

Ferroelectricity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and Its Solid Solutions*

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On the basis of dielectric studies on polycrystalline specimens, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been established as a ferroelectric with a Curie temperature of 675°C . The symmetry is orthorhombic with $a=5.411 \text{ \AA}$, $c=32.83 \text{ \AA}$, and $b/a=1.007$ at 25°C . A high-temperature x-ray study revealed a symmetry change to tetragonal at 675°C . The polar axis is probably the orthorhombic b axis. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a member of oxides with the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{Me}_{x-1}\text{R}_x\text{O}_{3x+1})^{2-}$. According to Aurivillius, the crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ comprises a stacking of Bi_2O_2 and perovskite-like $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ layers along the pseudotetragonal c axis. Multiple ion substitutions of $(\text{Bi}^{3+}\text{Ti}^{4+})$ in $(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ by $(\text{Me}^{2+}\text{Nb}^{5+})$ where $\text{Me}^{2+}=\text{Ba}$, Pb , or Sr lead to a steep decrease of the Curie temperature.

I. INTRODUCTION

IN a comprehensive study of bismuth compounds, Aurivillius¹ has synthesized a number of mixed bismuth oxides of the formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{Me}_{x-1}\text{R}_x\text{O}_{3x+1})^{2-}$. Here Me can be mono-, di-, or trivalent ions or a mixture of them, R represents Ti^{4+} , Nb^{5+} , Ta^{5+} , etc., and x can have values of 2, 3, 4, etc. Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, is an example of such compounds with $x=3$. The crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was determined by Aurivillius²

and is shown in Fig. 1. The symmetry is pseudotetragonal. The crystal structure may be described as a stacking of layers of (Bi_2O_2) and $(\text{Bi}_2\text{Ti}_3\text{O}_{10})$ along the pseudotetragonal c axis. In the $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ units, Ti ions are enclosed by oxygen octahedra, which are linked through corners forming O-Ti-O linear chains. Bi ions occupy the spaces in the framework of TiO_6 octahedra. Thus, $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ units possess a remarkable similarity to the perovskite-type structure. The height of the perovskite-type layer sandwiched between Bi_2O_2 layers in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is equal to six Ti-O distances or approximately to three ABO_3 perovskite units.

Matthias,³ and Smolenskii and Kozhevnikova⁴ have evolved, empirically, some crystal chemical conditions which favor the occurrence of ferroelectricity in oxides. Structures having favorable environment for ferroelectricity contain small, highly charged cations surrounded by oxygen octahedra which are linked through corners. Satisfying these conditions are the perovskite (e.g., BaTiO_3), pyrochlore (e.g., $\text{Cd}_2\text{Nb}_2\text{O}_7$), and tungsten bronze (e.g., PbNb_2O_6) type structures, in which a number of known oxide ferroelectrics crystallize.

Based on these considerations and the structural arrangement in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, this compound may be expected to exhibit ferroelectric behavior. A number of investigators have, however, examined the dielectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ but failed to detect ferroelectricity. Skanavi and Demeshina⁵ measured dielectric properties of a number of bismuth titanates with $\text{TiO}_2/\text{Bi}_2\text{O}_3$ ratios between 22.3 and 1. For the mixture ($\text{TiO}_2/\text{Bi}_2\text{O}_3=1.45$) that comes closest to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in composition, they observed a dielectric constant of 107 at 20°C and a marked positive temperature coefficient of dielectric constant in the interval 20° to 80°C . Similar results have also been obtained by Popper and co-workers⁶ for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics up to 125°C . More

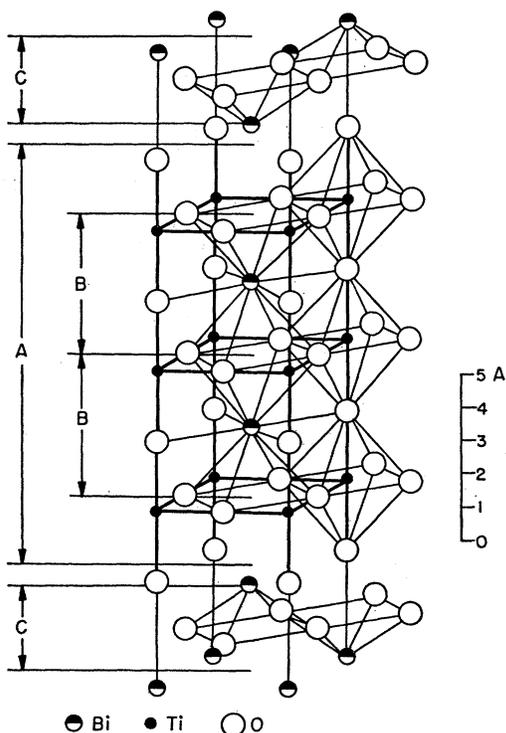


FIG. 1. One half of the pseudotetragonal unit cell of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (from $z \approx 0.25$ to $z \approx 0.75$). A denotes the perovskite layer $\text{Bi}_2\text{Ti}_3\text{O}_{10}^{2-}$, C $\text{Bi}_2\text{O}_2^{2+}$ layers, and B unit cells of hypothetical perovskite structure BiTiO_3 (after Aurivillius²).

