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deviations, however, are distributed in a regular way along the temperature region, and are several times those corresponding to the experimental errors.

The evidence that Eq. (1) or Eq. (2) expresses a physical relation seems to follow from the fact that the anomalous variations of a certain property can be predicted by means of other properties not exhibiting an anomaly in the region under consideration as is shown in Table I.

As a further concluding comment it may be worth mentioning that fairly recent theoretical work has

shown that there is a connection between partition functions and transport properties³ as well as with ordinary thermodynamic properties. Thus, all of the quantities examined here in the extrapolation comparisons have some kind of connection with partition functions. Further study may indeed be required to decide if the good extrapolation property shown arises accordingly from implicit but not obvious relationships among the various quantities used.

³ E. W. Montroll and J. C. Ward, *Physica* **25**, 423 (1959).

Dielectric Properties of Solid Solutions of BiFeO_3 with $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ at High Temperature and High Frequency*,†

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Solid solutions of BiFeO_3 with PbTiO_3 , $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$, and PbZrO_3 were prepared. The crystallographic data on these solutions, which are basically perovskitic, are given. The dielectric constants of the materials were determined at a frequency of 0.53 GHz and at temperatures up to 800°C. Dielectric Curie points were found in solutions containing up to 90 mole % BiFeO_3 . These results leave little doubt that BiFeO_3 is ferroelectric or antiferroelectric. The extrapolated Curie point for BiFeO_3 is above 850°C. BiFeO_3 appears more likely to be ferroelectric than antiferroelectric, but the distinction between the two classifications may not be sharp.

INTRODUCTION

BiFeO_3 is a perovskitic insulator whose exact crystal structure and electrical and magnetic properties have been the subject of considerable recent controversy, as exemplified in papers by Krainik *et al.*,¹ Roginskaya *et al.*,² and Smolenskii and Yudin.³ The purpose of this paper is to present dielectric evidence strongly indicating that the material is ferroelectric or antiferroelectric and that its Curie point is about 850°C. This conclusion is not in disagreement with earlier claims of unusual dielectric properties in BiFeO_3 ,^{4,5} but it is believed that the dielectric data presented here will offer reliable evidence in support of the claim, while the earlier data were primarily crystallographic and not

completely convincing in establishing classification on a dielectric basis. The data given are the results of measurements of the dielectric properties of polycrystalline materials in the BiFeO_3 - PbTiO_3 - PbZrO_3 system. All of these solid solutions have the basic perovskite structure at room temperature, though a number of different perovskitic phases are present.

The measurements of dielectric constant as a function of temperature were made at a frequency of 0.53 GHz using a special sample holder. The high measurement frequency was necessary because of the high conductivity of the samples near their Curie points. This conductivity would mask other dielectric effects at lower measurement frequencies.

Solid solution series having the compositions $(\text{BiFeO}_3)_x(\text{PbTiO}_3)_{1-x}$, $(\text{BiFeO}_3)_x(\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3)_{1-x}$, and $(\text{BiFeO}_3)_x(\text{PbZrO}_3)_{1-x}$ were prepared with x ranging from 0 to 1, and the dielectric properties of the solutions, in particular the Curie points, were determined. The Curie point of pure BiFeO_3 could not be measured, due to the high conductivity of this material, but it was possible to determine the Curie point of solutions containing up to 90 mol% BiFeO_3 . These data were then extrapolated over a relatively small compositional range to give the Curie point of BiFeO_3 .

PREPARATION AND CRYSTALLOGRAPHY

The solid solutions were prepared by reacting the constituent oxides (PbO , cp; Bi_2O_3 , cp; TiO_2 , certified

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¹ N. N. Krainik, N. P. Khuchua, V. V. Zhdanova, and V. A. Evseev, *Soviet Phys.—Solid State* **8**, 654 (1966).

² Yu. E. Roginskaya, Yu. Ya. Tomashpolskii, Yu. N. Venetsev, V. M. Petrov, and G. S. Zhdanov, *Soviet Phys.—JETP* **23**, 47 (1966).

³ G. A. Smolenskii and V. M. Yudin, *Soviet Phys.—Solid State* **6**, 2936 (1965).

⁴ Yu. N. Venetsev *et al.*, *Soviet Phys.—Crystallogr.* **5**, 594 (1961).

