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The X-ray Measurement of the Amorphous Content of Polythene Samples

By J. L. Matthews, H. S. Peiser and R. B. Richards

Research Department, Imperial Chemical Industries (Alkali Division), Northwich, Cheshire, England

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A method is described for the determination of the amorphous content of polythene samples, based on a microphotometric comparison of the intensities of the amorphous band and the two strongest crystalline lines on X-ray powder photographs obtained from the samples in sheet form. Corrections for two types of orientation are described. The results indicate that amorphous contents at ordinary temperatures may vary from below 10 % to above 50 %, normal samples having an amorphous content of about 25 %. The more amorphous samples have lower densities; the quantitative relation between density and degree of crystallinity is discussed.

Introduction

All crystalline polymers, of which polythene is an example, have a composite crystalline–amorphous structure at temperatures below their melting-point. The relative proportions of crystalline and amorphous regions vary from sample to sample of any polymer, for they are affected by details of molecular structure (for example, the extent of chain branching) and such factors as the rate of cooling from the molten state. This variation in amorphous content has an effect on physical and mechanical properties, and methods are therefore required for the quantitative measurement of the proportion of amorphous material.

Methods based on X-ray measurements have been used for stretched rubber by Field (1941), and Goppel (1947) has extended Field's work to samples of partly crystalline rubber in the unoriented state by comparing the intensities of the diffracted beams due to the amorphous regions in the same sample first in the partly crystalline state, and secondly after converting the samples to the completely amorphous state by raising the temperature. Bunn & Alcock (1945) have made semi-quantitative observations of the change in the amorphous content of polythene samples at varying temperatures up to the melting-point. A quantitative method is described in this paper for unoriented polythene samples which is similar in some respects to that described for rubber by Goppel. X-ray photographs of unoriented polythene sheet show sharp reflexions due to the crystalline region together with a more diffuse band due to the amorphous material. The ratio of the intensity of the amorphous band to that of any crystal reflexion on the same photograph is a measure of the proportion of amorphous material. Goppel's method cannot be applied directly to polythene because it is impossible to obtain a polythene sample in the completely amorphous state at ordinary temperatures.

The method here described cannot necessarily be adapted to the measurement of the amorphous content of any crystalline polymer in the unoriented state, especially if, as in nylon (Bunn & Garner, 1947), there are degrees of order which must be considered intermediate between the crystalline and the amorphous states. In the case of polythene, the possibility of a clear-cut differentiation between scattering by amorphous and by crystalline regions lends no support to a view that this polymer contains extensive regions of intermediate order. Fig. 1 shows how the X-ray photograph given by polythene is intermediate between those for entirely crystalline and entirely amorphous paraffins, and Fig. 2 illustrates the wide variation in amorphous content of polythene samples at ordinary temperatures.

Methods other than those based on X-ray measurement have been used for the determination of the proportion of amorphous material in polymers. In the case of polythene, measurements of density (Hunter & Oakes, 1945) and of heat content (Raine, Richards & Ryder, 1945) have been used to show the changes in amorphous content as the temperature is raised up to the melting-point.

Preparation of samples

A standardized procedure must be used for the preparation of the specimens. Small compression-moulded sheets 0·3 mm. thick are made between heated plates in a moulding press at a temperature of about 140° C. Sheets of 'Cellophane' (grade 600) between the sample and the plates of the press ensure the production of a sheet with a good surface. The sample is held for a time in the molten state after moulding and is then cooled slowly in the press. The tendency of the molecular chains to aline themselves parallel to the surface of the films ('chain' orientation) is not very pronounced, and in most samples this kind of orientation can be removed by an annealing treatment in boiling water for 10 min., to which all specimens must be subject. The samples are then cooled slowly to room temperature.

In the few samples in which any appreciable chain orientation persists after annealing this is found to be a characteristic of the sample and must be measured and

Fig. 1. X-ray powder photographs of (a) a crystalline paraffin, (b) a polythene, (c) an amorphous paraffin.

