

# NEUTRON POWDER PROFILE REFINEMENT OF FERROELECTRIC AND ANTIFERROELECTRIC CRYSTAL STRUCTURES: SODIUM NIOBATE AT 22°C

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The profile refinement of neutron powder patterns permits a rapid and precise determination of structural transitions. For example, the room temperature structure of the rather complex distorted perovskite  $\text{NaNbO}_3$  has been obtained independently in good agreement with the X-ray measurements of Sakowski-Cowley, Lukaszewicz and Megaw. The speed and ease of neutron powder data collection means that structures can be compared for many different conditions of temperature, pressure and chemical composition.

## 1 INTRODUCTION

Recently we have used the profile refinement technique to determine the structures of the tetragonal, orthorhombic and rhombohedral phases of ferroelectric  $\text{KNbO}_3$ ,<sup>1</sup> the rhombohedral phase of  $\text{BaTiO}_3$  [Ref. 2] and the antiferroelectric and paraelectric phases of DADP.<sup>3</sup> Profile refinement has advantages because powder samples are easy to obtain, systematic errors such as extinction are negligible, and data collection is rapid (typically one day per structure). The ease and rapidity of data collection means that a material can be examined at many different temperatures and pressures, and many different isomorphous materials can be compared. Sodium niobate is an example of a material having a large number of structural transitions, at least six between 77 K and 650°C, all of which result from the condensation of soft modes of vibration involving tilts of the rigid oxygen octahedra.<sup>4</sup> We have examined all of these phases using profile refinement, but we will restrict the discussion here to the room temperature orthorhombic (5.566 Å × 15.520 Å × 5.506 Å) phase for which careful X-ray results are available<sup>5</sup> for comparison.

## 2 PROFILE REFINEMENT

Figure 1 shows the profile obtained in 22 hours on the PANDA diffractometer at Harwell using a wave-

length of 1.5414 Å. The structure is obtained by calculating the profile point by point for a starting model, and then refining the structural parameters for this model to obtain the best fit to the observed profile. This is possible for neutron powder patterns because we know very precisely the gaussian shapes and positions of all of the Bragg reflexions which contribute.<sup>6</sup> To obtain a suitable starting model we must first know, or be able to guess, the space group, P6mm (No. 57) in this case.<sup>7</sup> The only other information used to proceed to the final solution was the observation that the oxygen octahedra in these distorted perovskites are likely to remain relatively undistorted themselves, merely tilting against each other<sup>4</sup> or being displaced relative to the other atoms.<sup>1</sup> This approximation, which can be discarded once a suitable starting model has been obtained, requires that in table I the displacements  $u_{03} = w_{03} = -u_{04} = -w_{04}$  and  $w_{01} = -w_{02} = 4u_{03} = -4u_{04}$ .  $u_{03}$  was chosen to be positive and of initial magnitude  $|u_{03}| \approx \frac{1}{2}|w_{01}| = 0.02$ , corresponding to equal octahedron tilts about the axes [101],  $[10\bar{1}]$  and [010]. We then examined the results of refinements starting with every combination of signs for the other parameters, whose initial magnitudes were arbitrarily set at 0.001. An overall isotropic temperature factor was also refined. Only two solutions emerged from this process, the (±) models of table II corresponding to the choice of  $w_{01}$  to have the same or the opposite sign to  $u_{03}$ . These two solutions are in fact crystallographically equivalent; the (−) model can be obtained from the (+) model by reversing the direction of the  $\hat{x}$  and  $\hat{z}$  axes and interchanging the labels 03 and 04.