⁵ S. A. Fedulov, P. B. Ladyzhinskii, I. L. Pyatigorskaya, and Yu. N. Venetsev, *Soviet Phys.—Solid State* **6**, 375 (1964).

reagent grade; ZrO_2 , K and K Labs; Fe_2O_3 , Baker's analyzed) in a closed system containing air after thorough mixing of the oxides and pelletizing of the resultant mixture. The reaction temperatures were between 700° and 1025°C , maintained for a period of 2 h, with the lower reaction temperatures being used for compositions of high BiFeO_3 content. The material was usually air quenched after reaction. The pellets were then ground and an x-ray-diffraction analysis was made to determine the crystallography. To make the samples for dielectric measurements the powder was again pelletized and then densified by simultaneous application of heat and pressure. The technique, called "hot-pressing," consisted of heating the pellet in a matrix of MgO powder to the densification temperature (750° – 900°C) inside a Hastelloy die, while applying a pressure of 5–10 000 psi. The surface material contaminated with MgO was then removed and the sample was shaped into a small disk for the high-frequency dielectric measurements. X-ray diffraction patterns of the disk surfaces

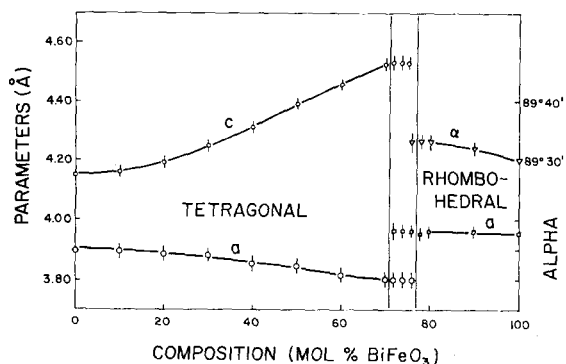


FIG. 1. Crystallographic parameters in the BiFeO_3 - PbTiO_3 system. In this figure, and in all following figures, the composition is specified by giving the mole % BiFeO_3 in the appropriate solid solution (in this figure, BiFeO_3 - PbTiO_3).

confirmed the similarity of the phases present in the solid to those present in the initial powder.

The results of the x-ray-diffraction analyses are given in Figs. 1–3. The results for the BiFeO_3 - PbTiO_3 system are in good agreement with the earlier work of Fedulov *et al.*,⁶ but it should be commented that the magnitude of the tetragonal distortion in compositions close to the rhombohedral phase boundary was dependent on the thermal history, probably because of varying oxygen stoichiometry. The width of the tetragonal-rhombohedral mixed phase region was also dependent on history. The extremely high c/a ratio found in this system is unique among perovskitic ferroelectrics and deserves emphasis.

The crystallographic results for the system BiFeO_3 - $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ have been partly given previously.^{6,7} The complete data are shown in Fig. 2. In this system the rhombohedral zone is greatly increased compared

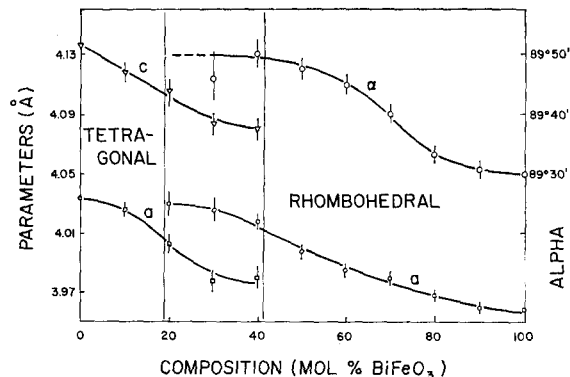


FIG. 2. Crystallographic parameters in the BiFeO_3 - $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ system. There is a wide mixed-phase region between the tetragonal and rhombohedral zones.

to the previous system, but the rhombohedral distortion is also considerably lower in much of the zone. This is consistent with the lower distortion of the adjacent tetragonal zone. These lowered distortions probably are due to a reduced degree of ferroelectric interaction, which is also indicated by lower ferroelectric Curie points (Fig. 7).

Finally, in Fig. 3 the crystallographic parameters of the BiFeO_3 - PbZrO_3 system are given. In a previous article⁸ two of the present authors had given the pseudocubic region in the central zone of this system, which is ferroelectric, a tentative indexing as orthorhombic. This seemed to be the best choice from x-ray data, but when neutron diffraction studies were run on this region,⁹ this choice was not confirmed. It seems best, at present, to relabel this region as pseudocubic. As was pointed out previously, the solid solutions rich in PbZrO_3 have a tendency to contain minor amounts of ZrO_2 as a contaminant (about 3 mole % as a maximum, although usually less).