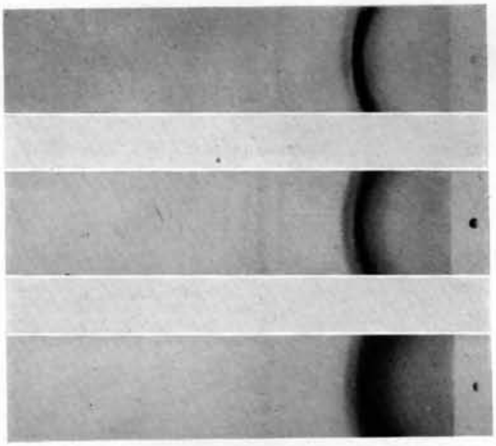

Fig. 2. X-ray powder photographs of three polythene samples differing widely in amorphous contents.

allowed for as described in the Appendix. Reference to another type of orientation ('plane' orientation), which is more common in these samples, is also made below.

For many special X-ray photographs (see Appendix) it is necessary to cut strips, square pillars or even cubes from the 0·3 mm. sheet. Careful examination by optical and X-ray methods has shown that specimens cut with a sharp razor blade have surface-oriented layers of a thickness less than $10\,\mu$, so that with a sample of dimensions of $\frac{1}{4}$–$\frac{1}{2}$ mm. the surface orientation effects are not liable to introduce appreciable errors.

The X-ray photographs

The 9 cm. X-ray powder camera used is fitted with an aperture, giving a narrow ($\leqslant 0\cdot5$ mm.) parallel X-ray beam, and with guard slits and trap systems to minimize the background intensity of X-ray scattering.

Filtered but not strictly monochromatic Cu $K\alpha$ radiation is used, and the exposure is controlled within 10–20 % in order to arrange for all the X-ray intensities to be measured to be within the most sensitive region of the microphotometer.

The direct beam is permitted to fall on to the X-ray film after passage through an absorbing metal disk (aluminium or brass) of uniform standard thickness, and in this way the direct beam can, where necessary, be photometered with the rest of the pattern to give a measure of total X-ray exposure.

The microphotometry

A non-recording Hilger microphotometer is used, and the blackening curve obtained is converted into X-ray intensities by comparison with the blackening along a standard intensity wedge printed on the same type of X-ray film and developed under identical conditions.

A Geiger-Müller counter method has also been found suitable for the amorphous-content determination in polythene. By courtesy of Messrs Philips Lamps Ltd., and in particular of Dr Barnes of that company, we have been able to try the North American Philips Geiger-Müller X-ray Spectrometer for an amorphous-content determination; excellent agreement is found between the intensity curves for the same sample obtained by the microphotometric technique and the Geiger-Müller counter method.

Whichever method is used the experimental errors involved in obtaining the intensity versus angle of diffraction graphs are small compared with those introduced during resolution of the amorphous and crystalline intensity curves.

The resolution of the photometer curve

A typical photometer plot, and the resolved curves derived from it, are shown in Fig. 3. The procedure includes the subtracting of the background curve followed by the resolution of the amorphous curve from those of the (110) and (200) crystal reflexions (cf. Bunn, 1939). The resolution is facilitated by the relatively large difference in spacings of the amorphous and crystalline diffraction patterns in polythene and would not be possible for many polymers.

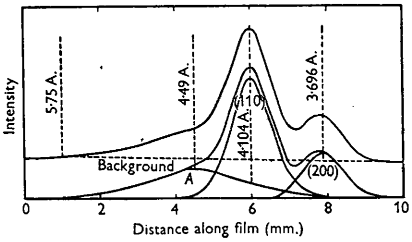

Fig. 3. Resolution of photometer plot for typical polythene sample of amorphous content 20·3 %.

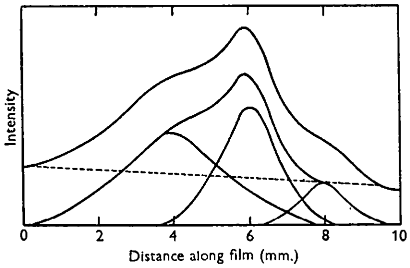

Fig. 4. Resolution of photometer plot of polythene sample with abnormally high amorphous content of 42·2 %. Abnormally large amorphous spacing; normal crystalline spacings.

