Supplementary Information

Lithium Dimer Formation in the Li-Conducting Garnets $Li_{5+x}Ba_xLa_{3-x}Ta_2O_{12}$ ($0<x\leq1.6$)

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Synthesis of $Li_{5+x}La_{3-x}Ba_xTa_2O_{12}$

Samples of $Li_{5+x}La_{3-x}Ba_xTa_2O_{12}$ were synthesised using standard ceramic methods from stoichiometric quantities of La_2O_3, Ta_2O_5 and $Ba(NO_3)_2$ and a 10 % excess of $^7LiOH.H_2O$ (>99% ^7Li). Isotopically enriched lithium hydroxide was used in order to reduce problems due to the high absorption cross section for neutrons of ^6Li. The powders were mixed and pressed into pellets of 13 mm diameter under a load of 2000 kg. The pellets were heated in air in an open alumina crucible from room temperature to 700 ^oC for 10 hours, followed by subsequent regrinding and heating from 700 ^oC to 900 ^oC for 24 hours. X–ray powder diffraction experiments showed that the sample contained a single phase that could be fitted as a garnet. Subsequent neutron diffraction experiments showed that the some of the samples contained small quantities of Li_2CO_3 (~1 wt%). Due to the negligible volatility of lanthanum and barium under the synthesis conditions the lithium content can be confidently assigned on the basis of charge balance. This is supported by the Vegard's law dependence of the lattice parameters as a function of target composition (see Figure 3 of main text).

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 a vanadium can 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 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.

$^{7}Li_{5.5}Ba_{0.5}La_{2.5}Ta_{2}O_{12}$ RT Polaris

The data were corrected for absorption using the GSAS “Debye-Scherrer” absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate. Impurities of 0.24 wt% Li_2CO_3 so sample is 99.76 wt% garnet. Weak Bragg peaks were also observed due to vanadium sample holder.

Space group Ia$\bar{3}$d: a = 12.91154(13) Å, vol. = 2152.46(7) Å^3

Bank E: R_{wp} = 3.26, R_p =3.96, Bank C: R_{wp} = 2.31 R_p =3.46, Bank A: R_{wp} = 3.93 R_p =4.41

Powder totals R_{wp} = 2.88, R_p = 3.93; χ^2 = 2.095 for 71 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 12 anisotropic and 2 isotropic displacement parameters, 1 phase fraction, 3 scale factors, 3 absorption corrections, 5 diffractometer constants, 6 profile parameters, 22 background parameters.

[Impurity variables, 5 lattice parameters, 2 phase fractions]

atom	site	frac	*x*	*y*	*z*
La	24*c*	$^5/_6$	$^1/_8$	0	$^1/_4$
Ba	24c	$^1/_6$	$^1/_8$	0	$^1/_4$
Ta	16*a*	1	0	0	0
Li	24*d*	0.677(6)	$^1/_4$	$^7/_8$	0
Li	48*g*	0.174(17)	$^1/_8$	0.6732(8)	0.5768(8)
Li	96*h*	0.202(7)	0.0932(9)	0.6883(6)	0.5771(5)
O	96*h*	1	0.28103(3)	0.10638(3)	0.20059(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	1.52(4)	0.92(2)	0.92(2)	0	0	0.48(2)	1.12
Ba	1.52(4)	0.92(2)	0.92(2)	0	0	0.48(2)	1.12
Ta	1.02(2)	1.02(2)	1.02(2)	0.09(2)	0.09(2)	0.09(2)	1.02
Li(Td)	~	~	~	~	~	~	3.74(12)
Li(Oh)	~	~	~	~	~	~	1.56(12)
Li(Oh)*	~	~	~	~	~	~	1.56(12)
O	1.83(3)	1.41(3)	2.08(3)	0.36(2)	0.26(2)	0.14(2)	1.78

