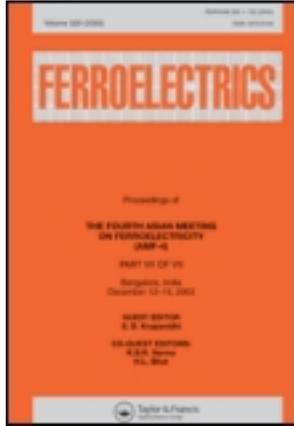


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# STRUCTURE OF RHOMBOHEDRAL FERROELECTRIC BARIUM TITANATE

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The Profile Analysis technique for neutron powder diffraction patterns has been used to show that the lowest temperature phase of barium titanate is rhombohedral  $R3m$  with cell angle  $\alpha = 89.868 \pm 0.004^\circ$  at 77.4 K. The atomic displacements from the cubic perovskite positions are along  $[111]$ , and have magnitudes of  $\delta(\text{Ba}) = 0.001 \pm 21 \text{ \AA}$ ,  $\delta(\text{Ti}) = 0.091 \text{ \AA}$  and  $\delta(\text{OI}) = \delta(\text{OII}) = \delta(\text{OIII}) = -0.091 \pm 14 \text{ \AA}$ . The oxygen octahedron is slightly distorted by an additional oxygen displacement of  $\delta_{\perp}(\text{O}) = 0.023 \pm 13 \text{ \AA}$  perpendicular to this ferroelectric axis. These values yield  $34 \pm 7 \mu\text{C} \cdot \text{cm}^{-1}$  for the spontaneous polarization in this phase, in good agreement with the measured value of  $33.5 \mu\text{C} \cdot \text{cm}^{-1}$ .

## 1 INTRODUCTION

Jona *et al.*<sup>1</sup> used a neutron powder pattern in 1956 to help with the structure determination of anti-ferrodistortive lead zirconate, but until recently single crystal measurements have been thought necessary for the solution of these distorted perovskite structures. It is often difficult to obtain single crystals though, and even then the experimental work is tedious and usually complicated by problems with anisotropic extinction and maintenance of a strong electric field across ferroelectric samples inside a cryostat or furnace. These difficulties have meant that the structure of the rhombohedral phase of perhaps the most important perovskite, barium titanate, has not been determined until now, although work on the tetragonal phase began more than 20 years ago.<sup>2</sup>

Recently,<sup>3</sup> we have found that the new Profile Refinement technique developed by Rietveld<sup>4</sup> makes neutron powder work much more competitive with single crystal measurements for these problems. Even though the individual powder reflexions may not be resolved, by fitting the structure to the detailed shape, or profile, or the complete pattern, we can extract almost as much information as we can by measuring integrated reflexion intensities for an ideal single crystal. In practice, this Profile Refinement of neutron powder patterns is often superior to single crystal work because systematic errors, such as those produced by extinction, are absent.

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## 2 THE NEUTRON POWDER PROFILE

Figure 1 shows the diffraction pattern obtained in 20 hr on the PLUTO reactor at Harwell from a  $4 \times 1.5 \text{ cm}$  diameter vanadium can full of "Puratronic" grade 1 barium titanate powder at 77.4 K (Johnson Matthey Chemicals Ltd., batch No. S8234; analysis yielded  $\text{Ca} = 3$ ,  $\text{Fe} = 2$ ,  $\text{Al} = 2$ ,  $\text{Si} = 2$ ,  $\text{Mg} < 1$ ,  $\text{Na} < 1$  parts per million and no detectable anion impurities). The full width  $H$  at half peak height for the PANDA diffractometer with a take off angle of  $\sim 90^\circ$  from a squashed germanium monochromator giving a wavelength of  $\lambda = 1.5399 \text{ \AA}$  from the (511) plane, is  $\sim 0.5^\circ$  over the entire range of scattering angles, up to the maximum of  $2\theta = 120^\circ$ .  $H$ , in hundredths of a degree, is in fact described by the resolution function  $H^2 = U \tan^2 \theta + V \tan \theta + W$

where  $U = 3704$ ,  $V = 4445$  and  $W = 3279$ . These parameters can be determined using a standard nickel sample which produces strong non-overlapping reflexions. In the rhombohedral phase the  $\text{BaTiO}_3$  peaks are simply broadened because of the splitting of the cubic perovskite reflexions, whereas in the tetragonal and orthorhombic phases this splitting can actually be resolved at high scattering angles (cf. the profiles observed for the various phases of  $\text{KNbO}_3$  where the splitting appears to vanish in the rhombohedral phase).<sup>3</sup> These structural transitions also produce small changes in the positions and strengths of the reflexions, and introduce asymmetry into the peak shape when two or more reflexions of different strength contribute to produce a compound peak. It is difficult to see these effects on such a small