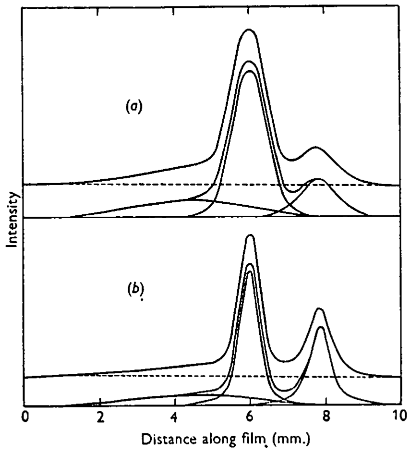

Fig. 5. 'Plane' orientation. (a) Photometer plot for photograph taken with plane of sheet perpendicular to X-ray beam. $I_{(110)}/I_{(200)} = 2\cdot67$. Apparent amorphous content 15·4 %. (b) Photometer plot for photograph taken with plane of sheet parallel to X-ray beam. $I_{(110)}/I_{(200)} = 1\cdot14$. Apparent amorphous content 12·7 %.

A number of rules which appear to be generally, but certainly not universally, valid for polythene samples are as follows:

(1) The height and slope of the background curve is approximately proportional to the total exposure time as recorded on each photograph.

(2) The amorphous band is assumed to have a low-angle limit at an arbitrarily chosen spacing of 5·75 A.

(see Fig. 3). The use of an empirical rule of this sort appears unavoidable at low angles, while at high angles the curve for the intensity of the X-ray line approaches the background curve much more smoothly and definitely.

(3) The spacings of the (110) and (200) crystal planes are taken to occur at 4·104 and 3·696 A. respectively. Small variations in spacings are observed from sample to sample, but are not great enough to affect amorphous-content determinations.

(4) The spacing corresponding to the peak of the amorphous band is constant and is taken to be 4·496 A. This is the value of the amorphous-band spacing in cold-drawn samples of polythene, where it can be measured without interference from the crystal diffraction pattern.

The application of this rule is probably well justified in most cases, because, if the anisotropically disposed forces which act on the amorphous regions in cold-drawn samples were to cause a change of spacing, one would expect a variation of amorphous spacing with orientation relative to the alined crystallites. This is not observed.

(5) The shape of the three intensity curves is approximately symmetrical about their centres. That this is so for the crystalline peaks near their maxima is evident by inspection of the total intensity curves, and photometer curves of the amorphous bands in cold-drawn polythenes also show this symmetry.

(6) The ratio of the intensities of the (110) to the (200) crystal reflexions is constant and equal to about 3·4 (or 2·4 after shape, absorption and θ-corrections (Bunn, 1945) have been applied). In the absence of anomalous orientation phenomena this rule implies merely that the crystal structure is the same in all samples.

These six guiding rules provide data more than sufficient to complete the resolution of the photometer curves. In practice it is not always possible to adhere to all of them rigidly, but it is desirable to use all in averaging the shapes of the derived resolved curves and never to allow an appreciable departure from any one of the rules without adequate and independent reason.

It is, we believe, significant that in the case of the two types of photometer plots for which considerable discrepancies from the rules are found unexpected information about the samples concerned is disclosed. The first example concerns unusually amorphous samples for which a reasonable resolution can be obtained only by an appreciable departure from rules (2) and (4) (see Fig. 4). The larger interchain spacing of the amorphous band indicated here is in agreement with the known high degree of chain branching in such polythenes.

The other example (see Fig. 5 (*a*)) concerns the photometer curves of samples which clearly violate rule (6), as the ratio of the areas under the (110) and (200) curves cannot be made equal to the normal values of 3·4. By cutting a small, roughly cubical chunk from the polythene films concerned and by taking X-ray powder photographs of these small cubes rotated, in turn, about an axis in the plane and about the unique axis perpendicular to the original sheet, photographs are obtained in which the ratio of the (110) and (200) intensities is normal. It follows that the crystal structure of the samples is normal, but that the arrangement of the crystallites is not. The 'plane' orientation so observed will be discussed in greater detail in an Appendix.