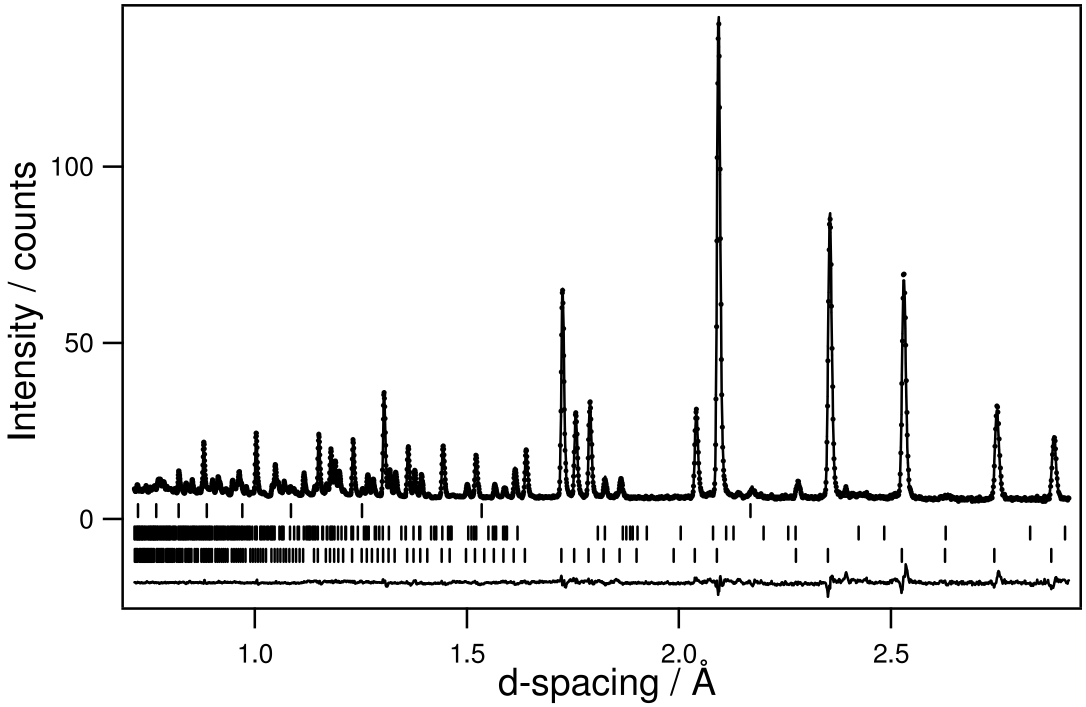


Fig. S1 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^{7}Li_{5.5}Ba_{0.5}La_{2.5}Ta_2O_{12}$ at room temperature using the C bank. The bottom, middle and top set of markers indicates the allowed reflections due to the garnet phase, Li_2CO_3, and the vanadium sample can respectively.

$^{7}Li_6BaLa_2Ta_2O_{12}$ RT Polaris

The data were corrected for absorption using the GSAS "Debye-Scherrer" absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate. The sample contains impurity of 0.96(2) wt% Li_2CO_3.

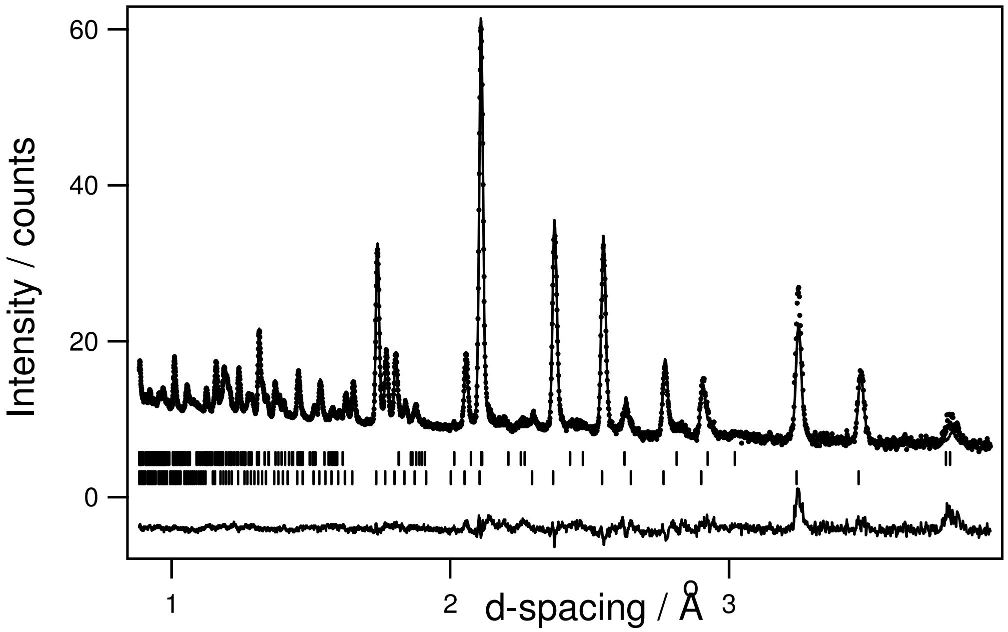
Space group $Ia\overline{3}d$: a = 13.0229(3) Å, vol. = 2208.64(13) Å^3
Bank E: R_{wp} = 2.38, R_p = 3.65, Bank C: R_{wp} = 1.98 R_p = 3.04, Bank A: R_{wp} = 3.98, R_p = 4.10

