Supplementary Material: Mechanism for the Combined Li–Na Ionic Conductivity in Sugilite ($Fe_2Na_2K[Li_3Si_{12}O_{30}]$)-Type Compounds

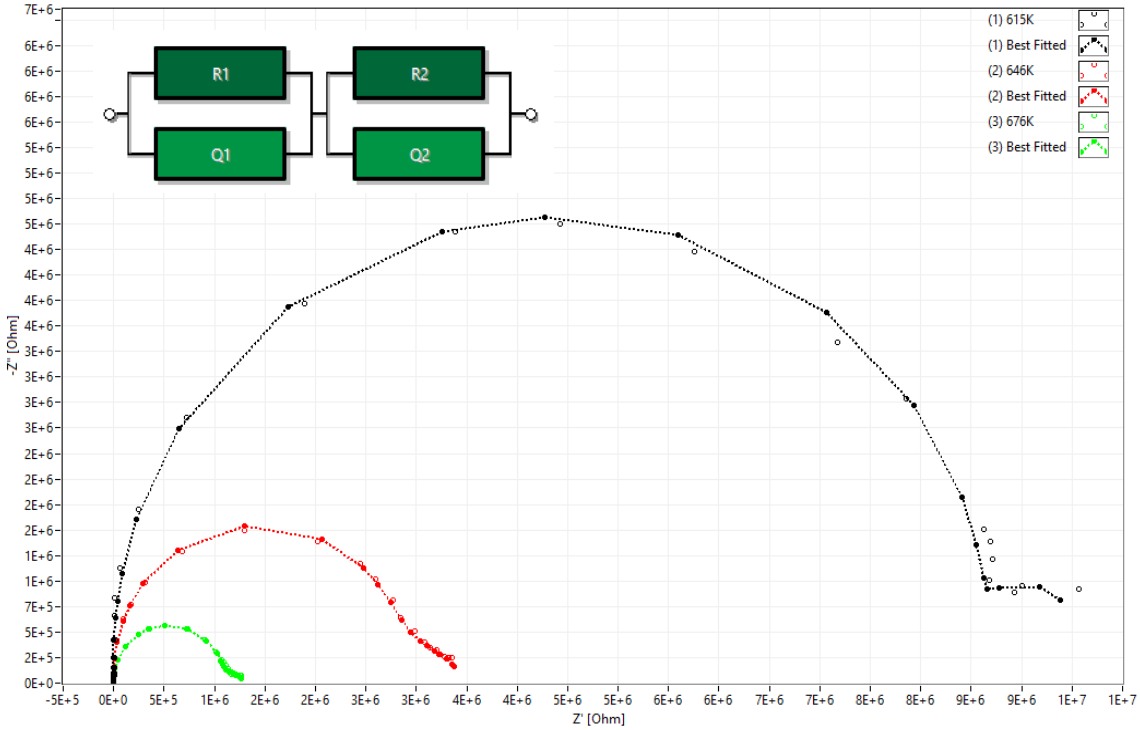
So-Hyun Park *, Carsten Paulmann, Markus Hoelzel and Rupert Hochleitner

Supplementary S1. Atomic parameters refined with HRNPD at 973 K of $(Fe_{1.3(2)}Mn_{0.3(0.1)}Al_{0.4(0.1)})Na_{2.0(2)}K_{1.03(1)}[Li_3Si_{12.000(3)}O_{30}]$,refined with HRNPD at 973 K. An occupation value of 0.1108 corresponds to full occupation at A sites with $Fe_{1.3(2)}Mn_{0.3(0.1)}Al_{0.4(0.1)}$, normalized by the neutron elastic scattering length of Fe. The other sites were refined with full occupation.