The intensities of the crystalline lines and of the amorphous band

Having completed the graphical resolution of the photometer curve into areas corresponding to the amorphous scattering and to the crystalline peaks (110) and (200), these areas are measured by means of a planimeter and a combined intensity correction for the temperature, absorption, atomic scattering and θ-factors (Bunn, 1945) is applied. Using a sheet specimen 0·3 mm. thick and Cu $K\alpha$ radiation, the areas under the amorphous, the (110) and the (200) crystalline curves must be multiplied by factors of 0·74, 1 and 1·43 respectively, in order to represent the relative intensities I_A, $I_{(110)}$ and $I_{(200)}$. The amorphous content determination proceeds by the evaluation of the ratio $I_A/(I_{(110)}+I_{(200)})$.

The sum of the intensities of the two strongest crystal reflexions is chosen to be compared with the intensity of the amorphous band intensity partly because in this way errors in resolution of these two crystal reflexions from one another are largely eliminated and partly because, for theoretical reasons, this ratio is expected to approximate to the actual weight ratios of amorphous to crystalline materials. It may be necessary to apply corrections for one or other of the two types of 'plane' and 'chain' orientation found in moulded polythene sheet; these corrections are described fully in the Appendix.

The absolute value of the amorphous content

We have now obtained a fully corrected value for $I_A/(I_{(110)}+I_{(200)})$ and are therefore in a position to arrange samples in order of increasing amorphous content, but for no sample do we know the actual weight ratio of amorphous to crystalline material, W_A/W_C. This can be evaluated only if the relative scattering efficiency, K, of unit weights of amorphous and of crystalline polythenes are known. We then have

$$K\frac{I_A}{I_{(110)}+I_{(200)}}=\frac{W_A}{W_C}.$$

From theoretical considerations, K can be expected to be close to unity, but it is still desirable to determine its value experimentally. Attempts so far to determine K practically by a number of methods indicate a value of 1·0 with an estimated probable error no greater than ± 0·1. The methods used or considered for the determination of K are as follows:

(1) Knowing the thickness and the density, and hence the total weight, W, of polythene in the X-ray beam, as

well as the X-ray exposure, I_0, as measured by the central spot on our X-ray films, we have for all samples:

$$(I_{(110)}+I_{(200)})/WI_0+KI_A/WI_0=\text{constant}.$$

The value of K can therefore be obtained from the slope of the linear plot of $(I_{(110)}+I_{(200)})/WI_0$ against I_A/WI_0. This method indicates that K is close to unity, but it is not entirely satisfactory because of (i) inaccuracies in measuring I_0, and (ii) the greater influence of both chain and plane orientation on this graph than on the determination of the intensity ratio (see Appendix).

(2) In a second method, related to the above, precisely similar sheets of two polythene samples, differing greatly in amorphous content, are examined side by side under rigidly controlled and identical conditions of exposure and development. We then have

$$K=\frac{(I_{(110)}+I_{(200)})-(I'_{(110)}+I'_{(200)})}{I'_A-I_A}.$$

This method has been tried for one pair of samples only, and in that case indicated a value of K slightly less than unity.

(3) Absolute intensity comparisons have been made between a polythene sample and a completely crystalline pure paraffin which has a crystal structure almost identical with that of the crystallites in polythene, both in powder form. In this method differences in the packing density of the specimens are difficult to allow for, but the result again indicated a value of K of the order of unity.

The amorphous content is generally expressed as a weight percentage. The reproducibility for samples on which two or more independent measurements have been carried out is usually better than ±0·6 %, and we estimate that the error in the absolute value of the amorphous percentage may be ±4 % for typical polythenes, the chief uncertainty being in the value of K.

Relation between the X-ray method and density measurements

Using the method described in this paper, the amorphous contents of more than 100 polythene samples have been measured. The results vary from about 7 % up to more than 50 % using a value of unity for K. Those obtained for a typical series of samples are shown in Fig. 6. The types of polythene available commercially and used for electrical insulation, e.g. 'Alkathene' 7, have amorphous contents of about 25 %. In the case of polymers of molecular weight above about 5000 there is a good general correlation between the amorphous content as measured by the X-ray method and the density of the same sample at ordinary temperatures. This is shown in Fig. 7. There may be a small variation of density for samples of the same amorphous content. This, we believe, is greater than the experimental error in the determination of either of these quantities, and the density of the sample may be affected by factors other than the amorphous content. This is particularly noticeable in the case of samples of low molecular weight, which, for a given amorphous content, have noticeably lower densities than the higher molecular weight samples.