Powder totals R_{wp} = 2.33, R_p = 3.48; χ^2 = 3.60 for 69 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 12 anisotropic and 2 isotropic displacement parameters, 3 scale factors, 3 absorption corrections, 5 diffractometer constants, 6 profile parameters, 22 background parameters.
[Impurity variables, 4 lattice parameters, 1 phase fraction]

Atomic coordinates and displacement parameters are provided in **Table 1** of the main text.

Selected Interatomic Distances

Ba/La-O	2.5628(8) Å × 4	Li(48*g*)-O	1.926(10) Å × 2
Ba/La-O	2.6729(9) Å × 4	Li(48*g*)-O	2.358(10) Å × 2
		Li(48*g*)-O	2.609(14) Å × 2
Ta-O	1.9994(8) Å × 6		
		Li(96*h*)-O	1.788(9) Å
Li(Td)-O	1.9537(8) Å × 4	Li(96*h*)-O	2.047(14) Å
		Li(96*h*)-O	2.176(14) Å
Li(Td) - Li(96*h*)	1.56(2) Å	Li(96*h*)-O	2.369(14) Å
Li(Td) - Li(96*h*)	2.44(2) Å	Li(96*h*)-O	2.709(16) Å
Li(Td) - Li(48*g*)	2.00(2) Å	Li(96*h*)-O	2.867(14) Å



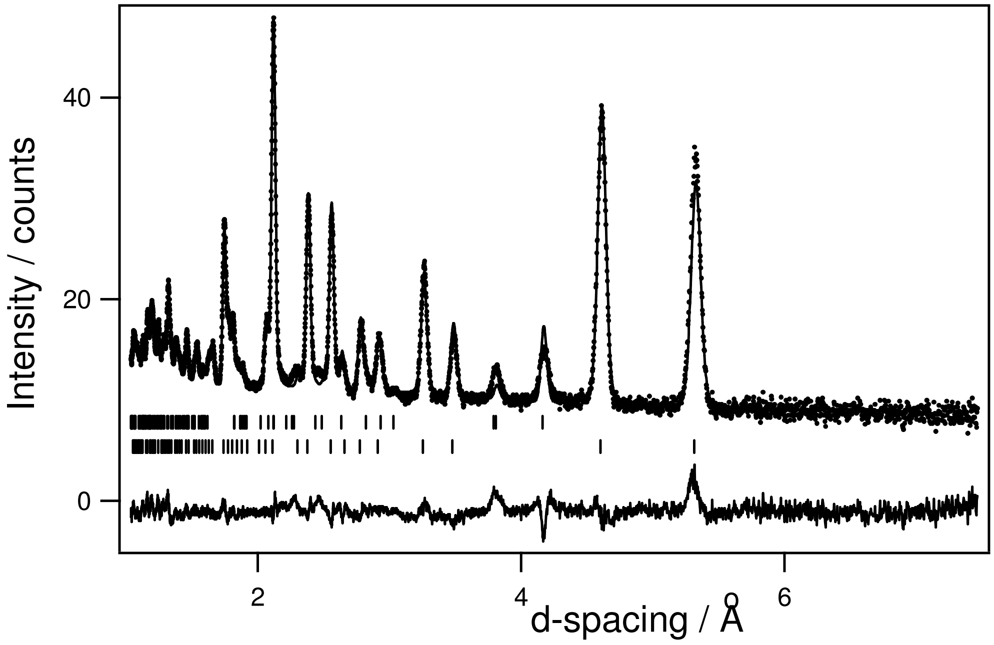


Fig. S2 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^7Li_6BaLa_2Ta_2O_{12}$ at room temperature using the A bank (top) and E bank (bottom). The lower and upper markers indicate the allowed reflections due to the garnet and Li_2CO_3 respectively.

