Lithium Diffusion Pathways in Metastable Ramsdellite-Like $Li_2Ti_3O_7$ from High-Temperature Neutron Diffraction

Supporting Information

Dennis Wiedemann[a,], Suliman Nakhal[a], Alexandra Franz[b], Martin Lerch[a]*

[a] Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

[b] Abteilung Struktur und Dynamik von Energiematerialien, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1,14109 Berlin, Germany

1 Neutron Diffraction

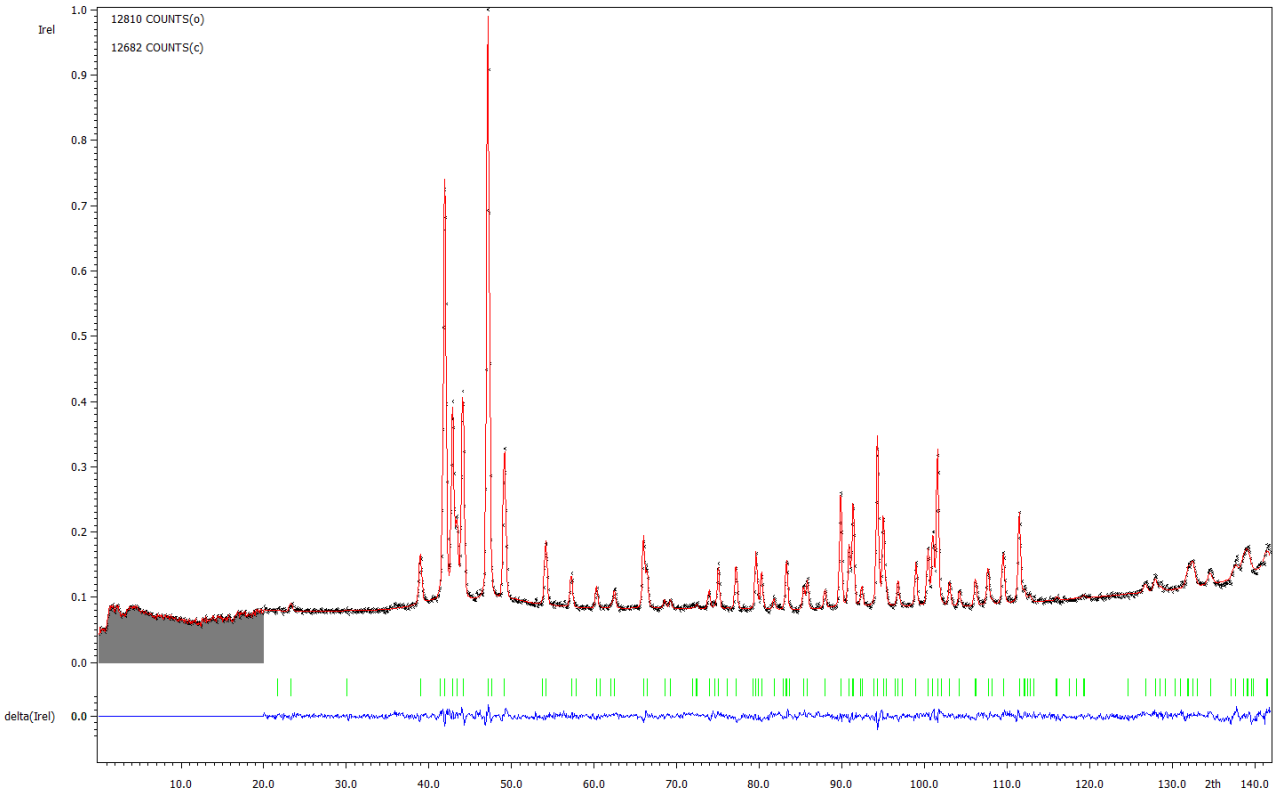

Fig. S1. Neutron powder diffractogram of $Li_2Ti_3O_7$ at 201 °C with results of Rietveld refinement (black: measured, red: calculated, gray: excluded region, green: Bragg position, blue: intensity difference).

