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Electrical Anisotropy in Single Crystals of Layer-structured $PbBi_4Ti_4O_{15}$

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Abstract

Single crystals of Lead Bismuth Titanate ($PbBi_4Ti_4O_{15}$) were grown by melting method. Electrical anisotropy of the crystals was investigated by measuring of dielectric permitivity, DC conductivity and complex impedance. The dielectric permittivity, measured at 1MHz, was 18300 in the direction parallel to bismuth layer (crystallographic a(b)-axis) at the Curie temperature of 570°C. This value was about 43 times higher than that in the perpendicular direction (c-axis). The DC conductivity at 700°C was about one order of magnitude higher in the direction parallel to bismuth layer than that in perpendicular direction. Results of complex impedance measurements suggested that the bismuth layer has a lower capacitance and a higher resistivity than those of the pseudo- perovskite blocks.

1. Introduction

$PbBi_4Ti_4O_{15}$ (PBT) is a member of a family of ferroelectric compounds with a layer-type structure of the general formula

$$(Bi_2O_2)^{2+} \ (M_{m-1}R_mO_{3m+1})^{2-}$$

where M=mono-, di-, or trivalent ions, or a mixture of them, R=Ti^{4+}, Nb^{5+}, Ta^{5+} etc., singly or in combination, and m=2,3,4 etc.. [1,2] The crystal structure of $PbBi_4Ti_4O_{15}$ comprises a stacking of pseudo-perovskite blocks($(Pb, Bi_2)Ti_4O_{13})^{2-}$ between bismuth oxide layers ($(Bi_2O_2)^{2+}$ layer) along the pseudo-tetragonal c-axis, as shown in Fig.1.

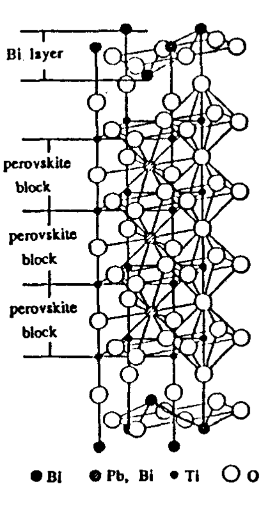


Fig.1. Crystal structure of $PbBi_4Ti_4O_{15}$ (one half of unit cell)

The octahedral cations R contribute strongly to the spontaneous polarization [3,4]. The continuous extention of the O-R-O chains in TiO_6 octahedrons along the c-axis is nterrupted by the presence of $(Bi_2O_2)^{2+}$ layers but the unbroken chains of O-R-O are present in the plane perpendicular to the c-axis. From such a structural arrangement, the electrical anisotropy is derived in bismuth layer-structured compounds. Positive use of the electrical anisotropy is assumed to be effective to develope new ferroelectric devices. However there is no report on electrical properties using single crystals in $PbBi_4Ti_4O_{15}$ because of difficulty in obtaining single crystals except very thin plate-like shaped crystals [5].

In the present paper, we report on the anisotropy of electrical properties in $PbBi_4Ti_4O_{15}$ (PBT) single crystals grown by melting method.

2. Experimental Procedure

2.1. Crystal growth

$PbBi_4Ti_4O_{15}$ were grown by melting method, as it has a congruent melting point at 1200° C. Powders of PbO, Bi_2O_3, and TiO_2 (purity>99. 99%) used as starting materials were ball-milled for 15 h with ZrO_2 balls and calcined at 700° C for 2 h. The calcined powders were set, using a double covered platinum crucible, in a vertical tube furnace with two thermocouples lied at the top and the bottom of the crucible. Heating was carried out at 1250° C for 4 h and cooling at a rate of 4° C/h to 1000° C, keeping the vertical temperature gradient of 1-2 ° C/mm. The obtained single crystals were cut with a size of about 3x3x1.2 mm^3, polished and electroded with Pt by sputtering

2.2. Polycrystalline preparation

In order to compare with the electrical properties in single crystals, polycrystalline samples were prepared by a conventional method using powders obtaind by crushing single crystals. Those powders were ball-milled for 15 h and calcined at 700° C for 2h. The calcined powders were pressed uniaxially at 69MPa and sintered at 1150° C for 2h. The sintered bodies were polished and electroded with Pt sputtering.

