Synthesis and conductivities of the garnet-related Li ion conductors, $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$

(Ln= La, Pr, Nd, Sm, Eu)

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Abstract

In this paper the synthesis and conductivities of the garnet-related Li ion conductors, $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ (Ln=La, Pr, Nd, Sm, Eu), are reported. These phases show high Li ion conductivity, similar to previously reported for the related $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M=Nb, Ta) materials. Neutron diffraction structural studies are also reported for $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ indicating a cubic unit cell, space group Ia-3d, with Li located in two partially occupied sites.

Keywords: Li ion conductivity, Garnet, Neutron diffraction

1. Introduction

Materials displaying fast ion conduction have attracted considerable interest due to their widespread technological applications. In the area of Li ion conductors, there is still an ongoing search for a solid state material with sufficiently high conductivity to allow the use as an electrolyte in an all solid state lithium ion battery. To this end, 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]. More recently there has been growing interest in Li ion conduction in garnet-related materials following the exciting discovery of high Li ion conduction in $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M=Nb, Ta) by Thangadurai and Weppner [3], with conductivities as high as $4 \times 10^{-5} \text{ Scm}^{-1}$ at 22°C reported for the alkaline earth doped analogues $\text{Li}_6\text{ALa}_2\text{M}_2\text{O}_{12}$ (A=Ca, Sr, Ba) [4-8].

Although these materials have cubic symmetry as for the traditional garnet materials, their structural features are somewhat complex, and have attracted a certain amount of controversy and confusion, particularly relating to the Li sites within the structure. This can be related to the fact that the early structural studies employed X-ray powder diffraction data [8-10], which makes location of the Li sites very difficult due to the low X-ray scattering factor of Li. More recently neutron diffraction structural studies have been reported for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M=Nb, Ta) by Cussen [11]. This work identified the space group as Ia-3d, with the Li occupying tetrahedral and distorted “octahedral” sites. Subsequently this structural interpretation has been confirmed by further work by Cussen *et al.*, and a similar study of the higher Li content phase $\text{Li}_6\text{SrLa}_2\text{Nb}_2\text{O}_{12}$ within our group [12, 13]. In the latter it was shown that the distorted nature of the “octahedral site” gave a coordination closer to 4 coordinate, the remaining two Li-O bonds being quite long ($>2.6 \text{ \AA}$).

In addition to the niobate/tantalate garnets described above, related antimony containing systems are also known. In this respect, the synthesis of $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ ($\text{Ln}=\text{La, Pr, Nd, Sm}$) have been reported by Isasi et al. [14, 15]. However, there was no characterisation of the Li ion conductivity of these Sb containing garnets. In a previous paper we reported, the synthesis, structure and conductivity of the Nd containing analogue, $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ [16]. The results showed a similar structure to $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb, Ta}$), while the room temperature conductivity was an order of magnitude lower and activation energy slightly higher.

In this paper we extend this work to investigate the effect of varying the rare earth size on the synthesis and conductivities. We also report neutron diffraction structural studies for $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$.

2. Experimental

The standard solid state reaction route was used to prepare the samples, $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ ($\text{Ln}=\text{La, Pr, Nd, Sm, Eu, Gd, Ho}$). Stoichiometric amounts of dried Ln_2O_3 ($\text{Ln}=\text{La, Nd, Sm, Eu, Gd, Ho}$), Pr_6O_{11} , Sb_2O_3 and a 10% excess of Li_2CO_3 were intimately ground and then heated at 700°C for 14 hours in air (for the $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ neutron diffraction sample isotopically enriched Li_2CO_3 , $>99\%$ ^7Li , was employed, so as to reduce problems with the high neutron absorption cross-section of ^6Li). The powders were then reground and pressed as pellets (2 cm diameter). The pellets were then heated at 925°C for 8-14 hours. Phase purity was established using X-ray powder diffraction ($\text{Cu K}_{\alpha 1}$ 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 hours at 925°C. Au electrodes were then affixed to the pellets using Au paste and the pellet fired again, at 700°C for 30 mins, 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. Data sets from two banks of detectors were used for the refinement; the first was the data from the backscattering detector bank and the second was the data from the 90° detector bank. Structural refinement employed the GSAS suite of Rietveld refinement software [17].

3. Results and Discussion

X-ray diffraction indicated the successful synthesis of the garnet-related phase for Ln=La, Pr, Nd, Sm, Eu. For the smaller rare earths (Gd, Ho), there was no sign of any garnet-related phase, but rather the main phase obtained was perovskite-type, $\text{Ln}_2\text{LiSbO}_6$. These results indicate that there is a minimum rare earth size for the stabilisation of the garnet phases, and they are consistent with previous reports by Isasi *et al.*, where the successful synthesis of $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ for Ln=La, Pr, Nd, Sm, was reported. The work here, however, shows that this range of samples can be extended to Ln=Eu.

Conductivity measurements

In all cases, high conductivities were obtained (figure 1), with the highest room temperature conductivity for the largest rare earth, Ln=La. In addition, all the samples showed a change in activation energy at elevated temperature (between 200-300°C), with the high temperature activation energy being reduced compared to the low temperature range (e.g. for Ln=Nd, E_a decreased from 0.67 eV to 0.35 eV). The higher activation energy in the low temperature region could be due to Li ion defect

trapping at low temperatures, and in this respect Cussen has proposed clustering of Li ions within the structure [11], which could account for such defect trapping.

