

Short communication

Synthesis and characterisation of the garnet-related Li ion conductor, $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$

J. Percival, E. Kendrick, P.R. Slater*

Department of Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK

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Abstract

In this paper the synthesis, conductivity, and structure of the garnet-related Li ion conductor, $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$, are reported. As for the related $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) materials, this phase shows high Li ion conductivity, with a conductivity at 300 °C of $9.2 \times 10^{-3} \text{ S cm}^{-1}$. Structural studies using neutron diffraction indicate a cubic unit cell, space group $Ia-3d$, with Li located in two partially occupied sites. One of the sites is the traditional garnet structure tetrahedral site, while the other Li site is considerably more distorted. Although the latter is nominally a six coordinate site, a close inspection suggests that the coordination could be described as distorted tetrahedral, with the remaining two bonds being significantly longer ($\approx 2.6 \text{ \AA}$).

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1. Introduction

The search for new materials showing fast ion conduction has been driven by the widespread technological applications of solid state ionic conductors. In the area of Li ion conductors, a wide range of structure types have been investigated [1], with the highest bulk conductivities observed for the perovskite system, $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ [2].

Recent work by Thangadurai et al. has extended this range of structures, with the observation of high Li ion conduction in garnet-related systems [3–7]. Initially the authors reported the synthesis and conductivities of the $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) materials, showing high conductivities, e.g. $\sigma_{\text{total}} (25^\circ\text{C}) = 3.4 \times 10^{-6} \text{ S cm}^{-1}$ for $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ [3]. Further work showed that the Li content could be increased by partial substitution of La by alkaline earths (Ca, Sr, Ba), with conductivities as high as $4 \times 10^{-5} \text{ S cm}^{-1}$ at 22 °C for $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ [4]. In order to understand the conduction characteristics of these materials, detailed evaluation of the structure has also attracted significant attention, and in this area there has been some controversy. Early work by Mazza using X-ray powder diffraction data reported the structures of the phases $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) as closely related to the garnet structure, with space group $Ia-3d$, and three of the Li ions located in the conventional tetrahedral garnet site, while the remaining two Li ions fully occupied an octahedrally coordinated site, normally vacant in the ideal garnet structure [8]. In contrast, Hyooma and Hayashi proposed a lower symmetry space group, $I2_13$ [9], which was also supported by studies by Isasi et al. on the related Sb containing systems, $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$) [10,11]. Subsequently,

* Corresponding author. Tel.: +44 1483 686847; fax: +44 1483 686851.

E-mail address: p.slater@surrey.ac.uk (P.R. Slater).

Thangadurai et al. reinvestigated the structures of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) utilising a bond valence approach, and proposed that the Li was located exclusively in the octahedral site, with no occupancy of the tetrahedral site [12].

The results above highlight the difficulty in conclusively identifying the Li site(s) using X-ray diffraction data, which is not surprising, considering the small X-ray scattering factor for Li, and consequently there is a need for detailed neutron diffraction studies of these phases. The importance of neutron diffraction structural studies was shown by Cussen [13]. In this work, the structures of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) were re-examined, with the data confirming the space group as $Ia-3d$, with the Li occupying tetrahedral and distorted octahedral sites. High thermal displacement parameters were observed for the latter site, and so the Li in this site was split into two sites, with 32% on the ideal site and the remaining 68% displaced off site. Since the conductivities of the related garnet phases, $\text{Li}_3\text{Ln}_3\text{Te}_2\text{O}_{12}$ ($\text{Ln} = \text{rare earth}$), containing Li only on the tetrahedral sites, are low [14], Cussen has proposed that the octahedral site is key to the conduction process.

In light of the recent work by Cussen, there is a clear need for further neutron diffraction studies of these systems, and in this paper we report the first such studies for the phase, $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$, and compare with the results for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$). In addition, we also report for the first time conductivity studies on this system, showing high Li ion conductivity as for the related niobate/tantalate systems.

2. Experimental

A large 3.5 g sample of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ was prepared by standard solid state synthesis from stoichiometric amounts of Nd_2O_3 , Sb_2O_3 and a 10% excess of isotopically enriched Li_2CO_3 ($>99\%$ ^7Li : so as to reduce problems with the high neutron absorption cross-section of ^6Li). The intimately mixed powders were first heated at 700°C for 14 h in air, before regrinding and pressing as pellets (2 cm diameter). The pellets were then heated at 925°C for 14 h. Phase purity was determined using X-ray powder diffraction (Cu $\text{K}\alpha$ 1 radiation, Panalytical X'pert pro system with an X'celerator detector).

