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Electrical anisotropy in single crystals of Bi-layer structured ferroelectrics

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Abstract

Single crystals of $PbBi_2Nb_2O_9$ (PBN), $PbBi_4Ti_4O_{15}$ (PBT) and $Pb_2Bi_4Ti_5O_{18}$ (P_2BT), belonging to the bismuth layer-structured ferroelectric compound, were grown and dielectric, conducting and ferroelectic properties were evaluated separately in directions of *a*(*b*)-axis and *c*-axis. The relationship between crystal structure (the number of oxygen octahedra in the perovskite block *m*) and electrical properties was discussed comprehensively. The dielectric permittivity at T_c in the *a*(*b*)-axis direction was more than 20 times larger than for the *c*-axis direction. The anisotropy depended on *m* and was larger in the compound with even-number *m* than that with odd-number *m*. The DC conductivity increased with increasing *m* in both *a*(*b*)-axis and *c*-axis directions. The spontaneous polarization in the *c*-axis direction was not recognized for PBN and PBT with even-number *m* but observed for P_2BT with odd-number *m*, although the value of remanent polarization was much smaller than for the *a*(*b*)-axis direction. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Anisotropy; Layer structure; Ferroelectrics; Single crystal

1. Introduction

Since the discovery of bismuth layer-structured ferroelectrics (BLSF) by Aurivillius in 1949 [1,2], more than sixty bismuth layer-structured compounds have been reported up to date and most of them have been recognized as ferroelectrics. Generally, the BLSF has the following properties; relatively low dielectric permittivity, low dielectric loss, high Curie temperature and anisotropy of electrical properties.

The BLSF has the general formula $(Bi_2O_2)^{2+}(M_{m-1}R_mO_{3m+1})^{2-}$, where *M* represents mono- to trivalent ions as Na, Ca, Ba, Sr, Pb, Bi etc., R represents tri- to hexavalent ions as Ti, Nb, Ta, W etc. and *m* is 1–5 [3,4]. The crystal structure is composed of pseudo-perovskite blocks $(M_{m-1}R_mO_{3m+1})^{2-}$ interleaved with bismuth oxide layers $(Bi_2O_2)^{2+}$ along the pseudo-tetragonal *c*-axis. The *m* means the number of oxygen octahedra of R in the perovskite block. $PbBi_2Nb_2O_9$ (PBN), $PbBi_4Ti_4O_{15}$ (PBT) and $Pb_2Bi_4Ti_5O_{18}$ (P_2BT) correspond to the compound with $m=2$, 4 and 5, and have a block with one, three and four ($=m-1$) perovskite units between two nearest $(Bi_2O_2)^{2+}$ layers [5]. Fig. 1 shows the crystal structure of the BLSF with $m=4$.

The BLSF has peculiar anisotropy in electrical and optical properties between *a*(*b*)-axis and *c*-axis directions due to the layered structure. Ferroelecticity in the BLSF arises from the oxygen octahedra in the perovskite block and the spontaneous polarization takes place mainly in the direction parallel to the two dimensional bismuth layer [the *a*(*b*)-axis direction] [4–9]. Many researches have been conducted on their anisotropic properties in grain-oriented polycrystalline, bulk and thin films [10–12]. Recently, $SrBi_2Ta_2O_9$ thin films were applied to ferroelectric random access memory (FRAM) with high fatigue endurance [12]. Research on the electrical anisotropies of single crystals is, therefore, important to apply the BLSF to various ferroelectric devices. However, there is few report on electrical properties of single crystals because of the difficulty in obtaining single crystals except for small thin plate-like shaped crystals [13–18].

