Supplementary Material (ESI) for Chemical Communications

Supplementary Information

The Structure of Lithium Ion Garnets: Cation Disorder and Clustering in a new family of fast Li$^+$ conductors

Edmund J. Cussen
Edmund.cussen@nottingham.ac.uk

Synthesis of $Li_5La_3M_2O_{12}$

Samples of $Li_5La_3M_2O_{12}$ were synthesised using standard ceramic methods from stoichiometric quantities of La_2O_3 and M_2O_5 and a 10 % excess of isotopically enriched Li_2CO_3 (>99% ^{7}Li). ^{7}Li was used in order to reduce the mean neutron absorption cross section which arises from the presence of ^{6}Li and also to increase the magnitude of the negative scattering from the lithium positions. The powders were intimately mixed, pressed into pellets of 13 mm diameter under a load of 1500 kg. The pellets were heated in air in an open alimina crucible from 550 ^oC to 900 ^oC at a rate of 1.5 ^oC min^{-1} and held at this temperature for 40 hours. The pellets were then reground, repelleted and heated at 925 ^oC for a total of 12 days with several regrindings. The progress of the reactions were followed by X–ray powder diffraction and subsequent neutron diffraction experiments showed that the samples contained small quantities of Li_2CO_3 (≤ 1.6(2) wt%) and $La(OH)_3$ (≤ 3.1(1) wt%)

Neutron powder diffraction experiments

Neutron diffraction data were collected using the time–of–flight instrument Polaris at Rutherford Appleton Laboratories, Didcot, OXON, UK. Approximately 6 g of sample was accurately weighed into vanadium cans of 11 mm internal diameter. The sample height was noted and all data were corrected for absorption. Data were collected using three banks of detectors and the Rietveld refinements were carried out against all data simultaneously using the GSAS suite of programs. The background was described using a shifted Chebyshev polynomial and the peak shape was modelled using a convolution of exponential and pseudo–Voigt functions.

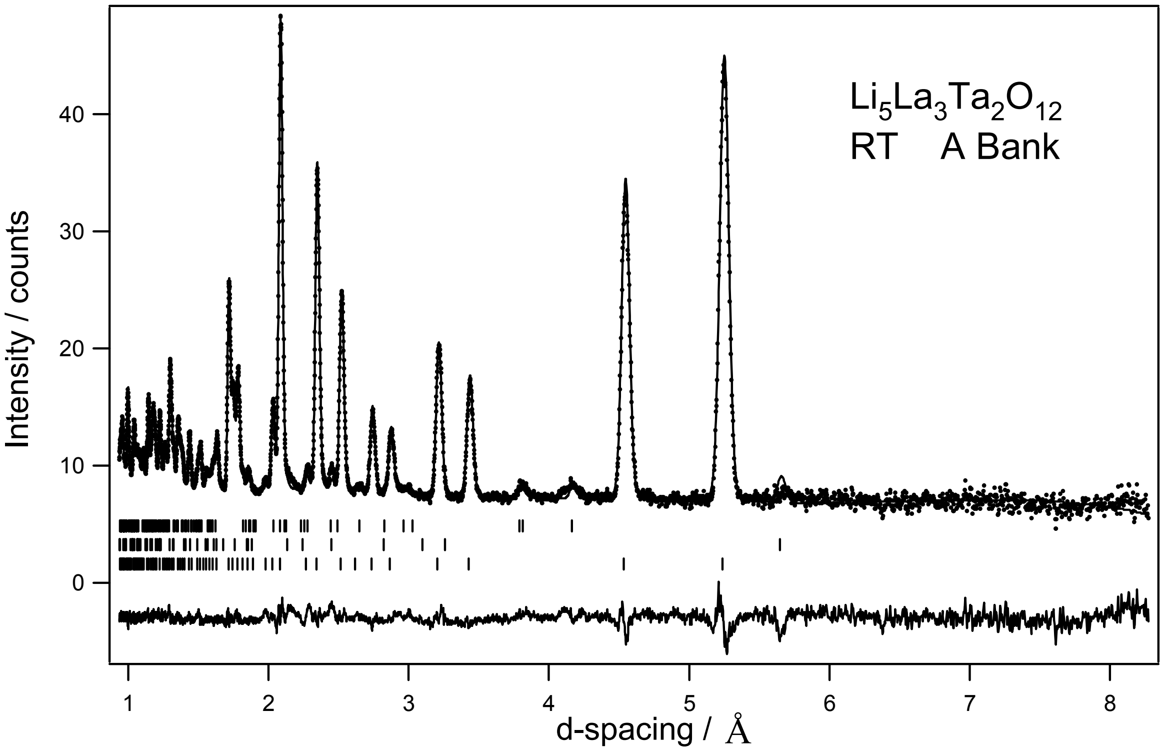
The details of the refinements and the resultant structural data are presented below for each of the data sets with representative figures showing the quality of the fits.

