Ferroelectricity in the Compound $Bi_4Ti_3O_{12}$

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Some ferroelectric and crystallographical properties of the compound $Bi_4Ti_3O_{12}$ are presented. The compound has a dielectric maximum at 685°C on increasing temperature and at 670°C on decreasing temperature. At these temperatures, an endothermic peak and an exothermic peak, respectively, occur. Ferroelectricity was observed along the c axis of the single crystal of this compound.

I. INTRODUCTION

THE compound $Bi_4Ti_3O_{12}$ was discovered in 1949 by one of us (B. A.) and a mixed-layer structure was proposed.[1] Recently, Subbarao and others found that this compound is ferroelectric.[2] Similar results were found by two of us (P. H. F. and C. R. R.).[3] In this note, we would like to report two points: (1) some supplementary dielectric data, and (2) the identification of a ferroelectric axis.

II. DIELECTRIC PROPERTIES

Subbarao reported a maximum in the dielectric constant at 675°C, measured at 100 kc/sec on a ceramic specimen. We used polycrystalline specimens (crystallite size≈0.1 mm) grown from the melt and observed a temperature hysteresis: a maximum in the real, as well as in the imaginary part of the dielectric constant at 685°C on raising the temperature and at 670°C on cooling. At these two temperatures, by a differential thermal analysis method, we observed an endothermic reaction on heating and exothermic reaction on cooling. Our measurements were made at the high frequency of 40 Mc/sec in order to avoid the appreciable intrinsic conductivity at high temperatures. Our value of the maximum dielectric constant is essentially equal to that of Subbarao's except that our maximum has a much narrower width in the temperature.

We observed ferroelectric hysteresis loops with both polycrystalline ceramics and single crystals. The single crystals were plates on the order of 10^{-3} cm thick. Hence, electrodes could be applied only on the (001) face (the identification is described in Part III).

In explaining the earlier failure of Popper *et al.*[4] to detect ferroelectricity, Subbarao[1] proposed that they did not study the material at sufficiently high temperatures. However, we would like to emphasize the importance of the applied field in this special material. When a field of 25 kv/cm was applied to a ceramic specimen having a coercive field of 30 kv/cm, we observed that the remanent polarization of the minor loop decreased to about one-half of that of the saturated loop. With an applied field of 15 kv/cm, only one-fortieth of the polarization remained, and the hysteresis loop appeared almost as a straight line. The maximum applied field used by Popper *et al.* was only 15 kv/cm. In agreement with our observations, no well-defined hysteresis loop would have been seen with such a low value of the applied field.

III. POLAR AXIS

On the basis of his x-ray data from polycrystalline ceramics, Subbarao suggested that the polar axis of $Bi_4Ti_3O_{12}$ is probably the b axis.

As mentioned in Part II, we observed ferroelectricity using single crystals. All of the crystals were thin plates such that electrodes could be attached only on their major surfaces. A precession photograph was taken of one of these crystal plates with the x-ray beam projected on the specimen in a direction parallel to its major surface.

In the photograph obtained, the (001) reflections (corresponding to the 33-Å c axis) were observed along a vertical line through the center of the film. This position of the (001) reflections shows unequivocally that the c axis is perpendicular to the crystal plate or major surface of the crystal. Since this is the surface on which the electrodes were applied, the polarization that we observed was along the c axis. We cannot rule on Subbarao's suggestion that the b axis is also a polar axis, but we have established that the orthorhombic c axis of $Bi_4Ti_3O_{12}$ is a polar axis.

[1] B. Aurivillius, Arkiv Kemi **1**, 499 (1949).
[2] E. C. Subbarao, Phys. Rev. **122**, 804 (1961); L. G. Van Uitert and L. Egerton, J. Appl. Phys. **32**, 959 (1961).
[3] Our work was mentioned in Compt. rend. **252**, 683 (1961) by P. H. Fang, C. Robbins, and F. Forrat. See also an erratum of E. Subbarao, Phys. Rev. **123**, 2202 (1961).
[4] P. Popper, S. N. Ruddlesden, and T. A. Ingles, Trans. Brit. Ceram. Soc. **56**, 356 (1957).