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# Electro-mechanical behaviour of single domain single crystals of bismuth titanate ($Bi_4Ti_3O_{12}$)

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The piezoelectric constants $d_{11}$, $d_{22}$ and $d_{33}$ for a single domain single crystal of $Bi_4Ti_3O_{12}$ have been measured at room temperature using appropriate crystal cuts on a Berlincourt $d_{33}$ meter. From the known temperature dependence of the spontaneous polarization, lattice strain and dielectric permittivity, the equivalent piezoelectric constants have been calculated assuming a simple proper ferroelectric in which, $P_s$, is the order parameter. Constants in the plane of the perovskite-like sheets in the $Bi_4Ti_3O_{12}$ structure ($d_{11}$, $d_{22}$) show good agreement with experimental values. The calculated value of the constant $d_{33}$ is more than an order of magnitude larger than the experimentally-measured value and gives clear indication of the "indirect" coupling to the strain in the tetrad axial direction and the need for a more sophisticated phenomenology.

## 1. Introduction

Bismuth titanate, $Bi_4Ti_3O_{12}$, is probably the most thoroughly investigated member of the very large family of mixed bismuth oxide layer structure ferroelectrics. In spite of this, however, there are no data upon the piezoelectric behaviour of this crystal in the most recent publication by Landholt-Börnstein [1] and we can find no data in the literature. The advent of processing techniques to develop grain-oriented ferroelectric ceramics [1–4] has renewed interest in the layer structure family materials as potential high-temperature piezoceramics and good single-crystal data upon the $d_{ij}$ coefficients is urgently needed. In this study the Berlincourt $d_{33}$ meter* was used to measure the piezoelectric $d_{11}$-, $d_{22}$- and $d_{33}$-coefficients of regular rectangular samples cut from large single-domain $Bi_4Ti_3O_{12}$ crystals. These measured values were then compared to values derived by fitting a simple Landau phenomenology [5] to the available polarization, strain and dielectric data so as to derive values for the electrostriction constants of the prototypic paraelectric phase, and from these constants and the known permittivity to derive appropriate $d$-coefficients.

## 2. Piezoelectric measurements

A large suite of bismuth titanate single-crystals which had been grown for electro-optic domain switching studies were kindly made available for this work by Cummins†. These crystals which are in the form of flat plates with major surfaces normal to the tetragonal $c$-axis of the prototype phase had been subjected to thermal annealing in a weak temperature gradient to eliminate 90°-type

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*Berlincourt CPDI 3300 $d_{33}$ meter from Cheannel Products, 16722 Park Circle Drive, Chagrin Falls, OH 44022, USA.
†The $Bi_4Ti_3O_{12}$ crystals kindly supplied by S. E. Cummins included batches grown at Wright Patterson Airforce Base by Cummins and Luke and crystals grown under Airforce contract as Sperry Rand by C. S. Sahagian.

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twins. Large area sections had then been pulse-poled to single-domain state using surface electrodes [6]. Rectangular sections with surfaces normal to the pseudo-orthorhombic axes of the ferroelectric single domain were string sawn from these sections, and hand polished. The major difficulty in this finishing operation is the small single-domain crystal thickness (~ 200 μm) which makes handling both delicate and tedious.

After preparation and cleaning, samples were checked using the tilted extinction method [7] to ascertain that they were single domain.

Piezoelectric measurements of the three axial $d$-coefficients were made on the Berlincourt $d_{33}$ meter using point contacting electrodes. To check the efficacy of the point-contact method, the $d_{33}$ values were checked using larger area contacts, but no measurable difference could be discerned.

From the Berlincourt meter the following values were obtained:

$$d_{11} = 39 \pm 1 \times 10^{-12}\ \mathrm{CN}^{-1};$$

$$d_{22} = 0;$$

$$d_{33} = 9 \pm 1 \times 10^{-12}\ \mathrm{CN}^{-1}.$$

In principle, the $d_{33}$ meter could be used to measure other components of the $d$-tensor in the single domain; however, the practical limitations imposed by the crystal geometry restricted reliable measurements to just the components above.

## 3. Calculation of the piezoelectric constants

If it is assumed that bismuth titanate is a simple proper ferroelectric derived from the prototype point group 4/mmm, it has been shown by Pohanka and Cross [8] that the elastic Gibbs, $\Delta \mathbf{G}_1$, function takes the form

$$\begin{aligned}\Delta \mathbf{G}_1 = {} & \alpha_1^{\mathrm{X}}(P_1^2+P_2^2) + \alpha_3^{\mathrm{X}}P_3^2 + \alpha_{11}^{\mathrm{X}}(P_1^4+P_2^4) \\ & + \alpha_{33}^{\mathrm{X}}P_3^4 + \alpha_{13}^{\mathrm{X}}(P_1^2P_3^2+P_2^2P_3^2) + \alpha_{12}^{\mathrm{X}}P_1^2P_2^2 \\ & + \alpha_{111}^{\mathrm{X}}(P_1^6+P_2^6) + \alpha_{333}^{\mathrm{X}}P_3, \qquad (1)\end{aligned}$$

where $P_1 \ldots P_3$ are the components of the piezoelectric constant, $P$, along the orthogonal tetragonal axes and $\alpha_i$ are related to the dielectric stiffness and higher order stiffnesses for finite elastic stress, $X$.

