the ratio of the total areas under the radial microphotometer curves parallel respectively to the equatorial and meridional directions.

It can then be shown that to correct for chain orientation the factor by which the value of $(I_{(110)}+I_{(200)})$ obtained from the perpendicular photograph must be multiplied is $\frac{2}{3}\left\{\frac{2(P_{\text{Par.}}/P_{\text{Perp.}})+1}{(P_{\text{Par.}}/P_{\text{Perp.}})+1}\right\}$. If $P_{\text{Par.}}/P_{\text{Perp.}}$ is 1·2 (an unusually high value), the correction in the final amorphous content is only 0·2 %, and hence chain orientation has been ignored in this work for all samples in which $0{\cdot}8 < P_{\text{Par.}}/P_{\text{Perp.}} < 1{\cdot}2$.

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Domain Orientation in Polycrystalline $BaTiO_3$

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X-ray diffraction patterns of polycrystalline $BaTiO_3$ show that, below the Curie temperature, the *c* axes of some of the individual crystallites can be oriented by large electric fields into a direction normal to their original direction and more nearly parallel to the applied field. For a field of 24 kV.cm.$^{-1}$ applied 35° C. below the Curie temperature about 80 % of the material was oriented so that the *c* axis made an angle of less than 45° to the electric field. At temperatures considerably above the Curie temperature the electric field had no effect; but at temperatures just above the average cubic–tetragonal transition temperature, the electric field appeared to increase the number of non-isometric crystals.

1. Introduction

The ferroelectric properties of $BaTiO_3$ (Wul & Goldman, 1945; Wainer, 1946; Jackson & Reddish, 1945; von Hippel, Breckenridge, Chesley & Tisza, 1946; Wul, 1946; Blattner, Matthias, Merz & Scherrer, 1947) require that the orientation of the polar axis depend upon field strength, as in the case of Rochelle salt (Mueller, 1935) and KH_2PO_4 (von Arx & Bantle, 1944; Zwicker & Scherrer, 1944; de Quervain, 1944) and such orientation has been observed directly in the polarizing microscope for single crystals of $BaTiO_3$ (Kay & Rhodes, 1947; Matthias & von Hippel, 1948). In the case of polycrystalline ceramic disks of $BaTiO_3$, such orientation by electric fields should result in marked changes in the intensity of X-ray scattering from some crystallographic planes. It is the purpose of this paper to discuss the experimental evidence for these predicted changes in intensity, the interpretation of these intensity changes in terms of domain orientation, and the limitations of this method for measuring preferred orientation in polycrystalline $BaTiO_3$.

2. Experimental

The samples were in the form of ceramic discs 15 mm. in diameter and 0·12 mm. thick with a layer of silver 10 mm. diameter and 0·8μ thick evaporated on each surface. The composition of the samples was 4 mol. $BaTiO_3$ to 1 mol. $SrTiO_3$, a mixture that lowers the cubic–tetragonal transition temperature from 120 to 60° C. The typical plot of dielectric constant versus temperature is shown in Fig. 3.

The experimental arrangement is shown in Fig. 4. The method of back-reflection allows one to resolve the pseudocubic structure, which was found to be tetragonal in confirmation of the results of Megaw (1947). For this composition the lattice constant a_0 at 25° C. was found to be 3·9782 A. and the axial ratio

$$c = c_0/a_0 = 1{\cdot}0045,$$

assuming, for Cu $K\alpha_1$, $\lambda = 1{\cdot}54050$ A. and, for Cr $K\alpha_1$, $\lambda = 2{\cdot}28962$ A. At 48·5° C. the value of a_0 was noticeably increased and the value of *c* decreased as expected. At 59·5° C. the structure of most crystals was cubic.