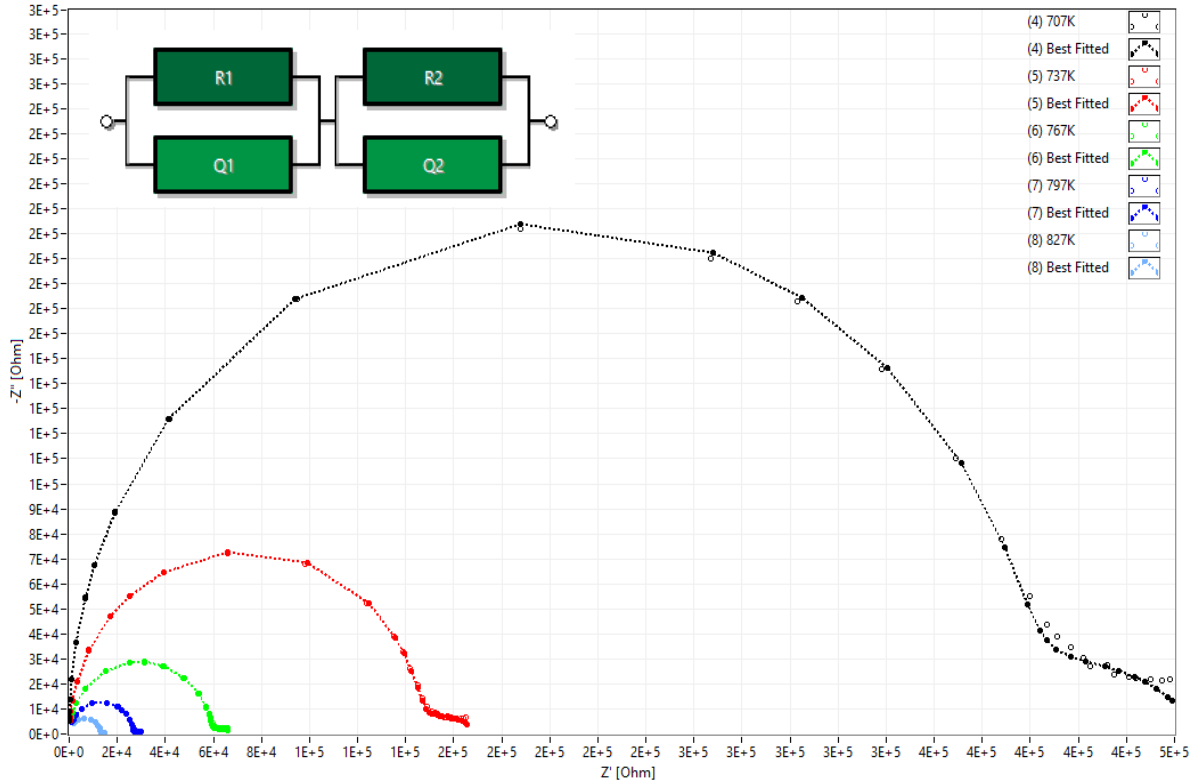
Site	Type	Coordinates			Eigenvalues of ADPs [Å]		
		x	y	z	U_1	U_2	U_3
A	Fe	0.33333	0.66667	0.25	0.008060	0.008060	0.008325
B	Na	0.33333	0.66667	0.5	0.019981	0.019981	0.087654
C	K	0	0	0.25	0.026607	0.130289	0.130289
T^{II}	Li	0.5	0.5	0.25	Average ADP = 0.035		
T^{I}	Si	0.2344(5)	0.3555(5)	0.3870(3)	0.017436	0.025254	0.027473
O1	O	0.1382(6)	0.3986(6)	0	0.003171	0.048717	0.096815
O2	O	0.2237(5)	0.2773(5)	0.1377(2)	0.011229	0.045480	0.081840
O3	O	0.1672(3)	0.5065(4)	0.1706(2)	0.028474	0.031663	0.040589

Supplementary S2. Observed and simulated impedance spectra of Sugilite#2.

