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Structure and ionic conductivity in lithium garnets

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Garnets are capable of accommodating an excess of lithium cations beyond that normally found in this prototypical structure. This excess lithium is found in a mixture of coordination environments with considerable positional and occupational disorder and leads to ionic conductivity of up to $4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. This high value for total conductivity, combined with excellent thermal and (electro)chemical resistance makes these candidate materials for operation in all solid-state batteries. This review looks at garnets with a wide range of stoichiometries and lithium concentrations and the impact of complex lithium distributions and crystallographic order/disorder transitions on the transport properties of these materials.

Introduction

The idea of ionic mobility in crystalline materials presents something of a paradox. The robust mechanical properties and excellent temperature resistance of many ceramic materials are at odds with an ionic assembly containing highly mobile species. The combination of fast ion mobility and the mechanical properties of a solid provides unprecedented properties. Thus there is considerable interest in such materials for electrochemical technologies where mechanical integrity under thermally and chemically demanding conditions is required.

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The twin problems of energy supply and global warming due to fossil fuel use are driving an overdue search for more efficient ways of storing and using energy. Advanced solid state electrochemical devices in the form of fuel cells, supercapacitors and batteries are anticipated to play a considerable role.² All three of these technologies rely on ionic conduction and this has given the search for new fast ion conducting materials considerable impetus.

The availability of high energy density batteries has permitted the huge growth in portable electronic devices. Lithium is the favoured ion as it provides a unique combination of high density and high potential. Current batteries employ solid state electrodes and electrolytes composed of lithium salts dissolved in an organic liquid.³ There is considerable ongoing research for new electrode

materials to give higher potentials and hence higher gravimetric and volumetric energy densities. As the energy contained in these batteries increases it is evident that the hazard posed by a rapid discharge due to short circuit will also increase.⁴ Lithium batteries currently used in a laptop computer typically provide *ca.* 200 kJ; a similar energy to that released by the combustion of 6 ml of petrol. The uncontrolled release of this energy would be capable of causing considerable damage, especially if additional sources of fuel, such as a polymer electrolyte, are present. In order to provide additional security against such occurrences there has been considerable research into developing solid, crystalline materials to replace the polymer. In addition to conducting lithium ions any electrolyte for this application must be an electronic insulator capable of withstanding both the electrochemical potential that exists between the electrodes of a fully charged cell, and the electrical overpotential necessary to charge the cell. The electrolyte must also provide a stable interface with the electrodes. To date no crystalline oxide has given long-term performance that matches all of these requirements. A number of materials, most notably the $\text{Li}_{3-x}\text{La}_x\text{TiO}_3$ perovskites and doped lithium nitrides,⁵ are capable of excellent lithium ion conductivity at room temperature but problems of electrochemical stability, high grain boundary resistance or synthetic challenges have limited their application.⁶ The conductivities of these materials and



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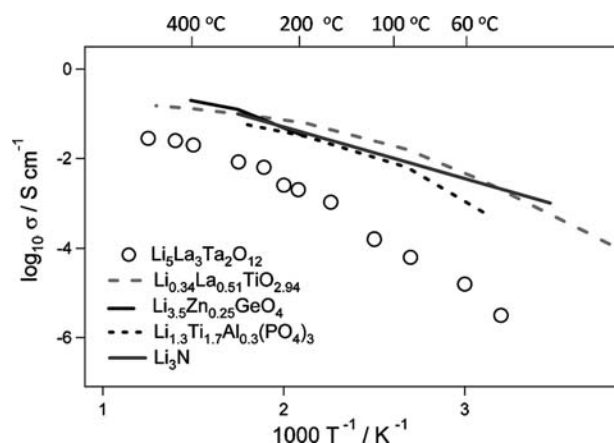


Fig. 1 The total conductivity⁷ of $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ compared with several other crystalline fast lithium ion conductors with composition indicated by the legend.³¹

other fast Li^+ conducting solids are collected in Fig. 1. This review is concerned with the recent development of the garnet as a host structure for fast Li^+ conduction.

