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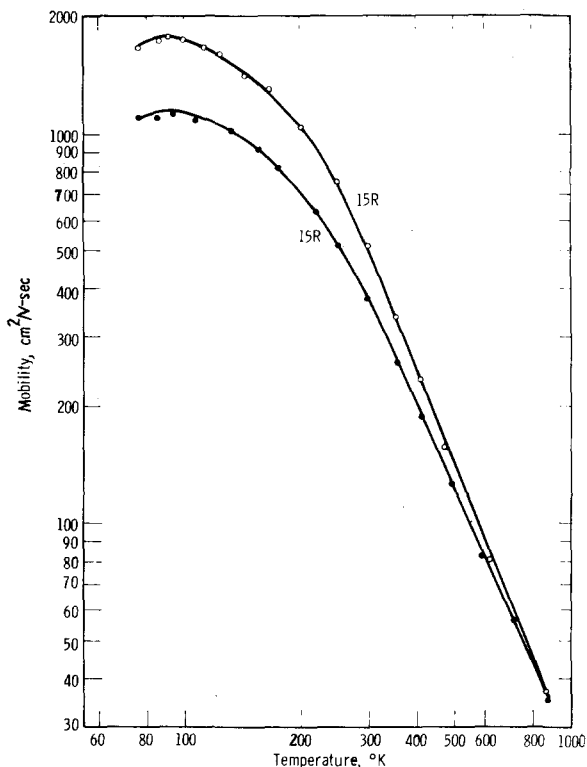
## Recommended Citation

FIG. 4. Electron mobility vs temperature for two $15R$ samples from preparations of different purity. The curves tend to converge at higher temperatures where impurity scattering is relatively unimportant.

## V. CONCLUSIONS

When measured perpendicular to the $c$ axis the electron mobility of high purity $15R$ SiC is at least 1.7 times that of $6H$ SiC. This ratio may prove to be even higher if samples of greater purity can be prepared and evaluated. Measurements on two samples suggest that the mobility is still greater in $4H$ SiC. Since the effective masses and deformation potentials of the different polytypes are not known, theoretical values of these ratios cannot be given. In the purest sample, the experimental value of $T^{-2.4}$ for the temperature dependence of mobility is almost identical for $6H$ and $15R$ polytypes above $300°K$. This suggests that acoustic and intervalley scattering are the dominant mechanisms in both polytypes.[4]

## ACKNOWLEDGMENTS

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# Ferroelectric Properties of PbZrO₃–BiFeO₃ Solid Solutions*†

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(Received 31 May 1966; in final form 12 September 1966)

Solid solutions of $BiFeO_3$ and $PbZrO_3$ were investigated for crystallographic and dielectric properties. A new pseudocubic perovskite phase was found, which has been tentatively indexed as orthorhombic with the same unit cell as $PbZrO_3$ but with dielectric properties characteristic of a ferroelectric substance. The Curie point in this series of solid solutions has a minimum of about 155°C at a composition of about $(PbZrO_3)_{0.80} (BiFeO_3)_{0.20}$, which at room temperature lies on the boundary between the orthorhombic antiferroelectric and the pseudocubic ferroelectric phases. This composition has a relative dielectric constant of 800 at room temperature and shows appreciable dielectric nonlinearity. The Curie point rises to about 400°C for $(PbZrO_3)_{0.50} (BiFeO_3)_{0.50}$ and is extrapolated to about 900°C for pure $BiFeO_3$, in agreement with previous data from similar solid solutions. It is felt that this is additional evidence that the distortion from cubic symmetry in $BiFeO_3$ may be of ferroelectric origin.

## INTRODUCTION

IT is known that $BiFeO_3$ is a perovskite with a rhombohedral crystal structure.[1] Its rhombohedral angle is $89°24'$. There are a number of ferroelectric materials which have the perovskite structure (slightly distorted in the ferroelectric state), and it thus appears that $BiFeO_3$ may be ferroelectric. If the distortion of $BiFeO_3$ from cubic symmetry is of ferroelectric or antiferroelectric origin, this is a very large ferroelectric effect. For comparison, the angle in rhombohedral $BaTiO_3$ is $89°52'$, roughly one-fourth the deviation from a 90° angle which is found in $BiFeO_3$.