T = 615- 676 K: fitting is made with two serially connected RC-circuits

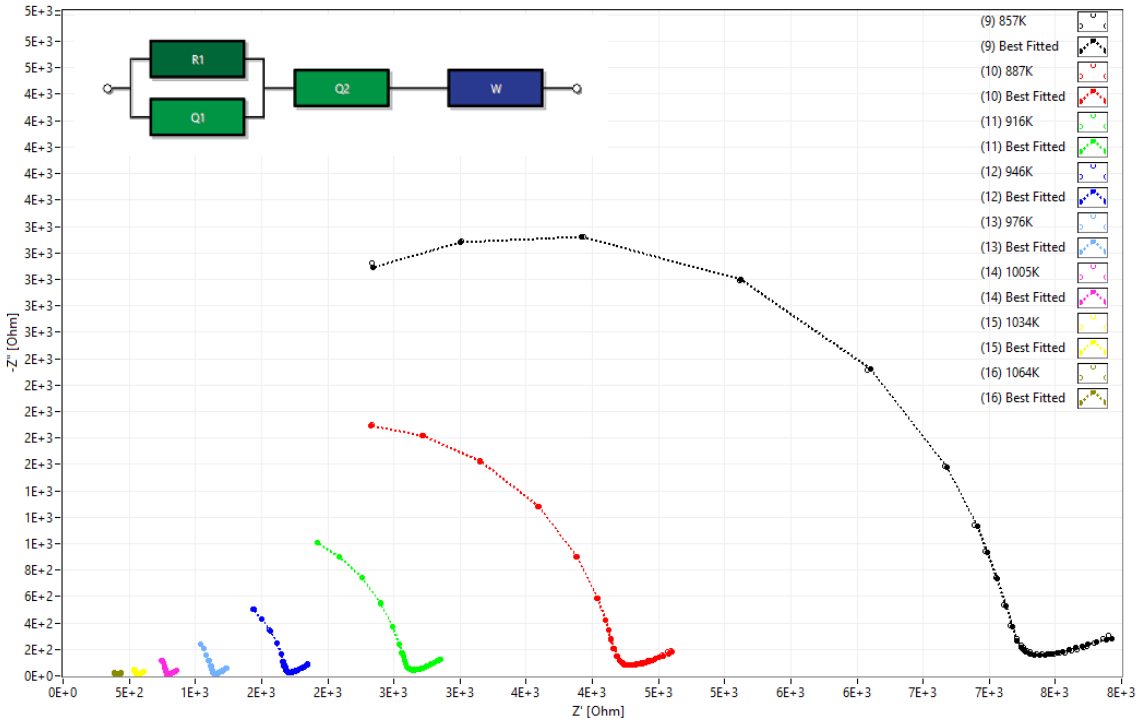


T = 707 – 827 K: fitting is made with two serially connected RC-circuits

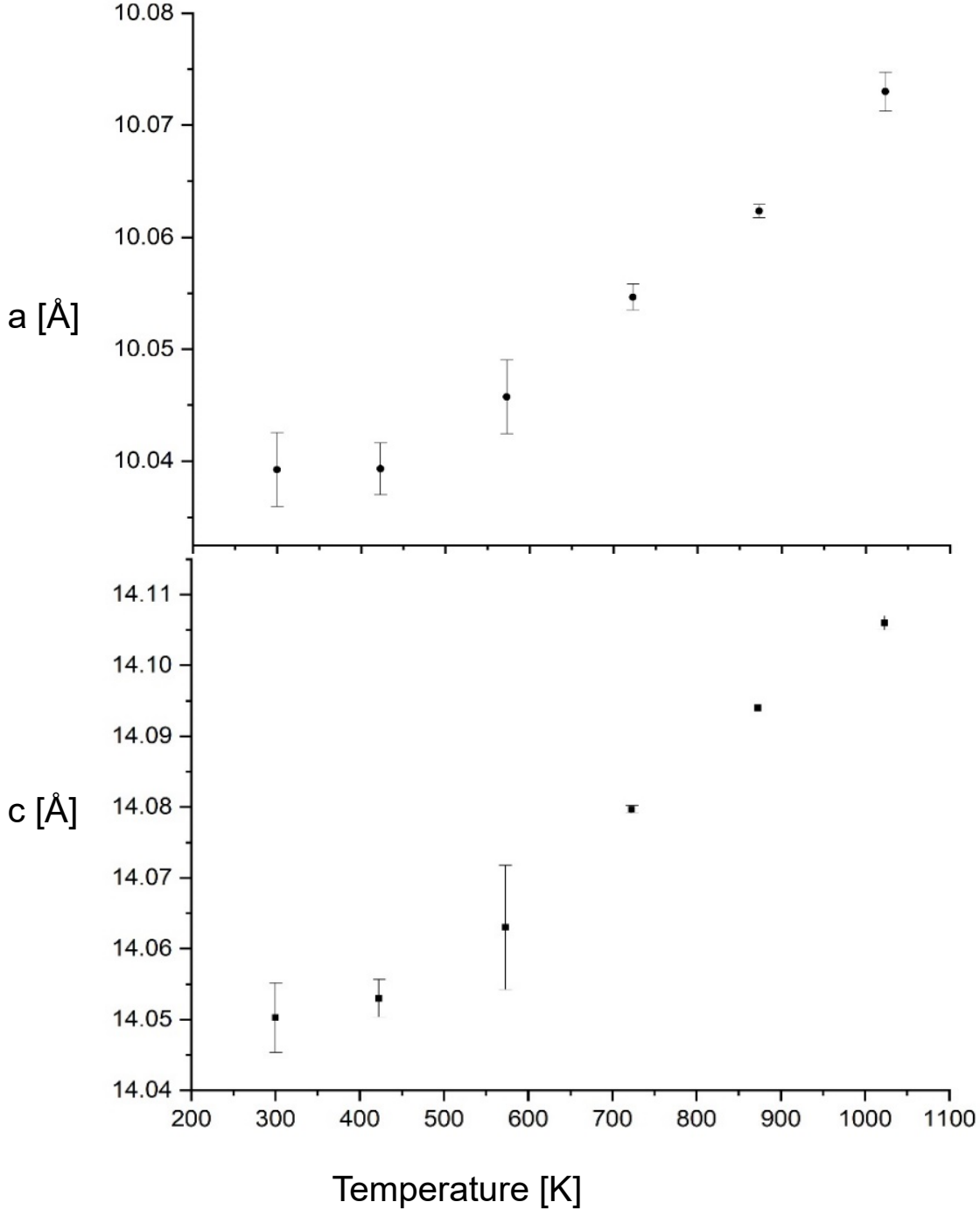