Interest in the lithium transport properties of the garnet structure was first aroused by the report of facile lithium conductivity in the compositions $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Nb}, \text{Ta}$).⁷ These materials show activation energies, *ca.* 0.5 eV, that indicate a low barrier to ion migration. Significantly the stability of the d^0 cations, especially Ta^{5+} , confers exceptional electrochemical stability on these compounds. Tests on these compounds and related materials have shown that garnets can be chemically compatible with metallic lithium⁸ and some common cathode materials.⁹ Moreover, the inter- and intra-grain conductivities are of the same order of magnitude; a key requirement of electrolytes that are required to deliver bulk transport of ions through a polycrystalline electrolyte. These compounds deliver a bulk conductivity of *ca.* $10^{-6} \text{ S cm}^{-1}$ at room temperature that compares favourably with the bulk transport properties of a range of other solid lithium electrolytes shown in Fig. 1. Consequently these compounds were identified as likely candidates for potential use in lithium ion batteries and this has spurred a search for other garnets capable of fast lithium conduction and a reinvestigation of the chemistry of the garnet structure.

The garnet structure

The determination of lithium environments in the prototypical garnet structure

has been a long-standing problem.^{10,11} The classic garnet formulation $A_3B_3C_2O_{12}$ contains three crystallographically distinct cation coordination environments with the *A*, *B* and *C* cations in eight, four and six coordination respectively. For conventional garnets each of these sites is fully occupied. The fast lithium conducting phases $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ represent a curious challenge; two additional lithium cations are found in each formula unit and there are no available sites. This difficulty has been recognised since the first reports of these compositions. However, the application of X-ray diffraction to resolve this uncertainty has been fraught with problems principally arising from the dominance of the X-ray diffraction process by the electron-dense species La^{3+} and M^{5+} that almost mask the contribution from Li^+ . An accurate determination of the lithium arrangement is most reliably

achieved using neutron scattering methods, where the negative scattering length of ^7Li provides excellent contrast to the positive scattering arising from the majority of nuclei. It should be noted that the strong absorption by ^6Li can present experimental challenges if a natural abundance of lithium is present in the sample.

Examination of lithium-containing garnets that show the conventional garnet stoichiometry, with a 3 : 3 : 2 ratio of cations, shows a straightforward distribution of cations. Neutron diffraction has provided a precise determination of the lithium distribution in a number of compositions $\text{Li}_3\text{Ln}_3\text{Te}_2\text{O}_{12}$ ¹² and $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ ¹³ and in every case showed that the Ln^{3+} and Te^{6+} or W^{6+} occupied the eight-coordinate *A* sites and six-coordinate *C* sites respectively. Refining a lithium distribution against these powder data showed that the lithium was exclusively found on the tetrahedrally coordinated positions occupied in the conventional garnet structure. Whilst this model indicates a fully occupied lithium position it should be noted that diffraction data are typically unable to detect vacancies at a level of $\leq 1\%$. The uncertainties in cation distribution are unlikely to be smaller than this for any structures without the introduction of other experimental observations.

Lithium coordination in conducting garnets

In order to understand the easy passage that lithium enjoys in some of these

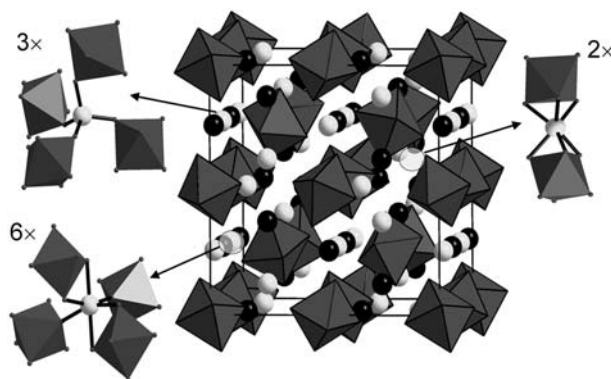


Fig. 2 The crystal structure of a conventional garnet $A_3B_3C_2O_{12}$ where octahedra indicate CO_6 units and black and grey spheres represent *A* and *B* cations respectively. In addition to the three *C* sites occupied in conventional garnets, suitable sites for lithium cations in $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ include the six octahedral and two trigonal prismatic sites indicated.¹⁸ Selected positions for these two additional coordination sites are indicated by translucent spheres within the garnet unit cell.