Since 4/mmm is a centric group, the lowest order elasto-electric coupling which is allowed is electrostrictive. Thus, to describe the crystal at finite elastic stress, $X$, the following additional terms must be added:

$$\begin{aligned}\Delta \mathbf{G}_1 = {} & (\Delta G_1)_P - \tfrac{1}{2}S_{11}^P(X_1^2+X_2^2) - \tfrac{1}{2}S_{12}^P X_1X_2 \\ & - S_{13}^P(X_1+X_2)X_3 - \tfrac{1}{2}S_{33}^P X_3^2 \\ & - \tfrac{1}{2}S_{44}^P(X_4^2+X_5^2) - \tfrac{1}{2}S_{66}^P X_6^2 \\ & + Q_{11}(P_1^2X_1+P_2^2X_2) + Q_{12}(P_1^2X_2+P_2^2X_1) \\ & + Q_{13}(P_1^2X_3+P_2^2X_3) + Q_{31}(P_3^2X_1+P_2^2X_1) \\ & + Q_{33}P_3^2X_3 + Q_{44}(P_2P_3X_4+P_1P_3X_5) \\ & + Q_{66}P_1P_2X_6 \\ & + Q_{144}(P_1^2P_2P_3X_4+P_2^2P_1P_3X_5) \\ & + Q_{366}P_3^2P_1P_2X_6, \qquad (2)\end{aligned}$$

where $X_1$ to $X_6$ are the components of elastic stress, $S_{11}$ to $S_{66}$ are the conventional elastic compliances measured at constant polarization and $Q_{11}$ to $Q_{66}$ are the electrostriction constants in polarization notation.

The spontaneous polarizations are derived from

$$\left(\frac{\partial \Delta \mathbf{G}_1}{\partial P_i}\right)_{T,X=0} = E_i = 0; \qquad (3)$$

the spontaneous elastic strains are derived from

$$\left(\frac{\partial \Delta \mathbf{G}_1}{\partial X_i}\right)_{TP} = -x_i. \qquad (4)$$

Cummins and Cross [9] have shown that only the stable ferroelectric phase in $\mathrm{Bi_4Ti_3O_{12}}$ has monoclinic symmetry and corresponds to solutions of Equation 3 in which

$$P_{1(\mathrm{S})} = P_{2(\mathrm{S})} \neq 0 \qquad (5)$$

and

$$P_{3(\mathrm{S})} \neq 0. \qquad (6)$$

Relations for the polarizations and dielectric permittivities in the single-domain state have been derived in [8].

From Equations 4 with $X_i = 0$ the spontaneous strains take the form

$$-x_1 = Q_{11}P_1^2 + Q_{12}P_2^2 + Q_{31}P_3^2, \qquad (7)$$

$$-x_2 = Q_{11}P_1^2 + Q_{12}P_2^2 + Q_{31}P_3^2, \qquad (8)$$

$$-x_3 = Q_{13}(P_1^2 + P_i^2) + Q_{33}P_3^2, \qquad (9)$$

$$-x_4 = Q_{44}P_2P_3 + Q_{144}P_1^2P_2P_3, \qquad (10)$$

$$-x_5 = Q_{44}P_1P_3 + Q_{144}P_2^2P_1P_3 \qquad (11)$$

and

$$-x_6 = Q_{66}P_1P_2 + Q_{366}P_3^2P_1P_2. \qquad (12)$$

The piezoelectric polarization coefficients, $b_{ijk}$, are given by the partial derivatives

$$\frac{\partial \chi_i}{\partial P_j} = \frac{\partial^2 \Delta G}{\partial X_i \partial P_j}, \tag{13}$$

which for the stable monoclinic ferroelectric phase may be written

$$\frac{\partial X_1}{\partial P_1} = b_{11} = b_{22} = 2Q_{11}P_1, \tag{14}$$

$$\frac{\partial X_1}{\partial P_2} = b_{21} = b_{12} = 2Q_{12}P_1, \tag{15}$$

$$\frac{\partial X_1}{\partial P_3} = b_{31} = b_{32} = -2Q_{31}P_3, \tag{16}$$

$$\frac{\partial X_3}{\partial P_1} = b_{13} = b_{23} = -2Q_{13}P_3, \tag{17}$$

$$\frac{\partial X_3}{\partial P_3} = b_{33} = -2Q_{33}P_3, \tag{18}$$

$$\frac{\partial X_4}{\partial P_2} = b_{24} = b_{15} = -Q_{44}P_3 - Q_{144}P_1^2P_3, \tag{19}$$

$$\frac{\partial X_4}{\partial P_3} = b_{34} = b_{35} = -Q_{144}P_1 - Q_{144}P_1^3, \tag{20}$$

