

Supporting Information

Direct Observation of Structural Changes near and at the Charge-Ordering Temperature of Ilvaite using High-flux Neutron Powder Diffraction

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Table S1. Variation of extracted lattice parameters and cell volume with temperature, D 20 data.

T / K	a/ Å	a error / Å	a/ao	a/ao error	b/ Å	b error / Å	b/bo	b/bo error	c/ Å	c error / Å	c/co	c/co error	$\beta/$	β error / Å	β/β_0	β/β_0 error	V / Å ³	V error /Å ³	V/Vo
138.0000	13.0221	5.3000e-4	1.0006	4.0726e-5	8.8164	3.1200e-4	1.0007	3.5415e-5	5.8409	2.2500e-4	1.0007	3.8548e-5	90.2300	2.0000e-3	1.0026	2.2223e-5	670.5790	0.0710	1.0019
145.0000	13.0222	5.3800e-4	1.0006	4.1340e-5	8.8166	3.1500e-4	1.0008	3.5756e-5	5.8407	2.2800e-4	1.0007	3.9062e-5	90.2290	2.0000e-3	1.0026	2.2223e-5	670.5840	0.0710	1.0019
152.0000	13.0217	5.3900e-4	1.0006	4.1417e-5	8.8161	3.1800e-4	1.0007	3.6096e-5	5.8404	2.2900e-4	1.0006	3.9233e-5	90.2270	2.0000e-3	1.0026	2.2223e-5	670.4770	0.0700	1.0017
159.0000	13.0219	5.3500e-4	1.0006	4.1110e-5	8.8164	3.1300e-4	1.0008	3.5529e-5	5.8406	2.2700e-4	1.0006	3.8891e-5	90.2310	2.0000e-3	1.0026	2.2223e-5	670.5060	0.0670	1.0018
166.0000	13.0218	5.3700e-4	1.0006	4.1264e-5	8.8164	3.1400e-4	1.0007	3.5642e-5	5.8409	2.2800e-4	1.0007	3.9062e-5	90.2300	2.0000e-3	1.0026	2.2223e-5	670.5550	0.0690	1.0019
173.0000	13.0223	5.3100e-4	1.0006	4.0803e-5	8.8172	3.1100e-4	1.0008	3.5302e-5	5.8415	2.2400e-4	1.0008	3.8377e-5	90.2310	2.0000e-3	1.0026	2.2223e-5	670.7170	0.0710	1.0021
180.0000	13.0226	5.2500e-4	1.0007	4.0341e-5	8.8174	3.0800e-4	1.0009	3.4961e-5	5.8421	2.2200e-4	1.0009	3.8034e-5	90.2320	2.0000e-3	1.0026	2.2223e-5	670.8160	0.0700	1.0022
187.0000	13.0218	5.4400e-4	1.0006	4.1801e-5	8.8175	3.2500e-4	1.0009	3.6891e-5	5.8424	2.3200e-4	1.0009	3.9747e-5	90.2320	2.0000e-3	1.0026	2.2223e-5	670.8160	0.0710	1.0022
194.0000	13.0223	5.3300e-4	1.0006	4.0956e-5	8.8184	3.1400e-4	1.0010	3.5642e-5	5.8433	2.2600e-4	1.0011	3.8719e-5	90.2350	2.0000e-3	1.0027	2.2223e-5	671.0190	0.0710	1.0025
201.0000	13.0217	5.3900e-4	1.0006	4.1417e-5	8.8184	3.2300e-4	1.0010	3.6664e-5	5.8437	2.3000e-4	1.0012	3.9405e-5	90.2370	2.0000e-3	1.0027	2.2223e-5	671.0290	0.0710	1.0026
208.0000	13.0217	5.3600e-4	1.0006	4.1187e-5	8.8189	3.1600e-4	1.0010	3.5869e-5	5.8446	2.2600e-4	1.0013	3.8719e-5	90.2370	2.0000e-3	1.0027	2.2223e-5	671.1730	0.0720	1.0028
215.0000	13.0209	5.3400e-4	1.0005	4.1033e-5	8.8193	3.1800e-4	1.0011	3.6096e-5	5.8453	2.2600e-4	1.0014	3.8719e-5	90.2400	2.0000e-3	1.0027	2.2223e-5	671.2390	0.0680	1.0029
222.0000	13.0207	5.3700e-4	1.0005	4.1264e-5	8.8198	3.2000e-4	1.0011	3.6323e-5	5.8461	2.2800e-4	1.0016	3.9062e-5	90.2420	2.0000e-3	1.0027	2.2223e-5	671.3630	0.0730	1.0031