$Li_5La_3Ta_2O_{12}$ RT Polaris

Space group Ia$\bar{3}$d: a = 12.80654(11) Å, vol. = 2100.37(6) Å^3
Bank C: R_{wp} = 1.28, R_p =2.62, Bank E: R_{wp} = 2.34 R_p =4.01, Bank A: R_{wp} = 3.56 R_p =4.12
Powder totals R_{wp} = 1.72, R_p = 3.45; χ^2 = 2.269 for 60 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre) vs Oh(displaced)], 4 atomic parameters, 11 anisotropic and 1 isotropic displacement parameters, 3 scale factors, 5 diffractometer constants, 9 profile parameters, 18 background parameters.
[Impurity variables, 2 isotropic temperature factors, 2 lattice parameters (La(OH)$_3$, 2 phase fractions]

atom	site	frac	x	y	z
La	24*c*	1	$^1/_8$	0	$^1/_4$
Ta	16*a*	1	0	0	0
Li	24*d*	0.802(4)	$^1/_4$	$^7/_8$	0
Li	48*g*	0.139(8)	$^1/_8$	0.6826(8)	0.5674(8)
Li	96*h*	0.147(9)	0.0927(9)	0.6840(6)	0.5795(5)
O	96*h*	1	0.27965(3)	0.10564(3)	0.19894(3)

atom	100U_{11}/ Å^2	100U_{22}/ Å^2	100U_{33}/ Å^2	100U_{12}/ Å^2	100U_{13}/ Å^2	100U_{33}/ Å^2	100$_{iso}$/ Å^2
La	1.21(3)	0.461(14)	0.461(14)	0	0	0.37(2)	0.71
Ta	0.426(10)	0.426(10)	0.426(10)	0.10(2)	0.10(2)	0.10(2)	0.43
Li(Td)	~	~	~	~	~	~	2.23(7)
Li(Oh)	~	~	~	~	~	~	0.64(12)
Li(Oh)*	~	~	~	~	~	~	0.64(12)
O	1.10(2)	0.50(2)	1.05(2)	–0.022(13)	0.092(14)	–0.14(2)	0.88



