Lithium dimer formation in the Li-conducting garnets $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ $(0 < x \leqslant 1.6)$†

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The garnet system $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ shows an unprecedented Li^+ content ($x \leqslant 1.6$) and short Li–Li distances of *ca* 2.44 Å between majority occupied sites suggesting that the high Li^+ mobility requires a complex cooperative mechanism.

The garnet structure has recently become of renewed interest due to the observation of high ionic mobility exhibited by phases[1–3] containing a surfeit of lithium cations. The conventional garnet stoichiometry, $A_3B_2C_3O_{12}$ contains cubic, octahedral and tetrahedral coordination environments filled with the *A*, *B* and *C* cations respectively. Garnets of the family $Li_3Ln_3Te_2O_{12}$ fill the tetrahedral sites with lithium and, interestingly the ionic mobility in $Li_3Nd_3Te_2O_{12}$ is at least three orders of magnitude less[4] than other lithium garnets, such as $Li_5La_3Ta_2O_{12}$,[1] which contain an excess of lithium beyond that which can be incorporated onto the tetrahedral sites.

The distribution of lithium in such cation-rich phases has been controversial since the first structural reports[5,6] of lithium-containing garnets. It has recently been shown[7] that in $Li_5La_3Ta_2O_{12}$ this excess of lithium is distributed across both the tetrahedral site usually occupied in the structure and an additional octahedral site that is capable of containing up to six lithium cations per formula unit. Both sites contain a large number of vacancies that permit clustering to avoid short lithium–lithium contacts. Considerable static displacements were observed on the partially occupied octahedral lithium position, and it was argued this positional and occupational disorder is responsible for the facile Li^+ mobility *via* a hopping mechanism between adjacent edge-shared octahedra. This hypothesis finds support in the negligible Li^+ mobility in $Li_3Nd_3Te_2O_{12}$ which contains no lithium on the octahedral site.[4]

The Li^+ conductivity[2] of $Li_6BaLa_2Ta_2O_{12}$, $\sigma_{RT} = 4.0 \times 10^{-5}$ S cm^{-1}, is enhanced beyond that observed in $Li_5La_3Ta_2O_{12}$ and is comparable to other fast Li^+ conductors.[8] Structural analysis of $Li_6BaLa_2Ta_2O_{12}$ has concluded[2] that the lithium fills the octahedral sites in the structure whilst the tetrahedral interstices remain vacant. Ionic mobility requires the presence of (i) ions capable of hopping from their equilibrium positions and (ii) vacant sites of comparable energy in close proximity to these positions to accept these cations and these requirements suggest that the fully occupied sites in $Li_6BaLa_2Ta_2O_{12}$ should inhibit Li^+ mobility. In order to examine this apparent contradiction we have studied this compound and related phases using neutron diffraction. This communication reports the results of these studies and shows that the lithium distribution in these compounds is more complex than has hitherto been appreciated.

All compounds were prepared by standard ceramic methods from stoichiometric quantities of La_2O_3, Ta_2O_5, $BaNO_3$ and a 10% excess of isotopically enriched (>99% ^{7}Li) $LiOH{\cdot}H_2O$. Neutron diffraction data were collected using the POLARIS diffractometer at Rutherford Appleton Laboratories. Data collected from $Li_6BaLa_2Ta_2O_{12}$ at room temperature were indexed in the space group $Ia\bar{3}d$. With the inclusion of 0.96(2) wt% Li_2CO_3 impurity, this satisfactorily indexed all observed diffraction peaks and close examination of the data showed no reduction in symmetry was necessary. Attempts to fit the data using exclusively octahedrally coordinated lithium failed to match the observed intensity (R_{wp} = 2.88, χ^2 = 5.50) and the fit was considerably improved (R_{wp} = 2.33, χ^2 = 3.60, Fig. 1) by allowing a distribution of lithium across both the tetrahedral and octahedral sites; the latter exhibiting positional disorder to a pseudo three-coordinate position towards a shared polyhedral face.

The lithium cations occupying the tetrahedrally coordinated sites show a significantly larger displacement parameter (U_{iso} = 0.074(4) Å^2) than either of the garnet phases $Li_5La_3Ta_2O_{12}$ or $Li_3Nd_3Te_2O_{12}$ which show high and low Li^+ conductivity respectively and highly localised tetrahedral lithium. The results of this structural refinement are collected in Table 1.