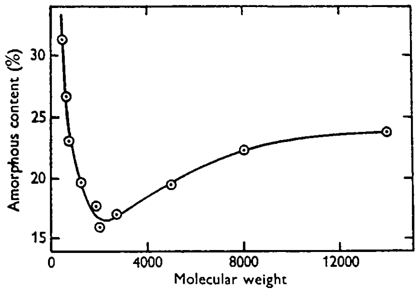

Fig. 6. Amorphous content of samples made by thermal degradation of polythene.

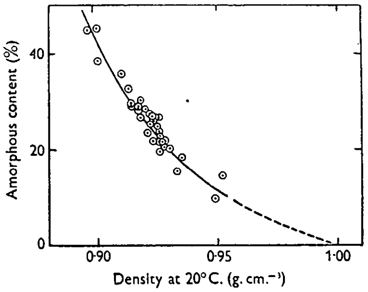

Fig. 7. Relation between amorphous content and density.

Since one cause of the variation in amorphous content from sample to sample is a variation in the degree of chain branching of the sample, and since the non-linear parts of the polythene molecule are likely to be concentrated in the amorphous regions, it is not to be expected that the density of the amorphous regions will be the same as that of an entirely amorphous paraffin of high molecular weight, or that it would agree with the figure obtained by an extrapolation to ordinary temperatures of the density–temperature curve for polythene above its melting-point. If we assume that the figures obtained for the amorphous content by the X-ray method are correct, we can calculate the average density of the amorphous regions in the polythene sample from the density of the sample as a whole and from the figure of 1·00 g.cm.$^{-3}$ for the density of the crystalline regions (based on the unit-cell dimensions). Results of about 0·73–0·78 g.cm.$^{-3}$ are obtained in this way. These should be compared with the value of 0·85 g.cm.$^{-3}$ obtained from extrapolation of the density–temperature curve for molten polythene and with the figures of 0·8–0·9 g.cm.$^{-3}$ for high molecular weight liquid paraffins at 20° C. We consider that the lower values calculated in this way for the density of the amorphous regions are significant, and that the structure of the amorphous regions differs appreciably from that of a liquid paraffin. If we assume a roughly hexagonal arrangement of the chain molecules in the amorphous regions of polythene, we find that the average interchain spacing is about 5·2 A., corresponding to a density of about 0·78 g.cm.$^{-3}$.

The amorphous content of one sample of polythene has been determined from its heat content–temperature curve (Raine *et al.* 1945). A value of about 25 % was obtained, in good agreement with the value for similar samples given by the X-ray method.

The authors wish to acknowledge the assistance given by many of their colleagues. They are especially grateful for the encouragement and advice given by Mr C. W. Bunn at all stages of this work.

APPENDIX

Corrections for orientation

(*a*) '*Plane*' *orientation*

For some samples of polythene the ratio of the intensities of the two crystal lines $I_{(110)}/I_{(200)}$ is not the characteristic one for the polythene structure when an X-ray photograph is taken of a sheet specimen perpendicular to the incident X-ray beam. For example, in Fig. 5 (*a*) the high value of $I_{(110)}/I_{(200)}$ is due to the orientation of crystallites with the (110) planes roughly perpendicular to the plane of the sheet (or the (200) planes parallel to the sheet), and X-ray photographs of pillars cut out of the sheet and oriented with the original plane of the sheet parallel to the X-ray beam and to the axis of the cylindrical photographic film show a relative defect of crystallites with (110) planes in a reflecting position and, consequently, a low value of $I_{(110)}/I_{(200)}$ (see Fig. 5 (*b*)). In other samples the intensity ratios when the beam is perpendicular to the beam is less than the normal value of 2·4. This 'plane' orientation is very different in character and in perfection from the well-known cold-drawing orientation in polythene fibres and strips.

If such 'plane' orientation occurs the main crystal planes will scatter more or less strongly relative to the amorphous scattering intensity, and the ratio

$$I_A/(I_{(110)}+I_{(200)})$$

for the perpendicular photograph is not characteristic for the sample as a whole. It is then essential to evaluate the parallel photograph in exactly the same way as we have discussed for the perpendicular photograph (cf. Fig. 5 (*b*)).