$^{7}Li_6BaLa_2Ta_2O_{12}$ 600 ^{o}C Polaris

The data were corrected for absorption using the GSAS "Debye-Scherrer" absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate. Impurities of 1.79 wt% Li_2CO_3 so sample is 98.21 wt% garnet. The apparent change in Li_2CO_3 impurity level compared to the room temperature data is not unexpected as an increase in crystallinity of Li_2CO_3 on heating the sample would lead to an increase in observed Bragg intensity. Minor Bragg peaks are also present due to the vanadium sample holder.

Space group Ia$\bar{3}$d: a = 13.1045(3) Å, vol. = 2250.39(14) Å^{3}
Bank E: R_{wp} = 2.21, R_p =3.23, Bank C: R_{wp} = 1.51 R_p =2.50, Bank A: R_{wp} = 3.64 R_p = 4.01
Powder totals R_{wp} = 1.90, R_p = 3.07; χ^2 = 2.064 for 72 variables including 1 lattice parameter, 2 fractional occupancies [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 11 anisotropic and 2 isotropic displacement parameters, 2 scale factors, 3 absorption corrections, 5 diffractometer constants, 9 profile parameters, 22 background parameters.
[Impurity variables, 5 lattice parameters, 2 phase fraction]

atom	site	frac	*x*	*y*	*z*
La	24*c*	$^{1}/_{3}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ba	24c	$^{2}/_{3}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ta	16*a*	1	0	0	0
Li	24*d*	0.601(13)	$^{1}/_{4}$	$^{7}/_{8}$	0
Li	48*g*	0.281(17)	$^{1}/_{8}$	0.6779(5)	0.5721(5)
Li	96*h*	0.209(5)	0.0820(9)	0.6899(8)	0.5834(6)
O	96*h*	1	0.28149(6)	0.10770(5)	0.20303(6)

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	2.15(8)	1.67(4)	1.67(4)	0	0	0.35(5)	1.83
Ba	2.15(8)	1.67(4)	1.67(4)	0	0	0.35(5)	1.83
Ta	1.51(3)	1.51(3)	1.51(3)	0.16(4)	0.16(4)	0.16(4)	1.51
Li(Td)	~	~	~	~	~	~	8.7(5)
Li(Oh)	~	~	~	~	~	~	1.64(18)
Li(Oh)*	~	~	~	~	~	~	1.64(18)
O	3.50(6)	2.23(5)	3.89(7)	0.62(4)	0.51(4)	0.27(4)	3.21