In the present paper, the anisotropy of electrical properties in as-grown single crystals of PBN, PBT and

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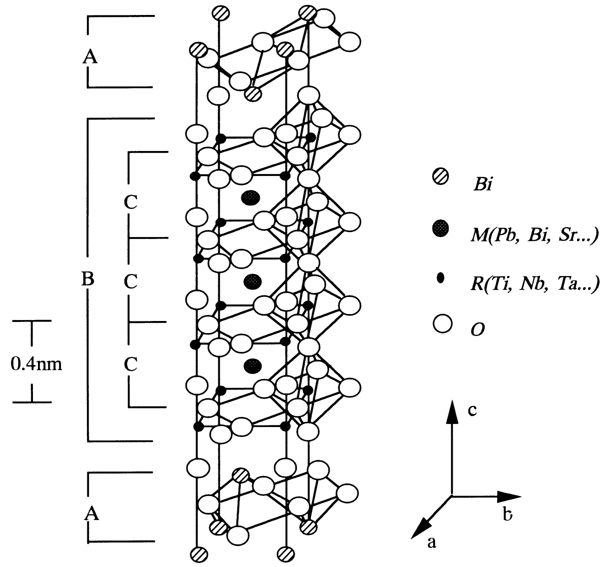

Fig. 1. Schematic drawing showing the crystal structure of bismuth layer-structured ferroelectric compound ($m = 4$). One half of the pseudo-tetragonal unit cell. A denotes the bismuth layers $(Bi_2O_2)^{2+}$, B denotes the perovskite layer $(M_3R_4O_{13})^{2-}$, and C a unit cell of the hypothetical perovskite structure (MRO_3).

P_2BT was studied. Electrical properties were evaluated by dielectric properties (dielectric permittivity, Curie–Weiss constant etc.), DC conductivity and ferroelectricity (remanent polarization, coercive field). Especially, the relationship between crystal structure (number of oxygen octahedra in the perovskite block) and electrical properties was discussed comprehensively.

2. Experimental

2.1. Crystal growth

The PBN, PBT and P_2BT single crystals were grown by the vertical gradient freeze method. As starting materials, reagent-grade (purity >99.99%) PbO, Bi_2O_3, TiO_2, Nb_2O_5 were mixed homogeneously. The mixed powders were then put into a double platinum crucible in order to minimize the evaporation of Pb and Bi components, and set in a vertical tube furnace with two thermocouples at the top and the bottom of the crucible. The platinum crucible was heated to 1230–1260°C at a rate of 5°C/min, kept for 4 h, because PBN, PBT and P_2BT have a congruent melting point at 1200, 1195 and 1190°C, respectively [13]. The entire zone was slowly cooled down to 1000°C at a rate of 3.5–4°C/h. The temperature at the top of the crucible was kept lower than that at the bottom providing a vertical temperature gradient of 1–2°C/mm in order to prevent spontaneous nucleation and natural convection flow to occur. The obtained single crystals were cut and polished to plates several millimetres square and 0.5∼1 mm thickness, and then electroded with Pt by sputtering for measurements of electrical properties.

2.2. Measurements

A Laue camera, a polarizing microscope and an X-ray diffractometer (CuK_α radiation) were used for characterizations of single crystals. For some sample, the atomic ratio was confirmed by ICP spectrometry. The dielectric properties were measured at room temperature to 700°C in the frequency range of 1 kHz to 1 MHz, using an LCR meter (Model 4284A, HP, Japan). The DC conductivity was measured at 200–500°C by 2-probe method, using a PA meter/DC voltage source (Model 4140B, HP, Japan) with an applied voltage of 1.0–2.0 V. The ferroelectric properties were evaluated by D–E hysteresis loops measured with RT6000HVS (Radiant Technologies, Inc.) in a silicon oil bath at 150–200°C.

3. Results and discussion

3.1. Characterization

The crystals were grown on the melt surface in the form of yellowish and transparent platelet aggregates with a layered habit. The large faces of the crystals were found to be parallel to the crystallographic plane (001), because the crystal growth is extremely slow in the direction perpendicular to the bismuth layer (the crystallographic *c*-axis) than for the direction parallel to bismuth layer (the crystallographic *a*(*b*)-axis). The crystals have a strong *c*-plane cleavage as bismuth layered high T_c superconductors [19,20].