Data collected at 2, 473, 673 and 873 K showed no substantial change in the lithium distribution in $Li_6BaLa_2Ta_2O_{12}$ indicating

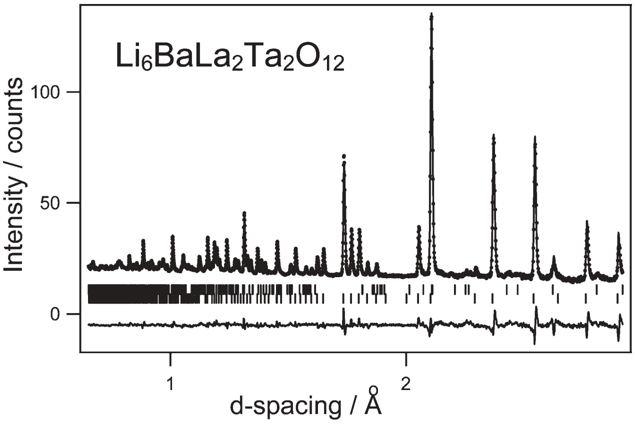

Fig. 1 Observed (dots), calculated (line) and difference neutron diffraction patterns collected from $Li_6BaLa_2Ta_2O_{12}$ at room temperature. The lower and upper tick marks indicate allowed Bragg reflections from the garnet and Li_2CO_3 phases respectively.

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Table 1 Structural parameters of $Li_6BaLa_2Ta_2O_{12}$ at room temperature

Atom	Site	Occup.	*x*	*y*	*z*	U_{iso}/Å^2
Ba; La	24*c*	$^1/_3$; $^2/_3$	$^1/_8$	0	$^1/_4$	^{a}
Li	24*d*	0.674(12)	$^1/_4$	$^7/_8$	0	0.074(4)
Li	48*g*	0.22(2)	$^1/_8$	0.6773(9)	0.5727(9)	0.014(2)
Li	96*h*	0.218(10)	0.0937(13)	0.6888(10)	0.5817(8)	0.014(2)
Ta	16*a*	1	0	0	0	^{b}
O	96*h*	1	0.28244(6)	0.10784(6)	0.20194(7)	^{c}

^{a} U_{11} = 0.0144(7), U_{22} = U_{33} = 0.0147(4), U_{12} = U_{13} = 0, U_{23} = 0.0080(4) Å^2; ^{b} U_{11} = U_{22} = U_{33} = 0.01182(4), U_{12} = U_{13} = U_{23} = 0.0034(5) Å^2; ^{c} U_{11} = 0.0268(6), U_{22} = 0.0187(5), U_{33} = 0.0357(7), U_{12} = 0.0058(4), U_{13} = 0.0074(4), U_{23} = 0.0049(4) Å^2; lattice parameter, *a* = 13.0229(3) Å

that the observed displacements on both the octahedral and tetrahedral sites are due to static disorder rather than dynamic processes. These two polyhedra are linked by shared faces such that every tetrahedron is linked to four octahedra and each octahedron is linked to two tetrahedra by opposing faces. Therefore, simultaneous occupation of adjacent octahedral and tetrahedral sites necessitates short Li···Li contacts (2.003(2) Å) and the observed displacement of Li^+ away from one of the shared faces as shown in Fig. 2 increases this separation to 2.44(2) Å.

This displacement from the centre of the octahedron away from one shared face requires the movement towards the other shared face and so the stability conferred by this mechanism is dependent on one of the two oxide tetrahedra remaining unoccupied. Despite this displacement, the Li···Li distance remains short and so is anticipated to destabilise the structure.

In order to establish both the effectiveness of this mechanism for stabilising these short Li···Li contacts and the maximum possible lithium content in this system, we examined the series of compounds $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$. Phases were prepared up to a maximum value of $x = 1.6$ ($Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$) giving a 120% excess of Li beyond the usual garnet stoichiometry. Attempts to synthesise compounds with higher lithium content failed to yield a garnet phase. We note that for $x > 1$ neither the octahedral nor tetrahedral site is capable of exclusively accommodating this concentration of Li^+.