garnets it is necessary to understand the differences in lithium distribution between the stoichiometric garnets and what we will refer to as the lithium-stuffed garnets, that is compositions that contain more than eight cations in the garnet formulation *i.e.* compounds $\text{Li}_x\text{Ln}_3\text{M}_2\text{O}_{12}$ where x is greater than three. Clearly it is not possible to accommodate this lithium on the sites occupied in conventional garnets.

Although the garnet structure that has not hitherto been considered to contain a significant amount of extra-framework volume, this structure type is actually more flexible than is commonly appreciated. Whilst the vast majority of garnets share the same space group symmetry, $Ia\bar{3}d$, it should not be inferred that the structure is not capable of substantial adjustment: the garnets $\text{Si}_3\text{Co}_3\text{Al}_2\text{O}_{12}$, $\text{Y}_3\text{Fe}_3\text{O}_{12}$ and $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ all crystallise^{14–16} in the space group $Ia\bar{3}d$ and consideration of the ionic radii¹⁷ of the ions contained within the unit cell volumes shows that the unit cell of these compounds are 71%, 60% and 58% filled respectively. Whilst the filled volume of $\text{Sr}_3\text{Co}_3\text{Al}_2\text{O}_{12}$ approaches that obtained for a close packed arrangement of spheres, $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ contains considerable void volume. Although the garnet lacks the epic range of structural distortions manifested in the perovskites it can be seen that considerable scope for structural variation exists.

Examination of the $[\text{La}_3\text{Ta}_2\text{O}_{12}]^{5-}$ framework¹⁸ reveals the presence of six octahedral and two trigonal prismatic sites per formula unit which could accommodate Li^+ in addition to the three tetrahedral interstices that are occupied

by lithium in the conventional garnets $\text{Li}_3\text{Ln}_3\text{Te}_2\text{O}_{12}$. The details of these different coordination environments are illustrated in Fig. 2.

By carrying out bond valence sums on these positions it is possible to obtain a description of how similar each of these sites is to a typical binding environment for Li^+ . The application of this approach to the sites in the $[\text{La}_3\text{Ta}_2\text{O}_{12}]^{5-}$ framework gives values that suggest that Li^+ should occupy the octahedral interstice rather than either of the other two candidate sites.¹⁵ However, it should be remembered that the bond valence approach is empirical and assesses likely coordination environments against a large number of known crystal structures. It may well be that such a comparison of structures which are known fast ion conducting phases (such as lithium garnets) with a library that is predominantly populated by ionically insulating phases may be inherently misguided and lead to misleading results as the bond valence parameters have been selected to identify coordination sites in which cations are robustly bonded and hence immobile.

An experimental determination of the lithium distribution has been obtained by a series of neutron diffraction experiments.¹⁸ These show that at room temperature the lithium is found in the centre of the tetrahedra as well as several sites in the distorted oxide octahedron. For $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Ta}, \text{Nb}$) the tetrahedra are *ca.* 80% occupied whilst the octahedra contain a complex arrangement of lithium across multiple sites that indicate *ca.* 40% of the octahedra are occupied by a single lithium cation as

shown in Fig. 3. Structural studies of these compounds at temperatures between 2 K and 873 K show that this complex distribution is largely temperature-independent indicating the presence of occupational disorder that is static over the diffraction timescale, rather than a dynamic process involving exchange between the different polyhedra. Lithium is found in oxide octahedra that are linked to two tetrahedra *via* shared faces and this results in short $\text{Li}\cdots\text{Li}$ distances; cations in the centre of each polyhedra would be at a distance of only 2.0 Å. Some of the lithium cations in the octahedra are displaced along an axis that takes them away from one shared face and towards the other in a manner that will reduce electrostatic repulsion between two cations occupying adjacent polyhedra by increasing this separation to 2.4 Å.¹⁸