It was confirmed that the crystals have four-fold symmetry axis based on single spots separated by 90° in back-reflection Laue patterns on (001) plane. Powder XRD analysis on crushed single crystals showed only peaks of single phases of PBN, PBT and P_2BT, respectively. The as-grown single crystals had a number of domains due to the phase transition below the Curie temperature as many ferroelectric crystals. The crystallographic *a*-axis could not be distinguished from the *b*-axis. The results of ICP spectrometry indicated that the single crystals have almost stoichiometric composition, such as 2.00: 4.00: 5.01 for P_2BT.

3.2. Dielectric properties

Figs. 2 and 3 show the temperature dependences of the dielectric permittivity along the *a*(*b*)-axis and the *c*-axis directions for PBN, PBT and P_2BT single crystals at frequency of 1 MHz, respectively. The temperatures showing the maximum of the dielectric permittivity are 561, 580 and 340°C for PBN, PBT and P_2BT, respectively in both *a*(*b*)-axis and *c*-axis directions. Those are

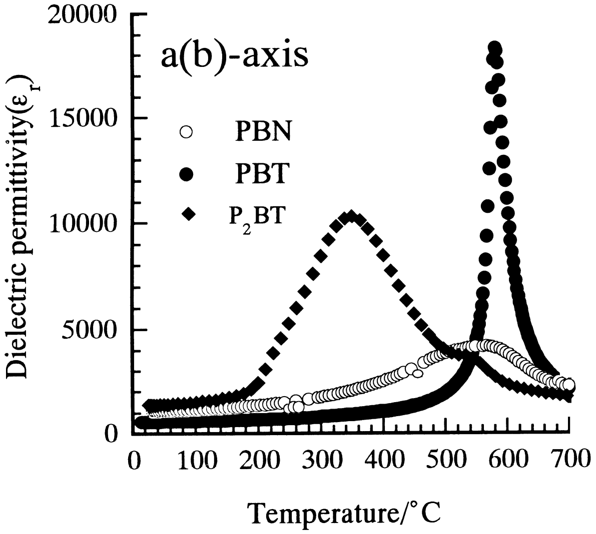

Fig. 2. Temperature dependences of dielectric permittivity for PBN, PBT and P_2BT in the *a*(*b*)-axis direction.

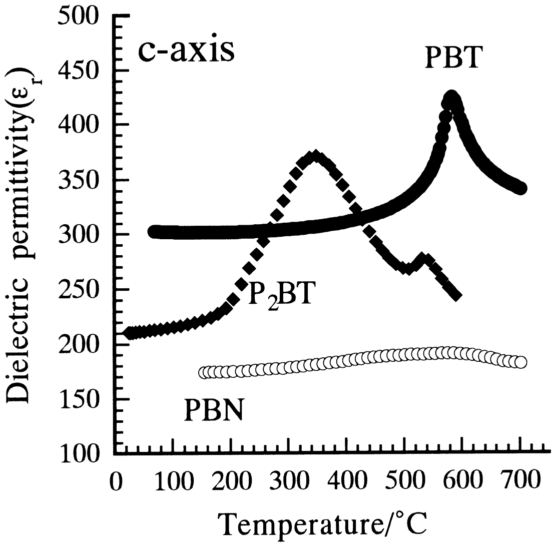

Fig. 3. Temperature dependences of dielectric permittivity for PBN, PBT and P_2BT in the *c*-axis direction.

close to the reported Curie temperature(T_c)s of 560, 570 and 310°C, respectively [6]. In the present work, the dielectric permittivities of PBN ($m = 2$), PBT ($m = 4$) and P_2BT ($m = 5$) were 4200, 18 300 and 10 400 in the *a*(*b*)-axis direction at the peak temperatures, respectively. Those values are much higher than the reported permittivities for polycrystalline samples at T_c; 2100, 5500 and 5900 for PBN, PBT and P_2B, respectively [6]. The permittivity in the *a*(*b*)-axis direction was also much larger than for the *c*-axis direction for single crystals. The anisotropy of permittivity [$\varepsilon(a(b))/\varepsilon(c)$] at T_c was about 22, 43 and 27 for PBN, PBT and P_2B, respectively. These values are much larger than those observed in grain-oriented polycrystalline samples [11].