229.0000	13.0205	5.3300e-4	1.0005	4.0956e-5	8.8203	3.1800e-4	1.0012	3.6096e-5	5.8471	2.2600e-4	1.0017	3.8719e-5	90.2450	2.0000e-3	1.0028	2.2223e-5	671.5030	0.0720	1.0033
236.0000	13.0202	5.4600e-4	1.0005	4.1955e-5	8.8210	3.2800e-4	1.0013	3.7231e-5	5.8479	2.3300e-4	1.0019	3.9919e-5	90.2490	2.0000e-3	1.0028	2.2223e-5	671.6300	0.0720	1.0035
243.0000	13.0196	5.4800e-4	1.0004	4.2109e-5	8.8212	3.3200e-4	1.0013	3.7685e-5	5.8487	2.3500e-4	1.0020	4.0261e-5	90.2490	2.0000e-3	1.0028	2.2223e-5	671.7060	0.0730	1.0036
250.0000	13.0195	5.4200e-4	1.0004	4.1648e-5	8.8221	3.2900e-4	1.0014	3.7345e-5	5.8497	2.3100e-4	1.0022	3.9576e-5	90.2510	2.0000e-3	1.0028	2.2223e-5	671.8870	0.0710	1.0038
257.0000	13.0193	5.2800e-4	1.0004	4.0572e-5	8.8226	3.1700e-4	1.0015	3.5983e-5	5.8505	2.2400e-4	1.0023	3.8377e-5	90.2520	2.0000e-3	1.0029	2.2223e-5	672.0130	0.0710	1.0040
264.0000	13.0187	5.5000e-4	1.0004	4.2263e-5	8.8233	3.3600e-4	1.0015	3.8139e-5	5.8514	2.3600e-4	1.0025	4.0433e-5	90.2550	2.0000e-3	1.0029	2.2223e-5	672.1290	0.0730	1.0042
271.0000	13.0188	5.6000e-4	1.0004	4.3031e-5	8.8240	3.4100e-4	1.0016	3.8707e-5	5.8524	2.3900e-4	1.0027	4.0946e-5	90.2540	2.0000e-3	1.0029	2.2223e-5	672.3030	0.0740	1.0045
278.0000	13.0183	5.4900e-4	1.0003	4.2186e-5	8.8247	3.3000e-4	1.0017	3.7458e-5	5.8530	2.3300e-4	1.0028	3.9919e-5	90.2540	2.0000e-3	1.0029	2.2223e-5	672.3980	0.0740	1.0046
285.0000	13.0183	5.6000e-4	1.0003	4.3031e-5	8.8253	3.4000e-4	1.0018	3.8593e-5	5.8537	2.4000e-4	1.0029	4.1118e-5	90.2560	2.0000e-3	1.0029	2.2223e-5	672.5320	0.0740	1.0048
292.0000	13.0185	5.4600e-4	1.0004	4.1955e-5	8.8261	3.2900e-4	1.0019	3.7345e-5	5.8545	2.3200e-4	1.0030	3.9747e-5	90.2530	2.0000e-3	1.0029	2.2223e-5	672.6890	0.0750	1.0050
299.0000	13.0183	5.6000e-4	1.0003	4.3031e-5	8.8267	3.4000e-4	1.0019	3.8593e-5	5.8549	2.3900e-4	1.0031	4.0946e-5	90.2520	2.0000e-3	1.0029	2.2223e-5	672.7680	0.0750	1.0052
306.0000	13.0189	5.5300e-4	1.0004	4.2493e-5	8.8277	3.3300e-4	1.0020	3.7799e-5	5.8556	2.3400e-4	1.0032	4.0090e-5	90.2490	2.0000e-3	1.0028	2.2223e-5	672.9530	0.0750	1.0054
313.0000	13.0182	5.7200e-4	1.0003	4.3953e-5	8.8279	3.4800e-4	1.0020	3.9501e-5	5.8556	2.4400e-4	1.0032	4.1803e-5	90.2450	2.0000e-3	1.0028	2.2223e-5	672.9380	0.0760	1.0054
320.0000	13.0187	5.8600e-4	1.0004	4.5029e-5	8.8288	3.5500e-4	1.0022	4.0296e-5	5.8560	2.4900e-4	1.0033	4.2660e-5	90.2380	2.0000e-3	1.0027	2.2223e-5	673.0790	0.0770	1.0056
327.0000	13.0202	5.8300e-4	1.0005	4.4798e-5	8.8300	3.5300e-4	1.0023	4.0069e-5	5.8566	2.4700e-4	1.0034	4.2317e-5	90.2290	2.0000e-3	1.0026	2.2223e-5	673.3240	0.0770	1.0060