It has been claimed that $BiFeO_3$ is ferroelectric or antiferroelectric with a very high Curie temperature,[2]

¹ V. S. Filp'ev, N. P. Smolyaninov, E. G. Fesenko, and I. N. Belyaev, Soviet Phys.—Cryst. 5, 913 (1960).

² S. A. Fedulov, Soviet Phys.—Doklady 6, 729 (1962).

possibly over 800°C. It is not possible to give direct dielectric evidence to support this claim. Single crystals of $BiFeO_3$ of size and perfection suitable for ferroelectric measurements have not been made. Ceramics of the material have been made, but they are too conductive at temperatures near the Curie point to measure dielectric properties, such as a possible dielectric anomaly at the Curie point. The measurement of dielectric nonlinearity or dielectric hysteresis at low temperatures is also prevented by the conductivity of the material, and possibly also by the necessity for a very high electrical field to cause domain reorientation. The latter is to be expected in a ceramic ferroelectric of high distortion well below its Curie temperature.

Instead of making direct measurements of dielectric hysteresis in $BiFeO_3$, the approach used by previous investigators to establish the presence of ferroelectricity has been to make solid solutions of $BiFeO_3$ with known perovskitic ferroelectrics. When a solid-solution series of the two perovskites was formed, the effect of the $BiFeO_3$ addition on the crystallographic and dielectric properties of the known ferroelectric was measured. The results from several of these series indicated that large additions of $BiFeO_3$ correspond to high values of the ferroelectric Curie point of the solid solutions. Moreover, the extrapolated values of the Curie point for several such series all showed roughly the same result (about 800°–900°C). Krainik has recently reviewed the evidence,[3] and in addition, presented new data on the $BiFeO_3$–$PbFe_{0.50}Nb_{0.50}O_3$ system. On the basis of his data, he concluded that $BiFeO_3$ is ferroelectric or antiferroelectric. Earlier a number of other Russian researchers had arrived at the same conclusion, their chief evidence being the remarkable effect of $BiFeO_3$ additions in increasing the ferroelectric distortion of $PbTiO_3$.[4] It is the purpose of the present work to augment these data with results for the $BiFeO_3$–$PbZrO_3$ series, and to show that these results also indicate ferroelectric properties in $BiFeO_3$. In addition, a new ferroelectric phase was found in the $BiFeO_3$–$PbZrO_3$ system, which appears to have the same crystal structure as antiferroelectric $PbZrO_3$.

It is of importance to establish whether $BiFeO_3$ is ferroelectric, because, if so, it is unique among the perovskitic ferroelectrics. With respect to formal valency rules, none of the other known perovskitic ferroelectrics and antiferroelectrics have two cations which are trivalent. Also, in these known materials, the six-coordinated cation has a noble-gas electronic configuration, while $Fe^{3+}$ does not. However $Fe^{3+}$ has a half-filled $3d$ level, corresponding to a $^6S$ state, which imparts a stability comparable to ions having a noble-gas configuration. Finally magnetic-susceptibility and neutron-diffraction studies show that $BiFeO_3$ is anti-

ferromagnetic. There are few other materials as simple structurally and chemically as $BiFeO_3$ in which a combination of ferroelectric and antiferromagnetic properties has been found.

The $PbZrO_3$–$BiFeO_3$ system has received some investigation in the past[5,6] though not with the thoroughness of the present work. It is a relatively difficult system to work with, because there is a strong tendency to form minor amounts of nonperovskitic phases which complicate the analysis of its properties. These phases appear mainly as $ZrO_2$ for compositions rich in $PbZrO_3$ and $\gamma$-$Bi_2O_3$ for compositions rich in $BiFeO_3$. For compositions which are close to pure $BiFeO_3$, there is also a third impurity phase, $Bi_2O_3$-$2Fe_2O_3$[7], but this phase is not detectable if more than 5 mole % $PbZrO_3$ is present. The amounts of impurity phase can be minimized by proper thermal treatment. In the samples reported on below, the main contaminant was $ZrO_2$, and its concentration did not exceed 3 mole %, although it was usually lower.

