Electronic Supplementary Information (ESI)

$Li_7Ba_3Al_3O_{11}$: A new super-tetrahedral oxide

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Table S1 Site occupancies, atomic coordinates and equivalent isotropic displacement parameters (U_{eq}) for $Li_7Ba_3Al_3O_{11}$

Atom	Wyckoff site	Occ.	*x*	*y*	*z*	U_{eq}*
Ba1	8*m*	1	0.20763(2)	0.50229(2)	0.50110(2)	0.00920(4)
Ba2	8*m*	1	0.00223(2)	0.29239(2)	0.50132(2)	0.00924(4)
Ba3	8*m*	1	0.00113(2)	0.00139(2)	0.20777(2)	0.00919(4)
Li1	8*m*	1	0.5888(6)	0.0968(6)	0.0925(5)	0.0139(15)
Li2	8*m*	1	0.4040(5)	0.0915(6)	0.0897(5)	0.0134(15)
Li3	8*m*	1	0.0939(5)	0.0880(5)	0.5954(5)	0.0124(15)
Li4	8*m*	1	0.0913(6)	0.5937(6)	0.0928(6)	0.0158(16)
Li/Al5	4*l*	0.532(7)/0.468	1/4	3/4	0.5881(2)	0.0101(8)
Li/Al6	4*l*	0.478(6)/0.522	1/4	3/4	0.0881(2)	0.0075(7)
Li/Al7	4*k*	0.152(6)/0.848	1/4	1/4	0.58603(14)	0.0072(5)
Li/Al8	4*k*	0.857(7)/0.143	1/4	1/4	0.0955(4)	0.0091(14)
Li/Al9	4*j*	0.977(7)/0.023	3/4	0.6042(7)	1/4	0.020(3)
Al10	4*j*	1	3/4	0.08523(12)	1/4	0.0063(3)
Li/Al11	4*i*	0.404(6)/0.596	1/4	0.58692(18)	1/4	0.0059(6)
Li/Al12	4*i*	0.614(7)/0.386	1/4	0.0887(3)	1/4	0.0115(9)
Li/Al13	4*h*	0.646(7)/0.354	0.5896(3)	1/4	3/4	0.0121(9)
Li/Al14	4*h*	0.358(6)/0.642	0.08672(18)	1/4	3/4	0.0072(6)
Li/Al15	4*g*	0.947(7)/0.053	0.6018(7)	1/4	1/4	0.019(2)
Li/Al16	4*g*	0.034(6)/0.966	0.08528(12)	1/4	1/4	0.0060(4)
O1	8*m*	1	0.6726(2)	0.1547(2)	0.3355(2)	0.0187(7)
O2	8*m*	1	0.67166(19)	0.0060(2)	0.17565(19)	0.0090(5)
O3	8*m*	1	0.3324(3)	0.6613(3)	0.1638(3)	0.0284(8)
O4	8*m*	1	0.3246(2)	−0.0020(2)	0.1717(2)	0.0121(6)
O5	8*m*	1	0.16956(17)	0.67823(17)	0.0008(2)	0.0119(5)
O6	8*m*	1	0.17810(17)	0.16959(17)	0.5045(2)	0.0104(5)
O7	8*m*	1	0.1612(3)	0.3262(2)	0.6580(2)	0.0219(7)
O8	8*m*	1	0.1550(3)	0.1662(3)	0.1706(2)	0.0229(8)
O9	8*m*	1	0.0059(2)	0.32381(18)	0.17144(18)	0.0098(5)
O10	8*m*	1	−0.0019(2)	0.67109(18)	0.17627(18)	0.0110(5)
O11	4*f*	1	0	0	0	0.0108(5)
O12	4*e*	1	1/2	1/2	1/2	0.0091(5)