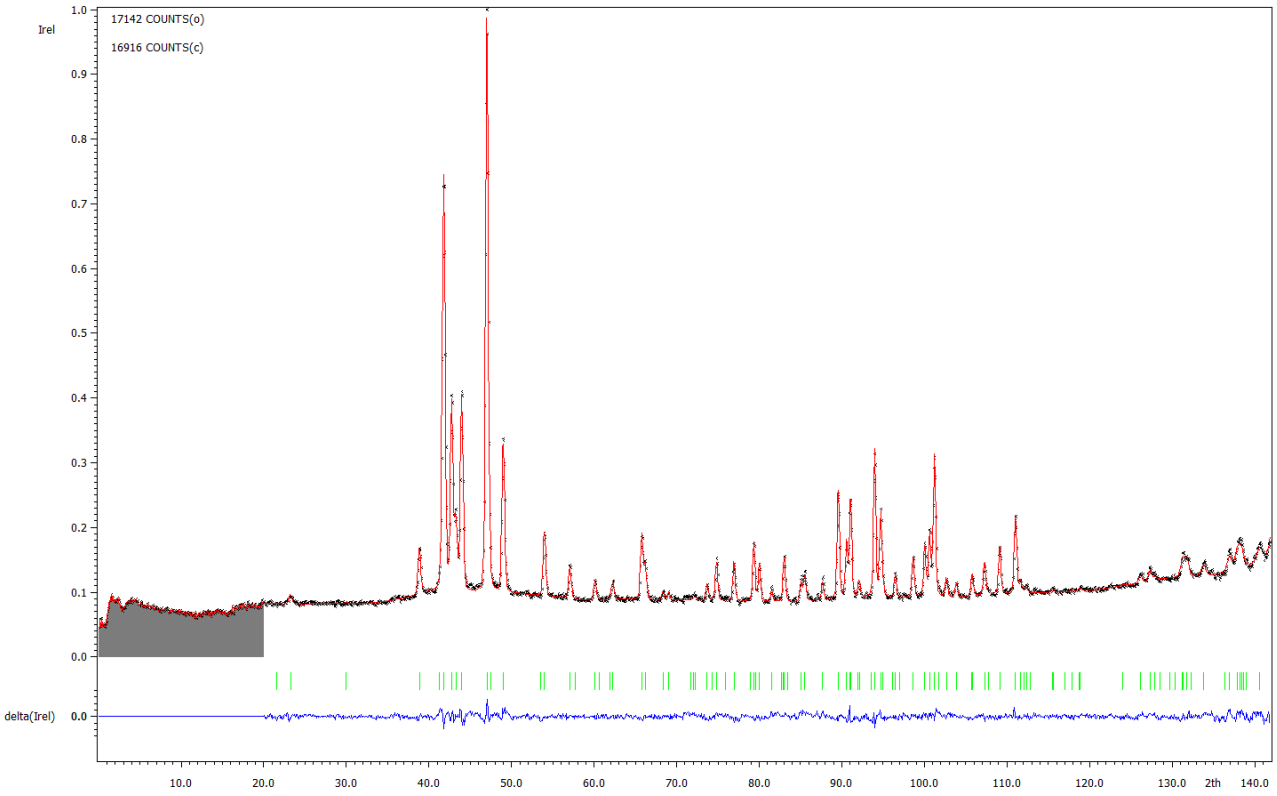

Fig. S2. Neutron powder diffractogram of $Li_2Ti_3O_7$ at 422 °C with results of Rietveld refinement (black: measured, red: calculated, gray: excluded region, green: Bragg position, blue: intensity difference).

