Supplementary Information for

"Control of Polymorphism in $NaNbO_3$ by Hydrothermal Synthesis"

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S1. Powder neutron diffraction structure refinement

Crystal data

Chemical formula	$NaNbO_3$
Chemical formula weight (g mol^{-1})	163.89
Cell setting	Rhombohedral
Space group	$R\bar{3}$
a (Å)	5.3430(9)
b (Å)	5.3430(9)
c (Å)	15.6493(27)
α (^{o})	90
β (^{o})	90
γ (^{o})	120
V ($Å^3$)	386.87(11)
Radiation type	Neutron
Temperature (K)	298
Colour	White
Data collection	
Diffractometer	GEM
Data collection method	Time-of-flight
Instrument location	ISIS, Rutherford Appleton Laboratory
Specimen mounting	6mm Vanadium Can
Refinement	
Rp	0.0479
Rwp	0.0472
Profile function	Pseudo-Voigt
Computer programmes	
Structure refinement	GSAS (Larson & Von Dreele, 1986)

	x	y	z	U_{iso}
Na	0.0	0.0	0.14291(10)	0.0113(4)
Nb	0.0	0.0	0.35158(5)	0.00166(20)
O	0.27024(10)	-0.05341(10)	0.26155(4)	0.00499(15)

S2 NMR experimental details

Spectra were recorded on a 400 MHz Bruker Avance spectrometer. For the ^{23}Na the reported spectrum is the result of averaging 24 transients with recycle intervals of 4 s from a sample packed into 4-mm standard ZrO_2 rotors and rotated at a rate of 10 kHz. For the ^{93}Nb spectra, a spin-echo pulse sequence was used with pulses selective for the central transition. The spectrum is the result of averaging 1600 transients with recycle intervals of 1 s. The sample was packed into a 2.5-mm standard ZrO_2 rotor and rotated at a rate of 33 kHz. On Figure 2b the red line in the ^{93}Nb spectrum is that fitted to extract spectral parameters.

S3 Variable Temperature powder XRD

A sample of ilmenite $NaNbO_3$ was heated to 1000 ^{o}C in steps of 25^{o}C on an MRI cell attached to a Siemens D5000 X-ray diffractometer. The sample was held at each temperature for 2 hours before each scan started. Data were measured using a CuK_α source (λ_1=1.5405 Å, λ_2=1.5443 Å, $\lambda_{Average}$=1.5418 Å) with a step size of 0.02 ^{o}2θ.

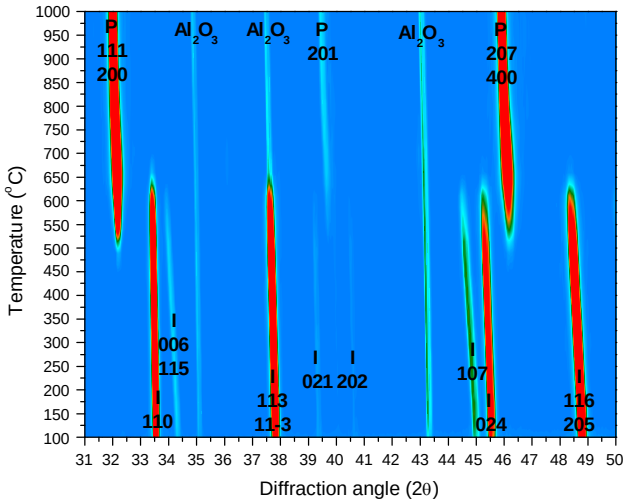


Figure S3.1: Contour map of powder XRD. Bragg peaks of the ilmenite and perovskite phase are labelled I and P, respectively, and the Al_2O_3 peaks are due to the sample holder. The perovskite peaks are indexed on the high temperature tetraganol (P4/mbm) phase) reported by Darlington and Knight.[1]