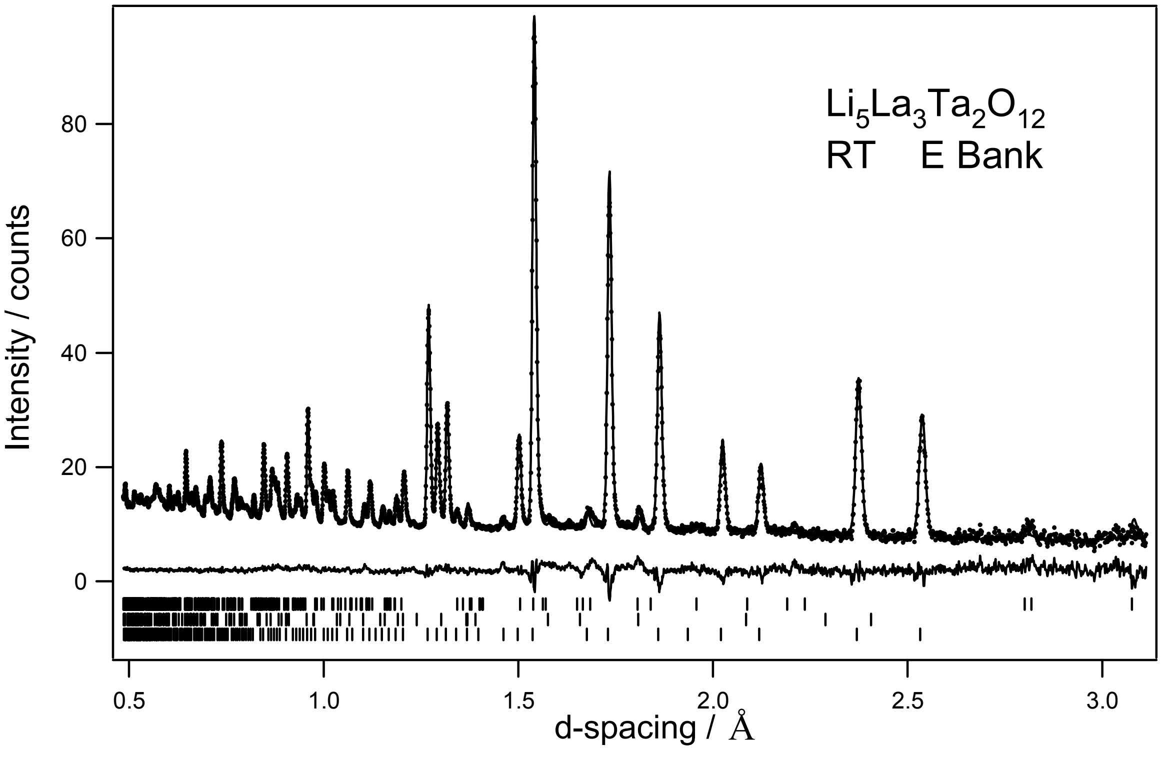


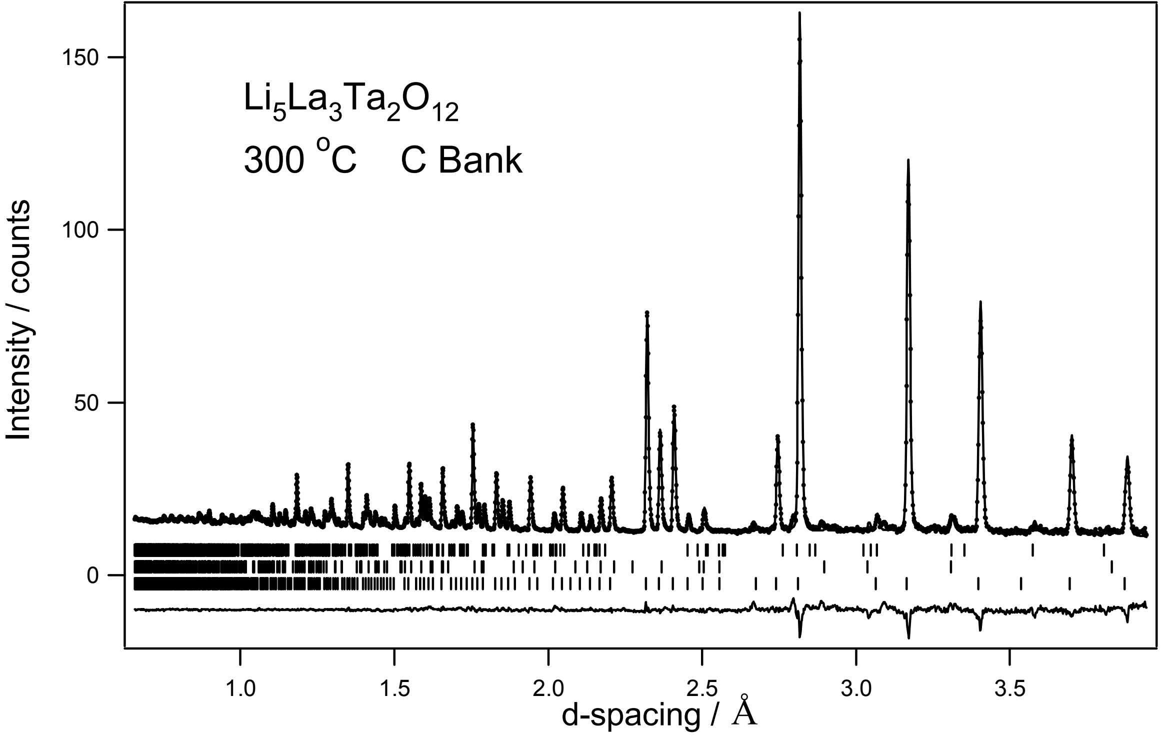
Fig. S1 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $Li_5La_3Ta_2O_{12}$ at room temperature. The lowest set of markers indicates the reflections due to the garnet phase.

$Li_5La_3Ta_2O_{12}$ 300 °C Polaris

Space group $Ia\overline{3}d$: a = 12.85508(12) Å, vol. = 2124.34(6) $Å^3$
Bank C: R_{wp} = 1.22, R_p =2.52, Bank E: R_{wp} = 2.21 R_p =3.78, Bank A: R_{wp} = 3.57, R_p =4.07
Powder totals R_{wp} = 1.61, R_p = 3.31; χ^2 = 2.196 for 58 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 4 atomic parameters, 11 anisotropic and 2 isotropic displacement parameters, 1 scale factors, 5 diffractometer constants, 9 profile parameters, 18 background parameters.
[Impurity variables, 2 isotropic temperature factors, 2 lattice parameters ($La(OH)_3$]