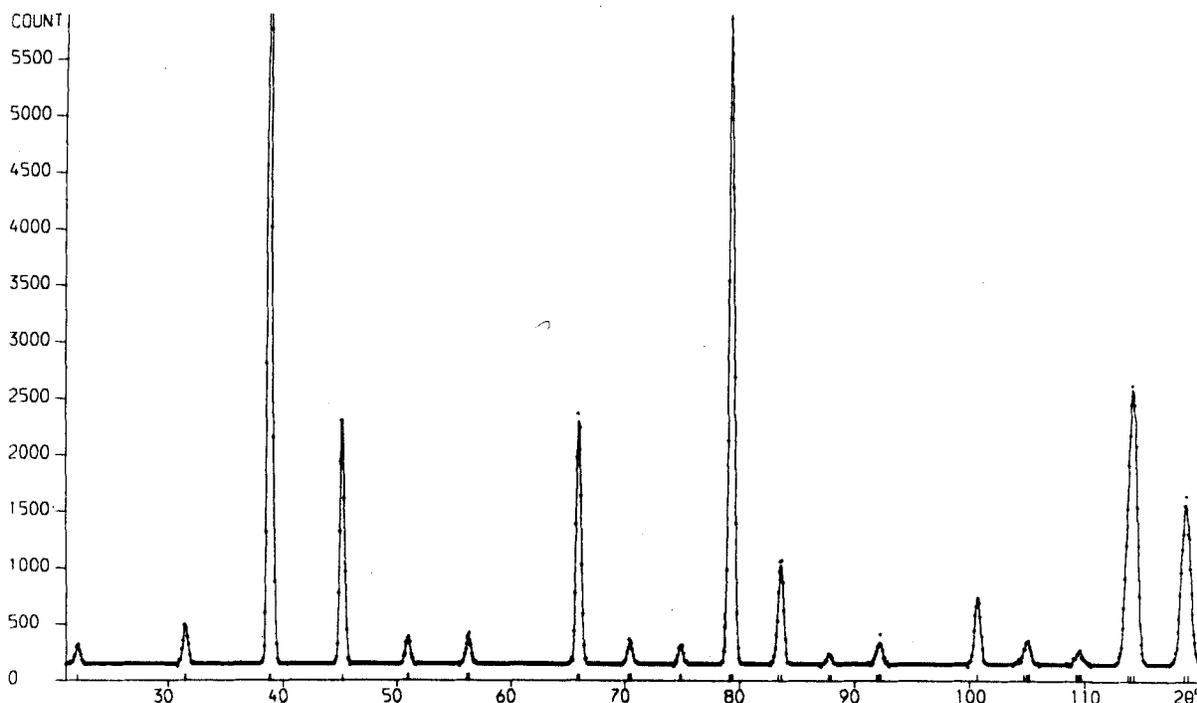


FIGURE 1 Observed (points) and calculated (lines) powder diffraction profile for the rhombohedral phase of  $\text{BaTiO}_3$  at 77.4 K for neutrons of wavelength 1.54 Å. The background was measured in the regions of the heavy horizontal lines, where there are no Bragg reflexions. (The Bragg angles are marked on the  $2\theta$  scattering angle axis.) Although the rhombohedral splitting cannot be resolved, the peaks are broadened and shifted relative to those for the cubic phase. The profile refinement technique requires that the scattering angle as well as the scattered intensity be measured very precisely. There is no evidence of systematic errors such as those produced by extinction in single crystal measurements, and the agreement between the calculated and observed profiles closely approaches the limit imposed by the count statistics.

scale plot as Figure 1, but in practice they are sufficiently large to fix the structural parameters quite precisely. For example, it is easy to see that a small change in the position of a peak will have a large effect with this Profile Refinement technique. For this kind of refinement the scattering angle must then be measured with high precision, and this is achieved on our diffractometer with the aid of Moiré fringe plates, with which the counter can be stepped in precise intervals of  $0.02^\circ$ . The points in Figure 1 represent the sum of the counts for five successive steps, i.e. at  $0.10^\circ$  intervals.