T = 857 – 1064 K: fitting is made with an additional Warburg impedance element(W) which describes a contribution to

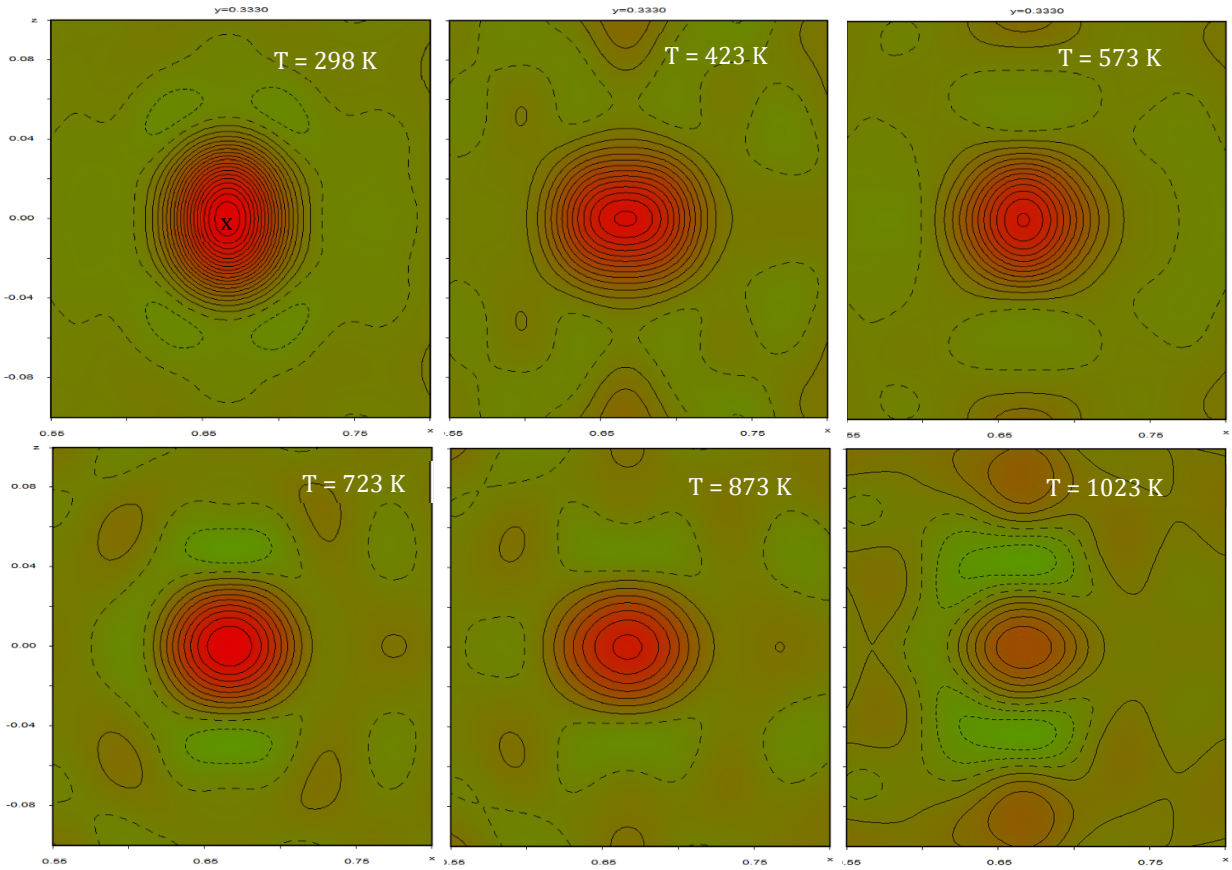
impedance caused by diffusion to and from an electrode (Pt in our case). This fitting support ionic bulk conductivity in Sugilite#2.