atom	site	frac	x	y	z
La	24*c*	1	$^1/_8$	0	$^1/_4$
Ta	16*a*	1	0	0	0
Li	24*d*	0.803(4)	$^1/_4$	$^7/_8$	0
Li	48*g*	0.182(8)	$^1/_8$	0.6822(6)	0.5678(6)
Li	96*h*	0.124(4)	0.0894(11)	0.6836(8)	0.5828(8)
O	96*h*	1	0.27935(3)	0.10593(3)	0.19941(4)

atom	$100U_{11}$/ $Å^2$	$100U_{22}$/ $Å^2$	$100U_{33}$/ $Å^2$	$100U_{12}$/ $Å^2$	$100U_{13}$/ $Å^2$	$100U_{33}$/ $Å^2$	$100U_{equiv}$/ $Å^2$
La	1.54(4)	0.82(2)	0.82(2)	0	0	0.46(2)	1.06
Ta	0.684(11)	0.684(11)	0.684(11)	0.01(2)	0.01(2)	0.01(2)	0.68
Li(Td)	~	~	~	~	~	~	4.32(11)
Li(Oh)	~	~	~	~	~	~	1.1(2)
Li(Oh)*	~	~	~	~	~	~	1.1(2)
O	1.44(2)	0.82(2)	1.67(3)	0.0006(2)	0.16(2)	–0.19(2)	1.31



