Electrical Properties of Layer-Structured $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ Single Crystals

In-Sook YI and Masaru MIYAYAMA*

Research Center for Advanced Science and Technology (RCAST), The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904

*Dept. of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656

層状構造 $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ 単結晶の電気的性質

李 仁淑・宮山 勝*

東京大学先端科学技術研究センター, 153-8904 東京都目黒区駒場 4-6-1

*東京大学大学院工学系研究科応用化学専攻, 113-8656 東京都文京区本郷 7-3-1

Single crystals of lead bismuth titanate ($\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$) were grown and their electrical properties were investigated by measuring the dielectric permittivity, conductivity and spontaneous polarization. The dielectric permittivity, measured at 1 MHz, was 10400 in the direction parallel to the bismuth layer (crystallographic $a(b)$ -axis) at the Curie temperature of 340°C. This value was about 30 times higher than that in the perpendicular direction (crystallographic c -axis). The DC conductivity was about two orders of magnitude higher in the direction parallel to the bismuth layer than that in the perpendicular direction at 200 to 500°C. A large anisotropy of the ferroelectricity was observed in $D-E$ hysteresis curves at 150°C, and the existence of spontaneous polarization in the c -axis direction was experimentally confirmed, though it was much smaller than that in the $a(b)$ -axis direction. Among the bismuth layer-structured ferroelectrics, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ in the $a(b)$ -axis direction was found to have a low coercive field and a large remanent polarization.

[Received August 11, 1997; Accepted November 14, 1997]

Key-words: Single crystal, $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, Ferroelectrics, Dielectric permittivity, Electrical conductivity, Spontaneous polarization

1. Introduction

$\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (P_2BT) is one of the bismuth layered ferroelectric compounds with the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{M}_{m-1}\text{R}_m\text{O}_{3m+1})^{2-}$, where M represents mono- to trivalent ions such as Na, K, Ca, Ba, Sr, Pb and Bi, R represents tetra- to hexavalent ions such as Ti, Nb, Ta, W, Fe and V and m is 1–5.^{1)–5)} The crystal structure of $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ is composed of a pseudo-perovskite block $(\text{Pb}_2\text{Bi}_2\text{Ti}_5\text{O}_{16})^{2-}$ interleaved with bismuth oxide layers $(\text{Bi}_2\text{O}_2)^{2+}$ along the pseudotetragonal c -axis, as shown in Fig. 1. The m means the number of oxygen octahedra of R in the perovskite block. P_2BT corresponds to the compound with $m=5$, and has a block with four ($=m-1$) perovskite unit cells between two neighbor $(\text{Bi}_2\text{O}_2)^{2+}$ layers.^{2),6)}

Ferroelectricity in the bismuth layered compounds arises from the oxygen octahedra in the perovskite block and the spontaneous polarization takes place mainly in the direction parallel to the bismuth layer (the crystallographic $a(b)$ -axis) originating from the two-dimensional layer structure.^{4)–8)} It has been proposed that there is no spontaneous polarization in the direction perpendicular to the bismuth layer (the crystallographic c -axis) in compounds having the perovskite block with even numbers of oxygen octahedra, due to a mirror symmetry, but a small degree of spontaneous polarization could be observed in compounds with odd numbers of oxygen octahedra below the Curie temperature T_c , as observed in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$).^{4)–7)} Therefore, P_2BT with odd numbers of oxygen octahedra is expected to exhibit a spontaneous polarization in the c -axis direction, but this has not yet been confirmed experimentally. Among the bismuth layered ferroelectric compounds, polycrystalline P_2BT has been reported to have relatively high dielectric permittivity of 5900 at 310°C (T_c) and 400 at 25°C and spontaneous polarization of $6 \mu\text{C}/\text{cm}^2$ at 235°C.²⁾

The bismuth layered ferroelectric compounds show a peculiar anisotropy in electrical and optical properties between $a(b)$ -axis and c -axis directions due to the layered structure,^{9),10)} and research on the electrical anisotropies us-

ing single crystals is important for enabling their application to various ferroelectric devices. However, there has been no report on electrical properties of P_2BT single crystals. In the present study, the anisotropy in dielectric permittivity, DC conductivity and spontaneous polarization was examined for P_2BT single crystals grown by the vertical gradient freeze method.