With copper radiation the application of an electric field decreases conspicuously the intensity of the innermost ring, due to scattering of $K\alpha_2$ radiation from the

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unresolved (431), (501) and (510) planes, and increases the intensity of the outer ring, due to scattering of $K\alpha_1$ radiation from the (105) planes. This is shown in Fig. 1. On the right side of the patterns we notice also that the intensity of the spot due to $K\alpha_1$ (224) relative to the intensity of the spot due to $K\alpha_1$ (422) is increased by the electric field. With chromium radiation and no electric field the intensity of the $K\alpha_1$ (311) reflection is four times the intensity of the $K\alpha_2$ (113) reflection, since the former has twice the radiation intensity and twice the multiplicity. With an electric field of 24 kV. cm.$^{-1}$ applied to the sample these two reflections become equal in intensity.

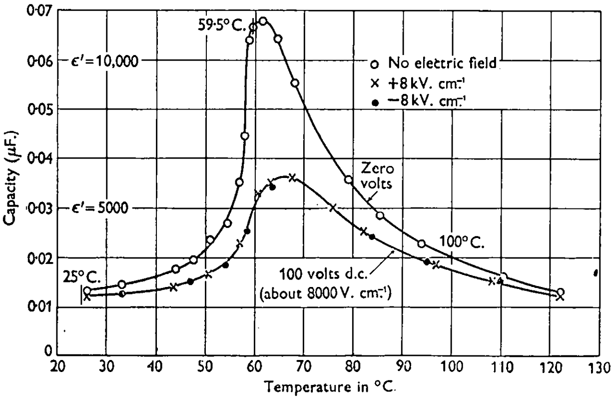


Fig. 3. Dielectric constant versus temperature for 4 $BaTiO_3$ + 1 $SrTiO_3$.

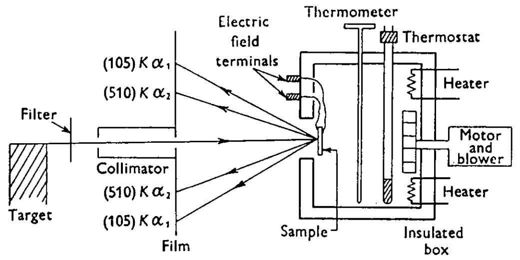
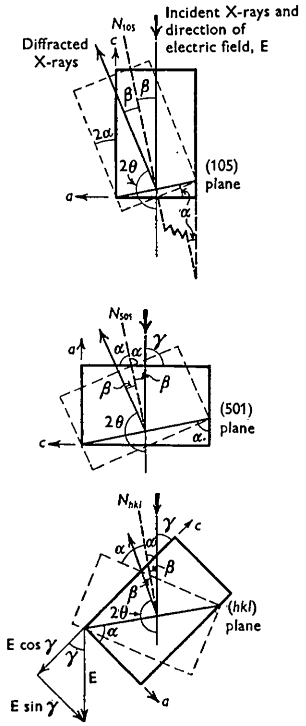


Fig. 4. Experimental arrangement for studying orientation of domains in $BaTiO_3$.

3. Interpretation

The explanation of these changes in intensity is shown in Fig. 5. We see that the (105) reflections are given by crystals oriented with their *c* axes nearly parallel to the X-ray beam (or electric field), while the (501) reflections are given by crystals oriented with their *c* axes nearly perpendicular to the X-ray beam. Hence the decrease in intensity of scattering from the (501) planes and increase in intensity of scattering from the (105) planes indicate that the field has oriented some of the *c* axes of the crystalline material from a direction normal to the field into a direction parallel to the field. The *c* axis is thus the polar axis in these tetragonal $BaTiO_3$ crystals. In cases where the same spot appears on both photographs, but with a different intensity upon application of the field, the crystal must be twinned; that is, it possesses more than a single domain.