Conductivity measurements were performed using AC impedance spectroscopy (Hewlett Packard 4182A Impedance Analyser). Samples for measurement were prepared by pressing into 13mm diameter pellets and firing for 2 h at 925°C . Au electrodes were then affixed to the pellets using Au paste and the pellet fired again, at 700°C for 30 min, to give good electrical contact between sample and electrode.

Time of flight neutron diffraction data were recorded on the diffractometer HRPD at the ISIS facility, Rutherford Appleton Laboratory. Structural refinement employed the GSAS suite of Rietveld refinement software [15].

3. Results

Conductivity measurements (Fig. 1) showed that $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ has high Li ion conductivity ($\sigma_{300^\circ\text{C}} = 0.0092 \text{ S cm}^{-1}$, $\sigma_{25^\circ\text{C}} = 1.3 \times 10^{-7} \text{ S cm}^{-1}$ (bulk conductivity)). The conductivity plot shows a change in slope just below 300°C , with the low temperature ($<300^\circ\text{C}$) activation energy being 0.67 eV, while the high temperature activation energy was significantly lower at 0.35 eV. A similar change in activation energy was apparent in the data for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) [3]. Compared to the literature data for the Nb, Ta containing systems, the

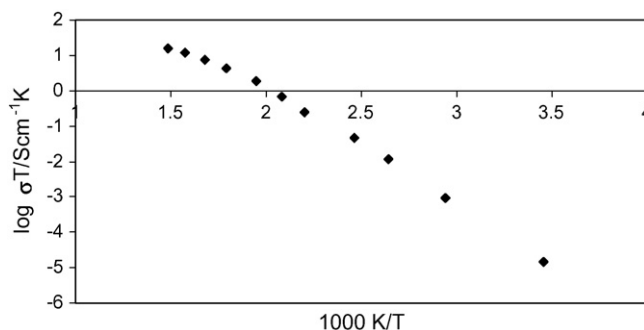


Fig. 1. Conductivity data for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$.

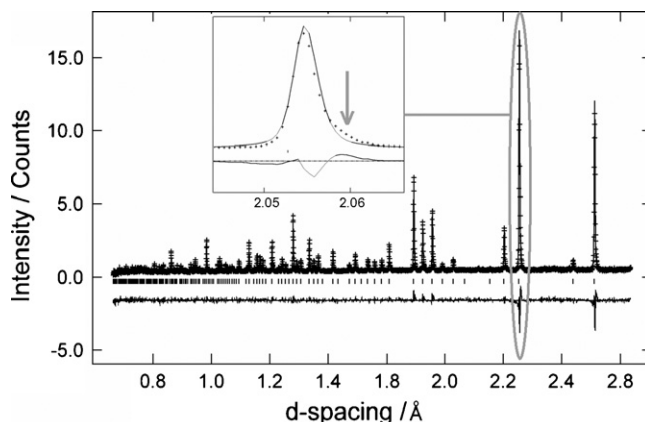


Fig. 2. Initial neutron diffraction data profile fit showing high d spacing shoulders (see inset).

room temperature conductivity of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ is an order of magnitude lower, while the low temperature activation energy is higher ($E_a(\text{Nb}) = 0.43$ eV, $E_a(\text{Ta}) = 0.56$ eV [3]).

For the refinement of the neutron diffraction data, two models were investigated based on previous studies on the related systems, $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$); that proposed by Thangadurai et al., in which the Li occupies 5/6 of an octahedrally coordinated site [12], and the Cussen neutron diffraction model, with occupancy of tetrahedral and octahedral sites [13]. In agreement with the work by Cussen, the former refinement resulted in a poor fit and a generally unstable refinement, and so further refinement continued with the Cussen structural model.