Structural refinement: $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$

For the refinement of the neutron diffraction data, two models were investigated; that proposed by Thangadurai *et al.* for $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M=Nb, Ta) from a combination of X-ray diffraction data and bond valence sum analysis, space group Ia-3 [8], and the Cussen model, based on analysis of the same samples by neutron diffraction, space group Ia-3d [11]. In agreement with the neutron diffraction structural studies by Cussen and our previous structural studies of $\text{Li}_6\text{SrLa}_2\text{Nb}_2\text{O}_{12}$ and $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ [11-13, 16], the former refinement resulted in a poor fit and a generally unstable refinement, and so further refinement continued with the Cussen structural model.

Initially refinement of the data employed the Li sites, Li1 at (1/4, 7/8, 0) (tetrahedral site) and Li2 at (1/8, y, z) (distorted “octahedral” site), resulting in a generally good fit to the data. However, the thermal displacement parameter for the Li2 site was high, and so in agreement with previous reports [11-13, 16], this Li was allowed to move off the ideal 48g site to give a 96h site, resulting in an improved fit, and a significantly reduced thermal displacement parameter. However, 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 $d=2.0 - 2.4 \text{ \AA}$) (figure 2a). 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 very closely related garnet phase in the sample. Therefore a further refinement was performed, with the inclusion of a second garnet phase with slightly different cell parameters. 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. Inclusion of this second phase improved the fit significantly (χ^2 reduced from 7.54 to 3.77) (figure 2b). The second phase had slightly higher cell parameters ($a = 12.8816(3) \text{ \AA}$) than the parent phase ($a = 12.84665(5) \text{ \AA}$), and the relative phase fractions were determined to be 9.8% and 90.2% respectively. A similar second phase was also observed previously for $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ [16]. The second garnet phase could be a result of Li volatility from the surface under the high synthesis temperatures, and so may suggest a certain degree of non-stoichiometry in these systems, which needs further investigation. Further evidence 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 $\text{\AA}$ reported for $\text{M}=\text{Ta}$, and 12.762 and 12.889 $\text{\AA}$ for $\text{M}=\text{Nb}$ [3,9,10,11]. The result highlights the complexity of these garnet systems.

The final refined structural parameters are given in table 1, with selected bond distances in table 2. The refined structure for $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ is in agreement with previous reports on $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($\text{M}=\text{Nb}, \text{Ta}$) and $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ [11,12,16], with Li present in both the ideal garnet tetrahedral site, and a more distorted second site normally vacant in the garnet structure. In agreement with our previous studies [12,16], a close inspection of the second sites suggests that the coordination is approaching 4-coordinate with a further two longer ($> 2.6 \text{ \AA}$) bonds. Compared to the previously reported $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$, the occupancy of the Li1 site is higher and consequently the Li2 site occupancy is lower ($\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$; Li1 occ. = 0.62(2), Li2 occ. = 0.262(5) [16]). Previously it has been suggested that the Li2 site is key to the high Li ion conductivity in these materials [11, 18], and so a close comparison of the conductivities of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ and $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ is warranted. Despite the reduced Li2 occupancy, the low temperature conductivity of $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ is slightly higher

than that of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$ (figure 1). However at higher temperatures, the conductivity of $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ drops below that of $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$. Given the previous suggestion, that Li ion trapping effects are important at low temperatures contributing to higher activation energies, it could be proposed that reduced Li ion trapping in $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ is responsible for the improved low temperature conductivity and lower activation energy in this sample. At elevated temperatures, when trapping effects are much lower, the higher Li2 site occupancy may then account for the higher conductivity in $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$.

Conclusions

In summary, we have reported the synthesis and conductivities of the series, $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ (Ln=La, Pr, Nd, Sm, Eu). The low temperature Li ion conductivity is shown to be highest for the larger rare earths (La, Pr, Nd). Structural studies of $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$ show a similar structure to $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$, although with higher occupancy of the Li1 site and lower occupancy of the Li2 site.

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Figure Legends

Figure 1. Conductivity data (bulk) for $\text{Li}_5\text{Ln}_3\text{Sb}_2\text{O}_{12}$ (Ln=La, Pr, Nd, Sm, Eu).

Figure 2(a). Initial neutron diffraction data profile fit showing high d spacing shoulders, particularly noticeable for the high intensity peaks between $d = 2.0$ and 2.4 Å.

Figure 2(b). 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 $\text{Li}_5\text{La}_3\text{Sb}_2\text{O}_{12}$

Atom	Site	x	y	Z	Frac.	100 U/Å ²
La	24c	1/8	0	1/4	1.0	1.78(4)
Sb	16a	0	0	0	1.0	1.37(4)
Li1	24d	1/4	7/8	0	0.73(1)	2.9(2)
Li2	96h	0.1002(8)	0.6821(8)	0.5741(7)	0.233(3)	2.7(3)
O	96h	0.27935(5)	0.10527(6)	0.20110(6)	1.0	1.84(3)
Space Group = I a -3 d			a = 12.84665(5)		Chi ² = 3.768	
W _{Rp} (BS) = 5.96%			Rp (BS) = 5.30%			
W _{Rp} (90°) = 4.55%			Rp (90°) = 3.49%			

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

Bond	Bond Distance/ Å	Bond	Bond Distance/ Å
La-O [4x]	2.4810(7)	Li2-O	1.900(10)
La-O [4x]	2.6230(7)	Li2-O	2.057(11)
Sb-O [6x]	1.9958(7)	Li2-O	2.070(10)
Li1-O [4x]	1.9323(7)	Li2-O	2.390(9)
		Li2-O	2.631(11)
		Li2-O	2.690(8)

Figure 1.

Figure 2a

Figure 2b.