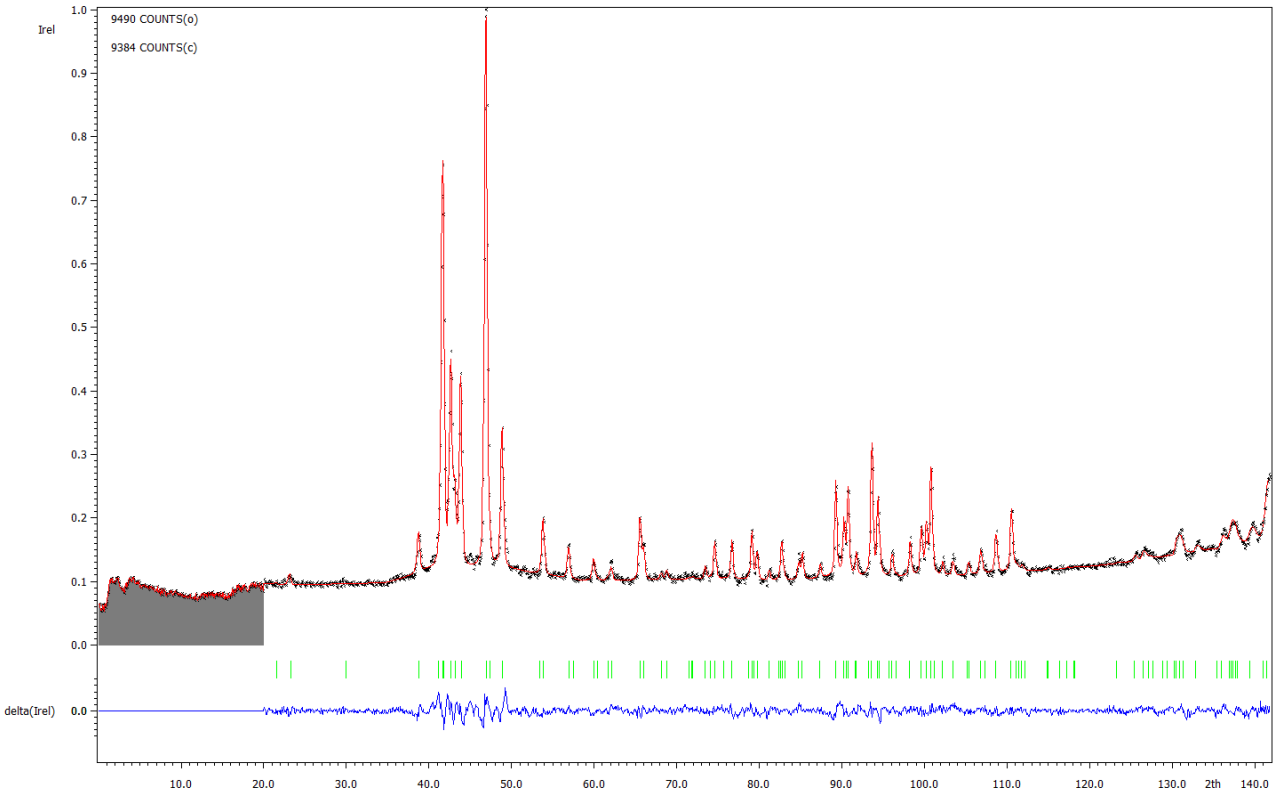

Fig. S3. Neutron powder diffractogram of $Li_2Ti_3O_7$ at 612 °C with results of Rietveld refinement (black: measured, red: calculated, gray: excluded region, green: Bragg position, blue: intensity difference).

Table S1. Anisotropic displacement parameters (harmonic/anharmonic terms) for $Li_2Ti_3O_7$ as derived from neutron diffraction.