* $U_{eq} = (\sum_i \sum_j U_{ij}\, a_i^* a_j^*\, a_i \cdot a_j)/3$

Table S2 Anisotropic displacement parameters (U_{ij} / Å^2) for $Li_7Ba_3Al_3O_{11}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.00645(7)	0.01051(8)	0.01064(7)	0.00039(7)	0.00021(10)	−0.00037(8)
Ba2	0.01010(8)	0.00692(7)	0.01071(8)	−0.00061(7)	−0.00049(9)	−0.00032(8)
Ba3	0.01015(8)	0.01059(8)	0.00682(7)	−0.00016(7)	0.00025(10)	0.00021(8)
Li1	0.014(4)	0.015(4)	0.012(3)	0.009(3)	0.004(3)	0.007(3)
Li2	0.012(4)	0.016(4)	0.012(3)	−0.004(3)	−0.007(3)	0.002(3)
Li3	0.013(4)	0.013(3)	0.012(3)	0.006(3)	0.001(3)	0.007(3)
Li4	0.016(4)	0.013(4)	0.018(4)	0.002(3)	0.004(3)	0.007(3)
Li/Al5	0.0076(14)	0.0124(15)	0.0104(14)	0.0002(11)	0	0
Li/Al6	0.0084(13)	0.0034(12)	0.0108(12)	−0.0013(10)	0	0
Li/Al7	0.0054(9)	0.0096(9)	0.0067(8)	−0.0018(7)	0	0
Li/Al8	0.010(3)	0.005(2)	0.012(3)	0.001(2)	0	0
Li/Al9	0.029(6)	0.003(4)	0.028(5)	0	−0.002(4)	0
Al10	0.0083(7)	0.0040(6)	0.0067(7)	0	−0.0021(6)	0
Li/Al11	0.0042(11)	0.0088(11)	0.0049(10)	0	−0.0015(9)	0
Li/Al12	0.0095(17)	0.0147(17)	0.0103(16)	0	0.0012(13)	0
Li/Al13	0.0114(18)	0.0116(17)	0.0132(18)	0	0	−0.0004(14)
Li/Al14	0.0081(11)	0.0089(11)	0.0048(10)	0	0	−0.0025(8)
Li/Al15	0.018(4)	0.020(4)	0.021(4)	0	0	−0.004(3)
Li/Al16	0.0042(8)	0.0070(7)	0.0069(7)	0	0	0.0019(6)
O1	0.0183(13)	0.0181(13)	0.0198(13)	0.0126(10)	−0.0035(11)	−0.0037(10)
O2	0.0090(12)	0.0091(14)	0.0089(12)	0.0002(10)	−0.0029(10)	−0.0006(10)
O3	0.028(2)	0.031(2)	0.0260(19)	−0.0045(15)	−0.0036(15)	0.0047(15)
O4	0.0087(12)	0.0168(17)	0.0108(12)	−0.0019(11)	0.0041(10)	−0.0012(11)
O5	0.0087(10)	0.0076(10)	0.0193(14)	−0.0027(8)	0.0010(13)	−0.0019(12)
O6	0.0078(10)	0.0094(10)	0.0140(13)	−0.0029(8)	−0.0009(12)	0.0018(11)
O7	0.0263(18)	0.0183(16)	0.0209(16)	−0.0103(13)	0.0029(14)	−0.0135(12)
O8	0.0194(17)	0.0282(18)	0.0212(17)	0.0072(13)	0.0139(13)	0.0023(13)
O9	0.0126(15)	0.0083(11)	0.0087(11)	0.0013(11)	0.0013(11)	0.0021(9)
O10	0.0146(16)	0.0096(11)	0.0088(11)	0.0013(11)	−0.0019(12)	−0.0033(9)
O11	0.0099(13)	0.0110(13)	0.0114(13)	−0.0011(14)	0.0018(17)	0.0005(15)
O12	0.0096(13)	0.0084(13)	0.0093(13)	−0.0023(13)	0.0000(18)	0.0016(15)