Manipulation of lithium content

By replacement of either La^{3+} or M^{5+} with cations of higher or lower oxidation state it is possible to continuously vary the lithium content of the garnet structure in order to maintain charge balance. Introduction of alkaline earth cations in place of lanthanides or a hexavalent cation such as Te^{6+} in place of pentavalent cations can give solutions that are lithium rich, such as $\text{Li}_{5+x}\text{La}_{3-x}\text{Ba}_x\text{Ta}_2\text{O}_{12}$,^{8,19} or lithium poor, such as $\text{Li}_{5-x}\text{Nd}_3\text{Sb}_{2-x}\text{Te}_x\text{O}_{12}$.²⁰ The lithium distribution of both of these series has been examined in detail using neutron diffraction data. As can be seen in Fig. 4, increasing the lithium content of the system leads to a systematic increase in the population of the octahedral sites and a simultaneous introduction of vacancies onto the tetrahedral sites. Moreover, for the most lithium rich compositions it can be seen that the increasing lithium population of the octahedra is predominantly found to be displaced away from one of the polyhedral faces that is shared with an adjacent tetrahedrally coordinated lithium site. This observation led to speculation that the lithium movement through the structure would involve considerable local rearrangement depending on the occupancy of adjacent lithium coordination sites and a strongly cooperative mechanism for ionic conduction.¹⁹

The lithium content can be increased further still by doping with Zr^{4+} or Sn^{4+} to

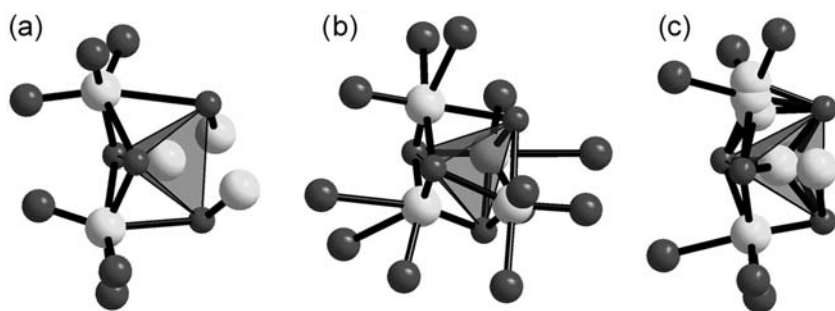


Fig. 3 The atomic arrangement of octahedrally coordinated lithium around (a) a filled tetrahedron and (b) an empty tetrahedron in the cation-ordered, tetragonally distorted phases $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ²² and $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$.²³ It can be seen that the positional disorder in the lithium distribution in the oxide octahedra observed in the cubic phase¹⁹ $\text{Li}_{6.6}\text{La}_{1.4}\text{Ba}_{1.6}\text{Ta}_2\text{O}_{12}$ (c) arises from displacements driven by the occupational disorder in the adjacent tetrahedron.

