Single-phase $Na_{1.0}TiO_2$: solid-state synthesis and characterisation by high-resolution powder diffraction

S. J. Clarke,[a] A. C. Duggan,[a] A. J. Fowkes,[a] A. Harrison,[b] R. M. Ibberson[c] and M. J. Rosseinsky*[a]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Department of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh, UK EH9 3JJ*
[c] *ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Oxon, UK OX11 0QX*

We report previously unsuspected multiple-phase behaviour in the Na_xTiO_2 ($x \approx 1$) system and a technique for the preparation of single-phase $Na_{1.0}TiO_2$: very high resolution powder diffraction data are needed for effective characterisation.

The preparation and characterisation of quantum spin systems on perfectly geometrically frustrated lattices (*i.e.* lattices with a topology such that all the exchange interactions cannot be simultaneously satisfied) is a subject of considerable interest.[1] $NaTiO_2$ has long been considered as a canonical two-dimensional frustrated $S = \frac{1}{2}$ system and as such may be a model for the quantum spin fluid ground state proposed by Anderson.[2] The $S = \frac{1}{2}$ Ti^{III} cations are arranged on a triangular lattice in the ordered rock-salt α-$NaFeO_2$ structure (Fig. 1 inset),[3] which consists of alternate layers of edge-sharing NaO_6 and TiO_6 octahedra [space group $R\bar{3}m$, a = 3.0 Å = r(Ti–Ti, intralayer), c = 16.3 Å = $3r$(Ti–Ti, interlayer)]: a sharp drop in the magnetic susceptibility (χ) on cooling at 250 K has been associated with the freezing of the $S = \frac{1}{2}$ spin system.[4] The appreciable sodium vapour pressure above $NaTiO_2$ at high temperature makes direct preparation by standard solid-state techniques challenging and adequate characterisation of the material, particularly with respect to the titanium oxidation state, is essential for confident interpretation of the physical properties.

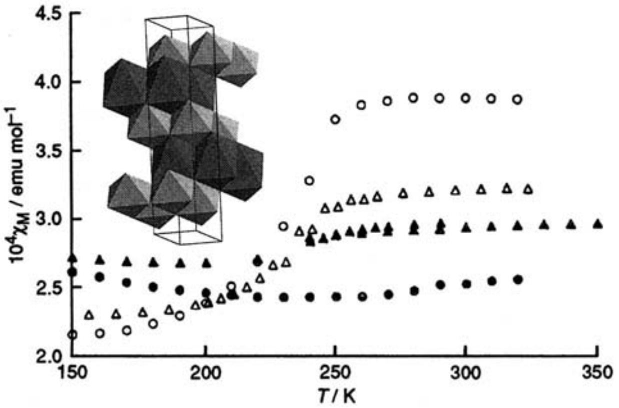

Fig. 1 The magnetic susceptibility, χ_M, depends strongly on the preparative route. The drop in χ below 250 K is particularly sensitive to the lattice parameters (reported here as pseudo-single phase values from the laboratory X-ray instrument to show the trend in Ti oxidation state). The samples shown are $Na_{1.2}TiO_2$ washed with NH_3 and used in the HRPD neutron refinement in Fig. 2 [○; a = 3.0458(1) c = 16.2472(5) Å], $Na_{0.9}TiO_2$ [●; a = 3.0128(2) c = 16.4143(26) Å] and two samples of composition $NaTiO_2$ [▲; a = 3.0196(1) c = 16.3719(14) Å: △; a = 3.0367(1) c = 16.2837(10) Å]. The correlation between the a parameter and the size of the χ anomaly at 250 K is apparent. *Insert:* The α-$NaFeO_2$ structure, consisting of stacked layers of edge-shared NaO_6 (dark) and TiO_6 (light) octahedra. The Ti–O bond length varies from 2.056 to 2.083 Å in the samples measured here.

Our initial Rietveld analyses of laboratory X-ray data† indicated that direct reaction at 1000 °C of 1 equiv. of sodium metal with anatase powder in sealed iron containers produced single-phase material. We observed, however, significant, and correlated, variations in the lattice parameters and magnetic properties in these preparations. The temperature dependence of the susceptibility of several Na_xTiO_2 samples is shown in Fig. 1.† It is thus apparent that the titanium oxidation state exerts a marked control over the electronic properties. We therefore attempted to avoid sodium loss in the high-temperature synthesis by running the reactions with excess (20–40%) sodium to fix the chemical potential of sodium in the reaction container, and subsequently removing unreacted excess sodium by washing with liquid ammonia. Although material prepared by this route appeared single phase on our laboratory X-ray instrument, with lattice parameters consistent with a high sodium content (a = 3.04 Å), and a large drop in χ at 250 K, high-resolution neutron powder diffraction data† could not be refined satisfactorily using a single-phase model. Detailed inspection of the profile shows the presence of *two* rhombohedral phases with the α-$NaFeO_2$ structure and very similar lattice parameters. Rietveld refinement of a model with two $R\bar{3}m$ phases rapidly converged [65(1)% phase I, a = 3.04585(3), c = 16.25631(20) Å; 35(1)% phase II, a = 3.05155(9), c = 16.2313(5) Å, χ^2 = 1.36, R_{wp} = 7.37%, Fig. 2]. Measurements on stoichiometric (x = 1.0) and sodium deficient samples (x = 0.97, 0.95, 0.90) on HRPD showed a similarly subtle two-phase behaviour, with refined lattice parameters for the phases within each sample differing by only 0.1%.