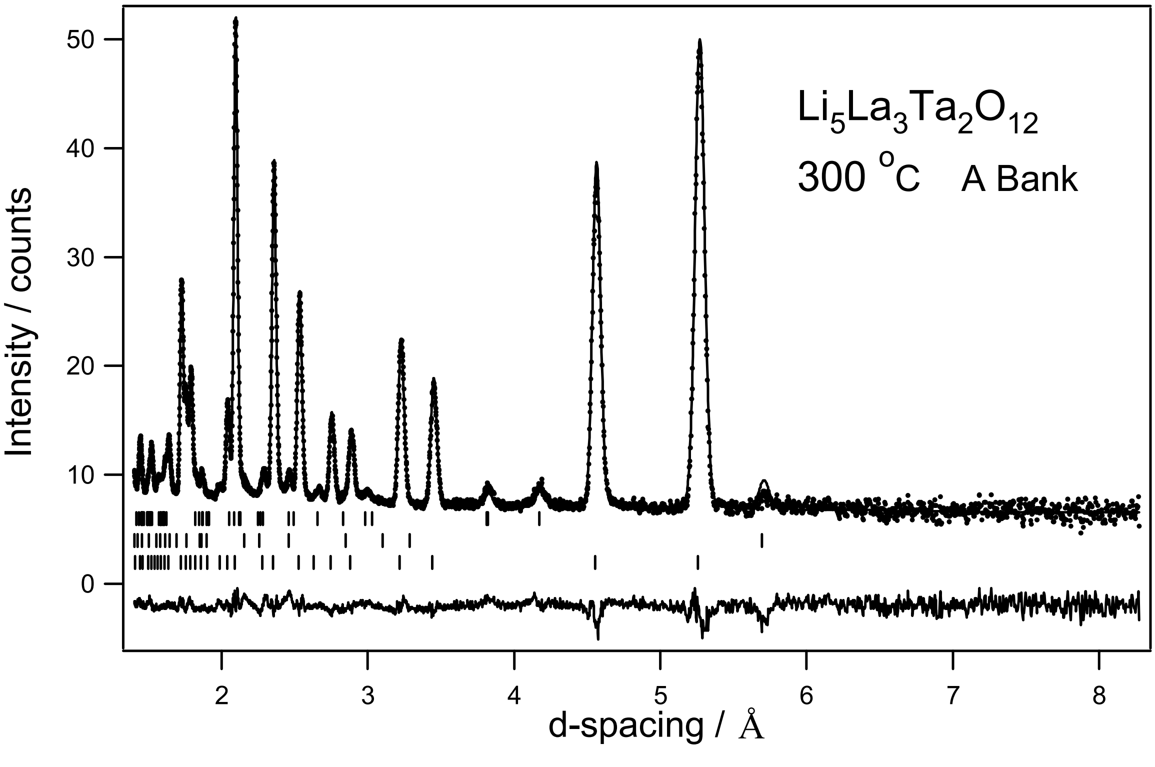


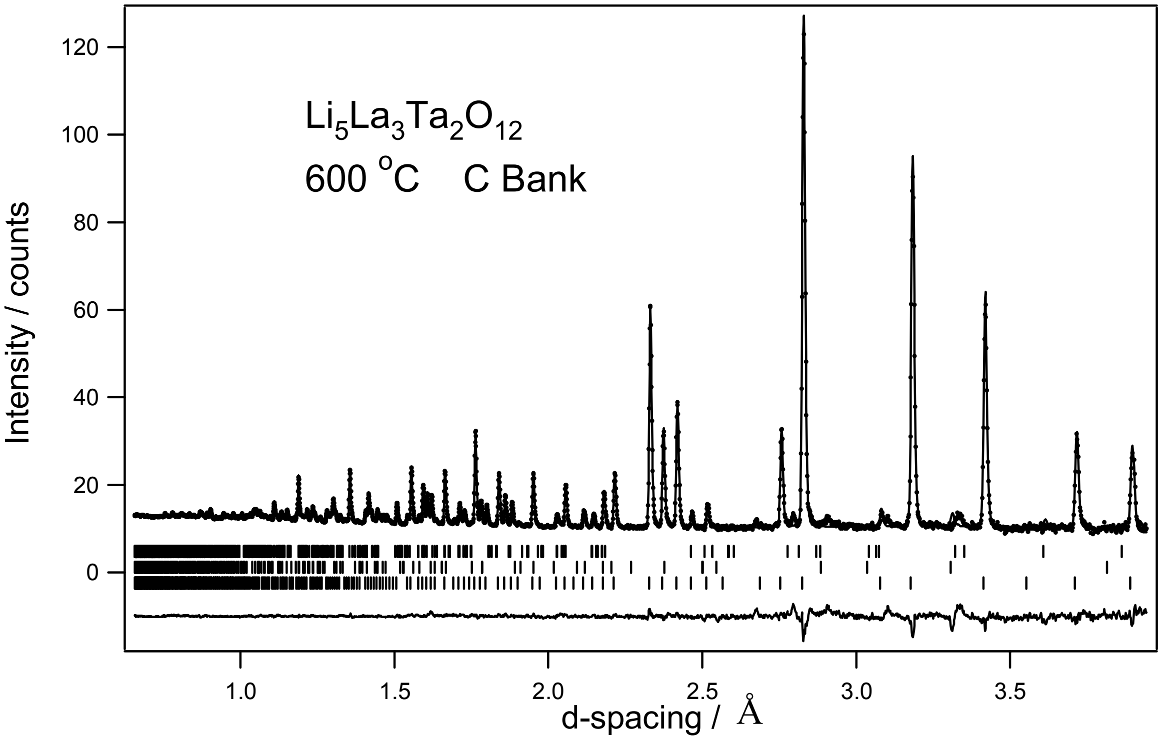
Fig. S2 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $Li_5La_3Ta_2O_{12}$ at 300 °C. The lowest set of markers indicates the reflections due to the garnet phase.

$Li_5La_3Ta_2O_{12}$ 600 °C Polaris

Space group $Ia\bar{3}d$: a = 12.9115(2) Å, vol. = 2152.44(8) $Å^3$
Bank C: R_{wp} = 1.26, R_p =2.73, Bank E: R_{wp} = 2.45 R_p =4.44, Bank A: R_{wp} = 4.31, R_p = 5.18
Powder totals R_{wp} = 1.74, R_p = 3.82; χ^2 = 1.531 for 62 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 4 atomic parameters, 11 anisotropic and 2 isotropic displacement parameters, 1 scale factors, 5 diffractometer constants, 9 profile parameters, 18 background parameters.
[Impurity variables, 2 isotropic temperature factors, 2 lattice parameters ($La(OH)_3$]

atom	site	frac	x	y	z
La	24*c*	1	$^1/_8$	0	$^1/_4$
Ta	16*a*	1	0	0	0
Li	24*d*	0.795(6)	$^1/_4$	$^7/_8$	0
Li	48*g*	0.188(9)	$^1/_8$	0.6812(7)	0.5688(7)
Li	96*h*	0.123(4)	0.088(11)	0.6868(10)	0.5828(8)
O	96*h*	1	0.27898(4)	0.10620(4)	0.20003(4)

atom	$100U_{11}$/ $Å^2$	$100U_{22}$/ $Å^2$	$100U_{33}$/ $Å^2$	$100U_{12}$/ $Å^2$	$100U_{13}$/ $Å^2$	$100U_{33}$/ $Å^2$	$100U_{equiv}$/ $Å^2$
La	1.99(5)	1.31(2)	1.31(2)	0	0	0.56(3)	1.54
Ta	0.99(2)	0.99(2)	0.99(2)	–0.08(2)	–0.08(2)	–0.08(2)	0.99
Li(Td)	~	~	~	~	~	~	6.7(2)
Li(Oh)	~	~	~	~	~	~	1.1(2)
Li(Oh)*	~	~	~	~	~	~	1.1(2)
O	1.99(3)	1.24(2)	2.39(4)	0.18(2)	0.25(2)	–0.23(2)	1.87