ϑ/°C	24	201	422	612
Li1/Ti1				
$U_{11}/10^4$ pm²	0.0130(16)	0.016(2)	0.022(3)	0.024(4)
$U_{22}/10^4$ pm²	0.0236(17)	0.035(2)	0.028(2)	0.033(3)
$U_{33}/10^4$ pm²	0.019(2)	0.027(3)	0.031(3)	0.036(4)
$U_{13}/10^4$ pm²	0.0010(12)	0.0010(16)	0.0014(17)	0.014(3)
Li2				
$U_{11}/10^4$ pm²	0.08(3)	—	—	—
$U_{22}/10^4$ pm²	0.12(2)	—	—	—
$U_{33}/10^4$ pm²	0.06(2)	—	—	—
$U_{13}/10^4$ pm²	0.028(12)	—	—	—
$C_{111}/10^3$	0	—	—	—
$C_{113}/10^3$	–0.10(2)	—	—	—
$C_{122}/10^3$	0.56(15)	—	—	—
$C_{133}/10^3$	0	—	—	—
$C_{223}/10^3$	0	—	—	—
$C_{333}/10^3$	0.80(19)	—	—	—
O1				
$U_{11}/10^4$ pm²	0.0231(11)	0.0291(15)	0.0314(15)	0.040(3)
$U_{22}/10^4$ pm²	0.0238(12)	0.0249(14)	0.0283(15)	0.029(2)
$U_{33}/10^4$ pm²	0.0325(12)	0.0358(14)	0.0412(15)	0.050(2)
$U_{13}/10^4$ pm²	0.0086(10)	0.0100(12)	0.0088(13)	0.012(2)
O2				
$U_{11}/10^4$ pm²	0.0240(12)	0.0274(14)	0.0327(15)	0.047(3)
$U_{22}/10^4$ pm²	0.0216(11)	0.0280(15)	0.0334(16)	0.039(3)
$U_{33}/10^4$ pm²	0.0183(9)	0.0196(10)	0.0264(11)	0.032(2)
$U_{13}/10^4$ pm²	0.0029(8)	0.0018(10)	0.0014(11)	–0.0049(18)

Table S2. Bond lengths (in pm) for $Li_2Ti_3O_7$ as derived from neutron diffraction.

ϑ/°C			24	201	422	612
Li1/Ti1						
	–O1	(1×)	196.4(4)	197.0(5)	197.1(5)	199.5(8)
		(2×)	196.0(2)	197.7(3)	197.9(3)	200.4(5)
	–O2	(1×)	202.9(4)	203.0(5)	204.4(5)	204.8(8)
		(2×)	200.6(2)	199.5(3)	200.3(3)	197.9(5)
Li2						
	–O1	(1×)	201(3)	215(3)	205(5)	206(10)
	–O2	(1×)	196(3)	181(2)	180(3)	177(7)
		(2×)	197.6(18)	205.2(17)	214(3)	220(7)
Li3						
	–O1	(1×)	220(7)	224(6)	240(6)	258(12) 261(11)
	–O2	(1×)	198(6)	190(5)	184(4)	196(7)
		(2×)	188(4)	196(3)	196(3)	187(4)

2 X-Ray Diffraction

The measurement was carried out on a "PANalytical X'Pert PRO MPD" diffractometer equipped with a "PIXcel" detector using nickel-filtered Cu-K_α radiation (λ_1 = 154.056 pm, λ_2 = 154.439 pm) in Bragg–Brentano (θ–θ) geometry. The drifted powder sample was mounted on an off-cut silicon holder. Data were in the final range of 10° ≤ 2θ ≤ 120° with $\Delta(2\theta)$ = 0.026°.

A model for the $Ti_3O_7^{2-}$ framework was imported [1] and refined with JANA2006 [2] against net intensities using the full-matrix least-squares algorithm with fixed elements per cycle. The background was modelled using ten Legendre polynomials with refined coefficients. Reflection profiles were fitted with a pseudo-Voigt function following the Thompson–Cox–Hastings approach [3]. Asymmetry was corrected for using the Bérar–Baldinozzi method [4] with four parameters. Additionally, displacement and transparency corrections as well as a roughness correction according to Pitschke, Hermann, and Mattern [5] (final values: C = 0.150[4], τ = 0.054911) were applied. Ionic form factors were used for Li^+ and Ti^{4+}.

First, the framework ions were refined with individual isotropic displacement parameters. Probable lithium positions were then searched for in difference Fourier maps, yielding Li2 and Li3. After setting U_{iso}(Li2, Li3) ≈ 2U_{iso}(Ti1/Li1), lithium positions and occupations were refined. *Note that, because of the strong disorder and low scattering power of the lithium ions, the final model appears lithium deficient with respect to the real composition!* Tables S3 and S4 list further experimental details.