Supplementary S3. Change of the lattice metrics a and c in [Å] in sugilite with increasing temperatures, determined by synchrotron X-ray single crystals diffraction data of Sugilite#1.



Supplementary S4. Observed Fourier maps evaluated with synchrotron X-ray single crystal diffraction data of Sugilite#1 without Na at B sites at all measuring temperatures from 298 up to 1023 K.



Supplementary S5. Components of harmonic ADP parameters U_{ij} which are the mean square displacements*, refined with synchrotron XSD data of Sugilite#2.

Site	T[K]	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A (Fe)	298	0.01845 (3)	0.01845 (3)	0.01912 (7)	0.00923 (1)	0	0
	423	0.02030 (3)	0.02030 (3)	0.0211 (1)	0.01015 (1)		
	573	0.02189 (3)	0.02189 (3)	0.0236 (1)	0.01095 (2)		
	723	0.02424 (2)	0.02424 (2)	0.02572 (6)	0.01212 (1)		
	873	0.02671 (2)	0.02671 (2)	0.02813 (7)	0.01335 (1)		
	1023	0.02967(2)	0.02967(2)	0.03139(6)	0.014833(11)		
B (Na)	298	0.0302 (2)	0.0302 (2)	0.090 (1)	0.015 (1)	0	0
	423	0.0368 (2)	0.0368 (2)	0.103 (1)	0.0184 (1)		
	573	0.0427 (3)	0.0427 (3)	0.108 (1)	0.0214 (1)		
	723	0.0493 (2)	0.0493 (2)	0.132 (2)	0.0247 (1)		
	873	0.0567 (3)	0.0567 (3)	0.145 (2)	0.0284 (2)		
	1023	0.0643 (3)	0.0643 (3)	0.123 (1)	0.0321 (5)		
C (K)	298	0.0291 (1)	0.0291 (1)	0.0335 (2)	0.0146 (1)	0	0
	423	0.0352 (1)	0.0351(1)	0.0407 (3)	0.0176 (1)		
	573	0.0388 (1)	0.0388 (1)	0.0456 (4)	0.0194 (1)		
	723	0.0471 (1)	0.0471 (1)	0.0561 (4)	0.0236 (1)		
	873	0.0535 (1)	0.0535 (1)	0.0637 (4)	0.0267 (1)		
	1023	0.06131(15)	0.06131(15)	0.0741(4)	0.03065(8)		

T(II) (Li)	298	0.0281 (5)	0.0214 (5)	0.026 (1)	0.0107 (2)	0	0
	423	0.0336 (7)	0.0247 (6)	0.034 (1)	0.0123 (3)		
	573	0.0414 (9)	0.0298 (9)	0.050 (9)	0.0149 (9)		
	723	0.0481 (8)	0.0311 (6)	0.045 (2)	0.0155 (3)		
	873	0.0590 (1)	0.0353 (7)	0.053 (2)	0.0177 (4)		
	1023	0.0758 (15)	0.0390 (8)	0.060 (2)	0.0195 (4)		
T(I) (Si)	298	0.01906 (3)	0.01858 (3)	0.01909 (6)	0.00941 (2)	0.00071 (2)	0.00020 (2)
	423	0.02094 (3)	0.02031 (3)	0.02096 (9)	0.01029 (3)	0.00104 (3)	0.00032 (3)
	573	0.02252 (4)	0.02184 (4)	0.0235 (1)	0.01108 (3)	0.00119 (4)	0.00043 (4)
	723	0.02482 (3)	0.02381 (3)	0.02487 (6)	0.01206 (2)	0.00167 (2)	0.00054 (2)
	873	0.02714 (3)	0.02592 (3)	0.02703 (6)	0.01313 (2)	0.00196 (3)	0.00064 (3)
	1023	0.02999 (3)	0.02840 (3)	0.02965 (5)	0.01444 (2)	0.00238 (2)	0.00088 (2)
O1 (O)	298	0.0308 (1)	0.0340 (2)	0.0187 (2)	0.0152 (1)	0	0
	423	0.0371 (2)	0.0413 (3)	0.0201 (3)	0.0181 (1)		
	573	0.0407 (3)	0.0447 (3)	0.0233 (4)	0.0195 (3)		
	723	0.0491 (3)	0.0555 (3)	0.0232 (3)	0.0239 (2)		
	873	0.0547 (3)	0.0632 (4)	0.0258 (3)	0.0265 (3)		
	1023	0.0625(3)	0.0731 (4)	0.0277 (3)	0.0309 (3)		
O2 (O)	298	0.0245 (1)	0.0187 (1)	0.0313 (2)	0.0075 (1)	-0.0005 (1)	-0.0001 (1)
	423	0.0285 (1)	0.0203 (1)	0.0368 (2)	0.0077 (1)	-0.0005 (1)	0.0001 (1)
	573	0.0312 (1)	0.0219 (1)	0.0413 (3)	0.0080 (1)	-0.0002 (2)	0.0004 (1)
	723	0.0368 (1)	0.02390 (6)	0.0486 (2)	0.00803 (6)	-0.0010 (1)	0.0003 (1)
	873	0.0416 (1)	0.02614 (7)	0.0544 (3)	0.00829 (7)	-0.0011 (1)	0.0005 (1)
	1023	0.0474 (1)	0.0290 (1)	0.0613 (3)	0.0087 (1)	-0.0007 (1)	0.0002 (1)
O3 (O)	298	0.0214 (1)	0.0226 (1)	0.0249 (1)	0.0108 (1)	0.0041 (1)	0.0016 (1)
	423	0.0241 (1)	0.0255 (1)	0.0289 (2)	0.0121 (1)	0.0061 (1)	0.0026 (1)
	573	0.0261 (1)	0.0278 (1)	0.0322 (3)	0.0130 (1)	0.0069 (1)	0.0030 (1)
	723	0.0297 (1)	0.0318 (1)	0.0374 (2)	0.0147 (1)	0.0096 (1)	0.0043 (1)
	873	0.0330 (1)	0.0358 (1)	0.0417 (2)	0.0163 (1)	0.0114 (1)	0.0052 (1)
	1023	0.0367 (1)	0.0402 (1)	0.0480 (2)	0.0181 (1)	0.0136 (1)	0.0058 (1)