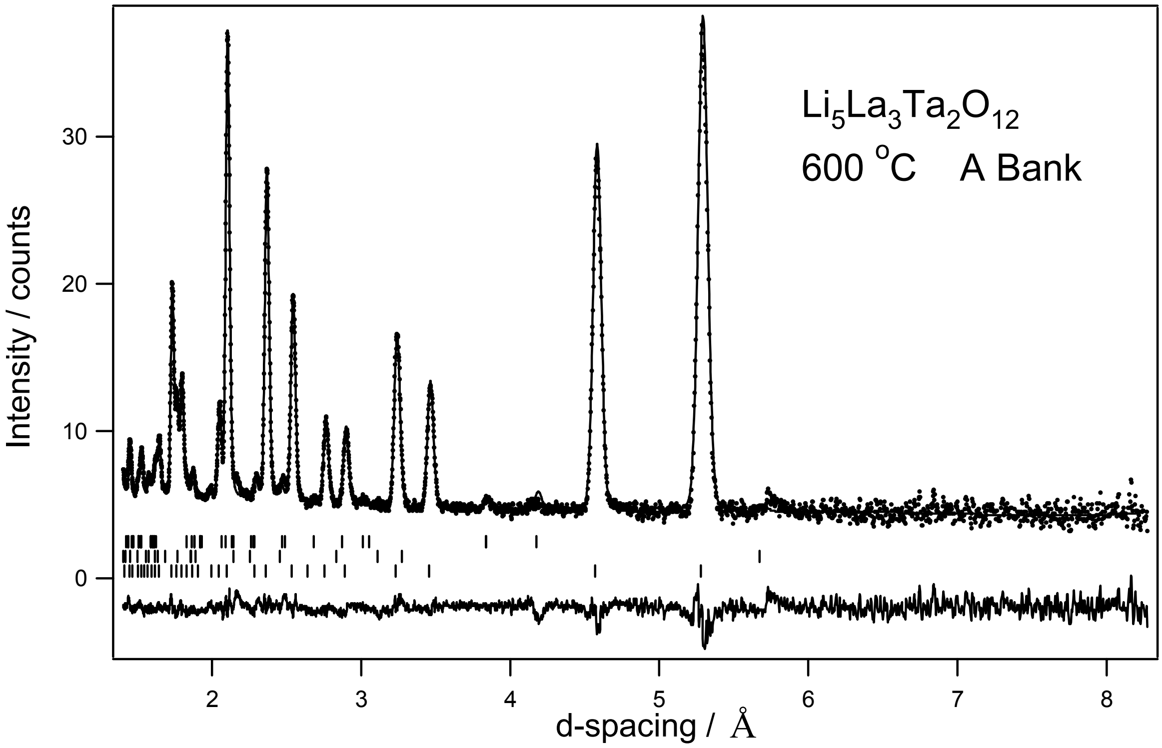


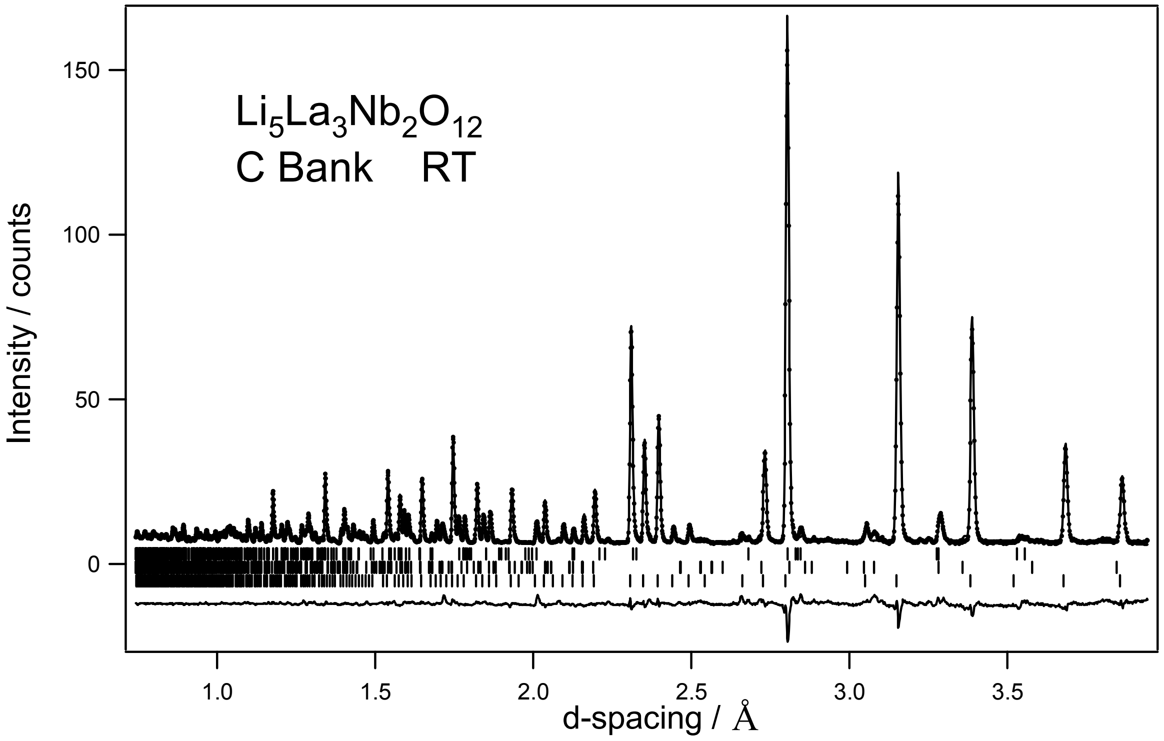
Fig. S3 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $Li_5La_3Ta_2O_{12}$ at 600 °C. The lowest set of markers indicates the reflections due to the garnet phase.