### 3 STRUCTURE REFINEMENT

If the space group for the rhombohedral phase is  $R3m$  (No. 160) with  $a = b = c = 4.001 \text{ \AA}$  and  $\alpha = \beta = \gamma = 89.85^\circ$ ,<sup>5</sup> the atomic co-ordinates are

$$\begin{array}{lll} \text{Ba} & \text{at} & \Delta_x(\text{Ba}), \quad \Delta_z(\text{Ba}), \quad \Delta_z(\text{Ba}) \\ \text{Ti} & \text{at} & \frac{1}{2} + \Delta_z(\text{Ti}), \quad \frac{1}{2} + \Delta_z(\text{Ti}), \quad \frac{1}{2} + \Delta_z(\text{Ti}) \end{array}$$

$$\begin{array}{lll} \text{O}_I & \text{at} & \frac{1}{2} + \Delta_z(\text{O}), \quad \frac{1}{2} + \Delta_x(\text{O}), \quad \Delta_z(\text{O}) \\ \text{O}_{II} & \text{at} & \frac{1}{2} + \Delta_x(\text{O}), \quad \Delta_z(\text{O}), \quad \frac{1}{2} + \Delta_x(\text{O}) \\ \text{O}_{III} & \text{at} & \Delta_z(\text{O}), \quad \frac{1}{2} + \Delta_x(\text{O}), \quad \frac{1}{2} + \Delta_x(\text{O}) \end{array}$$

One of these displacements (we chose  $\Delta_z(\text{Ti})$ ) is fixed in terms of the others by the requirement that the centre of mass of the cell is unmovable by the transition. If the oxygen octahedron is undistorted,  $\Delta_x(\text{O}) = \Delta_z(\text{O})$ , but this has not been assumed.

Various combinations of signs for the  $\Delta(\kappa)$  were tried as starting models for the refinement, but all yielded the same final set of parameters (Table I). The  $R$ -factor for integrated reflexion intensities, which is approximately twice the  $R$ -factor for structure factors usually quoted for single crystal work, is 1.86% for the refinement with isotropic temperature factors, which indicates a very good fit to the data. For comparison, the  $R$ -factor obtained when the atoms were assumed to be undisplaced from their cubic perovskite positions was 4.67%, well

TABLE I

Structural parameters for rhombohedral BaTiO<sub>3</sub>, with standard deviations, obtained from the profile refinement of the neutron powder pattern shown in Figure 1. The  $\Delta(\kappa)$  are the fractional displacements of the atoms from the cubic perovskite positions (see text). The  $R$ -factor has been calculated for the separated integrated Bragg intensities  $I_{hkl}$  as

$$R_I = \frac{\sum_{hkl} ||I_{obs}| - |I_{calc}||}{\sum_{hkl} |I_{obs}|}$$

The  $B$ -factors  $B(\kappa) = 8\pi^2 \langle u(\kappa)^2 \rangle$  represent the mean square atomic vibrational amplitudes  $\langle u(\kappa)^2 \rangle$ , and the  $b_\kappa$  the scattering lengths

$R_I \approx 2RF = 1.86$
$\Delta_z(\text{Ba}) = 0.013 \pm 3 \text{ \AA}$
$\Delta_z(\text{Ti}) = 0 \text{ \AA}$
$\Delta_x(\text{O}) = 0.024 \pm 2 \text{ \AA}$
$\Delta_z(\text{O}) = 0.031 \pm 2 \text{ \AA}$
$B(\text{Ba}) = 0.26 \pm 8 \text{ \AA}^2$
$B(\text{Ti}) = 0.10 \pm 15 \text{ \AA}^2$
$B(\text{O}) = 0.24 \pm 3 \text{ \AA}^2$
$a = b = c = 4.001 \text{ \AA}$
$\alpha = \beta = \gamma = 89.868 \pm 4 \text{ deg.}$
$b_{\text{Ba}} = 0.517 \pm 7$
$b_{\text{Ti}} = 0.347 \pm 6$
$b_0 = 0.58$

above that expected. When anisotropic temperature factors were introduced for the oxygen atoms, the  $R$ -factor was reduced to 1.50%, practically the minimum expected for the count statistics, but the large error limits calculated for these temperature factors indicate that there is insufficient data to fix them precisely: fortunately, the displacement parameters were not significantly changed when anisotropic temperature factors were introduced. It is also

encouraging that the quite precise values obtained for the rhombohedral angle, and for the atomic scattering lengths relative to that for oxygen, are in good agreement with the values expected. The cell dimension  $a_0$  was not determined because the neutron wavelength was also a parameter in the refinement.