Let us define γ as the angle between the electric field and the polar axis of a tetragonal $BaTiO_3$ crystal; and let δ be the smallest angle between the electric field and an *a* axis of the same crystal. If the electric field should happen to coincide with a face diagonal [101] direction, $\gamma = \delta = 45°$; while, if the electric field should happen to coincide with the body diagonal [111] direction, $\gamma = \delta = 54° 44'$. For values of γ lying between 45° and 54° 44′ there is, therefore, some uncertainty as to whether γ or δ is the smaller angle. For values of γ less than 45°, however, we can be certain that $\gamma < \delta$; and, for values of γ greater than 54° 44′, we can be certain that $\gamma > \delta$. If $\gamma < 45°$, $E \cos\gamma > E \cos\delta$, and the existing orientation of the polar axis will be maintained by the electric field E; if $\gamma > 54° 44'$, $E \cos\gamma < E \cos\delta$ and one of the non-polar axes may become a polar axis, if the electric field is large enough. The electric field thus tends to increase the number of crystals which have their *c* axes making an angle less than 45° with the electric field, and this orientation effect will be greatest when $E \cos\gamma \ll E \cos\delta$; that is, when γ is nearly 90°.



Domain *c* axis || *E*

$$|\alpha-\beta| < \gamma < |\alpha+\beta|.$$

If $|\alpha| = |\beta| = 90° - \theta$,

then $0 < \gamma < 2|\beta|$.

Domain *c* axis ⊥ *E*

$$|\alpha-\beta| < \gamma < |\alpha+\beta|.$$

If $\alpha = 90° - \beta = \theta$,

then $|90° - 2\beta| < \gamma < 90°$.

Domain *c* axis at angle γ to *E*

$$|\alpha-\beta| < \gamma < |\alpha+\beta|.$$

$$\cos\alpha = \frac{l^2/c^2}{\sqrt{(h^2+k^2+l^2/c^2)}},$$

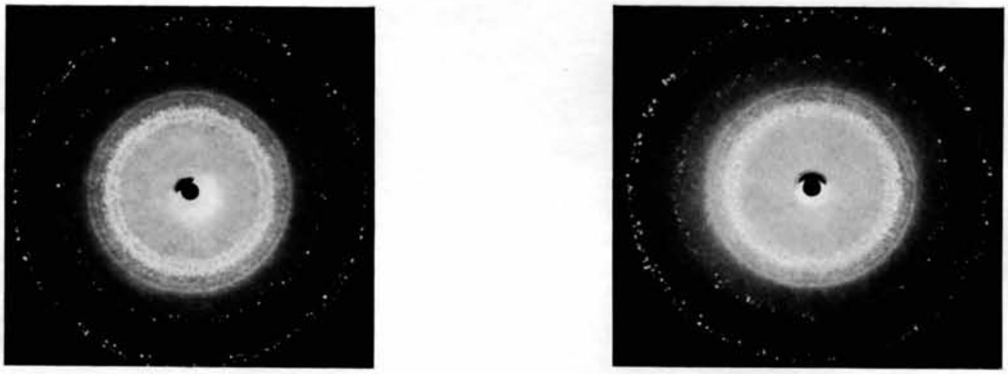
$$\cos\beta = \frac{\lambda}{2a_0}\sqrt{(h^2+k^2+l^2/c^2)}.$$

Fig. 5. Relationship between X-ray scattering in $BaTiO_3$ and *c*-axis orientation.

Our back-reflection X-ray diffraction pattern is produced by planes whose normals make a small angle with the incident X-ray beam, which is parallel to the electric field. Hence all planes which have their normals nearly parallel to the *c* axis, such as (105), will be increased in intensity by the electric field; and all planes which have

(a) (b)

Fig. 1. Effect of electric field of 50 kV.cm.$^{-1}$ at 25° C. upon X-ray scattering in 4 $BaTiO_3 + 1\ SrTiO_3$. (a) Without field, (b) with field.



(a) (b)

Fig. 2. Effect of electric field of 17 kV.cm.$^{-1}$ at 59·5° C. upon number of cubic crystals in 4 $BaTiO_3 + 1\ SrTiO_3$. (a) Without field, (b) with field.

their normals nearly perpendicular to the c axis, such as (501), will be decreased in intensity by the electric field.

