⁹³Nb NMR and DFT Investigation of the Polymorphs of NaNbO₃

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S1 Structures of *Pnma*, *P2*₁*ma*, *Pn2*₁*a* and *Pnm2*₁ niobate perovskites

In previous work⁵¹ the majority of synthetic samples of NaNbO₃, prepared using a variety of methods were shown to contain a mixture of perovskite phases. These were identified, through a combination of X-ray and neutron powder diffraction and ²³Na NMR spectroscopy as the commonly reported *Pbcm* phase, and a second, polar phase, probably $P2_1ma$. However, if only diffraction data was considered, refinements were unable to distinguish between models using space group *Pnma*, and three sub groups, resulting from a decrease in symmetry, $P2_1ma$, $Pn2_1a$ and $Pnm2_1$ for the nature of the second phase. All four produced fits of similar quality to the experimental diffraction data. However, both SHG measurements and ²³Na NMR did not support *Pnma* and *Pn2_1a* as possible space groups. Figure S1.1 shows the structures of the four possible perovskites, and Figure S1.2 shows the local Nb environment in each. All structures shown result directly from the refinement of the diffraction data and are prior to any optimisation of the geometry using DFT.



Figure S1.1 Structures of *Pnma*, $P2_1ma$, $Pn2_1a$ and $Pnm2_1$ NaNbO₃ perovskite structures derived from refinement of diffraction data.^{S1} Green spheres represent sodium atoms, and NbO₆ octahedra are shown in blue.



Figure S1.2. Expansion of the local Nb coordination environment in *Pnma*, $P2_1ma$, $Pn2_1a$ and $Pnm2_1$ NaNbO₃ perovskite structures derived from refinement of diffraction data.^{S1} Blue and red spheres represent niobium and oxygen atoms, respectively. Bond distances are shown with errors quoted in brackets.

S2 Overlay of two-dimensional ⁹³Nb MQMAS NMR spectra

Figure S2.1 shows an overlay of ⁹³Nb (14.1 T) triple-quantum MAS NMR spectra of commercial, solid-state and sol-gel NaNbO₃. The lineshape for sol-gel NaNbO₃ (major phase $P2_1ma$) is a little broader than that for the commercial sample (phase pure *Pbcm*), extending to lower δ_2 shifts. The ⁹³Nb MQMAS NMR spectrum of solid-state NaNbO₃, containing an almost equal mixture of the two phases, also looks very similar. It would appear, therefore, that the ⁹³Nb environment is similar in the two polymorphs and that it is not easy to either identify or distinguish between them by ⁹³Nb NMR, in contrast to the suggestion in previous work.^{S2}



Figure S2.1. Overlay of ⁹³Nb (14.1 T) MAS and two-dimensional triple-quantum MAS NMR spectra of commercial, solid-state and sol-gel NaNbO₃, shown in black, red and blue, respectively. Spectra were acquired using a phase-modulated split-t₁ shifted-echo pulse sequence⁵³ and result from averaging 1440 transients for each of 48 t₁ increments of 117.6 μs. In each case, the MAS rate was 30 kHz.

S3 Fitting and analysis of ⁹³Nb wideline NMR spectra

Lineshape analysis of variable field ⁹³Nb wideline static NMR spectra of commercial, solid-state and sol-gel NaNbO₃ was carried out using the SOLA lineshape simulation package within the Bruker Topspin software. Approximate values for δ_{isor} , C_Q and η_Q determined from ⁹³Nb MQMAS NMR data were used as initial parameters in the fits that were refined for spectra recorded at each magnetic field strength until consistency between each fit was reached. Figure S3.1 shows a comparison between the experimental ⁹³Nb static wideline NMR spectra for the two pure NaNbO₃ polymorphs (commercial and sol-gel samples) and spectra simulated using both values determined in this work and those quoted previously by Hanna *et al.*⁵² Good agreement with the experimental data is observed for both sets of fits, indicating that it is difficult to obtain a unique set of NMR parameters, even with data at variable fields. Figure S3.2 shows a comparison between experimental ⁹³Nb static wideline NMR spectra for spectra for solid-state NaNbO₃, and those simulated (for a variety of phase fractions) using the values obtained from analytical fitting of spectra for the *Pbcm* and *P*₁*ma* phases, given in Table 1 in the main text.



Figure S3.1. ⁹³Nb wideline static NMR spectra of (a) commercial and (b) sol-gel NaNbO₃ acquired using a spin-echo pulse sequence at 9.4, 14.1 and 20.0 T. Fits of the experimental data are shown below each spectrum in red. Spectra simulated using values quoted by Hanna *et al.*⁵² are shown in (c). In all simulated spectra, 2000 Hz Lorentzian line broadening was applied.



Figure S3.2. ⁹³Nb wideline static NMR spectra of solid-state NaNbO₃ acquired using a spin-echo pulse sequence at 9.4, 14.1 and 20.0 T. Also shown are lineshapes simulated (for various phase fractions) using the values obtained from analytical fitting of spectra for the *Pbcm* and $P2_1ma$ phases, given in Table 1 in the main text. In all simulated spectra, 2000 Hz Lorentzian line broadening was applied.