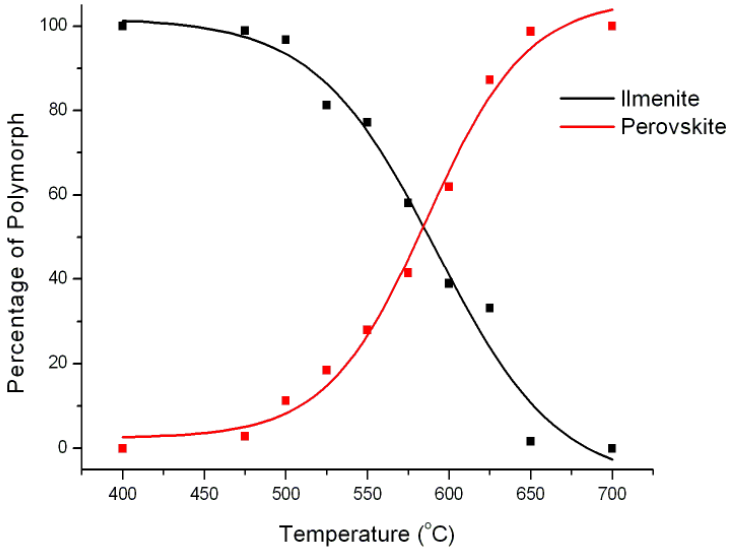


Figure S3.2: Percentage conversion of ilmenite to perovskite by peak area analysis of XRD data.

S4: EDXRD data

EDXRD experiments were performed on Station 16.4 of the Daresbury SRS with incident X-rays over the energy range 20 to 80 keV. Data are recorded using a fixed, three-element solid-state detector that permits three, overlapping regions of diffraction data to be measured simultaneously to maximise the amount of structural information measured.[2] Data were recorded from reactions in a 25 ml Teflon-lined stainless steel autoclave with windows thinned to 0.25 mm.[3] In the spectra below the black traces are from a detector at $2\theta = 1.81^{o}$ and the red traces from a detector at $2\theta = 4.7^{o}$. In the energy dispersive diffraction geometry the *d* spacing of a Bragg peak (in Å) is related to its observed energy, *E*, (in keV) by $d = 6.19926/E\sin\theta$.

The shift of the Teflon peak in the data presented in Figure 3 is due to thermal expansion and provides a measure of when reaction temperature is reached.

Bragg peaks of the crystalline phases observed were identified using published crystal structures. Peaks labelled * are due to the reaction cell.

Phase	Crystal Structure Reference
Nb_2O_5	[4]
$Na_7(H_3O)Nb_6O_{19}.14H_2O$	[5]
$Na_2Nb_2O_6.nH_2O$	[6]
Perovskite $NaNbO_3$	[7]
Ilmenite $NaNbO_3$	This work

1 C. N. W. Darlington and K. S. Knight, *Acta Cryst. B*, 1999, **55**, 24.
2 G. Muncaster, A. T. Davies, G. Sankar, C. R. A. Catlow, J. M. Thomas, S. L. Colston, P. Barnes, R. I. Walton, and D. O'Hare, *Phys. Chem., Chem. Phys.*, 2000, **2**, 3523.
3 J. S. O. Evans, R. J. Francis, D. O' Hare, S. J. Price, S. M. Clark, J. Flaherty, J. Gordon, A. Nield, and C. C. Tang, *Review of Scientific Instruments*, 1995, **66**, 2442.
4 K. Kato and S. Tamura, *Acta Crystallogr. B*, 1975, **31**, 673.
5 A. Goiffon, E. Philippot, and M. Maurin, *Rev. Chim. Min.*, 1980, **17**, 466.
6 H. W. Xu, M. Nyman, T. M. Nenoff, and A. Navrotsky, *Chem. Mater.*, 2004, **16**, 2034.
7 C. N. W. Darlington and K. S. Knight, *Physica B*, 1999, **266**, 368.