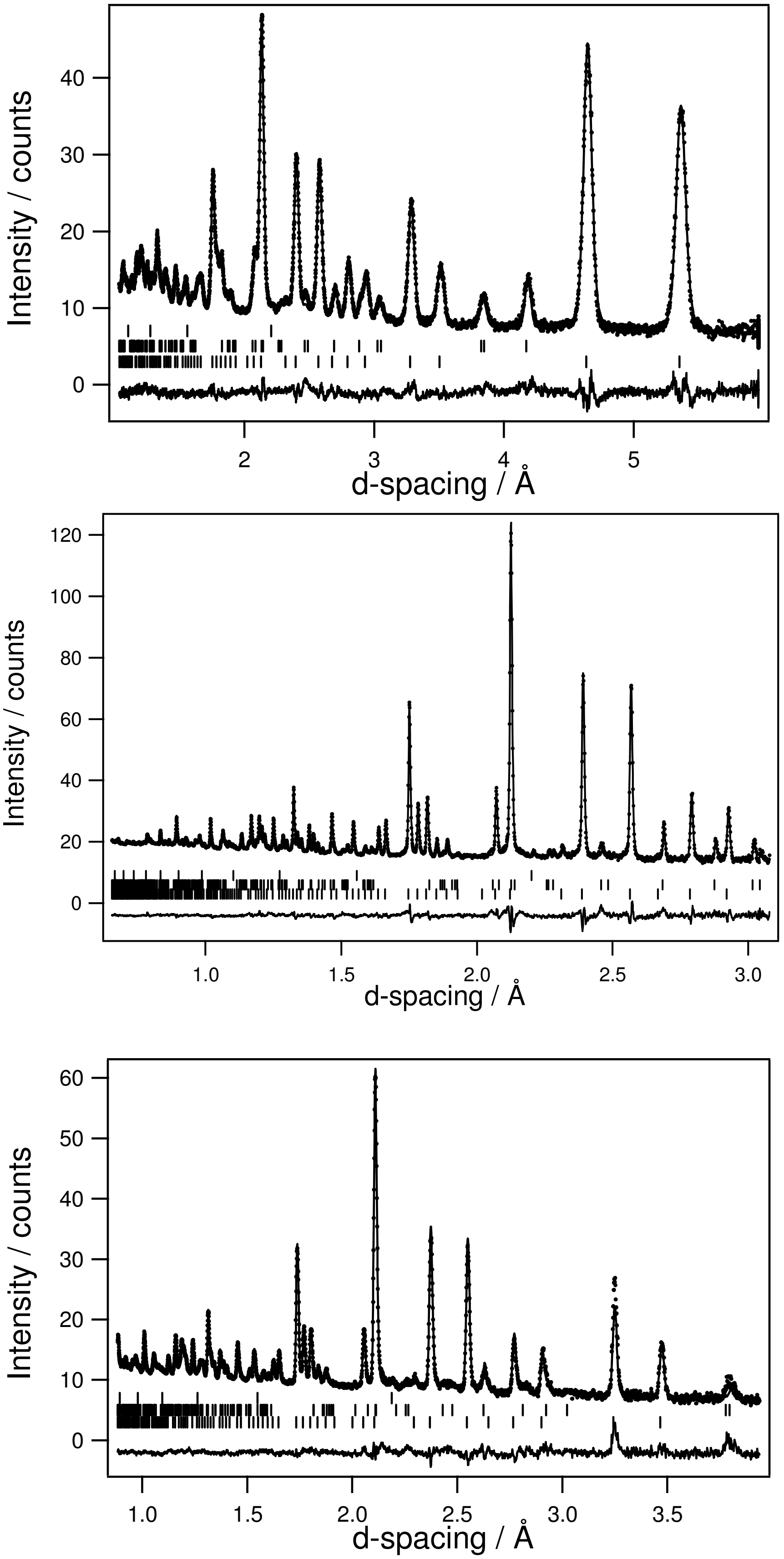


Fig. S3 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^{7}Li_6BaLa_2Ta_2O_{12}$ at 600 °C from (top to bottom) the A, C and E banks. The bottom, middle and top sets of markers indicates the reflections due to garnet, Li_2CO_3 and the vanadium sample can respectively.

$^{7}Li_{6.2}Ba_{1.2}La_{1.8}Ta_2O_{12}$ RT Polaris

The data were corrected for absorption using the GSAS “Debye-Scherrer” absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate.

Space group $Ia\bar{3}d$: a = 13.03391(16) Å, vol. = 2214.24(8) Å^3

Bank E: R_{wp} = 3.63, R_p =4.11, Bank C: R_{wp} = 2.35 R_p =3.92, Bank A: R_{wp} = 4.83 R_p =5.33

Powder totals R_{wp} = 2.78, R_p = 4.44; χ^2 = 3.369 for 65 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 12 anisotropic and 2 isotropic displacement parameters, 3 scale factors, 3 absorption corrections, 5 diffractometer constants, 7 profile parameters, 22 background parameters.

atom	site	frac	*x*	*y*	*z*
La	24*c*	$^{3}/_{5}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ba	24c	$^{2}/_{5}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ta	16*a*	1	0	0	0
Li	24*d*	0.567(8)	$^{1}/_{4}$	$^{7}/_{8}$	0
Li	48*g*	0.265(12)	$^{1}/_{8}$	0.6752(4)	0.5748(4)
Li	96*h*	0.243(4)	0.0882(5)	0.6909(4)	0.5820(4)
O	96*h*	1	0.28266(4)	0.10779(4)	0.20273(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	1.60(4)	0.95(2)	0.95(2)	0	0	0.31(2)	1.16
Ba	1.60(4)	0.95(2)	0.95(2)	0	0	0.31(2)	1.16
Ta	1.09(2)	1.09(2)	1.09(2)	0.24(2)	0.24(2)	0.24(2)	1.09
Li(Td)	~	~	~	~	~	~	4.91(18)
Li(Oh)	~	~	~	~	~	~	1.30(9)
Li(Oh)*	~	~	~	~	~	~	1.30(9)
O	2.76(3)	1.68(2)	2.80(3)	0.62(2)	0.62(2)	0.32(2)	2.41