The dielectric loss of PBN, PBT and P_2BT were very low, less than 0.1%, below the Curie temperatures in both *a*(*b*)-axis and *c*-axis directions at 1 MHz. They decreased with an increase in frequency but increased due to an increase in conductivity at higher temperatures above the Curie temperature.

The temperature dependence of the dielectric permittivity obeys the Curie–Weiss law; $\varepsilon = \varepsilon_0 + C/(T - T_0)$, where ε_0 is the temperature-independent part and is often neglected, C is the Curie constant and T_0 the Curie–Weiss temperature. The T_0 and C in the *a*(*b*)-axis and *c*-axis directions were estimated from the plot of reciprocal dielectric permittivity against temperature above the Curie temperature (in the paraelectric phase region). In the *a*(*b*)-axis direction, the Curie–Weiss constant C was 4.5×10^5, 2.5×10^5 and 6.0×10^5 °C for PBN, PBT and P_2BT, respectively, which agreed with the Curie constants (10^5 order of magnitude) of ferroelectric oxides such as $BaTiO_3$, $Cd_2Nb_2O_7$, etc. The Curie–Weiss temperature T_0 was 487, 578 and 340°C for PBN, PBT and P_2BT, respectively, which are close to the Curie temperatures. On the other hand, in the *c*-axis direction, though the Curie–Weiss constants C were of the same order of magnitude with for the *a*(*b*)-axis direction, the Curie-Weiss temperatures T_0 were much lower than for the *a*(*b*)-axis direction; below zero, 250 and 49°C for PBN, PBT and P_2BT, respectively. Accordingly, the bismuth layer is believed to be paraelectric from a lower temperature than the Curie temperature.

It has been proposed that there is no spontaneous polarization in the direction perpendicular to the bismuth layer (the *c*-axis direction) in compounds which consist of the perovskite blocks with even numbers of oxygen octahedra (*m*) due to a mirror symmetry below the Curie temperature, but small spontaneous polarization could be observed in compounds with odd numbers of oxygen octahedra, as in $Bi_4Ti_3O_{12}$ ($m = 3$) [4,5,8,9]. For the BLSF examined in the present study and $Bi_4Ti_3O_{12}$ [15], there is a tendency that the anisotropy in permittivity is larger in compounds with an even number of *m* (PBN and PBT) than for those with an odd number of *m*, which would be due to a small permittivity in the *c*-axis direction for even *m* compounds. In addition, the permittivity in the *a*(*b*)-axis direction at T_c showed a tendency to increase with increasing *m* for each even or odd *m* group, which is assumed to be due to a decreasing contribution of the bismuth layer.

3.3. Conductivity

Figs. 4 and 5 show the temperature dependences of DC conductivity of PBN, PBT and P_2BT in the *a*(*b*)-axis and *c*-axis directions, respectively. The DC conductivity was about one to two orders of magnitude higher in the *a*(*b*)-axis direction than for the *c*-axis direction in the temperature range from 200 to 500°C.

In the BLSF, similar anisotropy in conductivity has been reported for $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$ [14–16]. A low conductivity in the *c*-axis direction is assumed to be caused by the bismuth layer acting as an insulating layer against the charge transport, as explained for other BLSF [14–18].

When AC impedance was measured at 5–13 MHz, only one semicircle was observed in the complex impedance plot. However, in some cases, two semicircles can be observed in complex modulus plot only in the *c*-axis direction. It has been reported that the equivalent circuits for *a*(*b*)-axis and *c*-axis directions are identified as a single parallel RC circuit and two parallel RC circuits in a series array, respectively [16].