In general, all compositions were formed from the constituent oxides (PbO, C.P.; $ZrO_2$, K and K Labs; $Bi_1O_3$, C.P.; $Fe_2O_3$, Baker's analyzed) by reacting in a closed system for two hours (in some instances the materials were reground and resintered for two hours) at 870°C and then air quenching. In forming solid samples for dielectric measurements, the powders obtained from the above procedure were ground, the resulting fine power was compacted into cylindrical specimens, and finally it was densified. The compositions reported here were densified readily when both heat and pressure were applied simultaneously. The dielectric results reported below are given for materials whose relative densities were as follows: $PbZrO_3$, 95%; $(PbZrO_3)_{0.90}$ $(BiFeO_3)_{0.10}$, 98%; $(PbZrO_3)_{0.80}$ $(BiFeO_3)_{0.20}$, 91%; $(PbZrO_3)_{0.70}$ $(BiFeO_3)_{0.30}$, 94%; $(PbZrO_3)_{0.60}$ $(BiFeO_3)_{0.40}$, 85%; $(PbZrO_3)_{0.50}$ $(BiFeO_3)_{0.50}$, 91% of theoretical density. The structural results are given for the reacted powders.

## CRYSTALLOGRAPHIC STRUCTURE

The structure of $PbZrO_3$ has been investigated by both x-ray and neutron diffraction.[8] The unit cell at room temperature is multicell orthorhombic (pseudo-tetragonal), with $a=5.873$, $b=11.746$, $c=8.228$ Å. The space group is $Pba2$. The antiparallel dipole moments created by the antiferroelectric character of $PbZrO_3$ lie in the $ab$ plane. The $c$ axis is believed to be polar. The addition of $BiFeO_3$ to $PbZrO_3$ results in a

[3] N. N. Krainik, N. P. Khuchua, A. A. Berezhnoi, and A. G. Tutov, Soviet Phys.—Solid State 7, 100 (1965).

[4] S. A. Fedulov, P. B. Ladyzhinskii, I. L. Pyatigorskaya, and Yu. N. Venevtsev, Soviet Phys.—Solid State 6, 375 (1964).

[5] D. A. Berlincourt and H. H. A. Krueger, Annual Progress Report, 1963, Sandia Corporation, Purchase Order 51-6529 (Clevite Corporation).

[6] V. V. Ivanova, N. V. Tomeishvili, S. A. Fedulov, and Yu. N. Venevtsev, Vopr. Radioelektron. Ser. 3, Det. i Komp. Apparat. 10, 86 (1963).

[7] H. Koizumi, N. Niizeki, and T. Ikeda, Japan. J. Appl. Phys. 3, 495 (1964).

[8] F. Jona, G. Shirane, F. Mazzi, and R. Pepinsky, Phys. Rev. 105, 849 (1957).

reduction in the orthorhombic distortion (Figs. 1 and 2). At approximately the $(PbZrO_3)_{0.80}$ $(BiFeO_3)_{0.20}$ composition, a fairly sharp change of crystal parameters occurs. The unit cell becomes very nearly cubic at the transition composition and remains pseudocubic for compositions containing 20–70 mole % BiFeO₃. The dielectric Curie point reaches a minimum of about 155°C at the transition composition and rises very sharply when larger proportions of BiFeO₃ are used. The only other phase transitions found in the solid solution series occurs at about $(PbZrO_3)_{0.30}$



FIG. 2. Lattice parameters of the orthorhombic phases of PbZrO₃–BiFeO₃ at room temperature as a function of composition.