Initially the data was refined with Li1 at $(1/4, 7/8, 0)$ (tetrahedral site) and Li2 at $(1/8, y, z)$ (distorted octahedral site). This resulted in a good fit to the data, although the thermal displacement parameter for the Li2 site was high ($100 \text{ U} = 6.2 \text{ Å}^2$). Therefore a further refinement was performed allowing this Li to move off the ideal 48 g site to give a 96 h site. This resulted in an improved fit, and the thermal displacement parameter for the Li2 site was significantly reduced. Despite the apparent good fit to the data, a close inspection of the profile fit indicated the presence of small high d spacing shoulders on the peaks (most noticeable for the highest intensity peaks between $d = 2.0\text{--}2.4 \text{ Å}$) (Fig. 2). Attempts to fit these shoulders by varying the peak shape were unsuccessful, and it was therefore proposed that there was a small amount of a second closely related garnet phase in the sample. A further refinement was therefore performed, including this second phase with the same atom parameters as the main phase, but with slightly different cell parameters. Inclusion of this second phase improved the fit significantly (χ^2 reduced from 2.897 to 1.755) (Fig. 3). The second phase had slightly higher cell parameters ($a = 12.6884(2) \text{ Å}$)

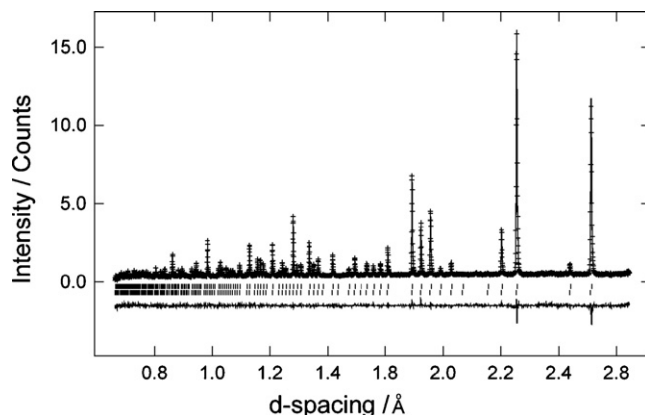


Fig. 3. Final neutron diffraction data profile fit with inclusion of second garnet phase (lower tick marks, main phase; upper tick marks, small amount of higher cell parameter second phase).

Table 1
Structural parameters for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Fractional occupancy	100 U (\AA^2)
Nd	24c	1/8	0	1/4	1.0	1.05(3)
Sb	16a	0	0	0	1.0	0.53(8)
Li1	24d	1/4	7/8	0	0.62(2)	0.4(2)
Li2	96h	0.1037(8)	0.6906(8)	0.5755(8)	0.262(5)	0.4(3)
O	96h	0.27830(7)	0.10391(8)	0.19927(8)	1.0	1.28(4)

Space group *Ia-3d*, $a = 12.66238(3)$, $R_{\text{wp}} = 5.93\%$, $R_p = 5.25\%$, $\chi^2 = 1.755$.

Table 2
Selected bond lengths for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$

Bond	Bond distance (\AA)
Nd–O [4 \times]	2.431(1)
Nd–O [4 \times]	2.563(1)
Sb–O [6 \times]	1.991(1)
Li1–O [4 \times]	1.9070(1)
Li2–O	1.85(1)
Li2–O	2.12(1)
Li2–O	2.15(1)
Li2–O	2.255(9)
Li2–O	2.55(1)
Li2–O	2.604(9)

than the parent phase ($a = 12.66238(3)$ \AA), and the relative phase fractions were determined to be 8.46 and 91.54%, respectively.

The final refined structural parameters for the main garnet phase are given in Table 1, with selected bond distances in Table 2, and the final refined neutron diffraction profiles shown in Fig. 3.

4. Discussion

The refined structure for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ is in agreement with the work of Cussen on $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) with Li present in both the ideal garnet tetrahedral site, and a more distorted second site normally vacant in the garnet structure (Fig. 4). This second site has been described as a distorted octahedral site, however a close inspection suggests that with the off-site displacement of the Li, the coordination is approaching tetrahedral with a further two longer (≈ 2.6 \AA) bonds. The geometry of this site is shown in Fig. 5 with the longer bonds highlighted. In terms of the occupancy of the two Li sites, a lower occupancy of the ideal tetrahedral Li1 site and higher occupancy of the distorted Li2 site is observed for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$. Considering the lower room temperature conductivity of the Sb containing system, this may suggest that the tetrahedral Li1 sites are involved in the conduction process along with the Li2 sites. However, it should be noted that the unit cell parameters are smaller for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ than for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$), which is related to the smaller size of Nd^{3+} compared to La^{3+} , and so a reduction in the size of the Li ion conduction bottleneck, thus hindering conduction, could explain the lower conductivity. In support of this latter explanation, the activation energy for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ is significantly higher than for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$). Regarding the activation energy, it is interesting to note the reduction in this parameter at high temperatures, and this needs further study with high temperature neutron diffraction experiments. One possible explanation could be Li “trapping” at low temperatures, and so the higher activation energy below 300 $^\circ\text{C}$ is due to the activation energy for “freeing” these Li ions combined with the activation energy for their migration. In this respect, Cussen has proposed clustering of Li ions within the structure [13], which could account for such Li ion “trapping” and hence the elevated activation energy at low temperatures.