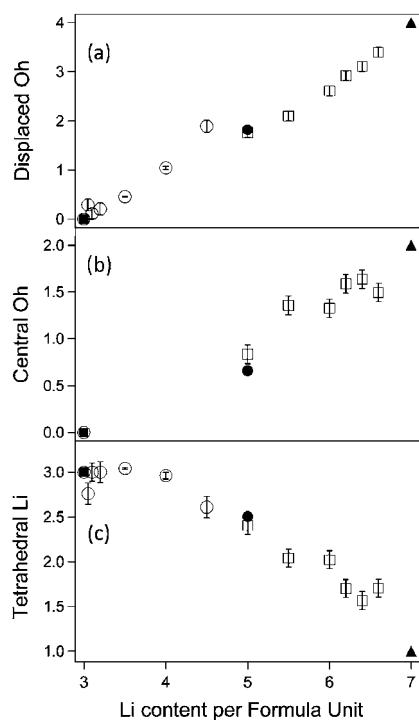


Fig. 4 The number of lithium cations found (a) displaced from the centre of the octahedra, (b) in the centre of the octahedra and (c) in the tetrahedra for a range of compounds with between three and seven lithium cations per formula unit. The compounds at each end of the series, $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$ (filled square)¹³ and $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ ²³ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (filled triangle),²² display complete cation ordering with sites either filled or empty. The other compositions $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$ (empty circles),²⁰ $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (filled circle)¹⁸ and $\text{Li}_{5+x}\text{La}_{3-x}\text{Ba}_x\text{Ta}_2\text{O}_{12}$ (empty squares)¹⁹ contain partially occupied sites.

give compositions of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$. There are two structural types associated with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; a cubic garnet²¹ with a structure presumed to be similar to the compounds adopting the $Ia\bar{3}d$ space group discussed previously and a tetragonally distorted phase.²² Simultaneously a study of $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ identified a similar distortion.²³ Both compounds show a complete ordering of the Li^+ cations over one third of the tetrahedral sites in the structure whilst each oxide octahedron contains a single lithium cation; 2/3 in positions strongly displaced from the centre of the octahedron to give pseudo four-coordination and 1/3 close to the centre of the octahedron. The displacement is away from the one third of the tetrahedra that are occupied and towards the two thirds of tetrahedra that are empty. As can be seen

in Fig. 3, the disordered distribution of lithium observed for lower lithium contents, such as $\text{Li}_{6.6}\text{La}_{1.4}\text{Ba}_{1.6}\text{Ta}_2\text{O}_{12}$,¹⁹ in the garnet can be considered as a composite of these two arrangements and this suggests that the positional disorder in the octahedral lithium is indeed coupled with the lithium occupancy of the adjacent tetrahedra. Comparison of the structural data of the ordered phases $\text{Li}_3\text{Nd}_3\text{W}_2\text{O}_{12}$,¹³ $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ ²³ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ²² with the lithium distribution of the disordered phases $\text{Li}_{5+x}\text{La}_{3-x}\text{Ba}_x\text{Ta}_2\text{O}_{12}$,¹⁹ $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$,¹⁸ and $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$ ²⁰ shows a continuous trend in site occupancies.

This complete chemical ordering of the lithium cations and vacancies drives a reduction in space group symmetry to give a tetragonal phase $I4_1/acd$, $a = 13.134(4) \text{ \AA}$, $c = 12.663(8) \text{ \AA}$.²² This is a relatively large metric distortion from cubic symmetry and should be readily detectable using a typical X-ray powder diffractometer. Given this clearly manifested distortion it is interesting that conductivity data have been reported for a compound with the same composition, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, that shows an absence of peak splitting that suggests a cubic structure, or at least a tetragonal distortion that is greatly reduced compared to the $I4_1/acd$ phase. The preparative conditions vary considerably between these two samples; the cubic phase was heated at 1230 °C whereas the tetragonal phase was prepared at 950 °C. It is possible that the higher temperature is responsible for the stabilisation of a higher symmetry phase, but a detailed study of the effect of synthetic conditions, and particularly cooling rate, on structural transitions is necessary to clarify this point. In the absence of a structural and chemical analysis of the cubic compound it may be possible that some change in composition is responsible for the variation in symmetry reported to occur for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. This is not the only variation observed in garnets reported to share the same composition; conductivities can also show a history dependence and this key property merits a detailed discussion.²⁴