undergo antiparallel shifts within the (001) plane and, in addition, unbalanced antiparallel shifts along the c axis. Examination of Fig. 1 reveals that, starting at the composition $(PbZrO_3)_{0.80}$ $(BiFeO_3)_{0.20}$, the reflections of the (004) and (240) planes merge into one peak and the intensities of (110), (112), (132) are nearly zero. This situation arises when all of the atoms are unshifted with reference to the ideal perovskite structure. Therefore, it is evident that the heavy atoms (oxygen contributions to the x-ray intensities are small) of the PbZrO₃ structure undergo considerable displacement upon introduction of BiFeO₃. These results suggest that the remaining distortion, which greatly influences the observed electrical properties, may be found mainly in the oxygen octahedra. Furthermore, the oxygen atoms in PbZrO₃ are so situated as to equalize the parameters
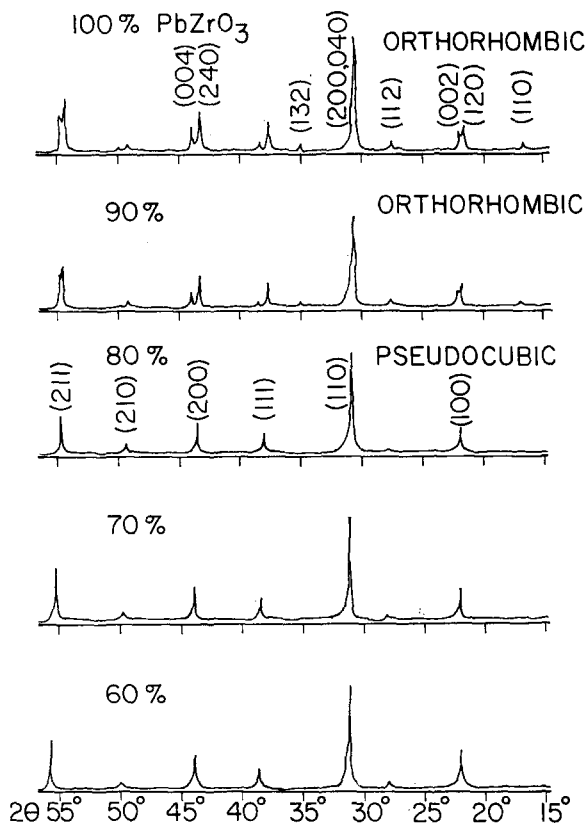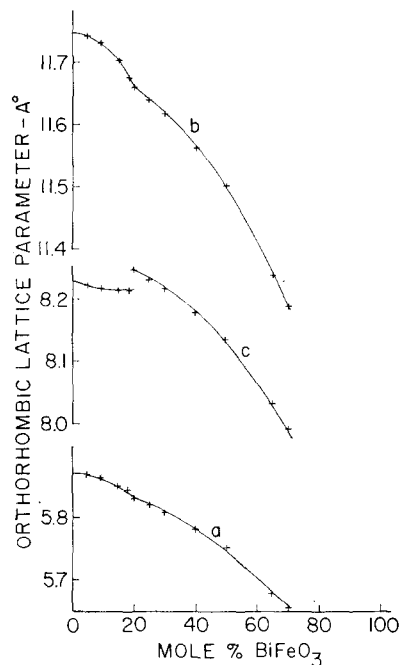


FIG. 1. X-ray diffraction patterns at room temperature of the orthorhombic phases in the system PbZrO₃–BiFeO₃. These patterns were produced using CuKα radiation on a Siemens diffractometer, model Crystalloflex IV.

$(BiFeO_3)_{0.70}$, where the pseudocubic structure changes to the rhombohedral BiFeO₃ structure. This transition has an appreciable mixed-phase region. Compositions containing 70–100 mole % BiFeO₃ have a rhombohedral angle of about 89°28', while the rhombohedral lattice parameter varies from about 3.985 at the phase boundary to 3.951 for pure BiFeO₃. The volume of the pseudocubic unit cell of the crystal decreases monotonically from PbZrO₃ to BiFeO₃ (Fig. 3).

The work of Jona et al.[8] showed that the lead atoms in PbZrO₃ shift with respect to the ideal perovskite structure, undergoing antiparallel displacements along the former cubic [100] direction. The oxygen atoms