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¹ B. Aurivillius, Arkiv Kemi **1**, 463, 499 (1949); **2**, 519 (1950).

² B. Aurivillius, Arkiv Kemi **1**, 499 (1949).

³ B. T. Matthias, Science **113**, 591 (1951).

⁴ G. A. Smolenskii and N. V. Kozhevnikova, Doklady Akad. Nauk S.S.S.R. **76**, 519 (1951).

⁵ G. I. Skanavi and A. I. Demeshina, J. Exptl. Theoret. Phys. (U.S.S.R.) **31**, 565 (1956) [translation: Soviet Phys.-JETP **4**, 524 (1957)].

⁶ P. Popper, S. N. Ruddlesden, and T. A. Ingles, Trans. Brit. Ceram. Soc. **56**, 356 (1957).

recently, Smolenskii *et al.*⁷ have indicated that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is not in all probability a ferroelectric. It is, however, significant that a number of mixed bismuth oxides with layer-type structure have recently been reported to be ferroelectric: $\text{PbBi}_2\text{Nb}_2\text{O}_9$,⁷ $\text{PbBi}_2\text{Ta}_2\text{O}_9$, $\text{BaBi}_3\text{Ti}_2\text{NbO}_{12}$, $\text{PbBi}_3\text{Ti}_2\text{NbO}_{12}$, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, and $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$.⁸

The present investigation is concerned with $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, which has the general formula $(\text{Bi}_2\text{O}_2)^{2+} \times (\text{Me}_{x-1}\text{R}_x\text{O}_{3x+1})^{2-}$ with $x=3$. An x-ray, dilatometric, and dielectric study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has been carried out through the phase change at 675°C. The investigation was extended to the influence of multiple ion substitution in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ on its ferroelectric behavior. Results of studies of layer-type compounds with $x=2$ and $x=4$ will be published separately.

II. SAMPLE PREPARATION

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and solid solutions based on this compound were prepared by solid state reaction of the constituent oxides or carbonates between 1000° and 1200°C. Bismuth oxide (Bi_2O_3) of specpure grade was supplied by Johnson, Matthey, and Company. Titanium dioxide (TiO_2) of high purity (largest impurity Ca, approximately 200 ppm) was obtained from National Lead Company. The other chemicals were of reagent grade. Firing was accomplished in covered platinum crucibles in gobar furnaces in air. A two-step firing procedure was used with the precalcination at about 100°C below the final firing temperature. The weight losses due to heat treatment were less than 0.5% in all cases. The density of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic disks used for dielectric measurements was 6.4 g cm^{-3} , or about 80% of theoretical.

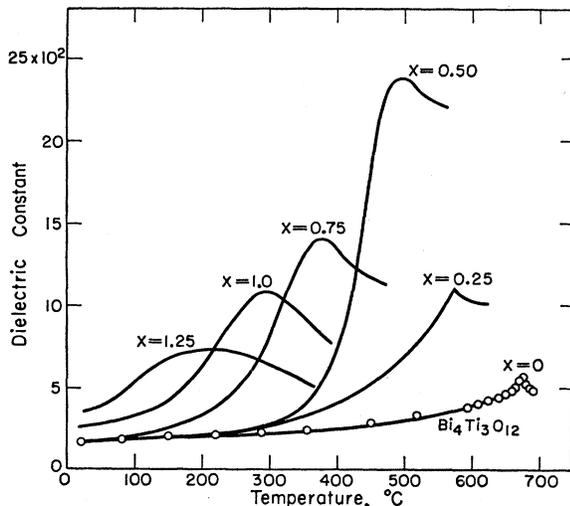


FIG. 2. Dielectric constant vs temperature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and of $\text{Bi}_{4-x}\text{Pb}_x\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ ($x=0$ to 1.25).

⁷ G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, *Fiz. Tverdogo Tela* **1**, 169 (1959) [translation: *Soviet Phys.-Solid State* **1**, 149 (1959)].