*related to $\beta^{11}h^2+\beta^{22}k^2+\beta^{33}l^2+2\beta^{12}hk+2\beta^{13}hl+2\beta^{23}kl$: $\beta^{11}=2\pi^2U^{11}a^{*2}$, $\beta^{22}=2\pi^2U^{22}b^{*2}$, $\beta^{33}=2\pi^2U^{33}a^{*2}$, $\beta^{12}=2\pi^2U^{12}a^*b^*\cos\gamma^*$, $\beta^{13}=2\pi^2U^{13}a^*c^*\cos\beta^*$, $\beta^{23}=2\pi^2U^{23}b^*c^*\cos\alpha^*$.

Supplementary S6. Principle mean square APDs from SXD data of Sugilite#1

6.1 ADP eigenvalues and eigenvectors at 298 K

Eigenvalues [Å²] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

10.0390	-5.0195	0.0000
0.0000	8.6940	0.0000
0.0000	0.0000	14.0500

Atom	Eigenvalues	Eigenvectors		
K	0.029127	0.000000	1.000000	0.000000
	0.029127	1.000000	0.000000	0.000000
	0.033484	0.000000	0.000000	1.000000
Fe	0.018450	0.000000	1.000000	0.000000
	0.018450	1.000000	0.000000	0.000000
	0.019119	0.000000	0.000000	1.000000
Li	0.021403	0.000000	1.000000	0.000000
	0.026375	0.000000	0.000000	1.000000
	0.030310	1.000000	0.000000	0.000000
Si	0.018367	0.674031	0.213608	-0.707144
	0.018541	-0.286801	0.957857	0.015970
	0.019820	0.680755	0.192046	0.706889
O1	0.018719	0.000000	0.000000	1.000000
	0.030814	0.830354	0.557236	0.000000
	0.035442	-0.557236	0.830354	0.000000
O2	0.018232	-0.198707	-0.980017	-0.009059
	0.029192	-0.946725	0.194330	-0.256805
	0.031416	-0.253433	0.042453	0.966421
O3	0.018630	0.767014	0.323865	-0.553896
	0.022867	-0.383113	0.923652	0.009544
	0.027686	0.514698	0.204884	0.832531
Na	0.030231	0.000000	1.000000	0.000000
	0.030231	1.000000	0.000000	0.000000
	0.090218	0.000000	0.000000	1.000000

6.2 ADP eigenvalues and eigenvectors at 423 K

Eigenvalues [Å²] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

10.0390	-5.0195	0.0000
0.0000	8.6940	0.0000
0.0000	0.0000	14.0530

Atom	Eigenvalues	Eigenvectors		
K	0.035162	1.000000	0.000000	0.000000
	0.035162	0.000000	1.000000	0.000000
	0.040670	0.000000	0.000000	1.000000
Fe	0.020298	1.000000	0.000000	0.000000
	0.020298	0.000000	1.000000	0.000000
	0.021094	0.000000	0.000000	1.000000
Li	0.024671	0.000000	1.000000	0.000000