S4.1: Perovskite crystallisation

- 1g Nb_2O_5
- 8mL (1.5M) NaOH
- 240 ^oC

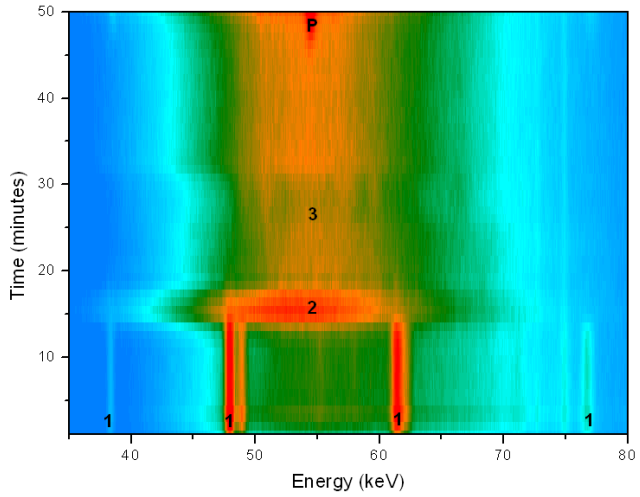
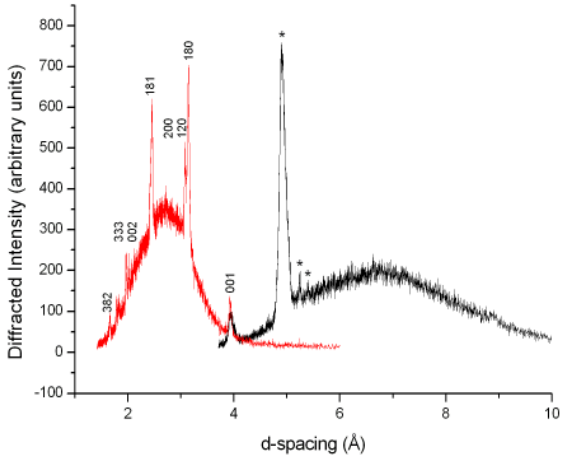


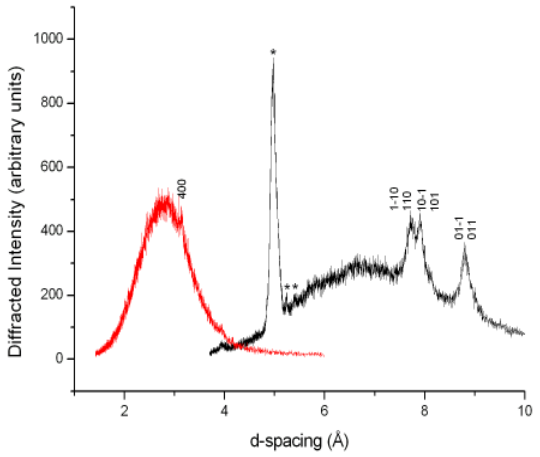
Figure S4.1: Contour map from detector at 4.7 $^o 2\theta$ for perovskite crystallisation (labels as for Figure 3)

Time: 1minute
Phase(s) Present: Nb_2O_5



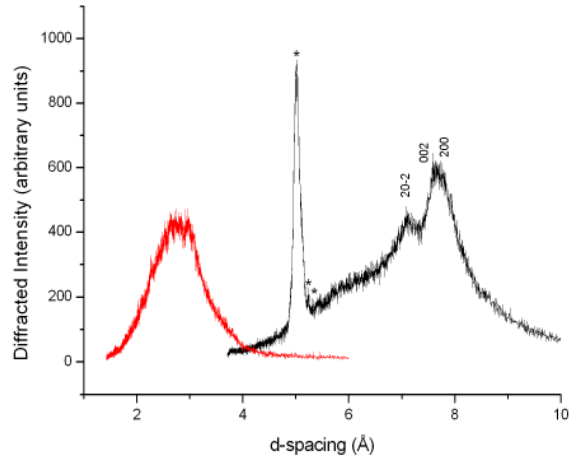
h	k	l	d_{calc}/Å	d_{obs}/Å
0	0	1	3.93	3.931
1	8	0	3.15	3.135
2 2	0 1	0 0	3.09 3.07	3.083
1	8	1	2.46	2.455
6	3	3	2.013	2.013
0	0	2	1.969	1.964
0	16	0	1.832	1.830
3	8	2	1.669	1.662
3	8	1	1.632	1.630

Time: 17 minutes
Phase(s) Present: $Na_7(H_3O)Nb_6O_{19}.14H_2O$



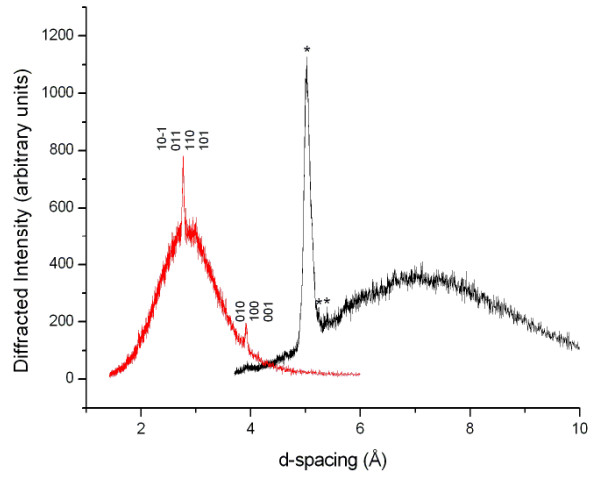
h	k	l	d_{calc}/Å	d_{obs}/Å
0 0	1 1	-1 1	8.786	8.817
1 1	0 0	-1 1	7.897	7.913
1 1	-1 1	0 0	7.754	7.720
4	0	0	2.518	2.515