We then used synchrotron powder diffraction† to explore a variety of synthetic routes to $NaTiO_2$. Reaction at the

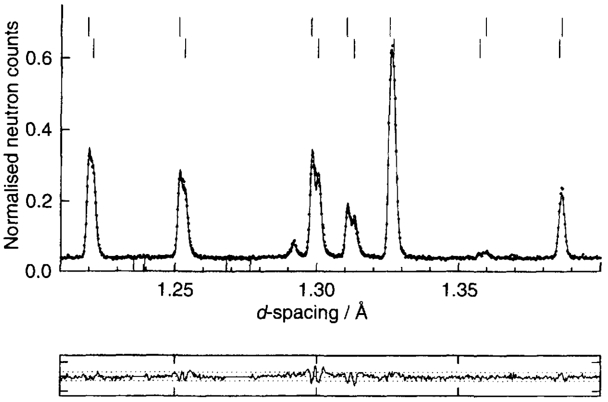

Fig. 2 Neutron powder diffraction Rietveld refinement [observed (●) and calculated (—)] shown over a limited region for $NaTiO_2$ prepared by high-temperature reaction at the composition $Na_{1.4}TiO_2$ followed by dissolution of excess sodium in liquid NH_3. The vertical tick marks represent calculated peak positions for the two phases. The lower trace is the difference profile divided by the standard deviation of each point; the dotted lines represent a level of ±3σ.

composition $Na_{1.0}TiO_2$ for 1 week at 1000 °C affords multiple-phase material [Fig. 3(*a*), inset]. Further reaction of this material at high temperature (regrinding followed by another week at 1000 °C) yields a single-phase product, at the cost of introducing significant sodium deficiency. This is apparent from the refined values of both the lattice parameters and the sodium occupancy in the Rietveld analysis [$Na_{0.905(5)}TiO_2$, a = 3.01360(2), c = 16.40983(18) Å; Fig. 3(*a*)]. Single-phase, high sodium concentration material [$Na_{1.001(4)}TiO_2$, a = 3.04406(3), c = 16.25950(19) Å] can be prepared by equilibrating multiphase, sodium deficient Na_xTiO_2 from the high-temperature reaction (initial composition $Na_{1.0}TiO_2$, 1 week at 1000 °C) with excess sodium metal at 300 °C for 5 days.‡ This avoids the loss of sodium at high temperature. Single-phase Rietveld refinement of this material proceeded smoothly, confirming the monophasic nature apparent on visual inspection [Fig. 3(*b*)]. High-temperature reaction with excess sodium (at the composition $Na_{1.4}TiO_2$) also produced material with a large a lattice parameter, characteristic of high sodium concentration [a = 3.04365(3), c = 16.25394(24) Å]. However, the composition $Na_{1.2}TiO_2$ produced material with lattice parameters characteristic of lower sodium concentrations [a = 3.0279(7), c = 16.3505(30) Å] and broad shoulders on many peaks.

Preparation of single-phase material with high sodium concentration is of extreme importance in the study of the physical properties. The a lattice parameter is very sensitive to the titanium oxidation state and is a good indication of the vacancy concentration on the octahedral sodium site. We have demonstrated that even material which appears good quality with a value of a appropriate to high sodium concentration can be multiphase when studied with high-resolution diffraction methods. We conclude by presenting preliminary data to show that the accepted view of the electronic structure of $NaTiO_2$ may be incorrect. The drop in χ at 250 K is only displayed in Na_xTiO_2 when $x \approx 1$ (Fig. 1). Variable-temperature powder neutron diffraction shows that a structural transition to a monoclinic phase occurs at 250 K [space group $C2/m$; a = 5.25040(6) b = 3.03202(1), c = 5.72377(5) Å, β = 108.44830(3)° at 100 K; the sheets of edge-sharing NaO_6 and TiO_6 octahedra slip relative to each other and the Ti–Ti distance in the plane contracts], so the drop in χ is associated with a structural, rather than purely magnetic, transition. The transition then appears to have many similarities to the transitions driven by metal–metal bonding in the early transition-metal oxides Ti_2O_3 and V_2O_3.[5] It is therefore possible that significant t_{2g} orbital overlap between the TiO_6 edge-shared octahedra produces delocalisation of the t_{2g} electrons in a narrow band. $NaTiO_2$ would then no longer be a canonical frustrated magnet; rather, the magnetism would be that of a correlated metal; the Ti^{III}–Ti^{III} separation is appropriate for itinerant electron behaviour.[6] In any event, the transition to monoclinic symmetry destroys the perfect triangular symmetry of the high-temperature rhombohedral structure.