Neutron diffraction data collected from all compounds in this series showed that as the Li^+ concentration increases, the occupancy of the tetrahedrally coordinated site is reduced with an associated increase in the concentration of octahedrally-coordinated lithium. Whilst the displacement of lithium from the centre of the octahedron remains constant (Li···Li distance is 2.471(12) Å in $Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$) it can be seen from Fig. 3 that the concentration of displaced lithium rises in an almost linear manner with composition to a maximum value in $Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$ which contains displaced Li^+ in 57(2)% of the octahedra. Comparison of this value with the tetrahedral site occupancy (56.8(14)%) shows a clear correlation between the occupancy of the tetrahedral site and the displacement of Li^+ away from the centre of the octahedron at this stoichiometric stability limit.

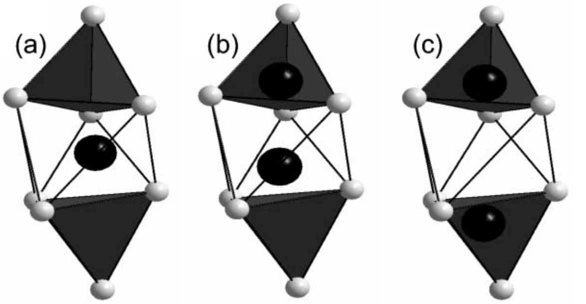

Fig. 2 In $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ lithium (black spheres) is accommodated in a tetrahedron or distorted octahedron of oxide anions (grey spheres). Physically reasonable arrangements occur if (a) both tetrahedra are unoccupied and the octahedral Li^+ occupies a central position, (b) a single tetrahedron is occupied with displacement of octahedral Li octahedron away from the shared face and (c) if both tetrahedra are occupied and the octahedron is vacant.

Diffraction experiments sample the contents of an average unit cell, and consequently occupational disorder can lead to the appearance of non-physically short interatomic distances in the averaged structure. Related phases contain Li···Li separations of 2.38(11) Å between sites that are 80% and 43% occupied.[7] However, a non-random distribution over these sites can prevent these short distances from occuring locally; such clustering is common in fast-ion conductors.[9,10] In the case of $Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$, the majority occupation of both the tetrahedral and (displaced) octahedral positions requires that the short interatomic separation (2.47(12) Å) must exist locally in a significant portion of the material. Thus these compounds behave wholly differently to the majority of ionic-conductors that show occupational disorder over well-separated sites. The most common lithium environment in this phase is associated with another Li^+ at a remarkably short distance and the repulsion associated with this arrangement may be a key factor in destabilising the Li^+ cations giving rise to the exceptionally high mobility in these structures. The displacement parameters of the tetrahedral lithium are unexpectedly high suggesting that the mobility of these cations may differ from Li^+ in the same crystallographic position in the Li-conducting phases $Li_5La_3M_2O_{12}$.

The observation of these Li···Li dimers suggests that hopping of Li^+ from either the tetrahedral or octahedral site will be associated with considerable local relaxation of the structure around the vacated site and the introduction of considerable strain at the newly occupied position. We conclude that lithium mobility in

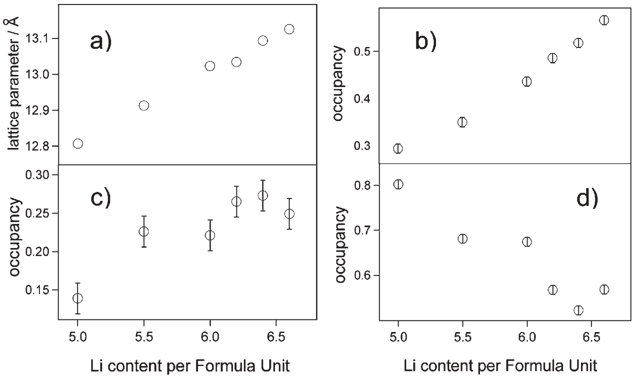

Fig. 3 The variation in (a) the lattice parameter and the fraction of octahedra containing (b) displaced Li^+ and (c) Li^+ on the centre of the octahedron and (d) the fractional occupancy of the tetrahedral site as a function of *x* in $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$. Data for $Li_5La_3Ta_2O_{12}$ are taken from literature values.[7] Error bars represent one standard deviation.

garnets is more complex than previously anticipated and that understanding and optimising this important property in these phases will be a challenging task.

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