If $\gamma > 90°$, reversal of the polar axis may occur. For example, suppose E is in the (100) plane and $\gamma = 150°$. Then

$$\cos\gamma = -\cos 30°,\ \cos\delta = \cos 60° \text{ and } E\cos\gamma < E\cos\delta.$$

Hence the polar axis may be changed in orientation by 90°. After this change in axes, however, $\cos\gamma = \cos 60°$, $\cos\delta = \cos 30°$ and again $E\cos\gamma < E\cos\delta$. The polar axis may thus be changed in orientation by 90° once more. The net result would be equivalent to 180° rotation of the polar axis. However, such a reversal of the polar axis, which would be expected to occur most readily when γ is nearly 180°, would not affect the intensities in our X-ray powder pattern.

The orientation angle γ is composed of two parts: the angle α between the c axis and the plane normal, and the angle β between the plane normal and the X-ray beam (or electric field) when reflection occurs. Since the X-ray diffraction pattern determines only β, the complement of the Bragg angle θ, there is an ambiguity in the orientation of the polar axis by an amount α. That is, $|\beta - \alpha| \leqslant \gamma \leqslant |\beta + \alpha|$, and we have an inherent numerical uncertainty in the orientation of the polar axis equal in magnitude to α or β, whichever is smaller. For the electric field parallel to the X-ray beam and the method of back-reflection used here, β is usually less than α. This uncertainty in the orientation of the c axis is shown in Fig. 5 by the solid and dotted rectangles.

The angles α and β may be calculated readily for any plane if we first determine the lattice constant a_0 and the axial ratio $c = c_0/a_0$:

$$\cos\alpha = \frac{l}{c}\left(h^2 + k^2 + \frac{l^2}{c^2}\right)^{-\frac{1}{2}},$$

$$\cos\beta = \sin\theta = \frac{\lambda}{2a_0}\left(h^2 + k^2 + \frac{l^2}{c^2}\right)^{\frac{1}{2}}.$$

If $c = 1 + \delta$, where δ is small, and $N = h^2 + k^2 + l^2$, we have for computational purposes

$$\cos\alpha = N^{-\frac{1}{2}}\, l\left[1 - \delta\left(1 - \frac{l^2}{N}\right)\right],$$

$$\cos\beta = \frac{\lambda}{2a_0} N^{\frac{1}{2}}\left(1 - \frac{l^2}{N}\delta\right).$$

The values of α, β, $\gamma_{\text{min.}}$, $\gamma_{\text{max.}}$ are shown in Table 1 for the planes observed by back-reflection using copper and chromium radiation.

The relationship between the angles α, β and γ is shown clearly by the stereographic projection in Fig. 6, which shows each crystallographic plane represented by a point and each cone of reflection by a circle. The radius of each circle is β and the displacement of its center from the origin is α. The orientation angle γ then lies between the angle measured from the origin to the nearest point on the circle and the angle measured from the origin to the farthest point on the circle. To a first approximation, the farther the circle is away from the 45° circle the more its intensity will be altered—increased if inside like (105), decreased if outside like (501).

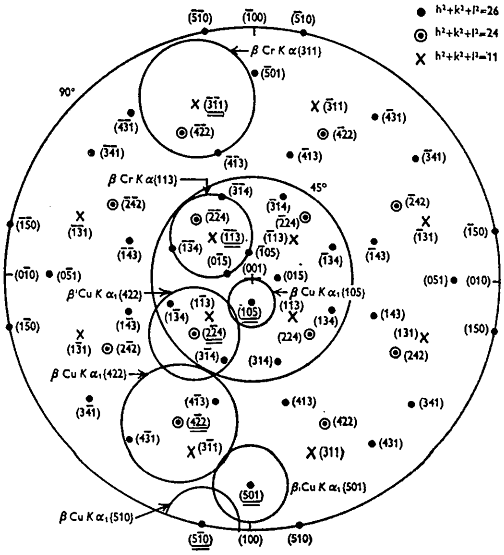


Fig. 6. Stereographic projection of BaTiO$_3$.