Ionic conductivity

Whilst interest in garnets was initially stimulated by the observation of

exceptional lithium ion conductivity of $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$, understanding the origin of this behaviour has required extensive study. A wide compositional range of garnets have been prepared with Ca, Sr and Ba^{8,25} in the 8-coordinate site and Bi,²⁶ Sb,^{25,27} W,¹³ Zr,²¹ Sn in the 6-coordinate site. All of the lithium-stuffed compositions have shown fast lithium conductivity. A number of studies have shown the inter- and intra-grain conductivity to be of the same order of magnitude.^{7,8,21,22} It is not possible to resolve these different processes at higher temperatures and so the ion transport in these systems have been described using a total conductivity. We will follow this convention here, but note that there is strong experimental support for using the total conductivity to follow the intra-grain conductivity. This allows meaningful correlation of the total conductivity of a material with the crystal structure of the garnet.

There is considerable variation in conductivity being reported for compounds with structures that, when crystallographically averaged by a neutron diffraction experiment, have the same lithium distribution and so would be expected to show very similar conductivities. Only by examining a range of compositions, and carefully characterising the lithium distribution using a variety of probes, has it been possible to infer details of the pathway and mechanisms for Li^+ transport in these compounds.

The complex distribution of Li^+ and vacancies across oxide tetrahedra and octahedra, combined with multiple lithium sites within the latter, means that the mechanism for lithium migration cannot be inferred simply by examining the structure of a single fast ion conducting phase e.g. $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$. Studies of compounds with a conventional garnet stoichiometry such as $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$ show that in this compound, containing lithium exclusively on a filled tetrahedral site, the conduction is orders of magnitude less than the fast conductors with their multiple, partially occupied Li^+ environments. The bulk conductivity at room temperature was immeasurably small but, based on the conductivity at 400 °C and the activation energy above this temperature, 1.2 eV, the room temperature conductivity of $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$ can be estimated as less than $10^{-10} \text{ S cm}^{-1}$.¹²

This observation of immobile lithium in these tetrahedral sites would suggest that the tetrahedrally coordinated lithium plays no part in the conductivity in garnets. However, there are two differences between the lithium-stuffed compositions and the stoichiometric garnet $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$. Most obviously, the lithium stuffed garnets contain lithium in multiple sites, but it is also important to note that they also contain vacancies in the tetrahedrally coordinated sites. These are absent in the stoichiometric garnets and tetrahedral vacancies provide potential hopping sites for lithium to access in the lithium-stuffed compounds.

A study of the series of compounds $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$ used replacement of Te^{6+} with Sb^{5+} to vary continuously the lithium content of the garnets. This provided a model system to study the transition from poor lithium conduction in the stoichiometric garnets to the fast ion conducting regime reported for compositions containing five or more lithium cations per formula unit.²⁰ As the lithium content is increased the occupancy of the oxide octahedra increases continuously as does the vacancy concentration of the tetrahedral site as shown in Fig. 4. Impedance measurements show a step change in the transport

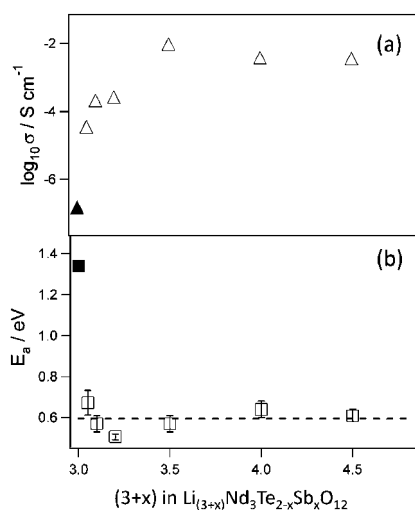


Fig. 5 The conductivity (a) at 400 °C and the activation energy (b) of $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$.²⁰ Solid symbols represent data from the cation-ordered phase $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$ which contains lithium exclusively in the octahedral sites in the structure. The dashed line in (b) indicated the mean value of the activation energy, 0.59 eV, for compounds with $x > 0$.

properties as the lithium content is increased from a conventional garnet to $\text{Li}_{3.05}\text{Nd}_3\text{Te}_{1.95}\text{Sb}_{0.05}\text{O}_{12}$; the conductivity increases by two orders of magnitude and the activation energy is reduced to a value, *ca.* 0.59(6) eV, that does not vary with increasing lithium content as shown in Fig. 5. This stepwise change in activation energy is a signature of the opening of a new mechanistic pathway for Li^+ conduction as the lithium content is increased above three.