Time: 30 minutes
Phase(s) Present: $Na_2Nb_2O_6.nH_2O$



h	k	l	d_{calc}/Å	d_{obs}/Å
2	0	0	7.892	7.843
0	0	2	7.537	7.618
2	0	-2	7.026	7.106

Time: 50 minutes
Phase(s) Present: Perovskite $NaNbO_3$



h	k	l	d_{calc}/Å	d_{obs}/Å
0 1 0	1 0 0	0 0 1	3.920	3.927
1 0 1 1	0 1 1 0	-1 1 0 1	2.779 2.771 2.771 2.764	2.767

S4.2: Ilmenite crystallisation

- 1g Nb_2O_5
- 8mL (1M) NaOH
- 240 ^oC

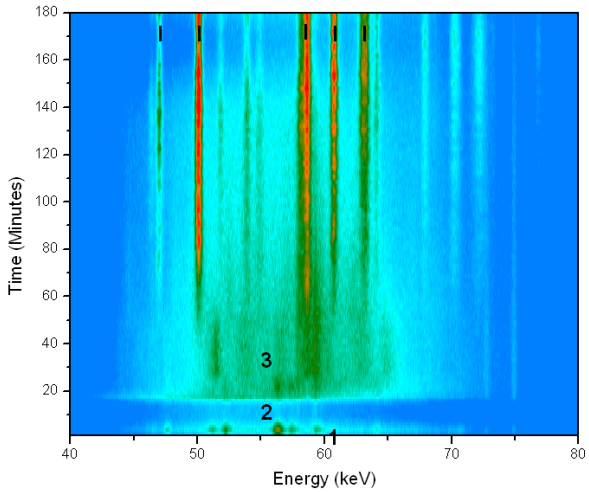
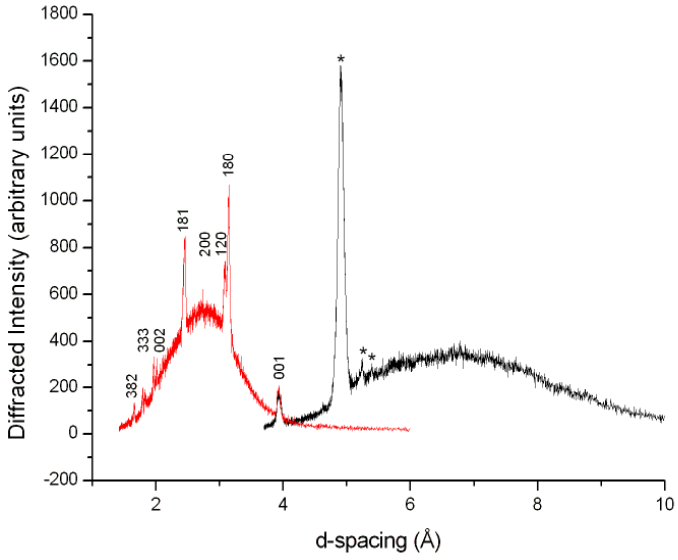


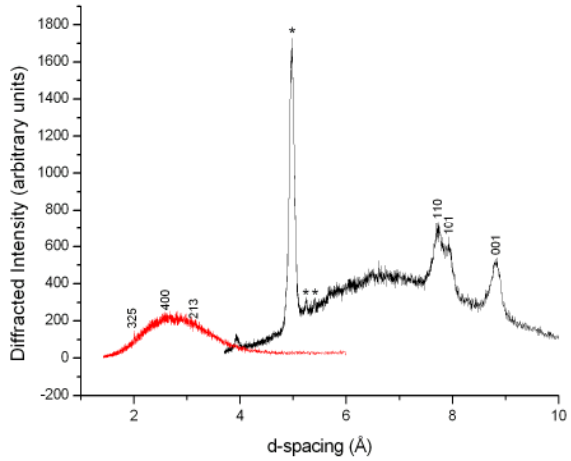
Figure S4.2: Contour map from detector at 4.7 º2θ for perovskite crystallisation (labels as for Figure 3)