	0.033660	0.000000	0.000000	1.000000
	0.036566	1.000000	0.000000	0.000000
Si	0.019911	0.634909	0.310099	-0.707622
	0.020282	-0.353352	0.931057	0.090971
	0.022040	0.687047	0.192281	0.700710
O1	0.020101	0.000000	0.000000	1.000000
	0.037008	0.821320	0.570468	0.000000
	0.043367	-0.570468	0.821320	0.000000
O2	0.019756	-0.191222	-0.981547	-0.000835
	0.034865	-0.928105	0.181088	-0.325313
	0.036989	-0.319461	0.061432	0.945606
O3	0.019989	0.738082	0.373615	-0.561825
	0.025928	-0.438892	0.898299	0.020789
	0.033039	0.512454	0.231237	0.826995
Na	0.036828	1.000000	0.000000	0.000000
	0.036828	0.000000	1.000000	0.000000
	0.103267	0.000000	0.000000	1.000000

6.3 ADP eigenvalues and eigenvectors at 573 K

Eigenvalues [Å²] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

	10.0460	-5.0230	0.0000
	0.0000	8.7001	0.0000
	0.0000	0.0000	14.0630

Atom	Eigenvalues	Eigenvectors		
K	0.038829	0.000000	1.000000	0.000000
	0.038829	1.000000	0.000000	0.000000
	0.045623	0.000000	0.000000	1.000000
Fe	0.021892	-0.334030	-0.942562	-0.000000
	0.021892	-0.942562	0.334030	0.000000
	0.023614	0.000000	0.000000	1.000000
Li	0.029761	0.000000	1.000000	0.000000
	0.045292	1.000000	0.000000	0.000000
	0.049901	0.000000	0.000000	1.000000
Si	0.021685	-0.438472	-0.773173	0.458199
	0.021872	0.719800	-0.607388	-0.336107
	0.024327	0.538173	0.182439	0.822852
O1	0.023314	0.000000	0.000000	1.000000
	0.040542	0.781171	0.624317	0.000000
	0.047284	-0.624317	0.781171	0.000000
O2	0.021198	-0.195148	-0.980663	0.014700
	0.038702	-0.959565	0.187806	-0.209674
	0.041391	-0.202859	0.055023	0.977661
O3	0.021592	0.744493	0.384990	-0.545448
	0.028433	-0.440698	0.897096	0.031674
	0.036747	0.501513	0.216796	0.837546

Na	0.042703	0.000000	1.000000	0.000000
	0.042703	1.000000	0.000000	0.000000
	0.107562	0.000000	0.000000	1.000000

6.4 ADP eigenvalues and eigenvectors at 723 K

Eigenvalues [Å²] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

10.0550	-5.0275	0.0000
0.0000	8.7079	0.0000
0.0000	0.0000	14.0800

Atom	Eigenvalues	Eigenvectors		
K	0.047097	0.707107	0.707107	0.000000
	0.047097	-0.707107	0.707107	0.000000
	0.056073	0.000000	0.000000	1.000000
Fe	0.024238	0.804589	0.593833	0.000000
	0.024238	-0.593833	0.804589	0.000000
	0.025715	0.000000	0.000000	1.000000
Li	0.031082	0.000000	1.000000	0.000000
	0.044742	0.000000	0.000000	1.000000
	0.053760	1.000000	0.000000	0.000000
Si	0.023176	-0.586369	-0.421196	0.691928
	0.023841	0.416153	-0.889481	-0.188787
	0.026619	0.694973	0.177249	0.696846
O1	0.023185	0.000000	0.000000	1.000000
	0.049080	0.823533	0.567269	0.000000
	0.058502	-0.567269	0.823533	0.000000
O2	0.023018	-0.190729	-0.981642	0.001342
	0.046374	-0.836388	0.161791	-0.523717
	0.049413	-0.513885	0.101010	0.851891
O3	0.023224	0.728473	0.393495	-0.560793
	0.032657	-0.457501	0.888726	0.029301
	0.043972	0.509922	0.235218	0.827437
Na	0.049292	0.804589	0.593833	0.000000
	0.049292	-0.593833	0.804589	0.000000
	0.131869	0.000000	0.000000	1.000000