Table S3 Selected inter atomic distances (Å) for $Li_7Ba_3Al_3O_{11}$

Ba1—O6	2.719(3)	Ba2—O5	2.717(3)	Ba3—O11	2.7296(3)
Ba1—O11	2.7348(3)	Ba2—O11	2.7353(3)	Ba3—O10	2.736(3)
Ba1—O4	2.743(3)	Ba2—O9	2.738(3)	Ba3—O2	2.744(3)
Ba1—O2	2.791(3)	Ba2—O10	2.799(3)	Ba3—O4	2.789(3)
Ba1—O5	2.827(3)	Ba2—O6	2.826(3)	Ba3—O9	2.797(3)
Ba1—O1	2.975(3)	Ba2—O7	2.970(4)	Ba3—O8	3.010(4)
Ba1—O3	3.059(4)	Ba2—O8	3.074(4)	Ba3—O1	3.105(3)
Ba1—O7	3.163(3)	Ba2—O3	3.151(4)	Ba3—O3	3.120(4)
Ba1—O8	3.240(4)	Ba2—O1	3.246(3)	Ba3—O7	3.213(4)
Li1—O9	1.930(8)	Li2—O6	1.939(8)		
Li1—O5	1.945(8)	Li2—O4	1.942(8)		
Li1—O2	1.953(8)	Li2—O9	1.951(8)		
Li1—O12	2.114(8)	Li2—O12	2.107(8)		
Li3—O2	1.922(8)	Li4—O10	1.936(9)		
Li3—O10	1.948(8)	Li4—O4	1.939(9)		
Li3—O6	1.952(8)	Li4—O5	1.940(9)		
Li3—O12	2.108(7)	Li4—O12	2.111(8)		
Li/Al5—O5 (2×)	1.839(3)	Li/Al6—O5 (2×)	1.825(3)		
Li/Al5—O1 (2×)	1.903(3)	Li/Al6—O3 (2×)	1.879(5)		
Li/Al7—O6 (2×)	1.779(3)	Li/Al8—O6 (2×)	1.935(5)		
Li/Al7—O7 (2×)	1.808(4)	Li/Al8—O8 (2×)	1.938(5)		
Li/Al9—O7 (2×)	1.916(6)	Al10—O2 (2×)	1.763(3)		
Li/Al9—O2 (2×)	2.031(8)	Al10—O1 (2×)	1.772(3)		
Li/Al11—O4 (2×)	1.810(4)	Li/Al12—O4 (2×)	1.858(4)		
Li/Al11—O3 (2×)	1.849(5)	Li/Al12—O8 (2×)	1.923(5)		
Li/Al13—O10 (2×)	1.863(4)	Li/Al14—O10 (2×)	1.807(3)		
Li/Al13—O3 (2×)	1.924(5)	Li/Al14—O7 (2×)	1.852(4)		
Li/Al15—O1 (2×)	1.925(6)	Li/Al16—O9 (2×)	1.762(3)		
Li/Al15—O9 (2×)	2.006(7)	Li/Al16—O8 (2×)	1.775(4)		

Table S4 Crystallographic data of $Li_7Ba_3Al_3O_{11}$ derived from Rietveld refinement of powder XRD data

Chemical formula		$Li_7Ba_3Al_3O_{11}$
Temperature, T (K)		300(2)
Crystal system		Orthorhombic
Space group		*Pnnn* (No.48)
Unit-cell dimensions	a (Å)	13.19876(19)
	b (Å)	13.21251(19)
	c (Å)	13.12913(13)
Unit-cell volume, V (Å^3)		2289.57(5)
Z		8
Calculated density, D_{cal} (Mg m^{-3})		4.1631(1)
Radiation wavelength, λ (Å)		1.54059/1.54432
2θ range for date collection (°)		5.0 – 140.0
Reflections collected		5448
R_p , R_{wp}		0.0412, 0.0562
R_B		0.01598

$R_p = \Sigma|Y_{o,m} - Y_{c,m}|/\Sigma Y_{o,m}$, $R_{wp} = [\Sigma w_m(Y_{o,m} - Y_{c,m})^2/\Sigma w_m Y_{o,m}^2]^{1/2}$, $w_m = 1/\sigma(Y_{o,m})$, $R_B = \Sigma|I_{"o",k} - I_{c,k}|/\Sigma I_{"o",k}$, where $Y_{o,m}$ and $Y_{c,m}$ are the observed and calculated data, respectively at data point m; $\sigma(Y_{o,m})$ is the error in $Y_{o,m}$, and $I_{"o",k}$ and $I_{c,k}$ are the observed and calculated intensities of the kth reflection.

Table S5 Site occupancies, atomic coordinates and isotropic displacement parameters (U_{iso}) refined by Rietveld analysis for the powder XRD pattern of $Li_7Ba_3Al_3O_{11}$