2.3. Characterizations and measurements

The characterizations of single crystals and polycrystalline samples were carried out with a Laue camera, a polarizing microscope, an X-ray diffractometer (Cu K_α radiation). 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, YHP, Japan). The DC conductivities were measured at room temperature to 700° C by 2-probe method using a pA Meter/DC Voltage Sorce (Model 4140B, YHP, Japan) with an applied voltage of 1-2V. The measurements of complex impedances were performed using an impedance analyzer (Model 4192A, YHP, Japan) with measureing frequency range of 5Hz-13MHz, and the oscillation level of 0.5V

3. Results and Discussion

As-grown crystals were translucent aggregates with yellow in colour and with thickness of about 1-2mm. Figure 2 gives a back- reflection Laue pattern, and Figure 3 shows a polarized photograph, on {001} plane of single crystal. The as grown crystals had a number of twins due to the phase transition below Curie temperature (570° C)[6] and the crystallographic a- and b-axes were not differentiated. Polyctystalline samples had relative densities of over 87% theoretical density.

Figure 4 (a), (b) shows the temperature dependences on dielectric permittivity along the a(b)-axis and the c-axis, respectively, for single crystals measured at various frequencies.

The dielectric permittivity decreased with increasing frequency and thedielectric dispersive penomena appeared at high temperatures in low frequency measurements. However, freqency dependence of the Curie Temperature as observed in the sigle crystals of BaBi$_4$Ti$_4$O$_{15}$ was not found[7].

Figure 5 shows the temperature dependence on the dielectric permittivity of single crystals and polycrystalline samples at 1 MHz. The dielectric permittivity was 18300 in the direction parallel to bismuth layer (the crystallographic a(b)- axis) at the Curie temperature of 570° C. This value was about 43 times higher than that in the perpendicular direction (the c-axis) and much higher than the anisotropy (about 10 times) in the single crystal of Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$)[8,9]. The dielectric permittivity of polycrystalline samples was 3000 at the Curie temperature and the value was situated between those of a(b)- and c-axes.

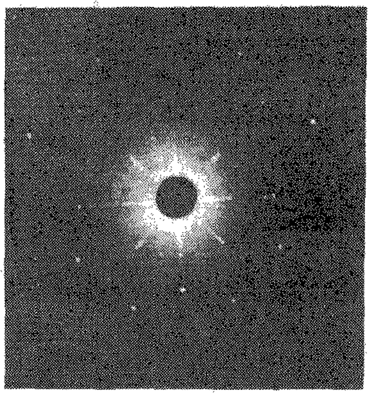


Fig. 2. Back-reflection Laue X-ray photograph of PbBi$_4$Ti$_4$O$_{15}$ sigle crystal