334.0000	13.0212	5.6800e-4	1.0006	4.3646e-5	8.8310	3.4100e-4	1.0024	3.8707e-5	5.8569	2.3900e-4	1.0034	4.0946e-5	90.2200	2.0000e-3	1.0025	2.2223e-5	673.4860	0.0770	1.0062
341.0000	13.0218	6.7800e-4	1.0006	5.2098e-5	8.8318	4.0900e-4	1.0025	4.6426e-5	5.8570	2.8700e-4	1.0034	4.9170e-5	90.2100	2.0000e-3	1.0024	2.2223e-5	673.5870	0.0900	1.0064
348.0000	13.0218	6.9100e-4	1.0006	5.3097e-5	8.8318	4.1500e-4	1.0025	4.7107e-5	5.8566	2.9000e-4	1.0034	4.9684e-5	90.1910	3.0000e-3	1.0022	3.3335e-5	673.5360	0.0920	1.0063
355.0000	13.0233	6.7400e-4	1.0007	5.1791e-5	8.8332	4.0300e-4	1.0027	4.5744e-5	5.8567	2.8500e-4	1.0034	4.8827e-5	90.1800	3.0000e-3	1.0021	3.3335e-5	673.7370	0.0890	1.0066
362.0000	13.0247	6.5600e-4	1.0008	5.0408e-5	8.8343	3.8500e-4	1.0028	4.3701e-5	5.8566	2.7600e-4	1.0034	4.7285e-5	90.1580	3.0000e-3	1.0018	3.3335e-5	673.8790	0.0890	1.0068
369.0000	13.0253	6.3800e-4	1.0009	4.9025e-5	8.8352	3.9200e-4	1.0029	4.4496e-5	5.8561	2.7200e-4	1.0033	4.6600e-5	90.1290	3.0000e-3	1.0015	3.3335e-5	673.9170	0.0870	1.0069
376.0000	13.0264	6.1700e-4	1.0010	4.7411e-5	8.8360	3.8900e-4	1.0030	4.4155e-5	5.8557	6.2300e-4	1.0032	1.0673e-4	90.0940	4.0000e-3	1.0011	4.4447e-5	673.9970	0.0840	1.0070
383.0000	13.0287	6.1500e-4	1.0011	4.7257e-5	8.8376	3.9600e-4	1.0032	4.4950e-5	5.8563	2.6200e-4	1.0033	4.4887e-5	90.0700	5.0000e-3	1.0008	5.5559e-5	674.2370	0.0840	1.0074
390.0000	13.0294	5.8000e-4	1.0012	4.4568e-5	8.8386	3.8000e-4	1.0033	4.3134e-5	5.8565	2.5000e-4	1.0034	4.2831e-5	90.0520	6.0000e-3	1.0006	6.6670e-5	674.4410	0.0780	1.0077

Table S2 . BVS calculations for iron sites in ilvaite. using the bond valance parameters given (for either Fe²⁺ or Fe³⁺ as stated) and using Fe-O bond length data extracted from GSAS refinements.