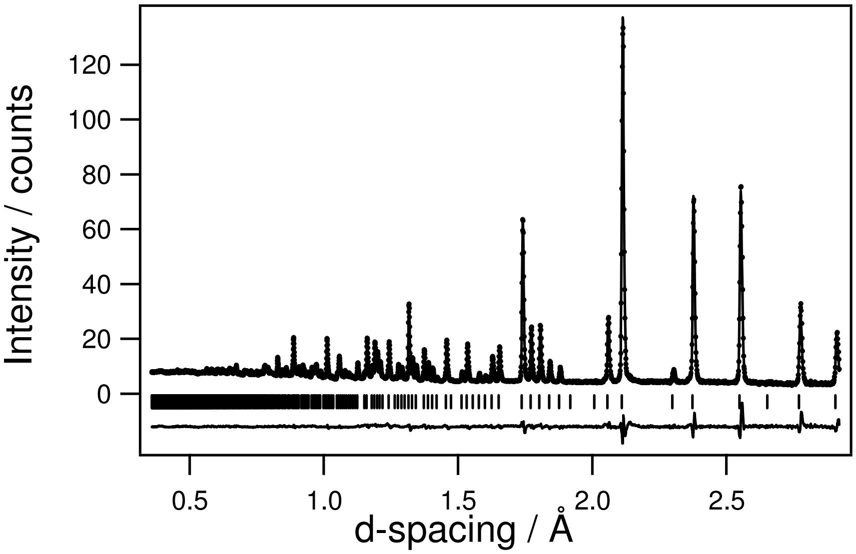


Fig. S4 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^{7}Li_{6.2}Ba_{1.2}La_{1.8}Ta_2O_{12}$ from the C bank at room temperature.

$^{7}Li_{6.4}Ba_{1.4}La_{1.6}Ta_{2}O_{12}$ RT Polaris

The data were corrected for absorption using the GSAS "Debye-Scherrer" absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate.

Space group Ia$\overline{3}$d: a = 13.07332(18) Å, vol. = 2234.38(9) Å^{3}

Bank E: R_{wp} = 3.83, R_p =4.25, Bank C: R_{wp} = 2.50 R_p =4.29, Bank A: R_{wp} = 4.69 R_p =5.09

Powder totals R_{wp} = 2.91, R_p = 4.53; χ^2 = 3.618 for 65 variables including 1 lattice parameter, 2 fractional occupancy [Td vs Oh, and Oh(centre)vs Oh(displaced)], 8 atomic parameters, 12 anisotropic and 2 isotropic displacement parameters, 3 scale factors, 3 absorption corrections, 5 diffractometer constants, 7 profile parameters, 22 background parameters.

atom	site	frac	*x*	*y*	*z*
La	24*c*	$^{8}/_{15}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ba	24c	$^{7}/_{15}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ta	16*a*	1	0	0	0
Li	24*d*	0.522(8)	$^{1}/_{4}$	$^{7}/_{8}$	0
Li	48*g*	0.273(13)	$^{1}/_{8}$	0.6749(4)	0.5751(4)
Li	96*h*	0.259(4)	0.0875(5)	0.6903(5)	0.5838(4)
O	96*h*	1	0.28324(4)	0.10832(4)	0.20314(5)

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	1.53(5)	0.89(2)	0.89(2)	0	0	0.24(3)	1.10
Ba	1.53(5)	0.89(2)	0.89(2)	0	0	0.24(3)	1.10
Ta	1.17(2)	1.17(2)	1.17(2)	0.25(3)	0.25(3)	0.25(3)	1.17
Li(Td)	~	~	~	~	~	~	5.18(22)
Li(Oh)	~	~	~	~	~	~	1.40(9)
Li(Oh)*	~	~	~	~	~	~	1.40(9)
O	3.05(4)	1.76(3)	2.89(4)	0.70(2)	0.72(3)	0.42(2)	2.57