Time: 1 minute
Phase(s) Present: Nb_2O_5



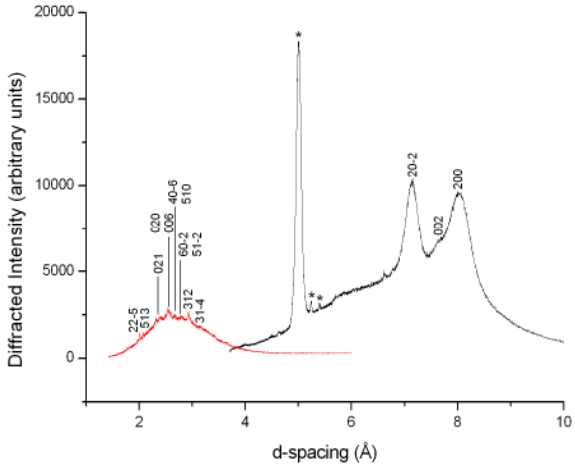
h	k	l	d_{calc}/Å	d_{obs}/Å
0	0	1	3.930	3.93
1	8	0	3.150	3.144
2	0	0	3.090	3.084
2	1	0	3.070	
1	8	1	2.460	2.453
6	3	3	2.013	2.012
0	0	2	1.969	1.963
3	8	2	1.669	1.661
3	8	1	1.632	1.628

Time: 18 minutes
Phase(s) Present: $Na_7(H_3O)Nb_6O_{19}.14H_2O$



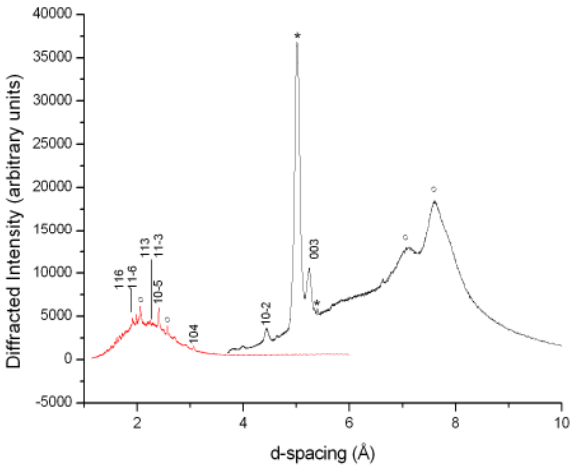
h	k	l	d_{calc}/Å	d_{obs}/Å
0	1	1	8.758	8.895
1	0	1	7.897	7.993
1	1	0	7.754	7.788
2	1	3	3.134	3.223
4	0	0	2.518	2.513
3	2	5	1.923	1.919

Time: 25-35 minutes
$Na_2Nb_2O_6.nH_2O$



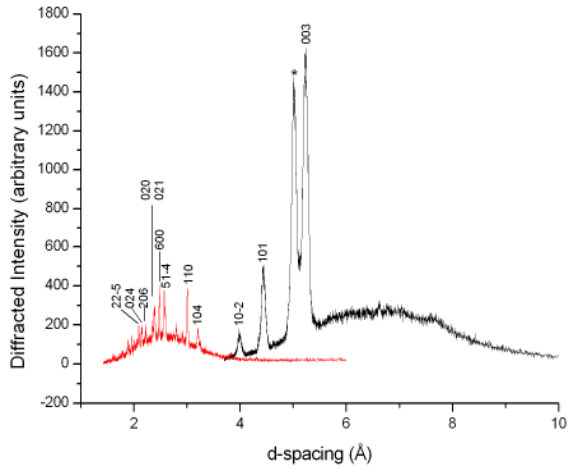
h	k	l	d_{calc}/Å	d_{obs}/Å
2	0	0	7.792	8.037
0	0	2	7.537	7.622
2	0	-2	7.026	7.141
3	1	2	2.950	2.959
6	0	-2	2.836	2.927
1	1	4	2.796	2.800
5	1	-4	2.637	2.667
6	0	0	2.597	2.581
0	2	0	2.515	2.540
0	2	1	2.480	2.497
2	2	0	2.393	2.392
2	2	1	2.319	2.319
2	0	6	2.150	2.146
0	2	4	2.092	2.072
2	2	-5	2.000	2.012
7	1	-6	1.982	1.970
0	2	6	1.777	1.788