$$\frac{\partial X_5}{\partial P_2} = b_{25} = b_{14} = -2Q_{144}P_1^2P_3, \tag{21}$$

$$\frac{\partial X_6}{\partial P_1} = b_{16} = b_{26} = -Q_{66}P_2 - Q_{366}P_3^2P_1 \tag{22}$$

and

$$\frac{\partial X_6}{\partial P_3} = b_{36} = -2Q_{366}P_3P_1^2. \tag{23}$$

Obviously, the $b$-coefficients derived in this manner may be converted to the more familiar $d$-coefficients by the relations of the form

$$d_{ij} = \epsilon_{ik}b_{kj}, \tag{24}$$

where $\epsilon_{ik}$ are the appropriate dielectric permittivities. It may be noted that two higher-order striction coefficients $Q_{144}$ and $Q_{366}$, have been included: these coefficients were inserted as, without them, the piezoelectric matrix for the monoclinic phase does not contain the required non-zero terms dictated by symmetry, i.e., $b_{36}$, $b_{25}$ and $b_{14}$ would become zero.

For the required $Q$-coefficients, the X-ray data from Subbarao [10] was used together with the monoclinic strain measurements of Cummins and Luke [11] to derive the components of the spontaneous strain in the ferroelectric phase. These strains were then used in Equations 7 to 12 with the polarizations calculated by Pohanka and Cross [8] to derive the $Q$-coefficients.

In making this derivation it was assumed that the $Q_{ij}$ are independent of temperature so that Equations 7 to 12 could be applied at a sequence of temperatures throughout the ferroelectric range. Since the number of equations then over determines the constant, a least-squares fitting was used to derive "best" values for the $Q$. From these calculated $Q$-values, Equations 14 to 23 were used with room-temperature (25° C) values of $P_S$ [$P_{1(S)}$ and $P_{3(S)}$] to calculate the $b$-constants at 25° C. These $b$-constants were then combined with the dielectric data from Fouskova and Cross [12], using Equation 13, to determine values of the $d$-constants at room temperature.

After rotating the $d$-matrix to correspond to the monoclinic symmetry with the mirror plane containing the 3, 1 axes, the values obtained were

$$d_{ij} = \begin{vmatrix} 44 & 18 & -48 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0.8 & 0 & {}_{\mathrm{m}}d_{26} \\ -75 & -76 & 269 & 0 & 12 & 0 \end{vmatrix}$$

where $d_{ij}$ is in units of $10^{-12}\,\mathrm{CN}^{-1}$ and where ${}_{\mathrm{m}}d_{26} = [2({}_{\mathrm{t}}d_{11} - {}_{\mathrm{t}}d_{12})]^{1/2}$ and the prefixes m and t refer to the monoclinic and tetragonal axes.

With the simple phenomenological theory it is not possible to derive ${}_{\mathrm{t}}d_{11}$ and ${}_{\mathrm{t}}d_{12}$ separately but only the sum ${}_{\mathrm{t}}d_{11} + {}_{\mathrm{t}}d_{12} = 43 \times 10^{-12}\,\mathrm{CN}^{-1}$.

The fitting process by which the values above are derived is quite complex, and utilize data from many different investigators. Much of this experimental data has been presented with no clear measure of error, so that it is very difficult to assess a level of confidence for the values derived above. If it is arbitrarily assumed that the X-ray lattice parameters are reliable to $\pm 5 \times 10^{-4}$ nm (relative), which is not unreasonable for good X-ray powder work, the assessed spontaneous strain may be in error by ± 20%. Taking the errors in the permittivity to be ± 2% and in the polarization to be ± 10%, the calculated $d$-values are estimated as

$$d_{11} = (44 \pm 12) \times 10^{-12}\,\mathrm{CN}^{-1},$$

$$d_{22} = 0$$

and

$$d_{33} = (269 \pm 100) \times 10^{-12}\,\mathrm{CN}^{-1}.$$

## 4. Discussion

The surprisingly close agreement between the measured and calculated $d_{11}$ values for $Bi_4Ti_3O_{12}$ suggest that the major part of the lattice distortion in the plane of the perovskite sheets of this layer structure material is simple electrostriction originating from the spontaneous polarization in the plane of sheet which occurs at $T_c$. The absence of any measurable $d_{22}$-value is clearly in agreement with the symmetry requirements of the monoclinic single domain, and further confirms that the samples were completely free from 90° twins. Experimental and theoretical values of $d_{33}$, however, are in very marked disagreement and appear to be well outside the range of possible error. Thus, it appears unlikely that the spontaneous strains outside the perovskite sheets can be attributed to the very small tilting of $P_S$ out of the $a$–$b$ plane. That the transition at $T_c$ was more complex is also evidenced by the X-ray measurements of Newnham and Dorrian [13] which show an obvious doubling of the unit cell in the ferroelectric phase.

The fact that the in-plane properties behave in a manner to similar to a simple proper ferroelectric, whilst the "$c$"-axis behaviour would certainly suggest a second-order parameter, aside from the polarization, does lend additional support to the concept of a triggered phase change, as has been suggested by Holakovsky [14].

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