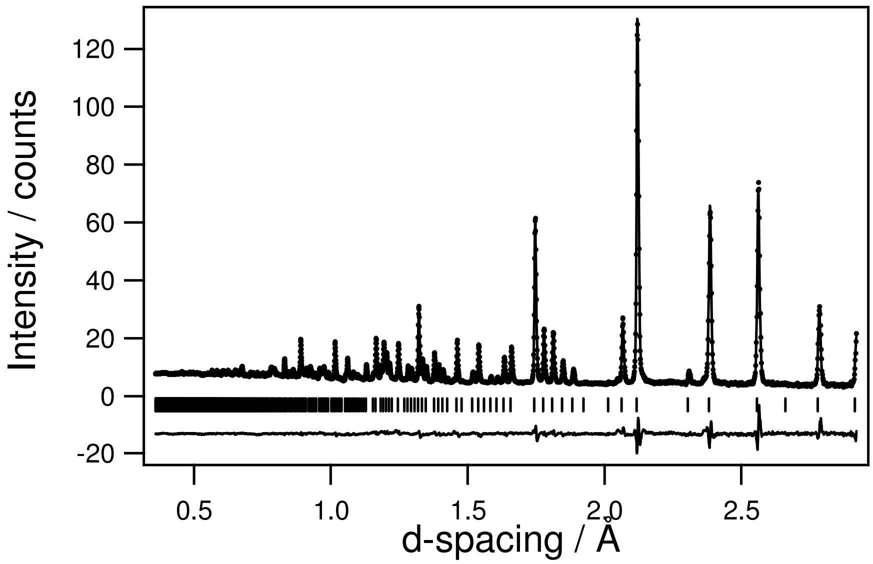


Fig. S5 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^{7}Li_{6.4}Ba_{1.4}La_{1.6}Ta_2O_{12}$ from the C bank at room temperature.

$^{7}Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$ RT Polaris

The data were corrected for absorption using the GSAS "Debye-Scherrer" absorption correction. The sample was made using 99.99% ^{7}Li, lithium hydroxide monohydrate. Impurities of 0.43 wt% Li_2CO_3 so sample is 99.57 wt% garnet

Space group $Ia\bar{3}d$: a = 13.12551(23) Å, vol. = 2261.25(12) Å^3

Bank E: R_{wp} = 1.96, R_p = 2.89, Bank C: R_{wp} = 1.62 R_p = 2.03, Bank A: R_{wp} = 2.85 R_p = 2.95

Powder totals R_{wp} = 1.79, R_p = 2.48; χ^2 = 3.212 for 70 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, 2 scale factors, 1 phase fraction, 3 absorption corrections, 5 diffractometer constants, 9 profile parameters, 22 background parameters.

[Impurity variables, 1 phase fraction, 4 lattice parameters]

atom	site	frac	*x*	*y*	*z*
La	24*c*	$^{8}/_{15}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ba	24c	$^{7}/_{15}$	$^{1}/_{8}$	0	$^{1}/_{4}$
Ta	16*a*	1	0	0	0
Li	24*d*	0.568(14)	$^{1}/_{4}$	$^{7}/_{8}$	0
Li	48*g*	0.249(24)	$^{1}/_{8}$	0.6690(8)	0.5810(8)
Li	96*h*	0.283(8)	0.0908(9)	0.6892(7)	0.5771(5)
O	96*h*	1	0.28364(7)	0.10897(6)	0.20368(7)

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	1.32(8)	1.06(5)	1.06(5)	0	0	0.43(5)	1.14
Ba	1.32(8)	1.06(5)	1.06(5)	0	0	0.43(5)	1.14
Ta	1.38(4)	1.38(4)	1.38(4)	0.34(5)	0.34(5)	0.34(5)	1.38
Li(Td)	~	~	~	~	~	~	7.9(5)
Li(Oh)	~	~	~	~	~	~	0.95(16)
Li(Oh)*	~	~	~	~	~	~	0.95(16)
O	2.87(6)	2.29(5)	2.96(7)	0.48(4)	0.70(4)	0.59(4)	2.71