DIELECTRIC MEASUREMENTS

A technique has been developed permitting admittance measurements to be performed with sufficient

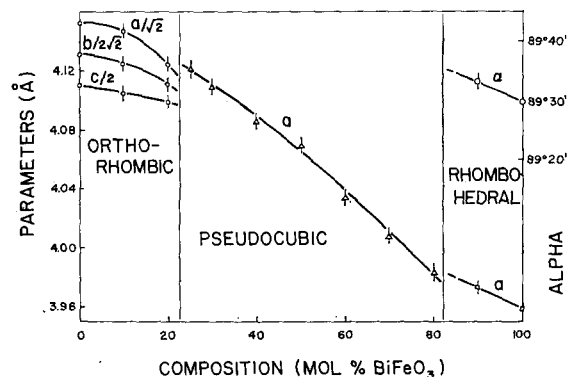


FIG. 3. Crystallographic parameters in the BiFeO_3 - PbZrO_3 system.

⁶ T. Ikeda and T. Okano, Japan J. Appl. Phys. 2, 63 (1963).

⁷ T. Ikeda and T. Okano, Japan J. Appl. Phys. 3, 63 (1964).

⁸ Robert Gerson, Pen-chu Chou, and W. J. James, J. Appl. Phys. 38, 55 (1967).

⁹ G. D. Achenbach, doctoral dissertation, University of Missouri at Rolla (1967).

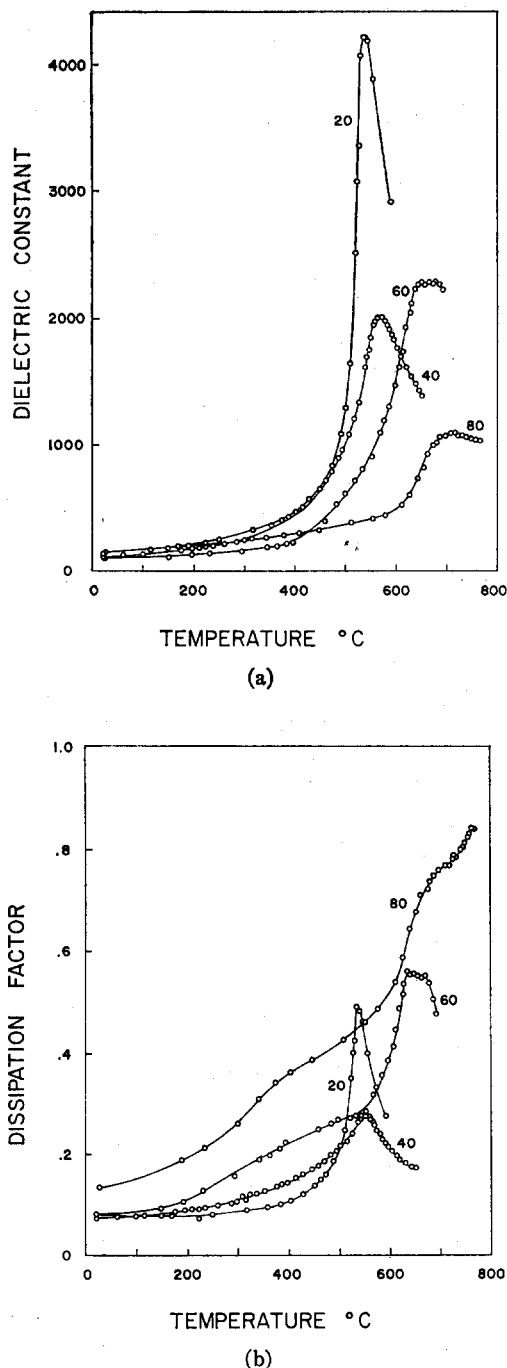


FIG. 4. The dielectric constant (a) and dissipation factor (b) of some BiFeO_3 - PbTiO_3 solid solutions, measured at 0.53 GHz. The numbers on the curves represent the mole % BiFeO_3 .