$Li_5La_3Nb_2O_{12}$ RT Polaris

Space group Ia$\overline{3}$d: a = 12.79432(11) Å, vol. = 2094.91(5) Å^3
Bank C: R_{wp} = 2.04, R_p =3.77, Bank E: R_{wp} = 2.62, R_p =3.79, Bank A: R_{wp} = 3.81, R_p =3.93
Powder totals R_{wp} = 2.35, R_p = 3.83; χ^2 = 4.380 for 62 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 11 anisotropic and 2 isotropic displacement parameters, 3 scale factors, 5 diffractometer constants, 9 profile parameters, 18 background parameters.

atom	site	frac	x	y	z
La	24*c*	1	$^1/_8$	0	$^1/_4$
Nb	16*a*	1	0	0	0
Li	24*d*	0.836(4)	$^3/_8$	0	$^1/_4$
Li	48*g*	0.11(1)	$^1/_8$	0.6798(10)	0.5702(10)
Li	96*h*	0.152(7)	0.0950(11)	0.6818(7)	0.5778(6)
O	96*h*	1	0.27953(3)	0.10553(3)	0.19846(3)

atom	$100U_{11}$/ Å^2	$100U_{22}$/ Å^2	$100U_{33}$/ Å^2	$100U_{12}$/ Å^2	$100U_{13}$/ Å^2	$100U_{33}$/ Å^2	$100U_{equiv}$/ Å^2
La	0.97(3)	0.606(12)	0606(12)	0	0	0.29(2)	0.73
Nb	0.621(9)	0.621(9)	0.621(9)	–0.019(13)	–0.019(13)	–0.019(13)	0.62
Li(Td)	~	~	~	~	~	~	2.52(6)
Li(Oh)	~	~	~	~	~	~	1.19(14)
Li(Oh)	~	~	~	~	~	~	1.19(14)
O	1.07(2)	0.709(14)	0.91(2)	–0.030(12)	–0.030(12)	–0.171(13)	0.89