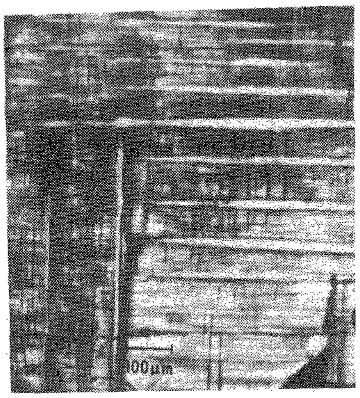


Fig. 3. Polarized photograph of PbBi$_4$Ti$_4$O$_{15}$ sigle crystal

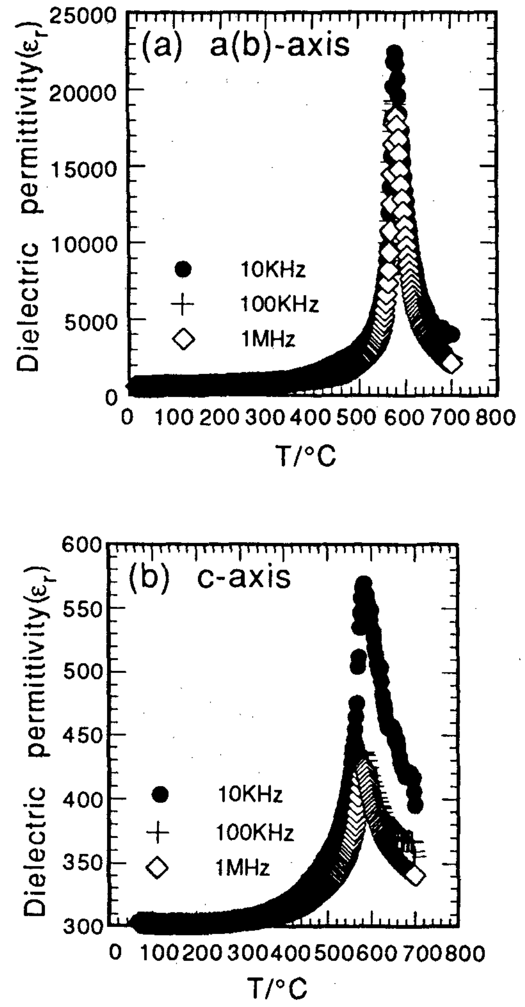


Fig.4. Temperature dependence of dielectric permittivity for $PbBi_4Ti_4O_{15}$; (a) a(b)-axis and (b) c-axis direction

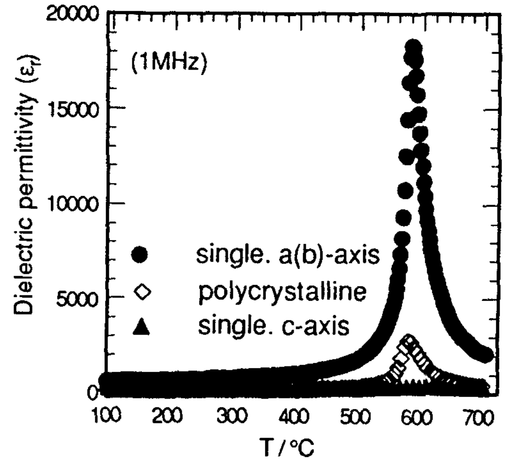


Fig.5. Temperature dependence of dielectric permittivity at 1 MHz for $PbBi_4Ti_4O_{15}$

Figure 6 stands the temperature dependences on DC conductivity for single crystals and polycrystalline samples. The DC conductivity above the Curie temperature was about one order of magnitude higher in the direction parallel to bismuth layer than that in perpendicular direction. The activation energies of the conductivity were decreased for a (b)- and c-direction above the Curie temperature and they were to 0.5 and 1.0eV above the Curie temperature, respectively. The higher activation energy and the lower DC conductivity in the perpendicular direction to bismuth layer proves that the bismuth layer acts as a barrier against the charge transport.

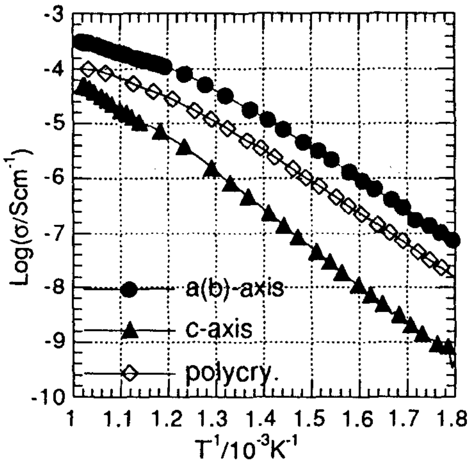
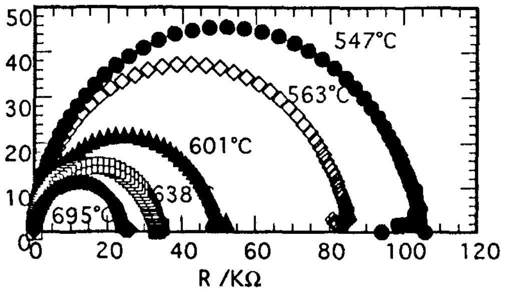