Time: 60-80 minutes
Phase(s) Present: Unknown Phase (o) and Ilmenite $NaNbO_3$



h	k	l	Phase	d_{calc}/Å	d_{obs}/Å
			Unknown Phase		8.140
			Unknown Phase		7.797
			Unknown Phase		7.588
			Unknown Phase		7.089
			Unknown Phase		5.247
0	0	3	Ilmenite $NaNbO_3$	5.204	5.019
			Unknown Phase		4.440
1	0	-2	Ilmenite $NaNbO_3$	3.976	3.991
			Unknown Phase		3.831
			Unknown Phase		3.647
			Unknown Phase		3.381
			Unknown Phase		3.209
1	0	4	Ilmenite $NaNbO_3$	2.981	3.009
			Unknown Phase		2.872
			Unknown Phase		2.797
1	0	-5	Ilmenite $NaNbO_3$	2.587	2.595
			Unknown Phase		2.570
			Unknown Phase		2.542
			Unknown Phase		2.481
1 1	1 1	3 -3	Ilmenite $NaNbO_3$	2.374	2.387
			Unknown Phase		2.350
			Unknown Phase		2.219
			Unknown Phase		2.146
			Unknown Phase		2.090
			Unknown Phase		2.072
2	0	-4	Ilmenite $NaNbO_3$	1.998	2.011
			Unknown Phase		1.966
			Unknown Phase		1.912
1 1	1 1	6 -6	Ilmenite $NaNbO_3$	1.863	1.879
			Unknown Phase		1.786
			Unknown Phase		1.775
			Unknown Phase		1.754
			Unknown Phase		1.727
			Unknown Phase		1.625
1 2	2 1	-4 4	Ilmenite $NaNbO_3$	1.594	1.598

Time: 180 minutes
Phase(s) Present: Ilmenite $NaNbO_3$



h	k	l	d_{calc}/Å	d_{obs}/Å
0	0	3	5.204	5.278
1	0	1	4.430	4.468
1	0	-2	3.976	4.016
1	0	4	2.981	2.991
1	1	0	2.668	2.668
0	0	6	2.602	2.613
1 1	1 1	3 -3	2.374	2.377
1	0	7	2.008	2.016
2	0	-4	1.998	1.991
1 1	1 1	6 -6	1.863	1.867
0	0	9	1.734	1.737
2	1	-2	1.704	1.704
1 2	2 1	-4 4	1.594	1.597
3	0	0	1.540	1.540
1	0	10	1.479	1.483
1 1	1 1	-9 9	1.454	1.460

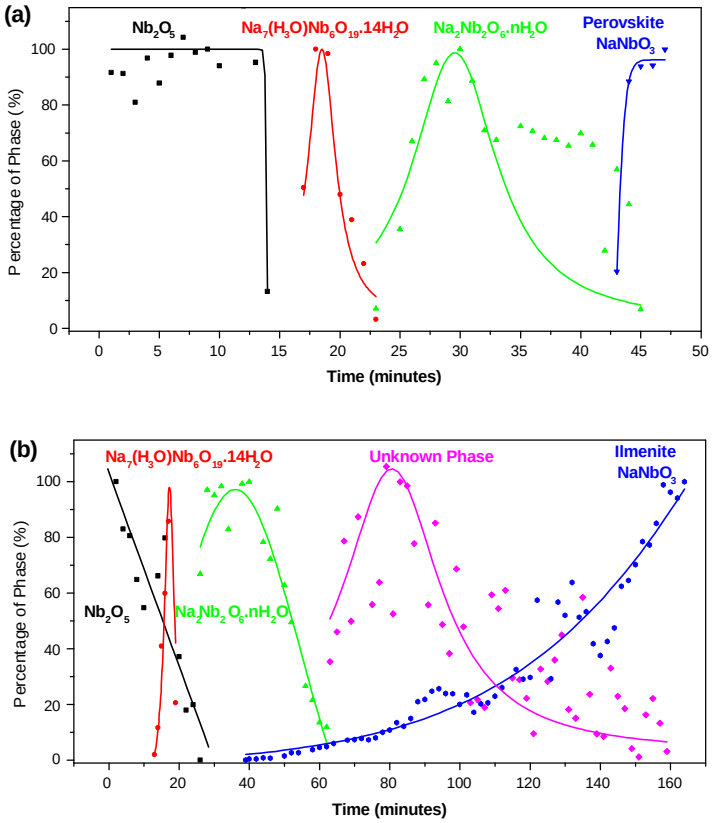


Figure S4.3: Evolution of normalised Bragg peak areas in the EDXRD experiments for (a) reaction performed at with 1.5 M NaOH and (b) with 1 M NaOH. Lines are for guidance only.

