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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 1½°/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 μC per cm^2 along the <100> direction, which represents 6.1 μC per cm^2 in the <111> 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 emprirical 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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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 study[5] and the previous dielectric measurements[3].

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 μC 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.

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Des monocristeaux de $BiFeO_3$ de type pérovskite ont été prépares, à l'aide d'un flux de Bi_2O_3, avec des dimensions de plus d'un millimètre. Des cycles d'hysterèse diélectrique ont été observés avec ces cristeaux. Bien que la polarization à saturation n'a pas été atteinte, l'observation de ces cycles prouve que $BiFeO_3$ est ferroélectrique.