6.5 ADP eigenvalues and eigenvectors at 873 K

Eigenvalues [Å²] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

10.0620	-5.0310	0.0000
0.0000	8.7139	0.0000
0.0000	0.0000	14.0940

Atom	Eigenvalues	Eigenvectors		
K	0.053521	0.000000	1.000000	0.000000
	0.053521	1.000000	0.000000	0.000000
	0.063717	0.000000	0.000000	1.000000

Fe	0.026707	0.000000	1.000000	0.000000
	0.026707	1.000000	0.000000	0.000000
	0.028135	0.000000	0.000000	1.000000
Li	0.035321	0.000000	1.000000	0.000000
	0.052647	0.000000	0.000000	1.000000
	0.066801	1.000000	0.000000	0.000000
Si	0.025119	-0.571114	-0.419246	0.705735
	0.025973	0.410165	-0.890467	-0.197063
	0.029181	0.711051	0.176922	0.680518
O1	0.025825	0.000000	0.000000	1.000000
	0.054593	0.826161	0.563434	0.000000
	0.067214	-0.563434	0.826161	0.000000
O2	0.025055	-0.192593	-0.981263	0.005639
	0.052740	-0.716188	0.136634	-0.684402
	0.055862	-0.670807	0.135850	0.729083
O3	0.025184	0.719540	0.401466	-0.566645
	0.036873	-0.469922	0.882252	0.028354
	0.049556	0.511306	0.245877	0.823474
Na	0.056717	1.000000	0.000000	0.000000
	0.056717	0.000000	1.000000	0.000000
	0.145218	0.000000	0.000000	1.000000

6.6 ADP eigenvalues and eigenvectors at 1023 K

Eigenvalues [Å^2] and eigenvectors are related to the orthonormal system defined by the following transformation matrix:

10.0730	-5.0365	0.0000
0.0000	8.7235	0.0000
0.0000	0.0000	14.1060

Atom	Eigenvalues	Eigenvectors		
K	0.061305	0.000000	1.000000	0.000000
	0.061305	1.000000	0.000000	0.000000
	0.074057	0.000000	0.000000	1.000000
Fe	0.029666	0.000000	1.000000	0.000000
	0.029666	1.000000	0.000000	0.000000
	0.031388	0.000000	0.000000	1.000000
Li	0.038972	0.000000	1.000000	0.000000
	0.060320	0.000000	0.000000	1.000000
	0.088057	1.000000	0.000000	0.000000
Si	0.027406	-0.516333	-0.485525	0.705454
	0.028503	0.462333	-0.851434	-0.247606
	0.032348	0.720866	0.198307	0.664098
O1	0.027675	0.000000	0.000000	1.000000
	0.062486	0.851615	0.524168	0.000000
	0.077064	-0.524168	0.851615	0.000000
O2	0.027634	-0.193519	-0.981095	0.001693
	0.060750	-0.480464	0.093266	-0.872041

	0.062991	0.855398	-0.169570	-0.489429
O3	0.027620	0.734168	0.390732	-0.555271
	0.041661	-0.443686	0.895138	0.043255
	0.057160	0.513945	0.214609	0.830544
Na	0.064275	0.000000	1.000000	0.000000
	0.064275	1.000000	0.000000	0.000000
	0.123221	0.000000	0.000000	1.000000

Supplementary S7. The Bond-Valence parameters (d_0,B_0) for Zachariasen formula (s= exp{(d_0-d)/B_0}) applied in this study.

Type 1: FE+3 with type 5: O-2 d_0= 1.759 B_0= 0.370 => Reference: Brown and Altermatt, (1985), Acta Cryst. B41, 244-247 (empirical)
Cation (Eff. radius): FE+3(0.640) Anion (Eff. radius): O-2 (1.400)

Type 2: LI+1 with type 5: O-2 d_0= 1.466 B_0= 0.370 => Reference: Brown and Altermatt, (1985), Acta Cryst. B41, 244-247 (empirical)
Cation (Eff. radius): LI+1(0.600) Anion (Eff. radius): O-2 (1.400)

Type 3: NA+1 with type 5: O-2 d_0= 1.803 B_0= 0.370 => Reference: Brown and Altermatt, (1985), Acta Cryst. B41, 244-247 (empirical)
Cation (Eff. radius): NA+1(0.950) Anion (Eff. radius): O-2 (1.400)

Type 4: SI+4 with type 5: O-2 d_0= 1.624 B_0= 0.370 => Reference: Brese and O'Keeffe, (1991), Acta Cryst. B47, 192-197 (extrapolated)
Cation (Eff. radius): SI+4(0.410) Anion (Eff. radius): O-2 (1.400)