⁸ E. C. Subbarao, *J. Chem. Phys.* **34**, 695 (1961).

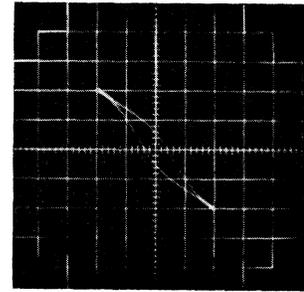


FIG. 3. Hysteresis loop of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic at 225°C (60 cps). $E_{\text{max}}=30 \text{ kv/cm}$; $P_{\text{max}}=6 \mu\text{coul/cm}^2$.

III. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

(a) Dielectric Study

The dielectric constant of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, measured on silvered ceramic disks at a frequency of 100 kc/sec and a measuring field of 10 v/cm, was approximately 180 at 25°C. This value increased with increasing temperature, reaching a peak value of about 570 at 675°C (Fig. 2). Beyond 675°C, the dielectric constant decreased according to the Curie-Weiss law. Using a standard Sawyer-Tower circuit, hysteresis loops were observed between 100° and 250°C, the maximum temperature employed. The loop shown in Fig. 3 was obtained with an applied electric field of 30 kv/cm at a frequency of 60 cps and at 225°C. The maximum polarization was approximately $6 \mu\text{coul/cm}^2$ and the estimated spontaneous polarization was about half that value. The dielectric constant peak and the existence of a hysteresis loop establish $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as a ferroelectric with a Curie temperature at 675°C. This appears to be the highest ferroelectric Curie temperature known. The earlier investigators^{5,6} did not detect ferroelectricity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ perhaps because their measurements were not extended to high enough temperature, presumably due to increased electrical conductivity.

Ceramic specimens of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, "poled" with a dc field of 40 kv/cm at 225°C, were tested for piezoelectric response under static loading. A value of about 20×10^{-12} coul/newton was obtained for the piezoelectric constant, d_{33} .

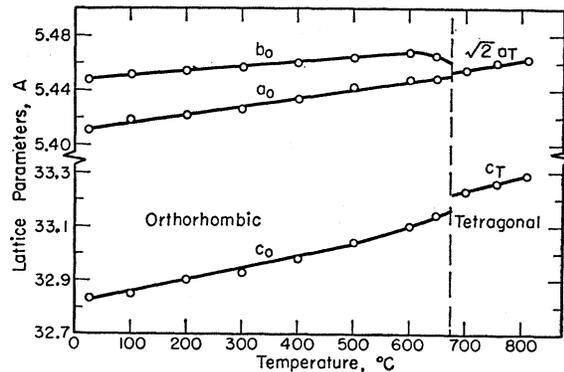


FIG. 4. Lattice parameters of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

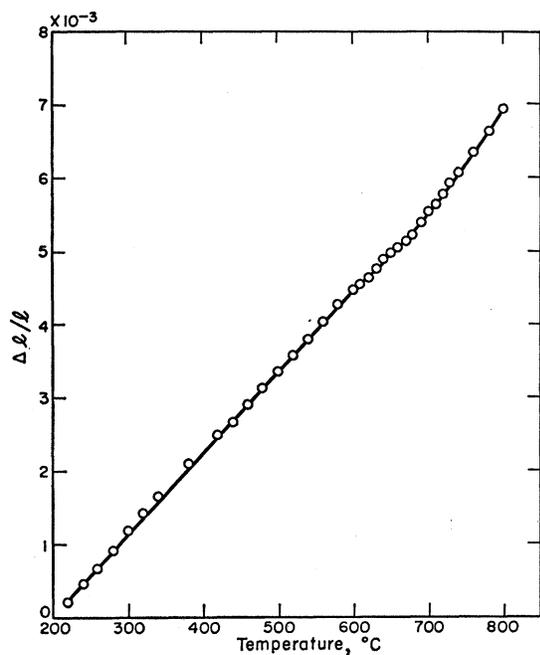


FIG. 5. Linear thermal expansion of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic.

(b) X-Ray Study

Using single crystals, Aurivillius² has established that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has orthorhombic symmetry with $a=5.410$, $b=5.448$, and $c=32.84$ Å at room temperature. The lattice parameters obtained in this study, viz., $a=5.411$, $b=5.448$, and $c=32.83$ Å, are in good agreement with those of Aurivillius. The orthorhombic distortion, b/a , of 1.007 may be compared with the value of 1.016 for orthorhombic PbNb_2O_6 , which is ferroelectric with a Curie temperature at 570°C .