Table S3. Details of X-ray powder diffraction at ramsdellite-like $Li_2Ti_3O_7$.

Sum Formula	$\mathbf{Li_{2.286}Ti_{3.429}O_8}$
Crystal system	orthorhombic
Space group	*Pnma*
$\boldsymbol{Z}$	1
$\boldsymbol{M}$**/g mol^{-1}**	308.04
$\boldsymbol{a}$**/pm**	9.5510(2)
$\boldsymbol{b}$**/pm**	2.94570(7)
$\boldsymbol{c}$**/pm**	5.01739(12)
$\boldsymbol{V}$**/10^6 pm^3**	141.161(6)
$\boldsymbol{\rho_{calc}}$**/g cm^{-3}**	3.6236
$\boldsymbol{\mu}$**/mm^{-1}**	40.355
$\boldsymbol{2\theta_{max}}$**/°**	119.5
Data, constr., parameters	131, 3, 40
$\boldsymbol{R_F}$ **(obs[a], all)**	0.0291, 0.0314
$\boldsymbol{R_B}$ **(obs[a], all)**	0.0481, 0.0486
$\boldsymbol{S}$ **(all)**	2.00
$\boldsymbol{R_p}$**,** $\boldsymbol{wR_p}$[b]	0.0196, 0.0286
$\boldsymbol{wR_{exp}}$[b]	0.0143
$\boldsymbol{\rho_{min}}$**,** $\boldsymbol{\rho_{max}}$**/10^{-6}** $\boldsymbol{e}$ **pm^{-3}**	0.31, –0.41
CSD No.	431132

[a] $I > 3\sigma(I)$. [b] $w = 1/[\sigma^2(I)+(0.01I)^2]$.