Fig. 1. Schematic drawing showing the crystal structure of $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$. One-half of the pseudotetragonal unit cell. A denotes the bismuth layers $(\text{Bi}_2\text{O}_2)^{2+}$, B denotes the perovskite block $(\text{Pb}_2\text{Bi}_2\text{Ti}_5\text{O}_{16})^{2-}$, and C a unit cell of the hypothetical perovskite structure $((\text{Pb}, \text{Bi})\text{TiO}_3)$.

2. Experimental

The P_2BT single crystals were grown by the vertical gradient freeze method.¹¹⁾ As starting materials, reagent-grade (purity > 99.99%) PbO , Bi_2O_3 , and TiO_2 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 1250°C at a rate of 5°C/min and kept at this temperature for 4h, because P_2BT has a congruent melting point at 1190°C. The entire zone was slowly cooled to 1000°C at a rate of 4°C/h. The temperature at the top of the crucible was kept lower than that at the bottom of crucible at a vertical temperature gradient of 1–2°C/mm in order to prevent a high number of spontaneous nucleations and to induce natural convection flow. The single crystals obtained were cut, polished, and electroded with Pt by sputtering for measurements of the electrical properties.

A Laue camera, a polarizing microscope, and an X-ray diffractometer ($\text{Cu K}\alpha$ radiation) were used for characterizations of single crystals. The chemical composition was examined by ICP emission spectroscopy. 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 conductivities were measured at 200 to 500°C by the 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 from D - E hysteresis loops measured with an RT6000HVS (Radiant Technologies, Inc.) in a silicon oil bath at 150°C.

3. Results and discussion

3.1 Characterization

Figure 2 shows an optical micrograph of as-grown crystals of P_2BT . The crystals were grown on the melt surface in the form of platelet aggregates with a layered habit and the crystals were pale yellow and transparent. The large faces of the crystals were found to be parallel to the crystallographic (001) plane because the growth of crystals is extremely slow in the c -axis direction (perpendicular to the bismuth layer) as compared with that in the $a(b)$ -axis direction (parallel to the bismuth layer). The crystals showed strong c -plane cleavage as in the case of bismuth layered high T_c superconductors.^{12),13)} It was confirmed that the crystal was in the tetragonal phase with the fourfold symmetry axis, based on single spots separated by 90° in a backreflection Laue pattern for the (001) plane, as shown

Fig. 2. Optical micrograph for as-grown $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal.

Fig. 3. Backreflection Laue pattern for as-grown $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal.

Fig. 4. Polarized photograph of cleaved (001) plane for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal.

in Fig. 3. Figure 4 shows a ferroelectric domain structure on the (001) plane, which is one of the ferroelectric properties. The as-grown crystals had a number of domains due to the phase transition, as do many ferroelectric crystals below the Curie temperature; thus the crystallographic a -axis could not be distinguished from the b -axis.¹⁴⁾

For powders prepared by crushing single crystals, only the peaks of P_2BT were observed in the XRD pattern, as shown in Fig. 5.¹⁵⁾ The atomic ratio of Pb, Bi and Ti was confirmed to be 2.00 : 4.00 : 5.01 by ICP spectroscopy, which indicates an almost stoichiometric composition.

3.2 Dielectric properties

Figures 6(a) and (b) show the dependences of dielectric permittivity on temperature measured along the $a(b)$ -axis and the c -axis directions for the P_2BT single crystal at frequencies of 10 kHz to 1 MHz. With increasing frequency, the dielectric permittivity decreased slightly and the temperature at which dielectric permittivity was maximum increased from 310°C to 340°C in both the $a(b)$ -axis and c -axis directions. The frequency dependences of the dielec-

Fig. 5. XRD pattern for powders prepared by crushing $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal.

tric permittivity and the Curie temperature are often revealed in ferroelectric relaxors, and these are explained by structure disorder due to a microscopic composition fluctuation in ferroelectric oxides with complex composition.¹⁶⁾

The dielectric permittivities showed another small peak in the vicinity of 550°C. This temperature corresponds to the Curie temperature of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$, which is a bismuth layered ferroelectric compound composed of a block with three perovskite unit cells between the bismuth layers. It is well known that intermixed layers often exist in bismuth layered ferroelectric compounds with a large number of perovskite layers.⁸⁾ The peak at 550°C is assumed to originate from a trace amount of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ component, though this was not confirmed by X-ray diffraction.