We thank EPSRC for access to ISIS and the SRS, a studentship to S. J. C. and research grants to M. J. R. and A. H. S. J. C. thanks St. Hugh's College, Oxford, for a Graduate Scholarship. We thank Dr D. M. O'Hare (ICL, Oxford) for access to the gradient furnace. We thank Professor F. J. DiSalvo (Cornell University) for useful discussions.

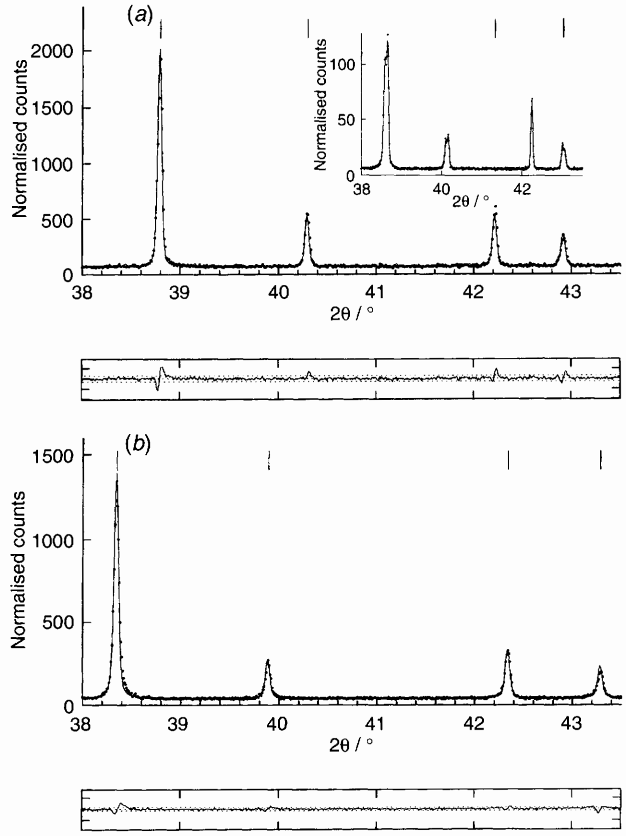

Fig. 3 (*a*) Synchrotron XRD powder Rietveld refinement shown over a limited region for single-phase $Na_{0.905(5)}TiO_2$. The observed, calculated and difference profiles are as in Fig. 2. χ^2 = 2.63, R_{wp} = 8.44%. Inset: example of a two-phase profile for comparison with the single-phase refinements. The profile is from a sample of reaction composition $Na_{1.0}TiO_2$ after 1 week at 1000 °C. The $Na_{0.905(5)}TiO_2$ phase is produced by further heating of this sample at 1000 °C for 1 week. (*b*) Synchrotron XRD powder Rietveld refinement shown over a limited region for single-phase $Na_{1.001(4)}TiO_2$. The observed, calculated and difference profiles are as in Fig. 2. χ^2 = 3.00, R_{wp} = 9.55%.

Footnotes

† Powder XRD data were collected on a Siemens D5000 instrument and at station 9.1 at the Synchrotron Radiation Source, Daresbury (λ = 0.9987 Å) on samples sealed under helium in 0.5 mm diameter capillaries. Rietveld refinement was carried out on synchrotron data collected in the range 8–116°. Powder neutron diffraction data were collected on the High Resolution Powder Diffractometer (HRPD) at ISIS, Rutherford Appleton Laboratory between 4 and 300 K. Rietveld profile refinement was performed using the CCSL code TF12LS and SR15LS with a Voigt peak shape function.[7] Magnetic measurements were made on a Cryogenics Consultants SCU 500C SQUID magnetometer at fields between 0.05 and 6 T.

‡ Na_xTiO_2 samples were prepared by direct reaction of sodium metal (99.9%, Aldrich) and anatase TiO_2 (99.999%, Aldrich). All starting materials and products were handled in a helium-filled dry box. Reaction mixtures were contained in arc-welded metal (iron or tantalum) reaction vessels. The best results are obtained using 9 mm o.d. tantalum containers subsequently sealed in evacuated 18 mm o.d. quartz tubes. Equilibration with sodium vapour was carried out with the Na_xTiO_2 sample contained in an open tantalum tube at 310 °C (to prevent direct contact with the glass vessel) and the sodium reservoir at 300 °C in a sealed Pyrex tube evacuated to 10^{-5} Torr.

References

1 A. P. Ramirez, *Ann. Rev. Mater. Sci.*, 1994, **24**, 453.
2 P. W. Anderson, *Mater. Res. Bull.*, 1973, **8**, 153.
3 P. Hagenmuller, A. Lecerf and M. Onillon, *Compt. Rend.*, 1962, **255**, 928.
4 K. Takeda, K. Miyake, K. Takeda and K. Hirakawa, *J. Phys. Soc. Jpn.*, 1992, **61**, 2156.
5 N. F. Mott, *J. Phys. Colloq.*, 1981, **42**, 277.
6 J. B. Goodenough, *Prog. Solid State Chem.*, 1971, **5**, 1.
7 W. I. F. David, R. M. Ibberson and J. C. Matthewman, Rutherford Appleton Laboratory Report, RAL-92-032, 1992.

Received, 6th October 1995; Com. 5/06592E