The presence of a small amount of a second garnet phase, with slightly higher cell parameters could also theoretically affect the conductivity. However, due to the low level of this second phase and the likely similar composition compared to the main phase, this is not considered significant.

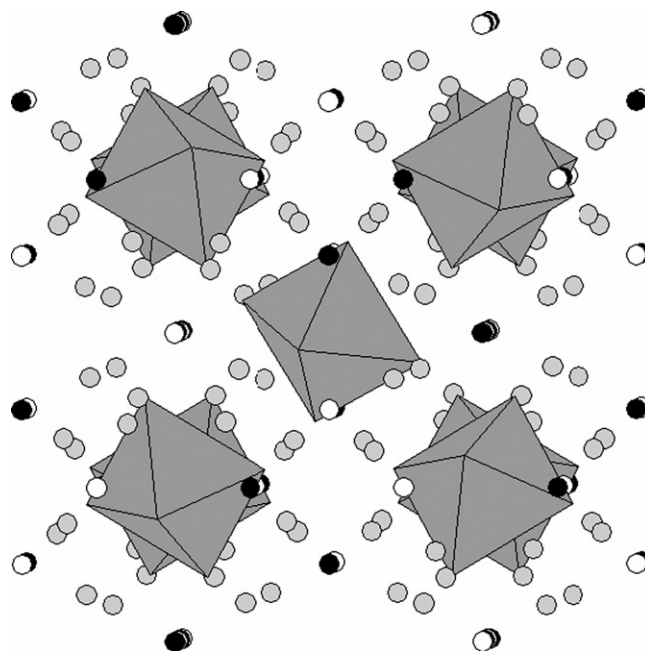


Fig. 4. Structure of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ (grey octahedral, SbO_6 ; black spheres, Nd; white spheres, Li1; grey spheres, Li2).

The presence of this secondary garnet phase is interesting and requires further discussion. Due to the low level of this phase, it was not possible to refine individual Li occupation factors, and so in the refinement it was assumed to have the same atomic parameters as the main garnet phase. Nevertheless, it is likely that this phase may have a slightly different Li content and/or site occupancies. In particular the presence of this second phase could be a result of Li volatility from the surface under the high synthesis temperatures, and thus have a slightly lower Li content. These results highlight the need for additional studies on optimising the synthesis and sintering of these Li containing garnet systems. In addition they suggest that there is some nonstoichiometry in these systems, which also warrants further investigation. In support of this conclusion is the significant spread of cell parameters reported in the literature for the $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) systems with values between 12.766 and 12.807 Å reported for $\text{M} = \text{Ta}$ and 12.762 and 12.889 Å for $\text{M} = \text{Nb}$ [3,8,9,13].

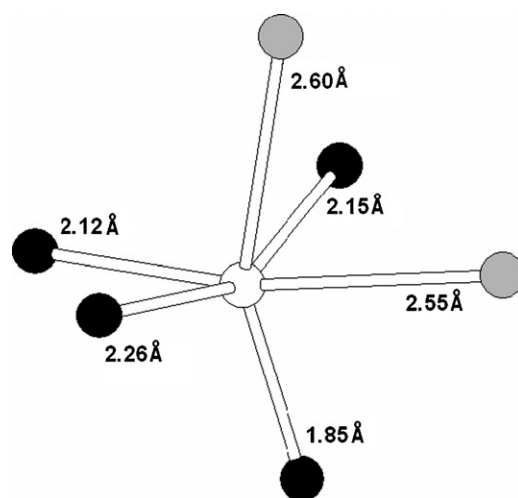


Fig. 5. Geometry of the Li2 site including bond lengths (white sphere, Li; black spheres, four closest oxygen atoms in a distorted tetrahedral arrangement; grey spheres, two most distant oxygen atoms).

5. Conclusions

In conclusion, the structure of the Li containing garnet $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ has been determined by neutron diffraction, with the results in agreement with studies on the related systems $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) by Cussen [13]. The Li is located both in the ideal tetrahedral garnet site, as well as a second more distorted site normally vacant in the garnet structure. Conductivity measurements show high conductivities, although the room temperature conductivity is lower, and the activation energy higher than for the related $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M} = \text{Nb}, \text{Ta}$) systems.

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