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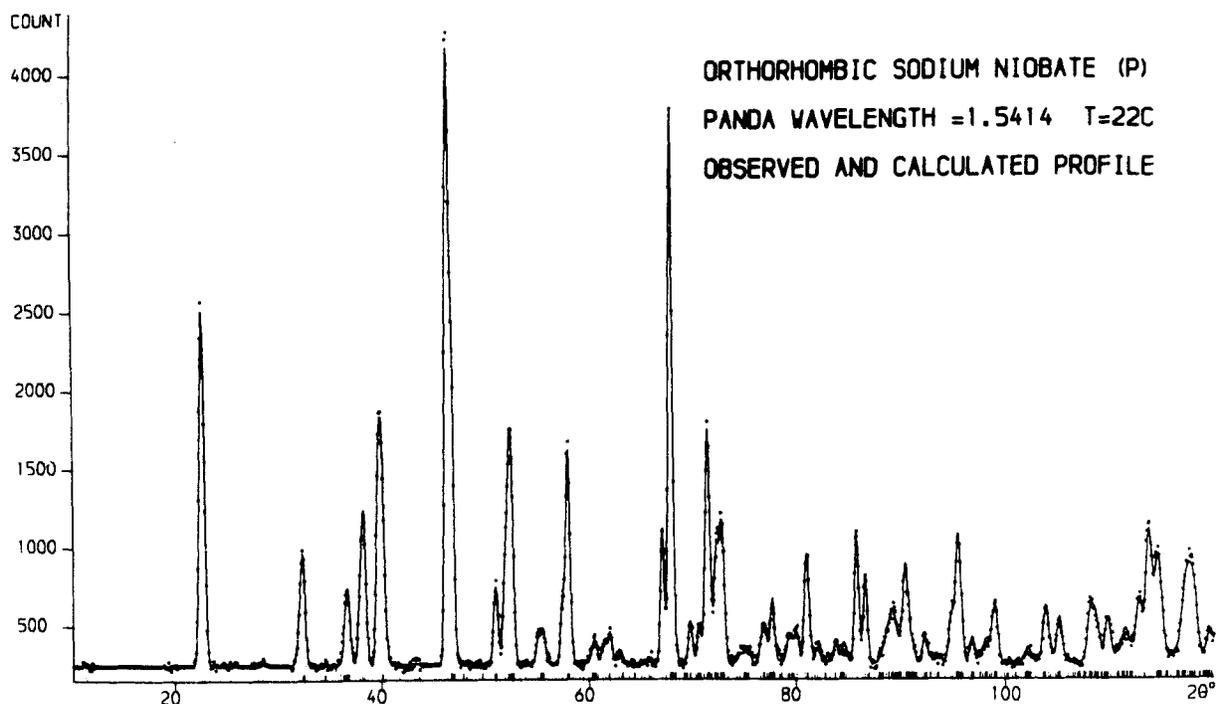


FIGURE 1 Observed (points) and calculated powder profile (line) for orthorhombic (Pbma)  $\text{NaNbO}_3$  at  $22^\circ\text{C}$ . The positions of the 371 individual Bragg reflexions are marked along the  $2\theta$  (scattering angle) axis. Each point on the profile is a summation over five counter steps, each of  $0.02^\circ$ .

TABLE I

Displacements  $u, v, w$  from the cubic perovskite positions, giving space group Pbma.<sup>5</sup>

Nb	8e	$\frac{1}{4} + u_{\text{Nb}}$	$\frac{1}{8} + v_{\text{Nb}}$	$\frac{1}{4} + w_{\text{Nb}}$
Na 1	4c	$\frac{3}{4}$	0	$\frac{1}{4} + w_{\text{Na1}}$
Na 2	4d	$\frac{3}{4} + u_{\text{Na 2}}$	$\frac{1}{4}$	$\frac{1}{4} + w_{\text{Na 2}}$
O1	4c	$\frac{1}{4}$	0	$\frac{1}{4} + w_{\text{O1}}$
O2	4d	$\frac{1}{4} + u_{\text{O2}}$	$\frac{1}{4}$	$\frac{1}{4} + w_{\text{O2}}$
O3	8e	$u_{\text{O3}}$	$\frac{1}{8} + v_{\text{O3}}$	$\frac{1}{2} + w_{\text{O3}}$
O4	8e	$\frac{1}{2} + u_{\text{O4}}$	$\frac{1}{8} + v_{\text{O4}}$	$w_{\text{O4}}$

At this stage the  $R$ -factor<sup>6</sup> for separated Bragg intensities,  $R = 7.5\%$ , already compared well with  $R = 8.5\%$  obtained for the profile calculated from the X-ray structure.<sup>5</sup> When the undistorted octahedra conditions were dropped, we obtained displacements not much different to the final values shown in Table II, with  $B(\text{Nb}) = 0.44$  (4)  $\text{\AA}^2$ ,  $B(\text{Na}) = 1.2$  (1)  $\text{\AA}^2$ ,  $B(\text{O}) = 0.83$  (3)  $\text{\AA}^2$  and  $R = 5.6\%$ . These displacements were not much changed even when unconstrained anisotropic temperature factors  $B_{ij}$  were introduced for all atoms, although the  $R$ -factor fell to 3.4%, close to the minimum expected from the statistics. How-

ever, the standard errors in these temperature factors were now of the same magnitude as the  $B_{ij}$  themselves, and in order to obtain more meaningful vibrational amplitudes  $\langle u_i^2 \rangle = (\frac{1}{3}\pi^2)B_{ii}$  we constrained the oxygen octahedra to vibrate as rigid units. ( $B_{33}(0) = B_{11}(0)$ ,  $B_{ii}(02) = B_{ii}(01)$ ,  $B_{ii}(04) = B_{ii}(03)$ ,  $B_{22}(01) = B_{11}(03) + B_{13}(03)$  and  $B_{22}(03) = B_{11}(01)$ ); the vibrational anisotropy of the Na and Nb atoms also had to be restricted ( $B_{33} = B_{11}$  and  $B_{ii}(\text{Na 2}) = B_{ii}(\text{Na 1})$ ). These constraints had very little effect on the displacement parameters, the quantities of most interest, but revealed oxygen octahedra librations (i.e.,  $B_{11}(01, 2) > B_{22}(01, 2)$  and  $B_{22}(03, 4) > B_{11}(03, 4)$ ). In Table 2 we compare the results of the constrained refinement ( $R = 4.6\%$ ) with those for the X-ray work.<sup>5</sup>

