

DIELECTRIC HYSTERESIS IN SINGLE CRYSTAL BiFeO_3 *

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Single crystals of BiFeO_3 of perovskite structure were grown with dimensions of greater than 1 mm from a Bi_2O_3 flux. Dielectric hysteresis loops were measured on these crystals. While the loops were not fully saturated, they confirm that BiFeO_3 is ferroelectric.

SINCE THE TIME of its original discovery,¹ the perovskite compound, BiFeO_3 , has been a subject of controversy. The X-ray diffraction pattern showed that the material was a rhombohedrally distorted perovskite and early neutron diffraction data showed that it is a G-type antiferromagnetic.² However, conclusive proof of the exact electrical and magnetic classification was lacking. Solids solutions consisting principally of BiFeO_3 showed electrical and crystallographic anomalies indicating that the material itself was ferroelectric or antiferroelectric.^{3,4} Neutron diffraction analysis of the exact atomic structure showed that the compound could not be antiferroelectric and that it was isostructural with a known ferroelectric solid solution of lead titanate zirconate.⁵ However, the classical evidence for ferro-electricity in BiFeO_3 , such as a dielectric hysteresis loop, reversible piezoelectricity, or a dielectric Curie point in the pure material, has not been reported.

We have recently succeeded in growing BiFeO_3 crystals with dimensions in the 1–2 mm range. These were grown by very slow cooling in a Bi_2O_3 flux contained in a nickel crucible. The initial Bi_2O_3 – Fe_2O_3 molar ratio was 1.75–1. The mixture was heated to 860°C and then cooled

at a rate of $1\frac{1}{2}^\circ/\text{hr}$ to 760°C, with a holding time of 18–20 hr at 820°C. The major faces of the crystals were (100) planes. There was unquestionably some loss of Bi_2O_3 through volatilization and reaction with the crucible, and the resulting concentration of Fe_2O_3 may have been an important factor in the formation of the crystals.

When electrodes were applied to the crystals (DuPont #4731 silver was used), it was possible to observe a dielectric hysteresis loop for a 60 Hz voltage (Fig. 1), applied when the crystal was held in liquid nitrogen. At room temperature the crystal was too conductive to give these results. The measured spontaneous polarization was $3.5 \mu\text{C}$ per cm^2 along the $\langle 100 \rangle$ direction, which represents $6.1 \mu\text{C}$ per cm^2 in the $\langle 111 \rangle$ direction. This is considerably lower than expected for a compound with such a high Curie temperature and distortion. For example, either a calculation of the polarization from the atomic coordinates, using the assumption that BiFeO_3 is fully ionic, or the use of the empirical relationship of Abrahams *et al.*⁶ between atomic shift and polarization, would indicate that the actual polarization of BiFeO_3 is an order of magnitude higher than we have measured. The maximum field applied to the sample was 55 kV per cm. The coercive field, as seen on the hysteresis loop, is not very well defined but is

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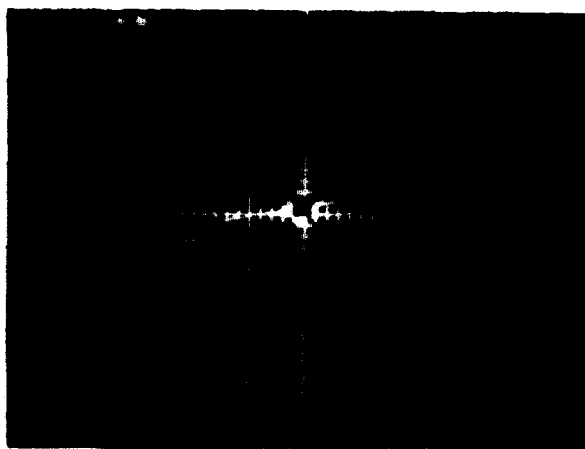


FIG. 1. Dielectric hysteresis loops obtained on a single crystal of BiFeO_3 in liquid nitrogen. The maximum field applied (largest loop) was 55 kV per cm, and the spontaneous polarization was $3.5 \mu\text{C per cm}^2$. The traces, presented for several values of applied field, were made with a device which applied the field during two complete cycles of 60 Hz voltage and also displaced the center of the loop from the center of the cathode tube. Note that one trace, with about 17 kV per cm maximum field, showed no measurable hysteresis.

about 20 kV per cm. This appears very high for a ferroelectric single crystal, but the true coercive field to reverse all of the polarization is undoubtedly substantially higher.

Accordingly, it is evident that the hysteresis loops are not saturated and represent only a partial reversal of the polarization. These data do serve to confirm, however, the evidence for ferroelectricity in BiFeO_3 as required by the space group $R3c$, found in the atomic structure study⁵ and the previous dielectric measurements³.

REFERENCES

1. ROYEN P. and SWARS K., *Angew Chem.*, 24, 779 (1957).
2. KISELEV S.V., OZEROV R.P. and ZHDANOV G.S., *Soviet Physics-Dokl.*, 7, 742 (1963).
3. SMITH R.T., ACHENBACH G.D., GERSON R. and JAMES W.J., *J. appl. Phys.*, 39, 70 (1968).
4. FEDULOV S.A., LADYZHINSKII P.B., PYATIGORSKAYA I.L. and VENEVTSEV Yu.N., *Soviet Phys.-Solid State*, 6, 375 (1964).
5. MICHEL C., MOREAU J.M., ACHENBACH G.D., GERSON R. and JAMES W.J., *Solid State Commun.*, 7, 701 (1969).
6. ABRAHAMS S.C., KURTZ S.K. and JAMIESON P.B., *Phys. Rev.*, 172, 551 (1968).

Des monocristaux de BiFeO_3 de type pérovskite ont été préparés, à l'aide d'un flux de Bi_2O_3 , avec des dimensions de plus d'un millimètre. Des cycles d'hystérèse diélectrique ont été observés avec ces cristaux. Bien que la polarisation à saturation n'a pas été atteinte, l'observation de ces cycles prouve que BiFeO_3 est ferroélectrique.