S5: TGA data from ilmenite $NaNbO_3$

Data were recorded using under a flow of air using a Perkin Elmer Pyris Diamond TG/DTA apparatus to 700 ^oC with a heating rate of 5 $^oC\ min^{-1}$.

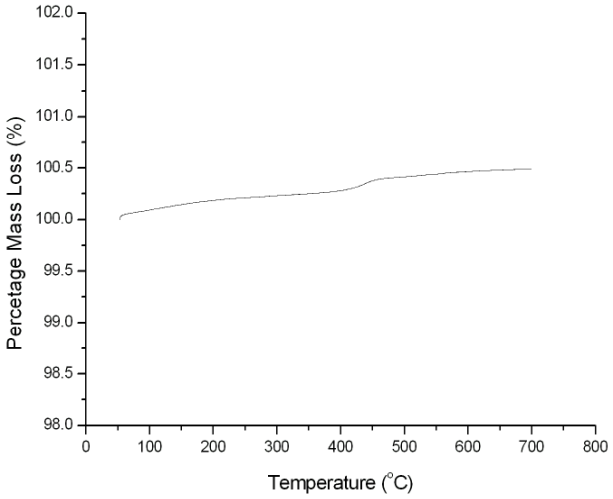


Figure S5.1: TGA trace of ilmenite $NaNbO_3$

S6: IR data from ilmenite $NaNbO_3$

Data were recorded from a freshly dried sample of the material (50 ^oC is air). The sample was studied undiluted using a Perkin Elmer Paragon 1000 FT-IR spectrometer in attenuated total reflection mode. This precludes the use of a diluent and so avoids contamination with water-containing material. The spectrum shows no features due to water or hydroxide.

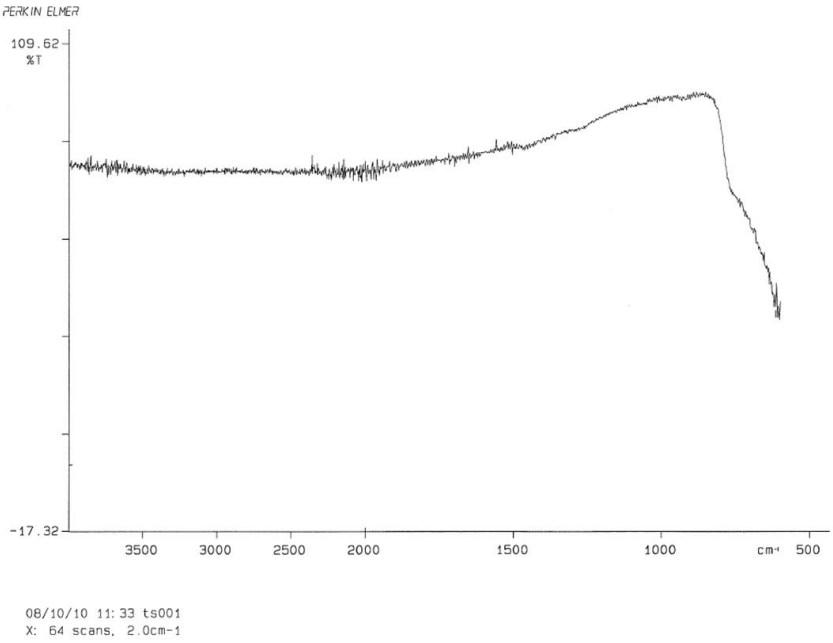


Figure S6.1: IR spectrum of ilmenite $NaNbO_3$

S7: ^{1}H NMR data from ilmenite $NaNbO_3$

The dominant signal in the ^{1}H NMR spectrum is a broad feature from the rotor and /or probe (usually not observed and part of the background of a typical spectrum of a hydrogen-containing sample). Weak additional features are due to additional contaminent water in the rotor, probe or sample, since they are seen even in anhydrous materials that have been prepared at extreme temperatures. As an example, the spectrum from Mg_2SiO_4, measured under identical conditions using the same rotor, is shown and this shows the same level of proton background, despite having been synthesised with an annealing step at 1500 ^{o}C.[8]

