lower densities than the samples with Pr doping on the Nb site (see Tables 1–3). Hence Pr doping on the Nb site appears to also enhance the sintering compared to Pr doping on the La site, which may be related to the higher lithium content in these \(\text{Li}_{5+\Delta}\text{La}_{3-\Delta}\text{Nb}_{2-\Delta}\text{Pr}_{\Delta}\text{O}_{12}\) systems.

Table 2  Pellet and conductivity data in addition to lattice parameters for \(\text{Li}_{5-\Delta}\text{La}_{3-\Delta}\text{Pr}_{\Delta}\text{Nb}_{2}\text{O}_{12}\) samples synthesised in air

| Sample  | Pellet density (g cm\(^{-1}\)) | Refined density (g cm\(^{-1}\)) | Relative density (%) | Lattice parameters (Å) | Conductivity at 50 °C (S cm\(^{-1}\)) | Activation energy 50–210 °C (eV) |
|---------|---------------------------|-----------------------------|----------------------|----------------------|---------------------------------|-------------------------------|
| LLNO    | 4.52                      | 5.248                       | 86                   | 12.7880(3)           | \(4.3 \times 10^{-6}\)           | 0.32                          |
| \(x = 0.5\) | 3.08                      | 5.289                       | 58                   | 12.7701(3)           | \(9.3 \times 10^{-6}\)           | 0.25                          |
| \(x = 1\)  | 3.21                      | 5.317                       | 60                   | 12.7481(3)           | \(6.9 \times 10^{-6}\)           | 0.28                          |
Table 3  Pellet and conductivity data in addition to lattice parameters for Li₅LaₓPrₓNb₂O₁₂ samples synthesised under H₂

| Sample               | Pellet density (g cm⁻³) | Refined density (g cm⁻³) | Relative density (%) | Lattice parameters (Å) | Conductivity at 50 °C (S cm⁻¹) | Activation energy 50–210 °C (eV) |
|----------------------|-------------------------|--------------------------|----------------------|------------------------|-------------------------------|---------------------------------|
| LLNO reference       |                          |                          |                      |                        |                               |                                 |
| LLNO synthesized     | 4.52                    | 5.259                    | —                    | 12.79432               | ~ × 10⁻⁶                     |                                 |
| x = 0.5              | 3.87                    | 5.286                    | 86                   | 12.7880(3)             | 4.3 × 10⁻⁶                   | 0.32                            |
| x = 1.5              | 3.40                    | 5.316                    | 64                   | 12.7727(3)             | 1.7 × 10⁻⁵                   | 0.31                            |
| x = 2                | 3.47                    | 5.346                    | 65                   | 12.7490(2)             | 9.2 × 10⁻⁶                   | 0.38                            |
| x = 2.5              | 3.91                    | 5.373                    | 73                   | 12.7250(5)             | 6.0 × 10⁻⁶                   | 0.35                            |
| x = 3                | 4.01                    | 5.407                    | 74                   | 12.6769(3)             | 8.1 × 10⁻⁶                   | 0.38                            |

Conclusions

In summary, we have shown for the first time a dopant (Pr) that can be substituted onto both the La and Nb site in Li₅LaₓNb₂O₁₂. Furthermore, the oxidation state of the Pr is dictated by the site substitution; +3 on the La site, and +4 on the Nb site. Due to the resultant increase in Li content for Nb site substitution, a significant increase in conductivity is observed. These Li₅⁺LaₓNb₂ₓPrₓO₁₂ samples show some of the highest conductivities for garnets with Li contents less than 6, with values up to 0.56 mS cm⁻¹ (at 50 °C) for x = 0.8. A final point of note, Pr doped phases at the Nb site (x ≤ 0.25) were a vibrant yellow, with a vibrant green colour obtained from H₂ based synthesis of Li₅⁺LaₓNb₂ₓPrₓO₁₂ garnets when x ≥ 2.5. Hence the optical properties of these garnets may merit further investigation, especially with respect to potential interest as pigments (see ESI†), however the effect of moisture on the Pr oxidation states, and therefore the sample colour, requires further investigation. It may also be of interest to study the optical properties of these Pr garnets under U.V. light.

Conflicts of interest

There are no conflicts of interest to declare.

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References

1  C.-X. Zu and H. Li, Energy Environ. Sci., 2011, 4, 2614–2624.
2  Y. Zhu, X. He and Y. Mo, ACS Appl. Mater. Interfaces, 2015, 7, 23685–23693.
3  V. A. Agubra and J. W. Fergus, J. Power Sources, 2014, 268, 153–162.
4  M. Armand and J. M. Tarascon, Nature, 2008, 451, 652.
5  N. Nitta, F. Wu, J. T. Lee and G. Yushin, Mater. Today, 2015, 18, 252–264.
6  M. Winter and R. J. Brodd, Chem. Rev., 2004, 104, 4245–4270.
7  J. M. Tarascon and M. Armand, Nature, 2001, 414, 359.
8  J. Li, C. Ma, M. Chi, C. Liang and N. J. Dudney, Adv. Energy Mater., 2015, 5, 1401408.
9  Q. Liu, Z. Geng, C. Han, Y. Fu, S. Li, Y.-B. He, F. Kang and B. Li, J. Power Sources, 2018, 389, 120–134.
10 A. C. Luntz, J. Voss and K. Reuter, J. Phys. Chem. Lett., 2015, 6, 4599–4604.
11 K. Fu, Y. Gong, B. Liu, Y. Zhu, S. Xu, Y. Yao, W. Luo, C. Wang, S. Lacey, J. Dai, Y. Chen, Y. Mo, E. Wachsman and L. Hu, Sci. Adv., 2017, 3, e1601659.
12 Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba and R. Kanno, Nat. Energy, 2016, 1, 16030.
13 V. Thangadurai, S. Narayanan and D. Pinzaru, Chem. Soc. Rev., 2014, 43, 4714–4727.
14 W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim and G. Ceder, Chem. Mater., 2016, 28, 266–273.
15 B. Dong, R. Jarkaneh, S. Hull, N. Reeves-McLaren, J. J. Biendicho and A. R. West, J. Mater. Chem. A, 2016, 4, 1408–1413.
16 C. Bernuy-Lopez, W. Manalastas, J. M. Lopez del Amo, A. Aguadero, F. Aguesse and J. A. Kilner, Chem. Mater., 2014, 26, 3610–3617.
17 H. Buschmann, J. Dölle, S. Berendts, A. Kuhn, P. Bottke, M. Wilkening, P. Heitjans, A. Senyshyn, H. Ehrenberg, A. Lotnyk, V. Duppel, L. Kienle and J. Janek, Phys. Chem. Chem. Phys., 2011, 13, 19378–19392.
18 S. Ohta, T. Kobayashi and T. Asaoka, J. Power Sources, 2011, 196, 3342–3345.
19 T. Thompson, S. Yu, L. Williams, R. D. Schmidt, R. Garcia-Mendez, J. Wolfenstine, J. L. Allen, E. Kioupakis, D. J. Siegel and J. Sakamoto, ACS Energy Lett., 2017, 2, 462–468.
20 A. F. Wells, Structural inorganic chemistry, Clarendon Press, 1984.
21 E. J. Cussen and T. W. S. Yip, J. Solid State Chem., 2007, 180, 1832–1839.