The temperature dependence of lattice parameters of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was determined from diffractometer tracings, using a furnace previously employed for a study of PbNb_2O_6 .⁹ $\text{Cu } K_\alpha$ radiation was used. The c parameter was computed from the $(00l)$ reflections with $l=12, 14, 16$, and 18 . The a and b parameters were obtained from (208) , (028) and $(2, 0, 14)$, $(0, 2, 14)$ pairs of reflections. On heating $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, the lattice parameters expand at essentially a linear rate until the phase change at 675°C . The a parameter expands at a faster rate than b , so that the orthorhombic distortion (b/a) decreases with increasing temperature. At 675°C , a and c parameters undergo a sudden expansion and b contracts (Fig. 4). These data are similar to those of PbNb_2O_6 .⁹ Above the phase transition, the orthorhombic distortion disappears, and the symmetry seems to be tetragonal. It may be noted that the tetragonal a of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is 3.86 Å, approximately the same as the lattice constants of perovskite-type compounds.

⁹ E. C. Subbarao, J. Am. Ceram. Soc. 43, 439 (1960).

(c) Dilatometric Study

Linear thermal expansion of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic, measured with a dilatometer having an optical level magnification of about 1800, is depicted in Fig. 5. These data are in substantial agreement with the expansion computed from the lattice parameters of Fig. 4. The coefficient of linear thermal expansion is $11 \times 10^{-6}/^\circ\text{C}$ below 675°C and $14 \times 10^{-6}/^\circ\text{C}$ above this temperature.

IV. SOLID SOLUTIONS BASED ON $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Ionic substitutions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, which has the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{Me}_{x-1}\text{R}_x\text{O}_{3x+1})^{2-}$, were restricted to the perovskite-type units $(\text{Me}_{x-1}\text{R}_x\text{O}_{3x+1})$. Replacement of Bi^{3+} in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by La^{3+} has previously been attempted by Popper *et al.*⁶ Their data seem to indicate that $\text{Bi}_2\text{La}_2\text{Ti}_3\text{O}_{12}$ is a single-phase composition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -type structure, suggesting that Bi^{3+} present in the perovskite-type units may be replaced by suitable trivalent ions whereas the Bi^{3+} ions in the (Bi_2O_2) layers may not be replaced. However, substitution of Bi^{3+} (0.93 Å)¹⁰ by Dy^{3+} (0.92 Å) or partial replacement of Ti^{4+} (0.68 Å) by Zr^{4+} (0.79 Å) did not yield a single phase at temperature used for heat treatment in the present study (1200°C).

Multiple-ion substitutions, e.g., of $(\text{Bi}^{3+}\text{Ti}^{4+})$ by a combination of divalent metal ion and a pentavalent ion such as BaNb , PbNb , SrNb , PbTa , etc., were feasible to an extent dependent primarily on the relative ionic sizes. Thus, as the size of the divalent metal ions in the above series decreases from Ba (1.34 Å) to Sr (1.12 Å), the number of Bi^{3+} ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ replaced increases from 0.75 to 1.50, respectively. These observations are consistent with the well-known critical

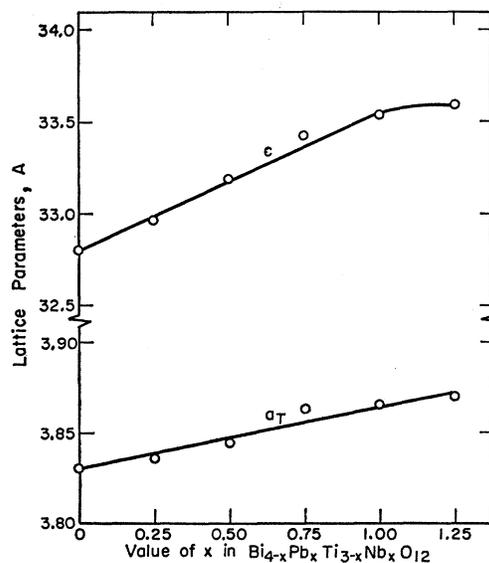


FIG. 6. Lattice parameters of $\text{Bi}_{4-x}\text{Pb}_x\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ ($x=0$ to 1.25).

¹⁰ All the ionic radii quoted are from L. H. Ahrens, Geochim. et Cosmochim. Acta 2, 155 (1952).