FIG. 3. Volume of the pseudocubic unit cell for PbZrO₃–BiFeO₃ solid solutions at room temperature as a function of composition. The change from the antiferroelectric to the ferroelectric orthorhombic phase shows little effect on the unit-cell volume, despite a pronounced effect on individual dimensions (see Fig. 2).
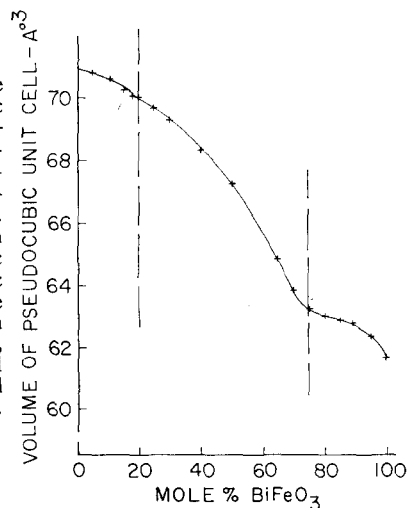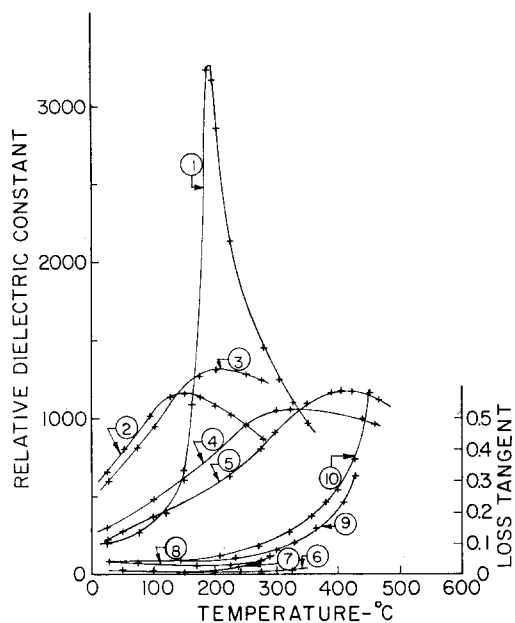
FIG. 4. Dielectric constant and loss tangent as a function of temperature for $PbZrO_3$–$BiFeO_3$ compositions. Curves 1–5 refer to relative dielectric constant and curves 6–10 to loss tangent. The materials and frequencies used are as follows: curves 1 and 6, $(PbZrO_3)_{0.90}$–$(BiFeO_3)_{0.10}$, 100 kHz; curves 2 and 7, $(PbZrO_3)_{0.80}$–$(BiFeO_3)_{0.20}$, 100 kHz; curves 3 and 8, $(PbZrO_3)_{0.70}$–$(BiFeO_3)_{0.30}$, 1 MHz; curves 4 and 9, $(PbZrO_3)_{0.60}$–$(BiFeO_3)_{0.40}$, 7.4 MHz; curves 5 and 10, $(PbZrO_3)_{0.50}$–$(BiFeO_3)_{0.50}$, 20 MHz. The measurements at 1 MHz and below were taken with a General Radio Company 716 C bridge, while the higher-frequency measurements were done with a Boonton Radio Corporation 260A Q-Meter. The high loss tangents at high temperature were due mainly to conductivity.

along the orthorhombic $a$ and $b$ axes, thus accounting for the pseudotetragonality.

The solid solutions containing 20–70 mole % $BiFeO_3$ are not exactly cubic, for their x-ray diffraction patterns show peaks (these peaks are small) which do not occur in the cubic system and the electrical properties are not those of cubic materials. Attempts to index the material in the rhombohedral, tetragonal, or monoclinic systems were unsuccessful. The exception is that the tetragonal indexing is close, for the reason discussed above. The only system in which these compositions could be indexed was orthorhombic, with the same unit cell as $PbZrO_3$. This is a somewhat tentative conclusion because of the small distortions in the system, and it must be granted that more exact compositional work may show that the orthorhombic symmetry is not a correct choice. It is, however, the best that can be made at present, and it is believed to be more informative to label the system as orthorhombic than pseudocubic. Moreover, the choice of the orthorhombic unit cell displays most clearly what may be happening to the crystal parameters at the phase transition (Fig. 2).

If the remaining distortion in the pseudocubic solid solutions is attributable primarily to the oxygen octahedra, one might expect the orthorhombic phase (phase II) beyond the transition composition to also

have $b=2a$, which is observed. Inasmuch as oxygen's scattering factor for x-rays is considerably less than that of lead or bismuth, the oxygen parameters cannot be determined from these measurements, but must be obtained from neutron diffraction data.