S4 Geometry optimisation of niobate perovskite structures

Geometry optimisation was carried out for all structures from the literature and refinement of diffraction data, using CASTEP^{S4-S5} (GGA PBE functional), with a cut-off energy of 60 Ry and k-point spacing of 0.04 Å⁻¹, and both the lattice parameters and internal atomic coordinates allowed to vary. Calculations were performed using the EaStCHEM Research Computing Facility, which consists of 136 AMD Opteron 280 dual-core processors running at 2.4 GHz, partly connected by Infinipath high speed interconnects. Calculation wallclock times ranged from 12 to 36 h using 12 cores, depending on the size of the unit cell.

Figures S4.1 and S4.2 show structures for the three *Pbcm* models considered (two from the literature^{S6-S7} and one from the refinement of diffraction data^{S1}), pre and post geometry optimisation. Very little change is observed in the overall structure, with some small variation in the Na position perhaps the most obvious change. Some small changes are observed in the local Nb coordination environment.

In contrast, large changes are observed, particularly in the local Nb structure, for the *Pmma*^{S8} phase upon geometry optimisation, as shown in Figure S4.3. These change are sufficient to result in a change in space group, to *Imma*, and are accompanied by significant changes in the ⁹³Nb NMR parameters, particularly C_Q .



Figure S4.1 Structures of *Pbcm* NaNbO₃ perovskite structures from (a) Ref. S6, (b) Ref. S7 and (c) Rietveld refinement of diffraction data.^{S1} Green spheres represent sodium atoms, and NbO₆ octahedra are shown in blue.



Figure S4.2. Expansion of the local Nb coordination environment in *Pbcm* NaNbO₃ perovskite structures from (a) Ref. S6, (b) Ref. S7 and (c) Rietveld refinement of diffraction data.^{S1} Blue and red spheres represent niobium and oxygen atoms, respectively.

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Figure S4.3 (a) Structures and (b) expansion of the local Nb coordination environment of *Pmma* NaNbO₃ perovskite.⁵⁸ Note that after optimisation the structure is described in space group *Imma*. In (a), green spheres represent sodium atoms, and NbO₆ octahedra are shown in blue. In (b), blue and red spheres represent niobium and oxygen atoms, respectively.

S5 Estimation of ⁹³Nb EFG using a point charge model

It is possible to estimate the relative contribution of differing atoms to the quadrupolar interaction using a simple electrostatic or "point charge" model.⁵⁹ In this approach, the electric field gradient at the nucleus, eq_{ionic}, is generated by summing the contribution to the shielding tensor components ($V_{\alpha\beta}$) of surrounding atoms (considered as simple point charges), at a position (x, y, z) from a Nb atom at the origin, assuming a purely ionic solid. For elements where $\alpha = \beta$ (*i.e.*, V_{xx} , V_{yy} or V_{zz}) the contribution to the tensor component for each point charge is given by

$$V_{\alpha\alpha} = ne (3\alpha^2 - r^2) / r^5$$
, (S1)

where ne is the charge on the atom and r is the distance of that charge from the origin. However if $\alpha \neq \beta$

$$V_{\alpha\beta} = ne (3\alpha\beta) / r^5 .$$
 (S2)

Here, a charge of -1 was assumed for the surrounding oxygen species (derived from empirical relationships described in more detail in Ref. S9), and a charge of +1 for the sodium cations. Diagonalisation of the full tensor produces the three principal components of the tensor V_{XX} , V_{YY} and V_{ZZ} . From this the magnitude of the EFG (from the largest of the three principal components V_{ZZ}) and the asymmetry, given by $(V_{YY} - V_{XX})/V_{ZZ}$, can be determined. If desired, the quadrupolar coupling constant C_Q can be determined using $C_Q = eQV_{ZZ}/h$, where Q is the nuclear electric quadrupole moment. If C_Q values for different nuclei are to be compared, the contributions of the inner electron shells to the observed field gradient, eq_{obs} , should also be considered. This is expressed by the Sternheimer anti-shielding factor (γ_{ex}), where $eq_{obs} = eq_{ionic}(1 - \gamma_{ex})$.

S6 Local Nb environment in ilmenite and perovskite polymorphs of NaNbO₃

As shown in Table 1 in the main text, there is a clear difference in the NMR parameters for the ilmenite (*R*–3) and perovskite (*Pbcm* and *P2*₁*ma*) polymorphs of NaNbO₃. The magnitude of the quadrupolar coupling is larger (~37 MHz compared to ~20 MHz for the perovskites) and a much larger Δ_{cs} is observed (of ~330 ppm). These differences are also confirmed by the DFT calculations (after geometry optimisation) in Table 2 of the main text. Although in both perovskite and ilmenite polymorphs the Nb is octahedrally coordinated by O, the NNN environment in the two is considerably different, as shown in Figure S6.1. In the *Pbcm* perovskite phase six O species are found within 2.2 Å, eight NNN Na cations within 3.6 Å, and a further six Nb (and also two O) within 4.05 Å. This general arrangement is reasonably similar for all the perovskites studied with the exact distances varying slightly with the polymorph. The NbO₆ octahedron in the ilmenite polymorph appears more distorted (resulting the higher shear and longitudinal strain observed in Figure 6 in the main text), with three longer and three shorter bond distances, respectively. The NNN is considerably different, with three Nb NNN (within 3.2 Å) and four NNNN Na⁺ cations within ~3.7 Å, as shown in Figure S6.1.



Figure S6.1 Expansion of the local Nb coordination environment of (a) *Pbcm* perovskite^{S6} and (b) R–3 ilmenite^{S10} polymorphs (after geometry optimisation) of NaNbO₃. Blue, red and green spheres represent niobium, oxygen and sodium atoms, respectively.

S7 References

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