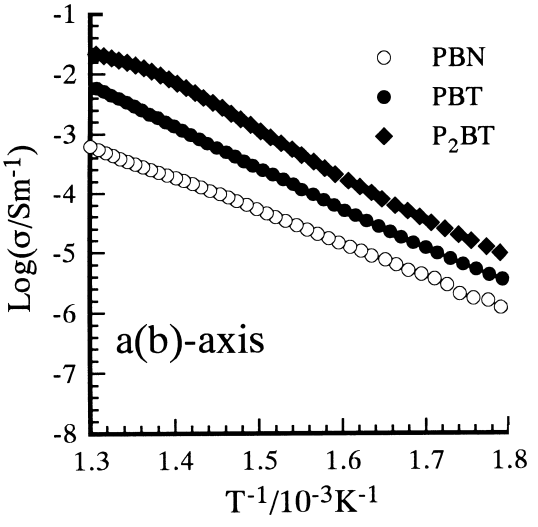

Fig. 4. Temperature dependences of DC conductivity for PBT, PBN and P_2BT in the *a*(*b*)-axis direction.

The DC conductivity increased with increasing number of *m* in both *a*(*b*)-axis and *c*-axis directions at temperatures above 350°C. However, the anisotropy of conductivity (ratio of conductivities in both directions) did not change significantly with increasing number of octahedra in the perovskite block *m*. It is thought that the insulating effect of the bismuth layer decreases with increasing *m*, that is, with increasing the distance between the bismuth layers.

3.4. Ferroelectric properties

Fig. 6 shows D–E hysteresis loops for PBN, PBT and P_2BT single crystals in the *a*(*b*)-axis within a temperature range of 150–200°C. The remanent polarization P_r and the coercive field E_c were 3, 8 and 17 μC/cm², and 8, 19 and 12 kV/cm for PBN, PBT and P_2BT, respectively, though they may be not in the well-saturated state. Among the above Pb-containing BLSF, the remanent polarization was larger in the compound containing a larger number of octahedra in the perovskite block. However, since $Bi_4Ti_3O_{12}$ has a larger P_r than for Pb-containing BLSF [21], the value of P_r seems to be much affected by component ions in the perovskite block.

Fig. 7 shows D–E hysteresis loops for PBN, PBT and P_2BT single crystals in the *c*-axis direction within the temperature range of 150–200°C. There is no spontaneous polarization in PBN and PBT which have even-layers of octahedra in the perovskite block in the *c*-axis direction. On the other hand, in P_2BT, a small component of spontaneous polarization was observed in the *c*-axis direction, which is expected for the BLSF with odd numbers of oxygen octahedra as $Bi_4Ti_3O_{12}$ ($m = 3$). The remanent polarization P_r and the coercive field E_c of

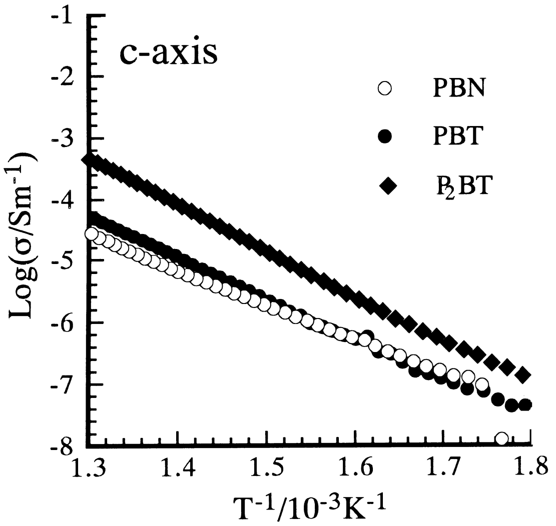

Fig. 5. Temperature dependences of DC conductivity for PBT, PBN and P_2BT in the *c*-axis direction.