accuracy to be useful in research on ferroelectrics at temperatures up to 800°C and at frequencies of about 1 GHz. The method requires a sample in the form of a thin disk terminating a coaxial transmission line of known impedance which constitutes the sample holder. The actual measurement device is a standard slotted line connected to the sample holder. The apparatus

differs from those in previously described work¹⁰⁻¹³ in that the coaxial transmission line is not fabricated of metal, but is made from a metallized ceramic. This permits the sample to be raised to high temperature without excessive heat loss along the line, although the metal skin is sufficiently conductive to maintain electrical contact with the sample. In this method of measurement, the disk sample is treated essentially as a lumped impedance, although a correction is applied because its diameter is an appreciable fraction of the wavelength in the sample at the measurement frequency. A detailed description of the apparatus and entire measurement procedure is given in the doctoral dissertation of Smith.¹⁴

The errors involved in the use of the apparatus depend on the sample measured. For a typical sample, with a moderate dissipation factor of about 0.1, the maximum dielectric constant and dissipation factor errors are about $\pm 10\%$ and $\pm 15\%$, respectively, in the vicinity of the Curie point, where K is high. The inaccuracy decreases to less than $\pm 5\%$ at room temperature, where K is usually below 1000.

The behavior of the dielectric constant as a function of temperature in the three solid solution series is the most important evidence bearing on the nature of BiFeO_3 . Since the qualitative nature of the dielectric

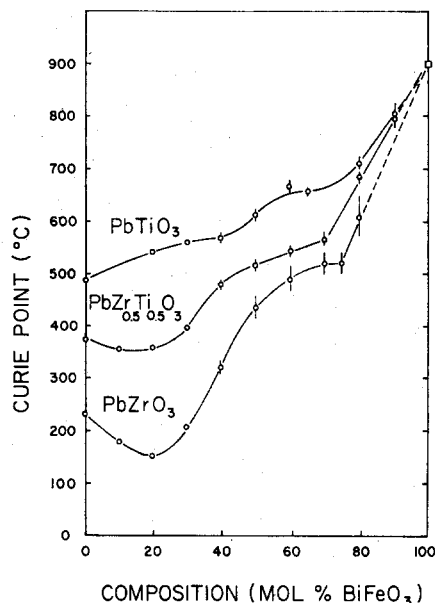


FIG. 5. The dielectric Curie point as a function of composition for the three solid-solution series labeled on the curves.

¹⁰ C. B. Sharpe and C. G. Brockus, *J. Am. Ceram. Soc.* **43**, 302 (1960).

¹¹ I. V. Ivanov and V. M. Petrov, *Bull. U.S.S.R. Acad. Sci.* **22**, 1516 (1958).

¹² R. Gerson, J. M. Peterson, and D. R. Rote, *J. Appl. Phys.* **34**, 3242 (1963).

¹³ W. J. Gemulla, *Tech. Memo., Electronic Defense Laboratories No. EDL-M246* (1960).

¹⁴ R. T. Smith, doctoral dissertation, University of Missouri at Rolla (1967).

constant vs temperature curves is the same for all of the systems, the curves are presented in detail only for the BiFeO_3 - PbTiO_3 series (Fig. 4). The detailed curves for all systems are in Ref. 14. The following trends are seen in considering all of the series:

(1) The Curie point temperature generally increases with increasing BiFeO_3 content for all solutions of high BiFeO_3 content (Fig. 5).

(2) The dielectric constant at the Curie point decreases in magnitude as BiFeO_3 content increases. If this maximum dielectric constant is plotted as a function of composition and then extrapolated (Fig. 6), a value of about 1300 is found for pure BiFeO_3 , using the BiFeO_3 - PbTiO_3 and BiFeO_3 - $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ series. The value for the BiFeO_3 - PbZrO_3 series was only half as high, but these solutions showed the maximum contamination with ZrO_2 and Bi_2O_3 , and might be expected to yield lower results.

An objection to the significance of these data might be raised on the basis that, for the solutions of high BiFeO_3 content, the dielectric loss was quite high at the Curie point, and consequently the real part of the dielectric constant might be increased substantially by a polarization due to space charges or an interfacial polarization. In examining the dielectric constant-temperature curves, however, no large irregularity in dielectric constant is found in the temperature range where the losses show their major increase. It does not seem, therefore, that space charge polarization plays a major role in the dielectric constant of these materials.