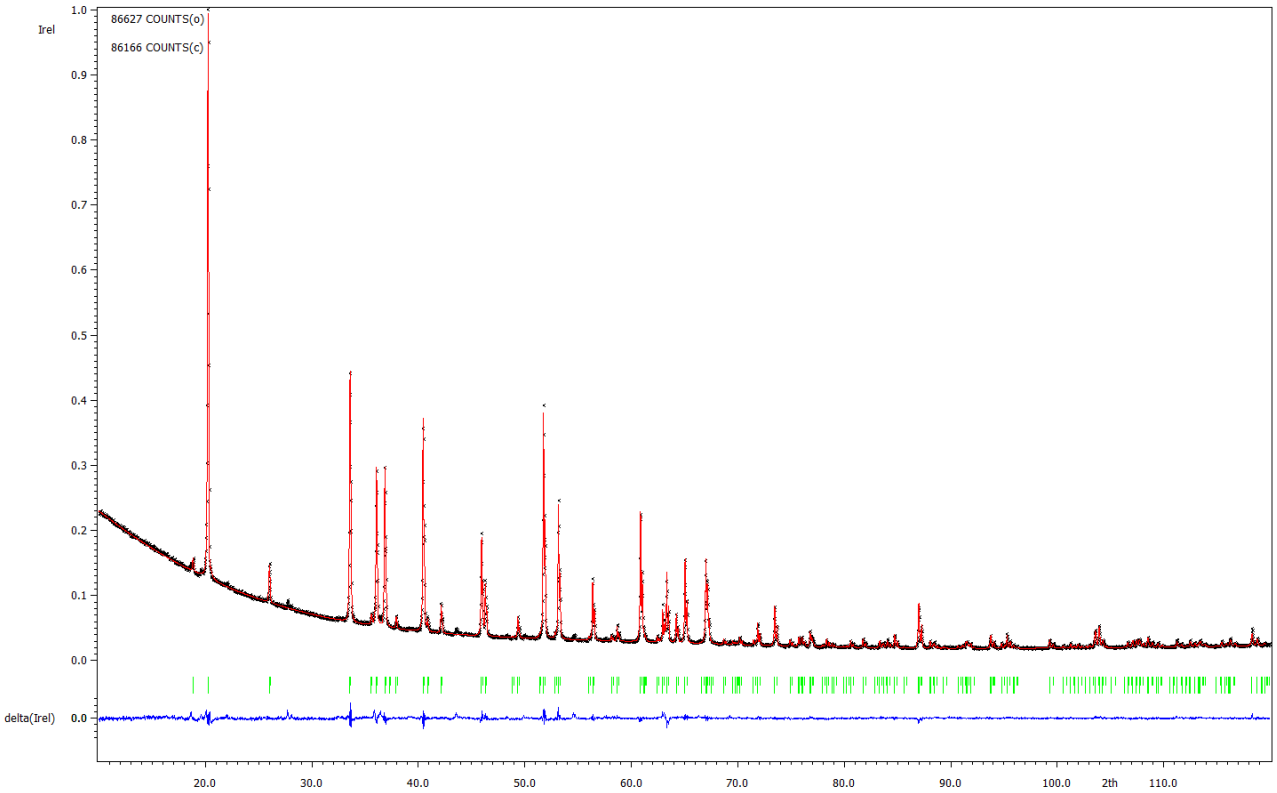

Fig. S4. X-ray powder diffractogram of $Li_2Ti_3O_7$ at room temperature with results of Rietveld refinement (black: measured, red: calculated, green: Bragg position, blue: intensity difference).

Table S4. Atomic coordinates, displacement parameters, and site occupation factors (s.o.f.) for $Li_2Ti_3O_7$ at ambient temperature as derived from X-ray powder diffraction.

Atom	Wyckoff site	x	y	z	$U_{iso}/10^4$ pm^2	s.o.f.
Ti1	4*c*	0.36093(7)	¼	0.03212(13)	0.0159(5)	0.8571
Li1	4*c*	0.36093(7)	¼	0.03212(13)	0.0159(5)	0.01(3)
Li2	4*c*	0.036(3)	¼	0.058(4)	0.03	0.276(12)
Li3	4*c*	0.432(7)	¼	0.424(12)	0.03	0.098(12)
O1	4*c*	0.22649(18)	¼	0.3281(4)	0.0215(10)	1
O2	4*c*	0.03209(16)	¼	0.7028(4)	0.0173(10)	1

3 MEM Reconstructions

Table S5. Number of reflections N_{ref}, weighting factors λ_n for generalized constraints, final residuals R and central moments C_n in the MEM reconstruction of scattering-length densities in $Li_2Ti_3O_7$.

ϑ/°C	24	201	422	612
N_{ref}	104	106	106	108
λ_2[a]	1	0.9	0.75	0.75
λ_4[a]	0	0.1	0.25	0.25
R_F	0.0508	0.0658	0.0602	0.0760
wR_F	0.0455	0.0574	0.0550	0.0648
C_2	0.99996	0.99955	0.99994	0.99964
C_4	1.25735	1.08515	1.22290	1.12503
C_6	1.40382	1.11606	1.35493	1.23372
C_8	1.32029	1.05712	1.26577	1.23841
C_{10}	1.04107	0.89945	0.98972	1.08980
C_{12}	0.69765	0.67960	0.65725	0.83360
C_{14}	0.40417	0.45524	0.37754	0.55826
C_{16}	0.20564	0.27142	0.19075	0.33100

[a] $\lambda_n = 0$ for $n > 4$.

4 References

[1] I. Abrahams, P.G. Bruce, W.I.F. David, A.R. West, *J. Solid State Chem.* 78 (1989) 170–177.

[2] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr. – Cryst. Mater.* 229 (2014) 345–352.

[3] P. Thompson, D.E. Cox, J.B. Hastings, *J. Appl. Crystallogr.* 20 (1987) 79–83.

[4] J.-F. Bérar, G. Baldinozzi, *J. Appl. Crystallogr.* 26 (1993) 128–129.

[5] W. Pitschke, H. Hermann, N. Mattern, *Powder Diffr.* 8 (1993) 74–83.