It is tempting to ascribe this change in lithium mobility to the introduction of lithium species into the oxide octahedra and so infer that it is these octahedral sites that are responsible for the fast Li^+ conduction. However, it should be recalled that this occurs simultaneously with the introduction of vacancies into the tetrahedrally coordinated site and these may be responsible for the step change in lithium conduction. In order to examine the relationship between the lithium on the different sites in the structure it was necessary to use ^6Li NMR to probe the local environments. Spectra collected from $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$ contain a single set of resonances, as could be expected from the fully ordered arrangement of lithium on only one (tetrahedral) site with the nuclear spin coupled with the paramagnetic cation Nd^{3+} . Spectra collected from more lithium-rich compositions in the series show the growth of a second set of resonances that increase in area as the concentration of lithium in the oxide octahedra is increased. There is no evidence of lithium hopping between these two sites over the timescale of the NMR experiment. Thus the lithium in the partially occupied tetrahedral sites of the fast conducting phases shows the same behaviour as in the fully ordered, ionically insulating compound $\text{Li}_3\text{Nd}_3\text{Te}_2\text{O}_{12}$.¹² Taken in sum, these observations show that in the series $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$ the tetrahedrally coordinated lithium remains essentially static for all compositions, whilst the lithium in the oxide octahedra is highly mobile. This suggests a mechanism for ionic motion that exclusively involves the edge-sharing oxide octahedra, shown in Fig. 6, and a single rate determining step for all compositions of *ca.* 0.6 eV.

This assignment finds strong support from the properties of the two compounds reported for the composition

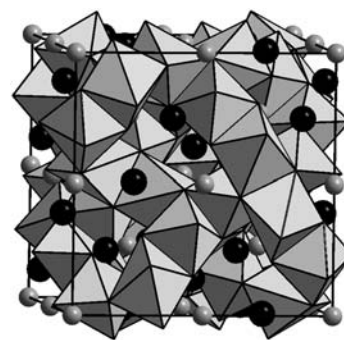


Fig. 6 The network of edge-sharing oxide octahedra that are occupied by mobile lithium cations in the lithium-stuffed cubic garnets. Immobile lithium is found in the centre of oxide tetrahedra that are enclosed by four polyhedral faces that are shared with octahedra and so are not visible in this diagram. Lithium occupancy of these central tetrahedra will significantly inhibit the passage of lithium through the adjacent octahedra and so the conduction pathway will be more complex than this cubic structure suggests.

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.^{21,22} This composition can form a cubic structure, presumed to contain a similar disordered arrangement of Li^+ across tetrahedral and octahedral sites observed for lithium-stuffed compositions up to and including $\text{Li}_{6.6}\text{La}_{1.4}\text{Ba}_{1.6}\text{Ta}_2\text{O}_{12}$. This phase shows a bulk room temperature conductivity of $4 \times 10^{-4} \text{ S cm}^{-1}$ that rivals the highest reported for crystalline materials.²¹ However, another polymorph of this compound has been structurally characterised. The complete ordering of Li^+ across all of the octahedra and one third of the tetrahedra occurs in the tetragonally distorted garnets $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ²² and $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ ²³ and both the intra- and inter-grain conductivities are around three orders of magnitude smaller than in the cubic variant. A detailed study of the temperature dependence of the structure and properties of $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ has shown that this undergoes a structural transition from tetragonal to cubic symmetry at 750 °C. This transition requires disordering of the lithium cations and presumably a substantial increase in conductivity, although carrying out such a measurement at these temperatures is not straightforward and data have not yet been reported.