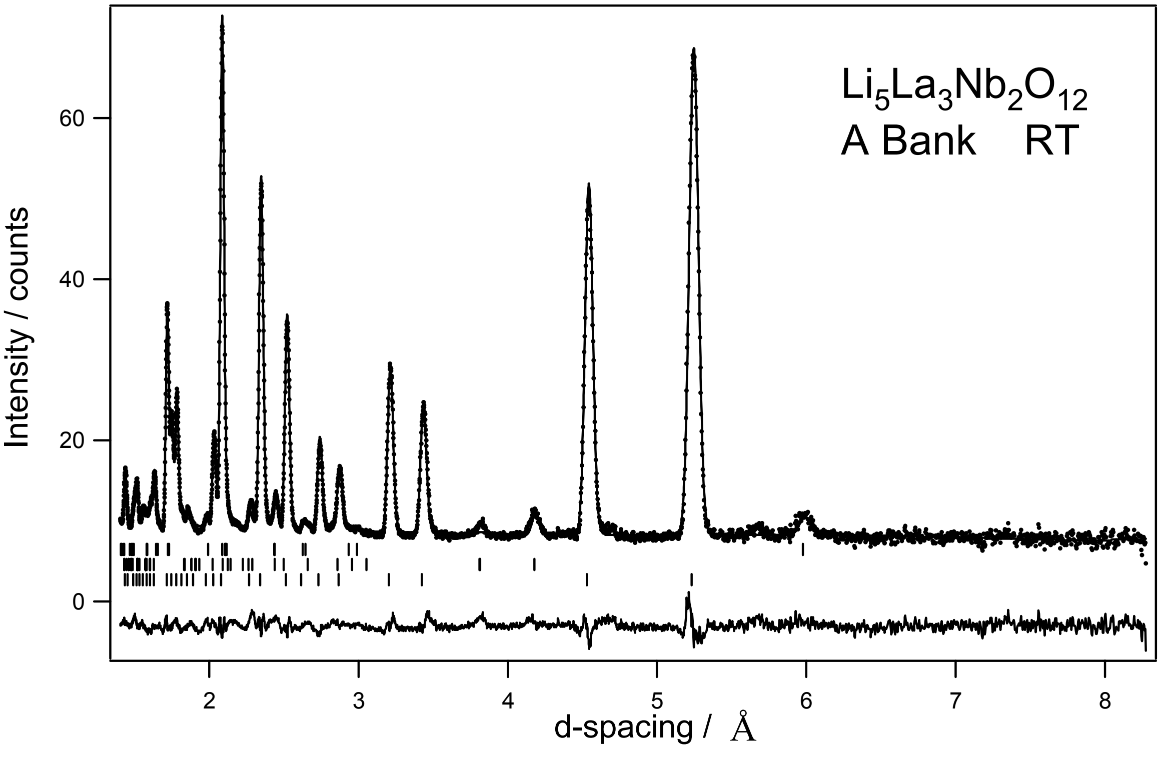


Fig. S4 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $Li_5La_3Nb_2O_{12}$ at room temperature. The lowest set of markers indicates the reflections due to the garnet phase.

Lattice Energy Calculations

Lattice energy calculations were carried out using the General Utility Lattice Program written and supplied by Dr J. D. Gale. The calculations used the interatomic potentials derived by Bush *et al.* from a range of oxide structures and supplemented by the Nb^{5+} potential derived by R. Jackson and M.E.G. Valerio, *J. Phys.: Condensed Matter,* 2005, **17**, 837. This Nb^{5+} potential was derived to be used in conjunction with the values of Bush *et al.* No suitable potential was available for Ta^{5+} so the calculations were all performed for the compounds of stoichiometry $Li_5La_3Nb_2O_{12}$ and used the structure refined from the room temperature neutron diffraction data as a starting model for the lattice energy minimisation. The minimisations were carried out in the space group determined from the neutron diffraction experiments ($Ia\bar{3}d$).

The Li^+ and Nb^{5+} cations were described with a core model with electrostatic charges of +1 and +5 respectively. The La^{3+} and O^{2-} species used a more complex description to model the polarisability of these cations. The La^{3+} was modelled using a core with charge +5.149 and a massless shell of –2.149 although the symmetry of the structure constrained both to the same fixed, special position 24*c*. The oxide anions were modelled with a core, +0.86902, and shell, –2.86902 which occupied independent general positions within the unit cell.

The Buckingham potentials and core/shell spring constants were taken from the literature examples.

Due to the similarity in the disordered octahedral lithium positions the calculations were performed with the octahedral lithium accommodated exclusively on the 96*h* site. The electrostatic interactions between the disordered Li^+ in the octahedral and tetrahedral positions could not be effectively modelled using mean–field theory due to the presence of clustering in the material. In order to account for this clustering the electrostatic interactions between Li^+ at a separation of <1.9 Å were excluded. i.e. Li^+ in the octahedra would not experience the charge associated with the nearest tetrahedrally coordinated Li^+ (1.50 Å)but would interact with the more distant neighbour at a distance of 2.38 Å.

The lattice parameters of the resulting minimised lattice (12.588 Å) showed a reasonable agreement ($\Delta a = -1.6$ %) with those derived experimentally from the neutron powder diffraction data (12.79432 Å). This level of agreement compares well with that calculated for the garnet $Y_3Fe_5O_{12}$ in the original paper by Bush *et al.* [$a_{obs} = 12.376$, $a_{calc} = 12.518$ Å $\Delta a = +1.6$ %].

Bond Valence Sum Calculations

Bond valence sums were calculated using the program Soft BVS written by S. Adams ad made available through the website:
http://kristall.uni-mki.gwdg.de/softbv/

This develops the bond valence parameters reported by N.E. Brese and M.O'Keeffe, *Acta Cryst.*, (1991), **B47**, 192 by using a variable bond softness parameter. The calculations were carried using the structures refined from the neutron powder diffraction data collected at room temperature.