## DIELECTRIC RESULTS

The nature of the difference between orthorhombic phase I ($BiFeO_3$ content less than 20 mole %) and orthorhombic phase II ($BiFeO_3$ content greater than 20 mole %) becomes more evident as the dielectric data are examined. Figure 4 shows dielectric constant and loss tangent as a function of temperature for compositions ranging from $(PbZrO_3)_{0.90}$ $(BiFeO_3)_{0.10}$ to $(PbZrO_3)_{0.50}$ $(BiFeO_3)_{0.50}$. (The same data for pure $PbZrO_3$ were originally given by Roberts[9]). It is seen that the Curie temperature decreases in phase I and increases in phase II with increasing $BiFeO_3$ content. This is emphasized in Fig. 5, which shows the Curie point plotted as a function of composition. A straight line extrapolation of these data yields a Curie point of approximately 900°C for pure $BiFeO_3$. Of course this extrapolation over such a wide range of composition, and into another phase, is a very uncertain quantitative estimate.

The dielectric constants of the series at room temperature are given as a function of composition in Fig. 6. The maximum dielectric constant occurs at the boundary composition between phase I and phase II. It is not unusual in series with ferroelectric properties to have a maximum dielectric susceptibility at a transition composition. In the present case, however, the minimum Curie point is also found at this transition composition. Both the low Curie point and the presence
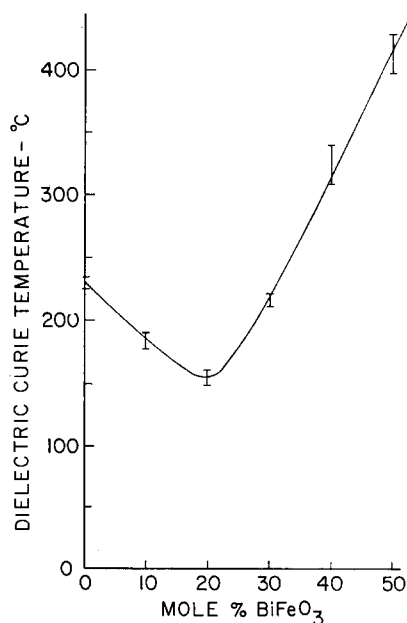


FIG. 5. Dielectric Curie point of solid solutions of $PbZrO_3$–$BiFeO_3$ as a function of composition, from Fig. 4. The highest values have large uncertainties because of the broad Curie peaks.

9 S. Roberts, J. Am. Ceram. Soc. **33**, 63 (1950).

of the phase boundary tend to raise the value of the dielectric constant at room temperature. The relative dielectric constant of about 800 measured for the boundary composition $(PbZrO_3)_{0.80}$ $(BiFeO_3)_{0.20}$ seems to be characteristic of all of the phase II compositions measured at temperatures 130°C below their Curie points. In phase I the dielectric constant is much lower at a corresponding temperature.

The dielectric linearities of phase I and phase II also show great differences, particularly for compositions near the transition. One indication of the change is seen in the behavior of the small-signal dielectric constant when a dc bias field is applied (Fig. 7). These measurements were made on samples about 0.3-mm thick at a frequency of 100 kHz, using a General Radio Company 716 C bridge and a large blocking capacitor between the bridge and the sample to prevent the dc potential from affecting the bridge.
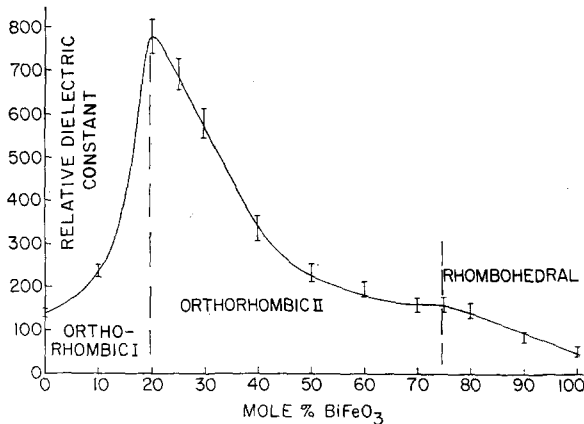


FIG. 6. Relative dielectric constant of PbZrO₃–BiFeO₃ solid solutions at room temperature measured at a frequency of 100 kHz. The loss tangent was less than 0.05 for all compositions.