In the present work, the dielectric permittivity of P_2BT was 10400 in the $a(b)$ -axis direction at 340°C and 1 MHz. This value was about 30 times higher than that in the c -axis direction at the same temperature, and about 6 times higher than that in the $a(b)$ -axis direction of single-crystal bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) at T_c (675°C).¹⁶⁾ Even at room temperature, the dielectric permittivity in the $a(b)$ -axis direction was as high as 1500. Since the anisotropy of dielectric permittivity in most bismuth layer-structured ferroelectrics are below about 25 at T_c ,^{10),17)} the single crystal of P_2BT was found to exhibit a large anisotropy in the dielectric property, among the bismuth layer-structured ferroelectrics.

Figure 7 shows the temperature dependences of dielectric loss in the $a(b)$ -axis and c -axis directions for the P_2BT single crystal. The dielectric loss decreased with increasing measurement frequency and increased with increasing temperature up to about 350°C. The dielectric loss at the Curie temperature, which is due to the motion of the domain wall, was less than 0.1% in both the $a(b)$ -axis and c -axis directions at the measurement frequencies. The increased dielectric loss at high temperature is assumed to be caused by an increase in conductivity, and also seems to be responsible for the dielectric dispersive phenomena recognized at a low (10 kHz) frequency at high temperatures in Fig. 6.

3.3 Conductivity

Figure 8 shows the temperature dependences of DC con-

Fig. 6. Temperature dependence of dielectric permittivity for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal (a) $a(b)$ -axis direction, (b) c -axis direction.

ductivity in the $a(b)$ -axis and c -axis directions for the P_2BT single crystal. The DC conductivity was about two orders of magnitude higher in the $a(b)$ -axis direction than that in the c -axis direction in the temperature range from 200 to 500°C. In bismuth layered compounds, similar anisotropies in conductivity have been reported in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, and $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$.^{14),17)-19)} A low conductivity in the c -axis direction is assumed to be due to the bismuth layer acting as an insulating layer against charge transport, as explained for other bismuth layered compounds.^{14),17)-19)}

3.4 Ferroelectric properties

Figures 9(a) and (b) show D - E hysteresis loops for the P_2BT single crystal in the $a(b)$ -axis and the c -axis directions. A small component of spontaneous polarization was observed in the c -axis direction, which is expected for bismuth layered structure ferroelectrics with odd numbers of oxygen octahedra. The remanent polarization (P_r) and the coercive field (E_c) at 150°C in the $a(b)$ -axis direction

Fig. 7. Temperature dependence of dielectric loss for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal in the $a(b)$ -axis and c -axis directions.

Fig. 8. Temperature dependence of DC conductivity for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ in the $a(b)$ -axis and c -axis directions.

were $17 \mu\text{C}/\text{cm}^2$ and $12 \text{ kV}/\text{cm}$, respectively, under an applied field of $30 \text{ kV}/\text{cm}$, while those in the c -axis direction were $0.7 \mu\text{C}/\text{cm}^2$ and $10 \text{ kV}/\text{cm}$ under $45 \text{ kV}/\text{cm}$. As a result, it was concluded that the crystal has a large anisotropy in ferroelectricity; the remanent polarization was more than 24 times higher in the $a(b)$ -axis direction than that in the c -axis direction. The anisotropy and the c -axis component of spontaneous polarization in P_2BT single crystals were confirmed experimentally for the first time in the present study. In the 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 not a saturated value and a higher value can be expected with a poling treatment or by

Fig. 9. D - E hysteresis loops for $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal (a) $a(b)$ -axis direction, (b) c -axis direction.

controlling the conductivity.