The conductivity of the compound $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ shows a significant dependence on the thermal history of the

sample; quenching the pellet from high temperature gives a slightly more conductive material than cooling more slowly.²³ Similar observations have been made in cubic lithium-stuffed garnets $\text{Li}_6\text{La}_2\text{ANb}_2\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}$).²⁴ It appears that the driver for structural distortion in the tetragonally distorted phase is the ordering of lithium that leads to the presence of a single lithium cation in each oxide octahedron. Whilst such ordering will clearly reduce the electrostatic energy associated with the short distances between Li^+ cations occupying adjacent octahedra, the ordering process reduces the disorder of the system and so there is an entropic driver that will favour the disordered, cubic structure at high temperature. It is possible that the history dependence of the conductivity arises from local ordering of the lithium and vacancies across the oxide tetrahedra and octahedra. An ^7Li NMR study of two samples of $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ showed some stark differences in the lithium signals depending on whether the sample had been prepared at 850 °C or 900 °C.²⁸ These could not be correlated with the lithium distribution observed *via* diffraction experiments, but it may be that the NMR data contained additional information on the local ordering of lithium that was taking place below the correlation lengths of the neutron diffraction experiments. Subsequent work has found that the fraction of mobile and immobile lithium nuclei does not correlate in a straightforward way with the distribution of lithium ions across octahedral and tetrahedral sites.²⁹ Internal frequency measurements have also shown a complex response with more than one type of lithium relaxation occurring.³⁰ Given the complexities implied by the local ordering between octahedrally and tetrahedrally coordinated lithium combined with the dynamic nature of the lithium occupancy of the octahedral site and the potential for local clustering and longer range ordering, indicated in the tetragonally distorted structures, it is clear that a model based on a simple, non-cooperative hopping from a single occupied site to a single vacant site involving a static potential well is likely to be a gross oversimplification of the conduction process in this structure.

The lithium pathway can be usefully visualised as being composed of the

network of edge-sharing octahedra shown in Fig. 6. However, the presence of lithium in some of the oxide tetrahedra is likely to perturb the local electric field and so influence the ease of passage of lithium cations through the four adjacent octahedral sites. Moreover, the lithium in the octahedra is not located on a single static position, but instead is displaced from the centre in order to (i) shorten the Li–O bonds to give an environment more typical of Li^+ and (ii) minimise repulsion if one of the two adjacent tetrahedra is occupied. Should both adjacent tetrahedra be occupied for any given octahedron, then this lithium occupancy of this vacant octahedron is likely to carry such a high electrostatic cost that it can be considered inaccessible and so play no part in the lithium conduction pathway. Consequently the energy landscape for lithium migration is likely to be significantly dependent on local cation arrangements and so have a considerable dependence on cooperative effects and lattice relaxation.

Conclusions

The garnet structure is capable of accommodating a surfeit of lithium in oxide octahedra that are vacant in conventional garnet stoichiometries. Population of these sites occurs simultaneously with the introduction of vacancies on the tetrahedral position that is filled with lithium for conventional stoichiometries. Occupational and positional disorder increases with lithium content until, for the highest lithium concentrations such as $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$, cation ordering occurs and lithium is precisely located on three, filled crystallographic sites in a tetragonally distorted structure. The displacements show that the disorder observed in the cubic garnets is driven by electrostatic repulsion between Li^+ in adjacent polyhedra. These phases show similar intra- and inter-grain conductivities and the total conductivity can reach values up to $4 \times 10^{-4} \text{ S cm}^{-1}$. Combined with excellent thermal and (electro)-chemical resistance this makes them candidates for application as solid state electrolytes. The conductivity does not show a straightforward dependence on either Li^+ or vacancy concentration. The mechanism for fast ion conductivity is switched on in a stepwise manner by

introducing lithium into the distorted oxide octahedra, although the local displacements observed in the cubic phases and the cooperative ordering shown in the tetragonal structure both suggest a strongly cooperative mechanism for lithium migration through the network of edge-shared octahedra.

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