The phase I compositions show little dependence of dielectric constant on bias field, while phase II compositions show a pronounced decrease of dielectric constant with bias field and a significant change in the dielectric constant after the bias field is removed. The behavior of the latter is characteristic of ferroelectric materials.

Another method of detecting dielectric nonlinearity is through measurement of the dielectric hysteresis loop. This measurement was made on the composition $(PbZrO_3)_{0.80}$–$(BiFeO_3)_{0.20}$ at room temperature and a frequency of 60 Hz, using a conventional Sawyer–Tower circuit. The loop did not show a sharp coercive field. When the maximum applied field was 60 kV/cm, the spontaneous polarization was 4 $\mu C/cm^2$ and the remanent polarization was about 0.7 $\mu C/cm^2$.

A more conclusive indication of dielectric non-linearity may be found by plotting the maximum dielectric polarization as a function of maximum applied electric field for a series of hysteresis loops
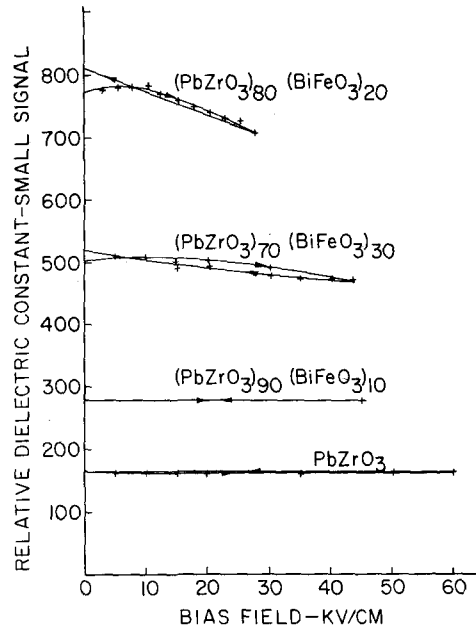


FIG. 7. Small signal dielectric constant of some PbZrO₃–BiFeO₃ solid solutions as a function of applied dc bias field. Pure PbZrO₃ showed a small increase in dielectric constant when the field was applied, although this effect is not visible on the scale of the drawing.

determined with slowly increasing electric fields (Fig. 8). In these data one finds evidence of both a threshold field for domain reorientation (the relatively abrupt polarization increase at 30–50 kV/cm) and dielectric saturation (the flattening of the curve above 50 kV/cm). The spontaneous polarization, estimated from the difference between the observed polarization near saturation and the value this quantity would have if the small-signal dielectric constant of 800 were used, is 6 $\mu C/cm^2$. This value is higher than the estimate from the simple high-field hysteresis loop, and is probably a better estimate of the actual polarization.
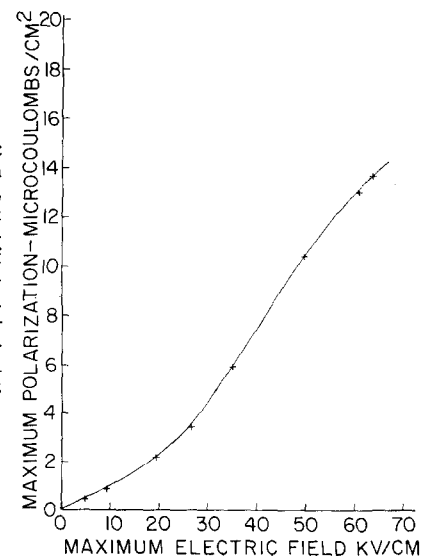


FIG. 8. Dielectric nonlinearity, from hysteresis loop data, showing maximum dielectric polarization as a function of the maximum applied electric field for $(PbZrO_3)_{0.80}$–$(BiFeO_3)_{0.20}$. A linear material would result in a straight line for this plot.