Essentially these independent X-ray and neutron determinations are in good agreement: Nb and Na 2 are displaced along  $\hat{x}$  and the relatively undistorted oxygen octahedra are tilted almost equally about the three axes  $[101]$ ,  $[1\bar{0}1]$  and  $[010]$ . There appear to be some differences though, especially for  $u_{\text{Nb}}$ ,  $w_{\text{Nb}}$ ,  $w_{\text{Na 1}}$  and  $w_{\text{Na 2}}$ . Our results indicate that these displacements are probably not significantly different from zero, and certainly it is difficult to distinguish

TABLE II

Displacements and standard errors ( $\epsilon$ ) obtained for this neutron powder profile refinement compared to those for the X-ray single crystal work.<sup>5</sup> The upper set of signs for the neutron parameters refer to the (+) solution and the lower set to the crystallographically equivalent (-) solution, which is obtained by reversing the  $\hat{x}$  and  $\hat{z}$  axes and interchanging the 03 and 04 displacements.  $B_{ij}$  for a particular atom is defined by the formula for the scattering length  $b_0$  corrected by the Debye-Waller factor for reflexion ( $h, k, l$ ),  $b = b_0 \exp \{-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]\}$  where  $\beta_{ij} = \frac{1}{4}a_i^*a_j^*B_{ij}$  depends on the reciprocal lattice lengths  $a_i^*$ .

	$u$	$v$	$w$
X-ray structure gives $R = 8.5\%$ with neutron powder data			
Nb	0.0222(2)	0.0012(2)	0.0066(1)
Na 1	0	0	-0.007(2)
Na 2	0.032(3)	0	-0.011(2)
01	0	0	0.054(3)
02	-0.017(3)	0	-0.052(3)
03	0.032(2)	0.0150(10)	0.036(1)
04	-0.033(2)	-0.0150(10)	-0.034(1)
Neutron structure gives $R = 4.6\%$ with neutron powder data			
Nb	$\pm 0.0205(7)$	$\mp 0.0019(6)$	$\mp 0.003(2)$
Na 1	0	0	$\pm 0.007(4)$
Na 2	$\pm 0.031(2)$	0	$\pm 0.004(4)$
01	0	0	$\pm 0.054(2)$
02	$\mp 0.018(2)$	0	$\mp 0.070(2)$
03	$\pm 0.025(1)$	$\mp 0.0160(4)$	$\pm 0.033(1)$
04	$\mp 0.044(1)$	$\mp 0.0160(4)$	$\mp 0.036(1)$
	$B_{11}$	$B_{22}$	$B_{33}$
Nb	0.4(1)	0.7(1)	0.4
Na 1, Na 2	1.0(2)	1.6(2)	1.0
01, 02	1.2(1)	0.9	1.2
03, 04	0.6(1)	1.2	0.6
03, 04		$B_{13} = 0.3(1)$	
	$a = 5.5679(3)^a \quad b = 15.5156(8)^a \quad c = 5.5029(3)^a$		

<sup>a</sup> Standard errors do not include error in  $\lambda$

between such small displacements and anisotropic vibrations.

Finally, we should mention that the difficulties anticipated by Katz and Megaw,<sup>8</sup> in the refinement of pseudosymmetric structures, were not encountered in this work. Only two crystallographically equivalent

solutions emerged after refinement, even though all combinations of signs were used as starting points for the displacements. These pseudosymmetry problems, first encountered in X-ray refinements of  $\text{BaTiO}_3$ ,<sup>9,10</sup> appear to be less serious for neutron diffraction.

### 3 CONCLUSION

Profile refinement of neutron powder patterns can be used to determine quite precisely the atomic displacements which occur in a structural transition. The results obtained for the rather complex distorted perovskite  $\text{NaNbO}_3$  at 22°C compare very well with the X-ray work, but were obtained for a fraction of the time and effort required for single crystal measurements. New powder diffractometers now being built will provide greatly increased resolution and intensity, and permit even more complex structures to be examined using profile refinement.

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