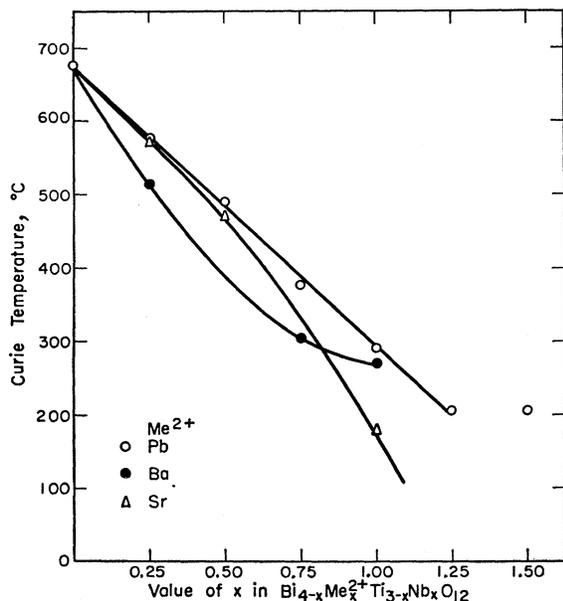


Fig. 7. Curie Temperatures of $\text{Bi}_{4-x}\text{Me}_x^{2+}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ ($\text{Me} = \text{Ba}, \text{Pb}, \text{Sr}$).

geometrical requirements for the stability of the perovskite structure.

Lattice parameter data for the solid-solution system $\text{Bi}_{4-x}\text{Pb}_x\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ with x between 0 and 1.25 are shown in Fig. 6. The pseudotetragonal a was used here instead of the orthorhombic a and b parameters, since the b/a ratio is small, it was not possible to measure these two parameters accurately in the solid solutions.

The temperature dependence of the dielectric constant of $\text{Bi}_{4-x}\text{Pb}_x\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ compositions is illustrated in Fig. 2 along with the data for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The dielectric behavior of systems in which Ba^{2+} or Sr^{2+} are introduced in place of Pb^{2+} , or Ta^{5+} for Nb^{5+} are similar. Curie temperatures, corresponding to the dielectric constant peak, of the investigated solid solutions are summarized in Fig. 7. The multiple-ion substitutions lead to a steep decrease in the Curie temperature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

In the light of data presented here, two compounds reported earlier,⁸ viz., $\text{PbBi}_3\text{Ti}_2\text{NbO}_{12}$ and $\text{BaBi}_3\text{Ti}_2\text{NbO}_{12}$, may be considered as solid solutions rather than as ordered phases.

V. DISCUSSION

It has been shown that ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is orthorhombic and that it becomes tetragonal above the phase transition at 675°C. Analogous to the perovskite-type ferroelectrics, the orthorhombic modification may be considered to be derived from the tetragonal form by a $[110]$ -type deformation, or the elongation of a face diagonal perpendicular to the c axis.

Inasmuch as single crystals are not available at present, the ferroelectric axis in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ cannot be determined by dielectric tests. However, on comparison of the lattice parameter data (Fig. 4) with those of perovskite-type ferroelectrics, it is suggested that the orthorhombic b is probably the polar axis in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. On cooling a crystal through the Curie temperature, the appearance of spontaneous strain associated with the spontaneous polarization causes an expansion along the polar axis and a consequent contraction along the other two axes.

A large number of oxide ferroelectrics crystallize with the perovskite structure (e.g., BaTiO_3 , PbTiO_3 , KNbO_3). It is noteworthy that perovskite-type arrangement forms an integral part of the structure of ferroelectrics with tungsten bronze type structure (e.g., PbNb_2O_6 and PbTa_2O_6) as well as those with layer-type structure (e.g., $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{PbBi}_2\text{Nb}_2\text{O}_9$, $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, etc.).

Structurally related to the mixed bismuth oxides with layer-type structure are a series of strontium titanates. A layer-type structure derived by a stacking of layers of NaCl-type SrO and perovskite-type SrTiO_3 along the tetragonal c axis has been proposed for Sr_2TiO_4 ,¹¹ $\text{Sr}_3\text{Ti}_2\text{O}_7$, and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$.¹² Kwestroo and Paping¹³ have reported that Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$ have dielectric constants of 38 and 50, respectively, at room temperature and show a strong negative temperature coefficient of the dielectric constant. A low-temperature study of these compounds seems worthwhile.

ACKNOWLEDGMENTS

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¹¹ S. N. Ruddlesden and P. Popper, *Acta Cryst.* **10**, 538 (1957).

¹² S. N. Ruddlesden and P. Popper, *Acta Cryst.* **11**, 54 (1958).

¹³ W. Kwestroo and H. A. M. Paping, *J. Am. Ceram. Soc.* **42**, 292 (1959).

FIG. 3. Hysteresis loop of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic at 225°C (60 cps). $E_{\text{max}}=30$ kv/cm; $P_{\text{max}}=6 \mu\text{coul}/\text{cm}^2$.