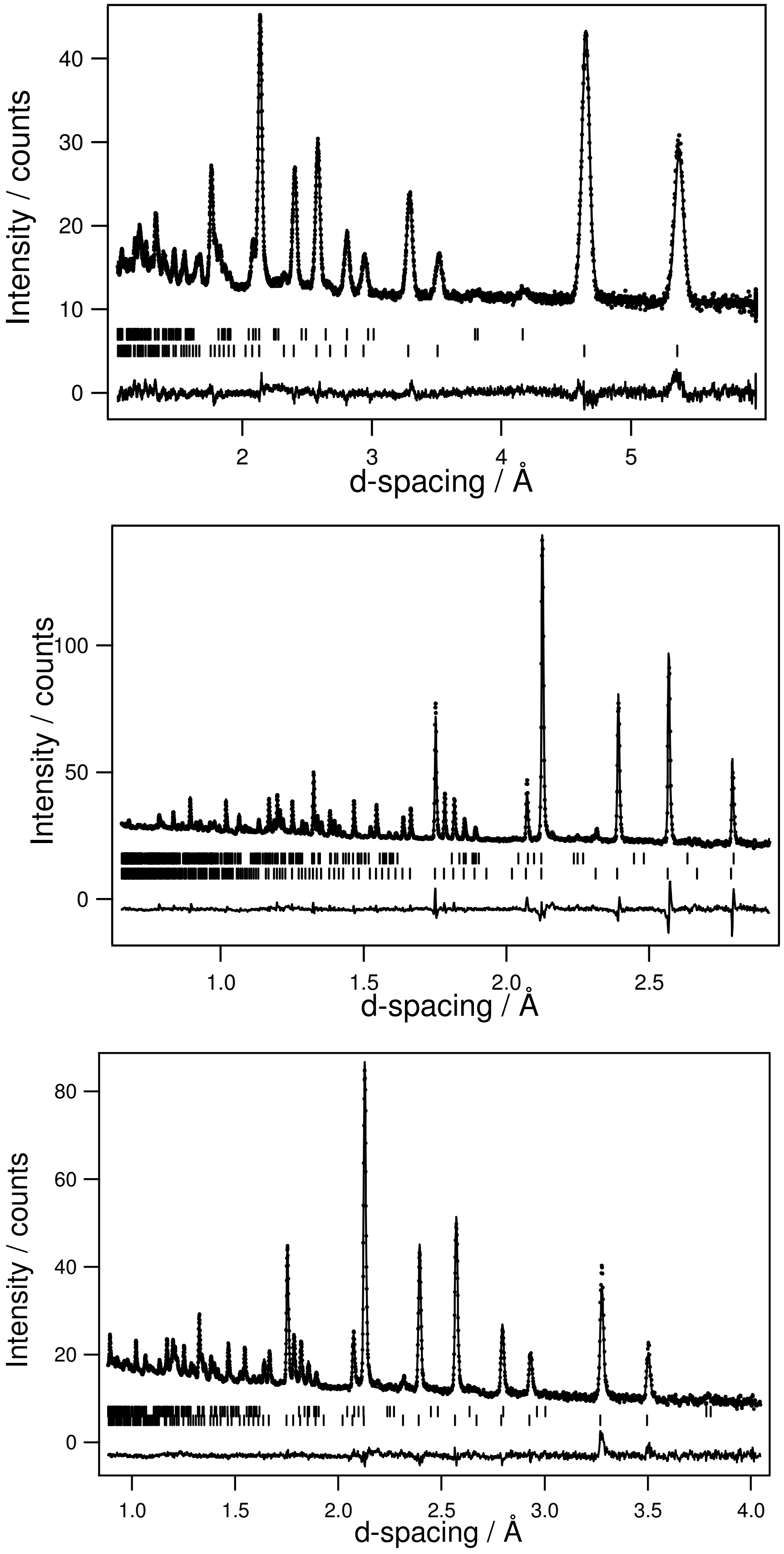


Fig. S6 Observed (dots), calculated (line) and difference neutron powder diffraction data collected from $^7Li_{6.6}Ba_{1.6}La_{1.4}Ta_2O_{12}$ from (top to bottom) the A, C and E banks at room temperature. The lower set of markers indicates the reflections due to the garnet phase, the top set are due to Li_2CO_3.