The ratio $[(I_{110}/I_{200})_{\text{Par.}}]/[(I_{110}/I_{200})_{\text{Perp.}}]$ can serve as a measure of the 'plane' orientation. Weissenberg X-ray photographs with continuously changing orientations show that for the polythene samples examined the orientation is always very imperfect and changes continuously with angle, while the maximum and minimum values of $I_{(110)}/I_{(200)}$ are always shown in the parallel and perpendicular positions. They also show that no appreciable orientation of the amorphous material occurs and that, in general, the (110) planes are much more evenly distributed parallel and perpendicular to the sheet specimens than are the (200) planes.

In samples in which a value of $(I_{(100)}/I_{(200)})_{\text{Perp.}}$ outside the limits 1·8–2·6 gives warning of appreciable plane orientation, the parallel photograph must be fully evaluated and an average value of the amorphous content must be calculated from the two photographs. It can be shown that the best method of averaging the ratios is

$$\left[\frac{I_A}{I_{(110)}+I_{(200)}}\right]_{\text{Av.}} = \frac{1}{3}\left\{2\left[\frac{I_A}{I_{(110)}+I_{(200)}}\right]_{\text{Perp.}} + \left[\frac{I_A}{I_{(110)}+I_{(200)}}\right]_{\text{Par.}}\right\}.$$

The values of $[I_A/(I_{(110)}+I_{(200)})]$ for perpendicular and parallel photographs rarely differ by as much as 20 %, corresponding to a difference of only about 2 % between the average amorphous percentage and the uncorrected value obtained from the perpendicular photograph.

(*b*) '*Chain*' *orientation*

Orientation of the molecular chains in the crystallites of the polythene samples parallel (or for that matter perpendicular) to the sheets cannot be detected from either the perpendicular or the parallel photograph alone, but might influence the value of

$$I_A/(I_{(110)}+I_{(200)}).$$

An independent test for the presence of chain orientation must therefore be made whenever plane orientation is absent. (The correction used for 'plane' orientation automatically corrects for 'chain' orientation if also present.) A flat-plate X-ray photograph is taken with a pillar specimen having the original plane of the sheet vertical and parallel to the incident X-ray beam. Now if θ is small compared with 90° and if the perfection of orientation is poor, the intensity of the crystalline reflexions on the equatorial radius of the photograph, $(I_{(110)}+I_{(200)})_{\text{Eq.}}$, can be shown to be approximately proportional to the number of chains per unit solid angle, $P_{\text{Par.}}$, which are in crystalline regions and which lie in a direction parallel to the sheet. The total crystalline line intensity on the meridional radius of the X-ray photograph, $(I_{(110)}+I_{(200)})_{\text{Mer.}}$, measures the arithmetic mean of $P_{\text{Par.}}$ and the number of chains per unit solid angle, $P_{\text{Perp.}}$, which are in crystalline regions and which are lying perpendicular to the polythene sheet. The chain orientation, which we may define quantitatively by the ratio $P_{\text{Par.}}/P_{\text{Perp.}}$, is therefore given by

$$\frac{P_{\text{Par.}}}{P_{\text{Perp.}}} = \left[2\left\{\frac{(I_{(110)}+I_{(200)})_{\text{Mer.}}}{(I_{(110)}+I_{(200)})_{\text{Eq.}}}\right\}-1\right]^{-1}. \qquad (2)$$

In practice the amount of this type of orientation is always small in annealed, pressed films of polythene, and no appreciable error is introduced by assuming that the orientation $P_{\text{Par.}}/P_{\text{Perp.}}$ can be evaluated from

$$\frac{(I_A+I_{(110)}+I_{(200)})_{\text{Eq.}}}{(I_A+I_{(110)}+I_{(200)})_{\text{Mer.}}},$$

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 $BaTiO_3$

By G. C. Danielson*

Bell Telephone Laboratories Inc., Murray Hill, New Jersey, U.S.A.

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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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* Now at Iowa State College, Ames, Iowa, U.S.A.