T/K	Fe1 (M12) 2+	Fe2 (M11) 2+	Fe3 (M2) 2+	Fe1 (M12) 3+	Fe2 (M11) 3+	Fe3 (M2) 3+
100.0000	2.1530	2.4100	1.9540	2.4410	2.7870	2.1610
138.0000	2.0850	2.4300	1.9000	2.3500	2.8140	2.0830
145.0000	2.0910	2.4280	1.9020	2.3570	2.8120	2.0950
151.5000	2.1110	2.4230	1.8990	2.3850	2.8040	2.0910
158.0000	2.0810	2.4600	1.9090	2.3450	2.8540	2.1040
165.0000	2.0970	2.4150	1.8990	2.3660	2.7930	2.0900
171.5000	2.0820	2.4270	1.8960	2.3460	2.8110	2.0860
178.0000	2.0940	2.4260	1.9000	2.3630	2.8090	2.0920
185.0000	2.0890	2.4270	1.9010	2.3560	2.8100	2.0938
191.0000	2.1160	2.4030	1.8990	2.3910	2.7760	2.0913
198.0000	2.1090	2.4100	1.8930	2.3820	2.7870	2.0830
204.0000	2.1030	2.3960	1.8970	2.3730	2.7690	2.0880
210.0000	2.1160	2.4030	1.9020	2.3910	2.7770	2.0970
217.0000	2.0950	2.3980	1.9060	2.3630	2.7700	2.1000
224.0000	2.1110	2.3930	1.9050	2.3860	2.7640	2.0990
230.0000	2.0880	2.4020	1.9040	2.3550	2.7760	2.0980
237.0000	2.1250	2.3610	1.8980	2.4040	2.7200	2.0900
244.0000	2.1280	2.3640	1.8930	2.4080	2.7250	2.0840
251.0000	2.0960	2.3790	1.9070	2.3650	2.7450	2.1030
257.0000	2.1010	2.3840	1.8930	2.3710	2.7520	2.0830
263.0000	2.0930	2.3890	1.9040	2.3610	2.7590	2.0980
270.0000	2.0670	2.4190	1.9000	2.3270	2.8000	2.0940
276.0000	2.0970	2.3880	1.8910	2.3670	2.7580	2.0810
289.0000	2.1070	2.3780	1.8910	2.3800	2.7440	2.0810
289.0000	2.0870	2.3900	1.8930	2.3540	2.7600	2.0840
290.0000	2.0800	2.3920	1.8940	2.3450	2.7640	2.0850
300.0000	2.1110	2.4340	1.8870	2.3870	2.8190	2.0760
296.0000	2.0740	2.3980	1.8950	2.3370	2.7710	2.0860
302.0000	2.0873	2.3790	1.8960	2.3540	2.7450	2.0880
308.0000	2.0790	2.3810	1.8920	2.3430	2.7490	2.0830
314.0000	2.0880	2.3690	1.8940	2.3559	2.7320	2.0860
320.0000	2.0820	2.3740	1.8960	2.3470	2.7400	2.0890
327.0000	2.1110	2.3520	1.8830	2.3880	2.7090	2.0720
332.0000	2.0450	2.4030	1.9050	2.2980	2.7790	2.1000
336.0000	2.0891	2.3640	1.8860	2.3570	2.7260	2.0760
347.0000	2.0842	2.3420	1.8970	2.3500	2.6970	2.0916
353.0000	2.1860	2.2400	1.8810	2.4870	2.5590	2.0710
360.0000	2.1970	2.2260	1.8860	2.5010	2.5410	2.0760
366.0000	2.1980	2.2490	1.8890	2.5041	2.5716	2.0790
372.0000	2.3240	2.1300	1.8890	2.5750	2.5100	2.0800
575.0000	2.2811	2.2630	1.9240	2.5210	2.5910	2.1290
800.0000	2.3140	2.1900	1.9020	2.5380	2.4810	2.1020