(3) The losses increase as the BiFeO_3 content increases, the maximum loss resulting in a dissipation factor somewhat below 1.0 at the Curie point. These losses are probably mainly conductive at higher tem-

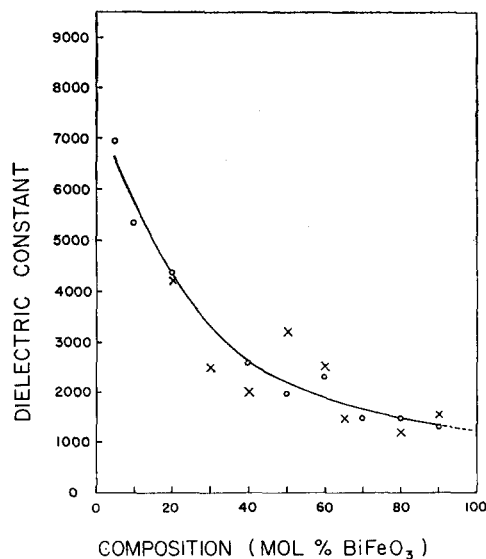
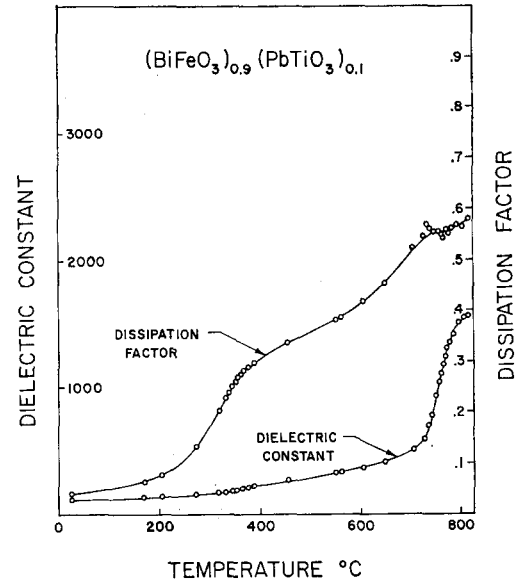
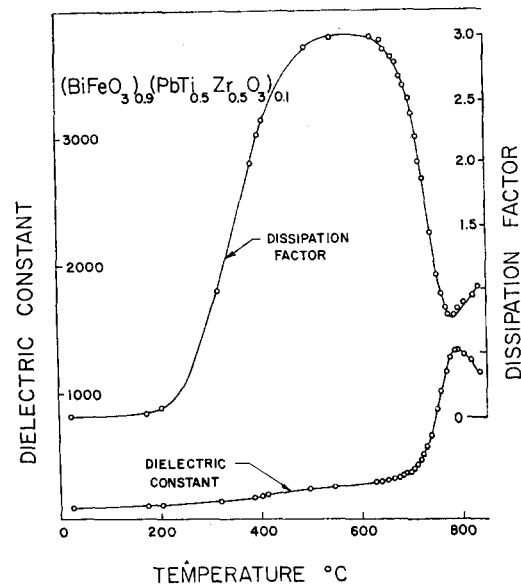


FIG. 6. The maximum (Curie point) dielectric constant as a function of composition for the BiFeO_3 - PbTiO_3 (crosses) and BiFeO_3 - $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ (circles) systems.



(a)



(b)

FIG. 7. The dielectric constant and dissipation factor as a function of temperature for the compositions $(\text{BiFeO}_3)_{0.9}(\text{PbTiO}_3)_{0.1}$, (a) and $(\text{BiFeO}_3)_{0.9}(\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3)_{0.1}$, (b) measured at 0.53 GHz.

peratures, and are sharply increased when the measurements are made at lower frequencies.

(4) There is a small anomaly in the dielectric constant curve at about 300° - 400°C for all solutions of high BiFeO_3 content. At the same temperatures there is a very marked rise in dissipation factor. These effects may be associated with the antiferromagnetic transition which takes place slightly below the above temperatures.

The behavior of solid solutions containing 90 mole % BiFeO_3 is of particular interest because these approach so closely to pure BiFeO_3 . The data for two of these

solutions are given in Fig. 7. It is noteworthy that in spite of the large difference in dissipation factor (conductivity) the two dielectric constant curves would almost superimpose if plotted on the same axes. The Curie points in both cases are clearly seen, although temperature limitations in the measurement apparatus prevented the Curie peak from being completely measured in one of the compositions. These data strongly indicate the presence of a Curie peak in BiFeO_3 at about 850°C , in excellent agreement with crystallographic and other data.

DISCUSSION

After the discovery of BiFeO_3 as a perovskite, the question which arose was whether the material was ferroelectric, antiferroelectric, or had no electrical anomalies at all. The work presented in this report leaves little doubt that the material is ferroelectric or antiferroelectric, but does not completely resolve the choice. The discussion below examines the evidence to see whether either choice is more probable.