## 4 DISCUSSION

Our results (Table I) show that, as in the tetragonal and orthorhombic phases, the oxygen octahedron in the rhombohedral phase of BaTiO<sub>3</sub> is slightly distorted, whereas in KNbO<sub>3</sub> there is very little distortion in any of these phases.<sup>3</sup> The standard deviations quoted for the parameters have been defined elsewhere.<sup>3,4</sup> In Table II we compare the actual atomic displacements for the three phases in directions parallel to ( $\delta_{\parallel}(\kappa)$ ) and perpendicular to ( $\delta_{\perp}(\kappa)$ ) the ferroelectric axis, which in terms of the cubic cell axes is [001] for the tetragonal phase, [011] for the orthorhombic phase, and [111] for the rhombohedral phase. These displacements are relative to the centre of mass, so that the heavy Ba atom ( $m = 137.36$ ) is essentially unmoved, while the displacements of the titanium atom ( $m = 47.90$ ) and oxygen half octahedron ( $m = 48.00$ ) are necessarily equal and in opposite directions for the rhombohedral phase. We have also calculated for each of the phases the spontaneous polarization  $P_s(\text{calc}) = (e/v_c) \sum_{\kappa} z_{\kappa} \delta_{\parallel}(\kappa)$ , which is the product of the atom displacements  $\delta_{\parallel}(\kappa)$  and the apparent ionic charges  $z_{\kappa}$ ;  $e$  is the electron charge and  $v_c$  the volume of the cell containing the atoms  $\kappa$ . These apparent ionic charges,  $z_{\text{Ba}} = 3.6 \pm 0.5$ ,  $z_{\text{Ti}} = 5.7 \pm 0.9$  and  $z_{\text{O}} = 3.1 \pm 0.3$  electrons, include the contribution from

TABLE II

Atomic displacements parallel to ( $\delta_{\parallel}(\kappa)$ ) and perpendicular to ( $\delta_{\perp}(\kappa)$ ) the ferroelectric axis [ $hkl$ ] for the low-temperature phases of BaTiO<sub>3</sub>, relative to the fixed centre of mass. In each case there is an appreciable distortion of the oxygen octahedron. These displacements have been used to calculate the spontaneous polarization  $P_s(\text{calc})$  for comparison with the macroscopic measurements,  $P_s(\text{obs})$ , of Weider<sup>7</sup>

	Tetrag. [001] 20°C <sup>9</sup>	Ortho. [001] -10°C <sup>10</sup>	Thom. [111] 77.4 K	
$\delta_{\parallel}(\text{Ba})$	0.004	0.002	0.001 ± 21	Å
$\delta_{\parallel}(\text{Ti})$	0.058 ± 2	0.059	0.091	Å
$\delta_{\parallel}(\text{OI})$	-0.093 ± 4	-0.055	-0.091 ± 14	Å
$\delta_{\parallel}(\text{OII})$	-0.057 ± 4	-0.072	-0.091	Å
$=\delta_{\parallel}(\text{OIII})$	-0.057	-0.072	-0.091	Å
$\delta_{\perp}(\text{OI})$	0	0.017	0.023	Å
$P_s(\text{calc})$	25 ± 3	24	34 ± 7	μC . cm <sup>-1</sup>
$P_s(\text{obs})$	26.3	30.7	33.5	μC . cm <sup>-1</sup>

the ionic polarizability, and have been estimated<sup>6</sup> from calculations of the lattice dynamics and infrared dipole strengths. The experimental values  $P_s(\text{obs})$  come from Wieder's<sup>7</sup> measurements of the component of the spontaneous polarization along [001] in selected c-domain crystals. There is good agreement between the calculated and observed values of  $P_s$  for the tetragonal and rhombohedral phases, but less good agreement for the orthorhombic phase where the error limits for the atomic displacement have not been given.

## 5 CONCLUSIONS

The neutron powder pattern for the lowest temperature phase of barium titanate can be fitted to within the limits imposed by the statistics to a rhombohedral  $R3m$  cell in which the oxygen octahedron is displaced along the pseudocubic [111] direction, relative to the barium and titanium atoms. This oxygen octahedron is rather more distorted in all three low-temperature phases of  $\text{BaTiO}_3$  than it is in the corresponding phases of  $\text{KNbO}_3$ . These structural results yield values for the spontaneous polarization which are in good agreement with macroscopic measurements on the tetragonal and rhombohedral phases, although there appears to be a discrepancy for the orthorhombic

phase. The determination of the rhombohedral structure completes Cochran's<sup>8</sup> picture of the ferroelectric transitions in barium titanate as the successive condensation of soft modes of vibration.

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