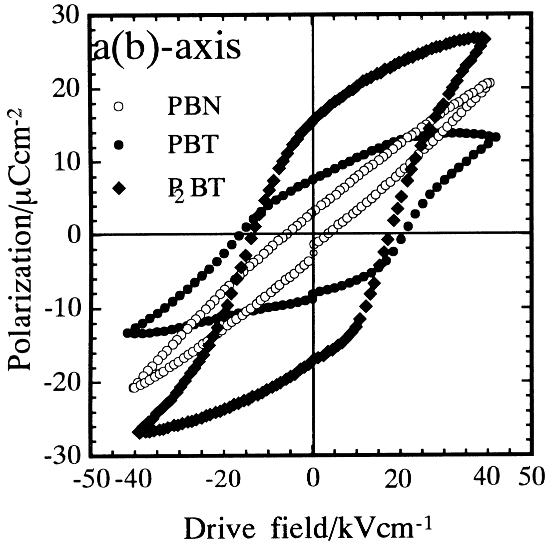

Fig. 6. D-E hysteresis loops of PBT, PBN and P_2BT in the *a*(*b*)-axis direction.

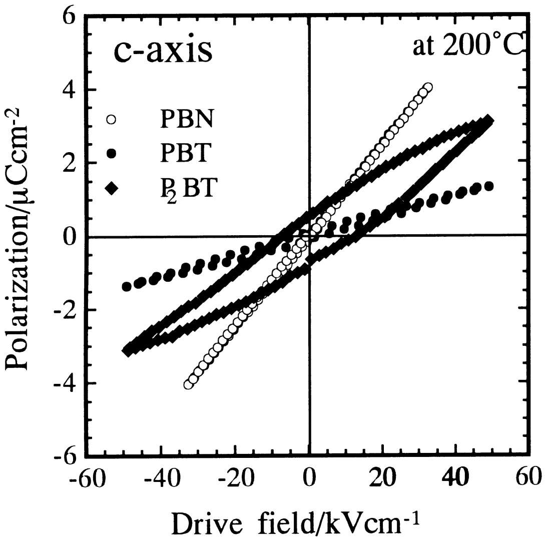

Fig. 7. D–E hysteresis loops of PBT PBN, and P_2BT in the *c*-axis direction.

P_2BT in the *c*-axis direction at 150°C were 0.7 μC/cm^2 and 10 kV/cm, respectively, under an applied field of 45 kV/cm.

The anisotropy of ferroelectricity and the spontaneous polarization in the *c*-axis for PBT, PBN and P_2BT single crystal are confirmed experimentally for the first time in the present study. In these measurements, the maximum applied field was restricted by current leakage but the value of P_r in the *a*(*b*)-axis direction continued to increase with an increase in the applied field in the measured range. Accordingly, the measured value of P_r is considered not to be the saturated value and a higher value can be expected by a poling treatment or by controlling the conductivity.

4. Conclusions

Single crystals of PBT, PBN and P_2BT were grown by the vertical gradient freeze method, and the relationship between crystal structure (number of octahedra in perovskite block *m*) and electrical properties is comprehensively discussed.

The dielectric permittivities of the PBN ($m = 2$), PBT ($m = 4$) and P_2BT ($m = 5$) in the *a*(*b*)-axis direction were about 22, 43 and 27 times higher than for the *c*-axis direction at T_c under 1 MHz, respectively. The anisotropy was dependent on *m* and was larger in the compound with an even-number *m* than that with an odd-number *m*. The Curie–Weiss temperature (T_0) was 487, 578 and 340°C in the *a*(*b*)-axis direction, in contrast it was below 0, 250 and 49°C in the *c*-axis direction for PBN, PBT and P_2BT, respectively. From these results, the bismuth layer was found to have paraelectric property from a low temperature below T_c.

The DC conductivity increased with increasing *m* in both *a*(*b*)-axis and *c*-axis directions in the temperature range from 280–500°C. However, anisotropy of the conductivity did not change significantly with increasing *m*. It is assumed that the insulating effect of the bismuth layer decreases with increasing *m* in both directions.

In ferroelectricity, the remanent polarizations of PBN, PBT and P_2BT increased with increasing *m*. High remanent polarization and low coercive field of P_2BT are especially suited as a candidate material for ferroelectric memory devices. It was confirmed experimentally that there is no spontaneous polarization in the *c*-axis direction in compounds with an even-number *m* as PBT and PBN. On the other hand, in P_2BT with an odd-number *m*, a small component of spontaneous polarization was observed in the *c*-axis direction.

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