With respect to conclusions drawn from the structure of BiFeO_3 , the introduction of some puckering in the iron-oxygen octahedron could be responsible for the multiple unit cell found using neutron diffraction.⁹ Since the bismuth atoms are essentially unshifted from their positions in the simple unit cell, it seems unlikely that the puckering, which could result in antiferroelectricity, represents the dominant behavior of BiFeO_3 , even though it may be responsible for raising the electrical coercive field. This is in contrast to the behavior of PbZrO_3 , which is ordinarily classified as antiferroelectric despite its polar structure.¹⁵ In PbZrO_3 the puckering is strong enough so that the Pb sublattice is also affected and a multiple unit cell can be found by x-ray diffraction.

There is strong evidence that BiFeO_3 is noncentrosymmetric. Kurtz¹⁶ has recently measured appreciable second harmonic generation from laser light incident on BiFeO_3 powder. The magnitude of this frequency conversion showed that BiFeO_3 is noncentrosymmetric, a requirement for frequency conversion.

There are three rhombohedral point groups which are noncentrosymmetric: $R3$, $R3m$, and $R32$. The first two groups are polar and permit ferroelectricity. The last group, $R32$, is nonpolar and, if the crystal belongs to this group, it must be antiferroelectric. While recent neutron diffraction studies⁹ were unable to differentiate conclusively among the three point groups, a structure based on $R32$ did not seem to be possible, while one based on $R3$ offered the best fit to the data. It therefore seems likely that BiFeO_3 is not only noncentrosymmetric but also polar, and thus can be a ferroelectric.

It should be noted that a multiple-cell structure, such as possessed by BiFeO_3 , may result from either ferroelectricity or antiferroelectricity, as has been discussed

by Megaw,¹⁷ so that the existence of this structure in BiFeO_3 does not prove that it is antiferroelectric, as has sometimes been implied.

In some recent work, Krainik¹ measured the dielectric constant of BiFeO_3 at its Curie point at a frequency of 7×10^9 Hz. A relatively low value of 140 was found, and it was claimed that this low value indicated antiferroelectricity rather than ferroelectricity. The technique used was a filled waveguide method. It is felt that, using this technique over an appreciable temperature range, it would be quite easy to obtain erroneous results. The present measurements, obtained by extrapolation of data from solid solutions, yield a value of the Curie point dielectric constant an order of magnitude higher than that obtained by Krainik. The higher values in these measurements are consistent with the theory that BiFeO_3 undergoes a ferroelectric transition.

It is clear that in perovskitic substances there may not be a phenomenological distinction in electrical properties between a puckered ferroelectric with a high coercive field and an antiferroelectric with a polar axis. If a distinction is to be made between the two classifications, one possible way of doing this is to compare the size of the electrical dipole moment along the polar axis (the ferroelectric polarization) with the magnitude of the opposed antiferroelectric dipole moments. If either polarization is clearly dominant, it would be reasonable to classify the material as primarily belonging to the dominant category. Since the nuclear positions are not known in BiFeO_3 , it is not possible at this time to make an unequivocal classification on this basis. Based on the dielectric evidence presented in this article, the best tentative classification of BiFeO_3 would appear to be as a ferroelectric (with puckered structure) rather than as an antiferroelectric. This conclusion is also consistent with the dilatometric measurements of Krainik,¹ which show a marked decrease in volume for BiFeO_3 as it is heated through its Curie point. (In perovskitic materials the ferroelectric state has been found to have a higher volume than the paraelectric state, while the best known antiferroelectrics have a lower volume just below the Curie point than above it. This point is briefly discussed in the monograph by Jona and Shirane.¹⁸)

It will be difficult to confirm the classification of BiFeO_3 completely until the exact atomic coordinates of the atoms in the unit cell are established or until single crystals of high resistivity are available for electrical testing.

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We are very grateful for the assistance of Dannie R. Clarida, who prepared many of the solid solutions and made preliminary x-ray analyses, and of James P. Canner, who densified the powders.

¹⁵ F. Jona, G. Shirane, F. Mazzi, and R. Pepinsky, *Phys. Rev.* **105**, 849 (1957).

¹⁶ S. K. Kurtz (private communication).

¹⁷ Helen D. Megaw, *Ferroelectricity in Crystals* (Methuen and Co. Ltd., London, 1957), Chap. 6, p. 133.

¹⁸ Franco Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962). Chap. 5, p. 246.