Fig. 6. Temperature dependence of DC conductivity for $PbBi_4Ti_4O_{15}$

In order to confirm the dielectric and the DC conducting properties, the complex impedances were measured. The R-X plots of the single crystals revealed very slightly distorted single semicircles both in the two crystallographic axes, as shown in Fig. 7 (a), (b). With increasing temperature, resistances decreased and semicircles became smaller. The conductivity calculated from the intercepts at low frepuency side of the R-X plots with the real axis is shown in Fig. 8. The AC conductivity agreed with that obtained from the DC measurements. Figure 9 shows the temperature dependence of the reciprocal of capacitance estimated at the top position of a semicircle in the R-X plot, assuming a simple equivalent circuit consisted of a parallel resistance and capacitance. In the paraelectric phase region the extrapolated line to 1/C=0 points out the Curie-Weiss temperature. The Curie-Weiss temperature in the a(b)-axis was 560°C, which is very similar to the peak temperature of the dielectric permittivity.

On the other hands,that in the c-axis was extremely low about 280°C. When two capacitance components are seriously connected, the total capacitance in mainly dominated by that of a smaller capacitance component. Accordingly, the result in the c-axis direction suggests that the bismuth layer would have paraelectric properties from a very low temperature below Tc.

(a) a(b)-axis



(b) c-axis

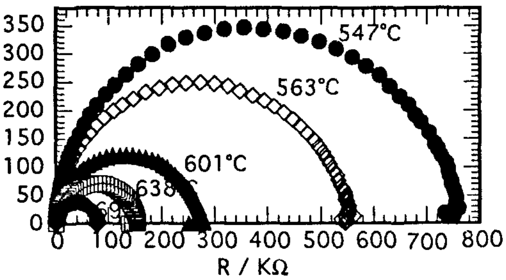


Fig. 7. Complex impedance plots for $PbBi_4Ti_4O_{15}$; (a) a(b)-axis and (b) c-axis direction

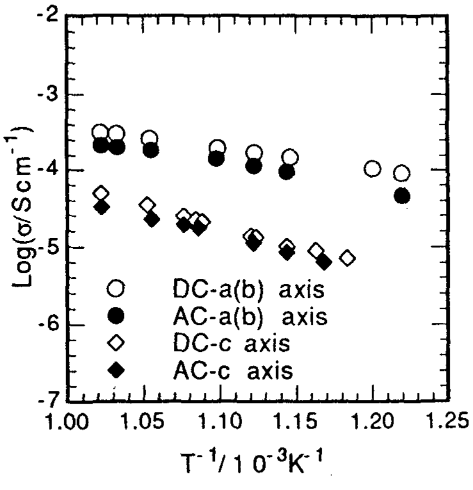


Fig. 8. Temperature dependence of DC and AC conductivity for $PbBi_4Ti_4O_{15}$

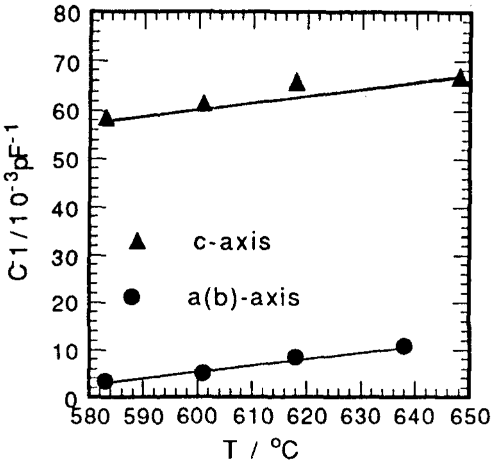


Fig. 9. capacitance from R-X plot of $PbBi_4Ti_4O_{15}$ single crystal as a function of temperature

The anisotropy in the dielectric properties originated from the structure anisotropy was confirmed even on the paraelectic phase above the Curie temperature. From the results of dielectric permittivity and DC/AC conductivity measurements, the bismuth layer in $PbBi_4Ti_4O_{15}$ single crystal acts as an insulating and a paraelectric layer.

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