The values of P_r and E_c of single-crystal $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a typical bismuth layer-structured ferroelectric with $m=3$, have been reported to be $\sim 50 \mu\text{C}/\text{cm}^2$ and $50 \text{ kV}/\text{cm}$, respectively, in the a -axis direction.²⁰⁾ Also, P_r and E_c of $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ with $m=4$ have been reported to be $6 \mu\text{C}/\text{cm}^2$ and $20 \text{ kV}/\text{cm}$, in the $a(b)$ -axis direction for the single crystal under application of $30 \text{ kV}/\text{cm}$,¹⁸⁾ and to be $11 \mu\text{C}/\text{cm}^2$ and $68 \text{ kV}/\text{cm}$ in ceramics grain-oriented to the $a(b)$ -axis direction.²¹⁾ After comparison with these data, P_2BT was found to exhibit a relatively large remanent polarization with a low coercive field in the $a(b)$ -axis direction. These results suggest that this compound has suitable properties for use as a material for ferroelectric memory devices.

4. Conclusions

Single crystals of $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ were grown by the vertical gradient freeze method, and their dielectric, conducting and ferroelectric properties were examined separately in the directions of $a(b)$ - and c -axes. The dielectric permittivity was 10400 in the $a(b)$ -axis direction at 340°C , which

was about 30 times higher than that in the c -axis direction. The DC conductivity was about two orders of magnitude higher in the $a(b)$ -axis than that in the c -axis direction in the temperature range from 200 to 500°C. By using D - E hysteresis loops of the $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal, a large anisotropy in ferroelectricity was observed and the existence of spontaneous polarization in the c -axis direction was confirmed experimentally. The remanent polarization was $17 \mu\text{C}/\text{cm}^2$ and the coercive field was $12 \text{ kV}/\text{cm}$ in the $a(b)$ -axis direction at an applied bias of $30 \text{ kV}/\text{cm}$ at 150°C . It was found that the $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ single crystal has large anisotropies in dielectric permittivity, conductivity and ferroelectricity, due to the layered structure.

References

- 1) E. C. Subbarao, *J. Chem. Phys.*, **34**, 695-96 (1961).
- 2) E. C. Subbarao, *J. Phys. Chem. Solids*, **23**, 665-76 (1962).
- 3) G. A. Smolenskii, V. A. Isupov and A. I. Agranovskaya, *Sov. Phys. Solid State*, **3**, 651-55 (1962).
- 4) R. E. Newnham, R. W. Wolfe and J. F. Dorrian, *Mater. Res. Bull.*, **6**, 1029-40 (1971).
- 5) R. E. Newnham, R. W. Wolfe, R. S. Horsey, F. A. Diaz-Colon and M. I. Kay, *Mater. Res. Bull.*, **8**, 1183-96 (1973).
- 6) J. F. Dorrian, R. E. Newnham and D. K. Smith, *Ferroelectrics*, **3**, 17-27 (1971).
- 7) R. A. Armstrong and R. E. Newnham, *Mater. Res. Bull.*, **7**, 1025-34 (1972).
- 8) B. Aurivillius and P. H. Fang, *Phys. Rev.*, **126**, 893-96 (1962).
- 9) A. Fouskova and L. E. Cross, *J. Appl. Phys.*, **41**, 2834-38 (1970).
- 10) T. Takenaka, *J. Mater. Sci. Soc. Jpn.*, **27**, 136-44 (1990).
- 11) K. Suzuki and A. Tanaka, *Jpn. J. Appl. Phys.*, **31**, 2479 (1992).
- 12) H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, *Jpn. J. Appl. Phys.*, **27**, L209-12 (1988).
- 13) K. Hiraga, M. Hirabayashi, M. Kikuchi and Y. Syono, *Jpn. J. Appl. Phys.*, **27**, L573-77 (1988).
- 14) S. K. Kim, M. Miyayama and H. Yanagida, *J. Ceram. Soc. Japan*, **102**, 722-26 (1994).
- 15) E. C. Subbarao, *J. Am. Ceram. Soc.*, **45**, 166-69 (1962).
- 16) G. A. Smolenskii, *J. Phys. Soc., Supplement*, **28**, 26-36 (1970).
- 17) S. K. Kim, M. Miyayama and H. Yanagida, *Mater. Res. Bull.*, **31**, 121-31 (1996).
- 18) K. Homma and M. Wada, *Electronic Ceramics*, **4**[8], 9-14 (1973).
- 19) I. S. Yi and M. Miyayama, *Mater. Res. Bull.*, in press.
- 20) S. E. Cummins and L. E. Cross, *J. Appl. Phys.*, **39**, 2268-74 (1968).
- 21) T. Takenaka, Doctor Thesis, Kyoto University (1984) p. 36.