In the special case of chromium radiation we see that, for almost any orientation of the c axis, reflection either from the (311) plane or from the (113) plane (but not both) is possible. As mentioned previously, without a field the intensity of $K\alpha_1$ (311) is four times $K\alpha_2$ (113), as one expects, but with a field of 24 kV. cm.$^{-1}$ these intensities are observed to be about equal. This means

Table 1. *Orientation angles in* 4 BaTiO$_3$ + 1 SrTiO$_3$

$h^2+k^2+l^2$	Plane	α	β	$\gamma_{\text{min.}}$	$\gamma_{\text{max.}}$
		Copper radiation			
26	510	90°	9° 8′	80° 52′	90°
	(501) (431)	78° 44′	9° 12′	69° 32′	87° 56′
	413	54° 5′	9° 40′	44° 25′	63° 45′
	314	38° 27′	10° 4′	28° 23′	48° 31′
	105	11° 21′	10° 34′	0° 47′	21° 55′
24	422	66° 0′	18° 35′	47° 25′	84° 35′
	224	35° 24′	18° 58′	16° 26′	54° 22′
		Chromium radiation			
12	222	54° 51′	5° 28′	49° 23′	60° 19′
11	311	72° 32′	17° 26′	55° 6′	89° 58′
	113	25° 20′	17° 54′	7° 26′	43° 14′

that, with an electric field applied, four times as much crystalline material has γ between 7° 26′ and 43° 14′ as has γ between 55° 6′ and 89° 58′. That is, about 80 % of the material has the polar axis of the domains making an angle of less than 45° with the electric field.

4. Limitations

We have seen that this method of studying domain orientation does not give a unique determination of the angle γ owing to the inherent uncertainty α. In addition, the angular distribution of domain orientations is not plotted continuously. It has been pointed out by E. A. Wood that it might be possible to overcome both of these limitations by the method shown in Fig. 7. The angle α is reduced to zero by using iron radiation and comparing the intensities of the (400) and (004) reflections. The angular distribution can be plotted continuously by rotating the sample-normal through a known angle σ. Since the angle ρ between the c axis and the sample-normal is $|\beta-\sigma|$, we can measure the amount of crystalline material oriented at any angle ρ by an appropriate setting of σ. In order to prevent spottiness due to large crystal size the sample may be rotated continuously about its normal P.

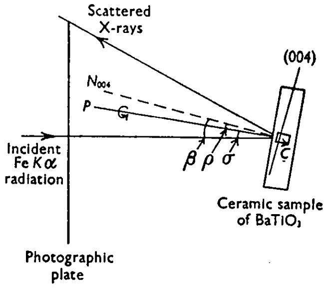


Fig. 7. Proposed method for measuring angular distribution of c axes in $BaTiO_3$.

N_{004}, normal to (004) plane,
P, normal to rotating sample,
$\rho=|\beta-\sigma|$, where ρ is angle between c axis and sample normal.

$$\beta=90-\theta.$$

$$\begin{aligned}\cos\beta&=\frac{\lambda}{2a_0}\sqrt{\left(h^2+k^2+\frac{l^2}{c^2}\right)}\\&=2\lambda/a_0c \text{ for } (004)\\&=2\lambda/a_0 \text{ for } (400).\end{aligned}$$

σ, angle between incident beam and sample normal.

This method of obtaining a continuous angular distribution of domain orientations has been attempted but with little success. The heavy background caused by the iron radiation exciting the titanium in the sample and the weak scattering by the (400) and (004) planes have made even estimates of intensities impossible. Hence the method does not appear very suitable for a quantitative determination of the angular distribution of domain orientations in polycrystalline $BaTiO_3$ ceramics.

5. Conclusion

The method of X-ray diffraction is very useful, however, in the qualitative study of $BaTiO_3$ domains in polycrystalline ceramics. The effect of applied electric fields at room temperatures in altering the orientation of the c axes has been described. The effect of increasing the temperature is shown in Fig. 2. At temperatures considerably above the Curie temperature the electric field had no effect; but at temperatures just above the average cubic–tetragonal transition temperature, the electric field appeared to increase the number of non-isometric crystals.

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