Atom	Wyckoff site	Occ.	*x*	*y*	*z*	U_{iso}
Ba1	8*m*	1	0.2073(3)	0.5016(9)	0.5011(14)	0.811(15)
Ba2	8*m*	1	0.0032(8)	0.2922(3)	0.5024(8)	0.811†
Ba3	8*m*	1	−0.0007(13)	0.0014(9)	0.20786(12)	0.811†
Li1	8*m*	1	0.541(6)	0.097(7)	0.120(7)	0.35(8)
Li2	8*m*	1	0.41(2)	0.10(2)	0.095(17)	0.35‡
Li3	8*m*	1	0.087(19)	0.091(17)	0.587(11)	0.35‡
Li4	8*m*	1	0.100(14)	0.604(15)	0.093(16)	0.35‡
Li/Al5	4*l*	0.532/0.468*	1/4	3/4	0.59(1)	0.35‡
Li/Al6	4*l*	0.478/0.522*	1/4	3/4	0.087(11)	0.35‡
Li/Al7	4*k*	0.152/0.848*	1/4	1/4	0.586(7)	0.35‡
Li/Al8	4*k*	0.857/0.143*	1/4	1/4	0.127(5)	0.35‡
Li/Al9	4*j*	0.977/0.023*	3/4	0.618(11)	1/4	0.35‡
Al10	4*j*	1	3/4	0.087(6)	1/4	0.35‡
Li/Al11	4*i*	0.404/0.596*	1/4	0.596(8)	1/4	0.35‡
Li/Al12	4*i*	0.614/0.386*	1/4	0.074(8)	1/4	0.35‡
Li/Al13	4*h*	0.646/0.354*	0.59(1)	1/4	3/4	0.35‡
Li/Al14	4*h*	0.358/0.642*	0.074(5)	1/4	3/4	0.35‡
Li/Al15	4*g*	0.947/0.053*	0.58(2)	1/4	1/4	0.35‡
Li/Al16	4*g*	0.034/0.966*	0.093(4)	1/4	1/4	0.35‡
O1	8*m*	1	0.679(6)	0.144(7)	0.330(5)	0.35‡
O2	8*m*	1	0.676(6)	0.006(6)	0.170(6)	0.35‡
O3	8*m*	1	0.331(6)	0.644(7)	0.161(6)	0.35‡
O4	8*m*	1	0.325(7)	0.0030(9)	0.176(7)	0.35‡
O5	8*m*	1	0.173(6)	0.671(6)	0.007(6)	0.35‡
O6	8*m*	1	0.173(6)	0.171(6)	0.495(6)	0.35‡
O7	8*m*	1	0.172(7)	0.334(6)	0.667(5)	0.35‡
O8	8*m*	1	0.164(7)	0.168(7)	0.159(5)	0.35‡
O9	8*m*	1	−0.003(8)	0.326(5)	0.170(5)	0.35‡
O10	8*m*	1	−0.004(9)	0.666(4)	0.185(4)	0.35‡
O11	4*f*	1	0	0	0	0.35‡
O12	4*e*	1	1/2	1/2	1/2	0.35‡

***** The values were fixed with the occupancies shown in Table S1.

† U_{iso} was constrained with U_{iso} of Ba1.

‡ U_{iso} was constrained with U_{iso} of Li1.

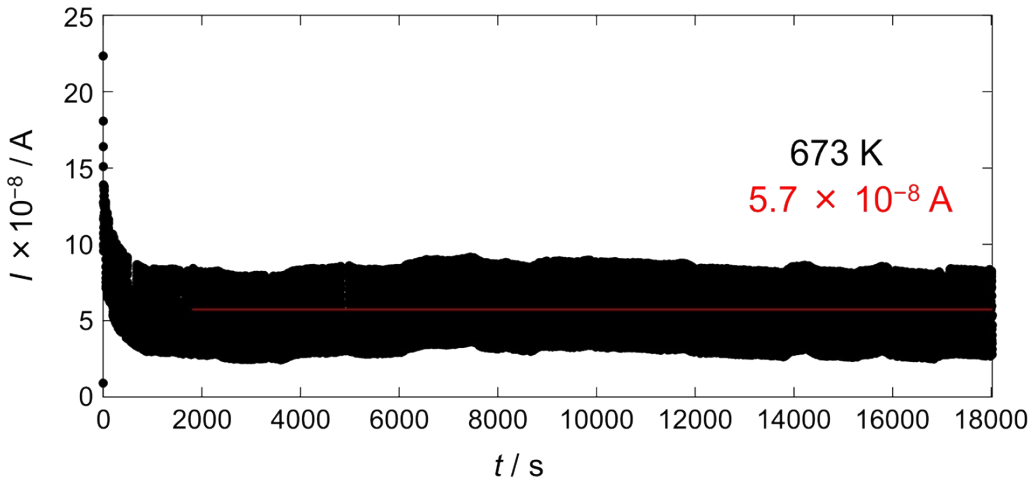

Fig. S1 Current versus time measured with Ni plate electrodes (0.1 mm thick) under an applied voltage of 5V for the polycrystalline sample of $Li_7Ba_3Al_3O_{11}$ in an Ar-filled glove box at 673 K.