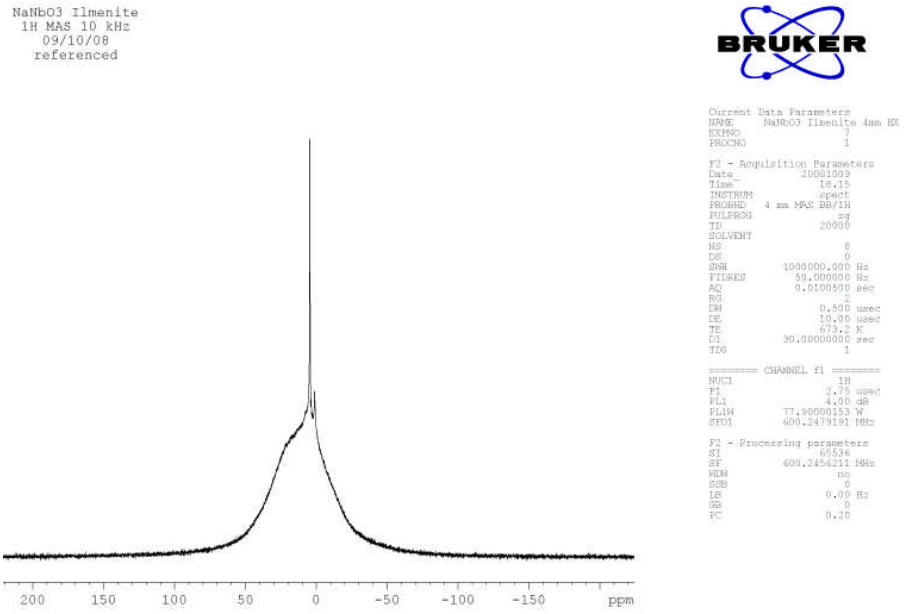


Figure S7.1: ^{1}H NMR spectrum of ilmenite $NaNbO_3$.

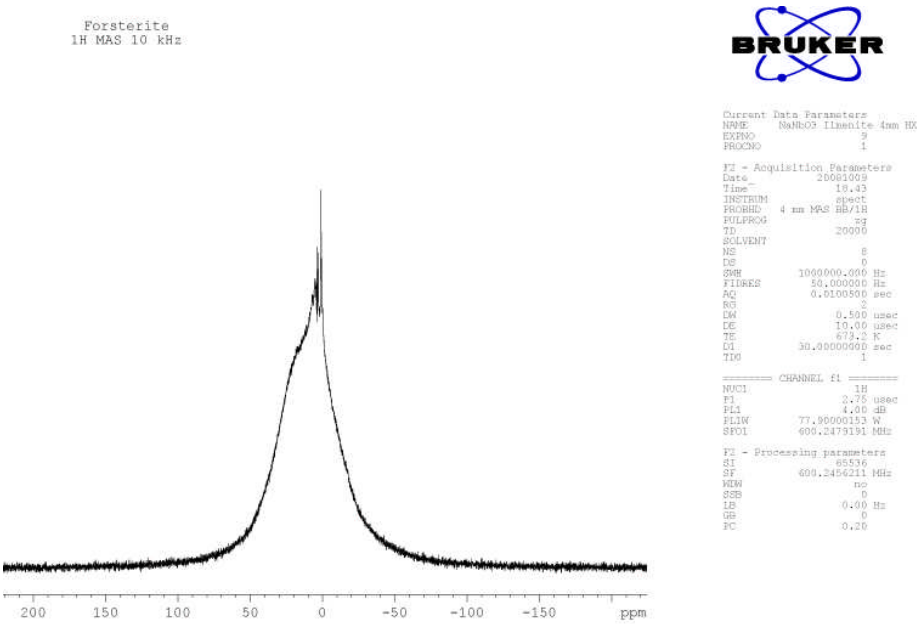


Figure S7.2: ^{1}H NMR spectrum of Mg_2SiO_4

8. S.E. Ashbrook, A.J. Berry and S. Wimperis, *Amer. Mineral.* 1999, **84,** 1191.