## DISCUSSION

The appearance of the pronounced nonlinearity at the transition composition between phase I and phase II shows that phase II is ferroelectric. The polarization measured in phase II is small for a ferroelectric perovskite, in agreement with the x-ray diffraction pattern which shows that the material is close to being cubic. Since the para-electric–ferroelectric transitions are diffuse in these solid solutions, it appears likely that a greater spontaneous polarization would be found below room temperature.

The fact that the addition of $BiFeO_3$ transforms antiferroelectric $PbZrO_3$ into a ferroelectric, and that within the ferroelectric phase the Curie point rises with increasing $BiFeO_3$ content, suggests the possibility of ferroelectric properties in $BiFeO_3$ itself. The combined evidence of the behavior of solid solutions of $BiFeO_3$ with $PbTiO_3$, $PbFe_{0.50}Nb_{0.50}O_3$, and $PbZrO_3$, where all of these series extrapolate to dielectric transitions at 800–900°C for pure $BiFeO_3$, is a further indication that pure $BiFeO_3$ may be ferroelectric (or antiferroelectric).

The crystal structure of the orthorhombic phase II is quite unexpected. In other antiferroelectric–ferroelectric transitions, whether induced by slight compositional changes or by an electrical field, there is usually a pronounced change in crystal structure accompanying the change of phase. For example, the orthorhombic antiferroelectric structure of lead zirconate changes to a rhombohedral ferroelectric, with a decrease in cell multiplicity by a factor of eight, when 10 mole % of lead titanate is added in solid solution.[10] In the transition described in the present paper, there is little discontinuity in the unit-cell volume at the phase boundary. There is, however, a pronounced reduction in the deviation from cubic symmetry in going from the antiferroelectric to the ferroelectric phases, the ferroelectric phase being nearly cubic at room temperature. The system which is most similar to the present study is possibly the $KNbO_3$–$NaNbO_3$ solid solution series, which also shows a transition between an orthorhombic ferroelectric (with a simple unit cell) and an orthorhombic antiferroelectric due to varying composition.[11]

Jona et al. pointed out,[8] in their report on the x-ray and neutron diffraction pattern of $PbZrO_3$, that this material is polar in the c direction, while the opposed dipole moments characteristic of antiferroelectricity lie in the ab plane. They hypothesized that the large distortion, particularly of the Pb sublattice, prevents the reversal of the c polarization under an applied electric field, so that no ferroelectricity is detected. This conclusion is in agreement with the results described here for orthorhombic phase II. It appears possible that when the extreme puckering in orthorhombic phase I is reduced by $BiFeO_3$ additions, the ferroelectric properties which have been concealed by the puckering become measurable. This seems to occur only after the disorder associated with the random $BiFeO_3$ addition has considerably reduced both the antiferroelectric and ferroelectric polarizations. Perhaps most of the remaining polarization is associated with distortion of the oxygen octahedra and can be readily reversed by an electrical field. There is, incidentally, no evidence of any superstructure lines in the x-ray diffraction patterns of the solid solutions which would indicate positional ordering of the $BiFeO_3$ cells in the $PbZrO_3$–$BiFeO_3$ matrix.

It is also very interesting that the Curie point decreases with increasing $BiFeO_3$ content in orthorhombic phase I, while the reverse is true in phase II. This is not a matter of the effect of $BiFeO_3$ being different in an antiferroelectric and a ferroelectric phase, for the same behavior occurs when $BiFeO_3$ is added to $(PbZrO_3)_{0.90}$–$(PbTiO_3)_{0.10}$, a rhombohedral ferroelectric at room temperature. It should be pointed out that the phase boundary and the change in dielectric behavior do not occur until enough $BiFeO_3$ is present so that almost all of the ion atoms have at least one iron atom as a neighbor in the six-coordinated position in the lattice. This points to the possible influence of chains of –O–Fe–O–Fe–O– atoms in causing the phase change.

We are not able at present to account satisfactorily for the difference between phases I and II. It is hoped that a neutron diffraction study, now being undertaken, will reveal the position of the oxygen atoms and clarify the manner in which $BiFeO_3$ raises the Curie point of phase II. This should help to clarify the reportedly high Curie temperature of $BiFeO_3$ itself.

## ACKNOWLEDGMENTS

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