

Dielectric Properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ below the Curie Temperature

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The dielectric permittivity, optical transmission spectrum and temperature dependence of resistance were investigated in single crystals of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. It is found that the dielectric anomalies previously reported below the Curie temperature are due electron space charges of inhomogeneous distribution in the material and near the non-ohmic electrodes.

§1. Introduction

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is the most typical and well known material in the family of complex bismuth oxides with layered structure (CBOL), generally described as $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$ (M and R indicate cations).¹⁻³⁾

The symmetry of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was reported to be orthorhombic by X-ray investigation, while observation with a polarizing microscope showed that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is monoclinic rather than orthorhombic. Dorrian *et al.*⁴⁾ refined the crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ from X-ray and neutron diffraction patterns, and they stated that the diffraction data were consistent with a polar orthorhombic structure with B2cb, $a=5.448(2)$, $b=5.411(2)$, $c=32.83(1)$ Å, and $Z=4$.

There have been several investigations on the dielectric properties of ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ⁵⁻⁷⁾ before now. Pulvari⁵⁾ first observed a few sharp peaks in the dielectric constant along the c axis of a single crystal of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, besides a peak at the Curie temperature (T_c), and he considered them to represent some sort of phase transition. Hisano *et al.*⁸⁾ reported observing a soft mode which freezes at about 250°C in the Raman spectrum of ceramic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and they considered this soft mode to be evidence of a phase transition below T_c . On the other hand, Fouscova and Cross⁷⁾ measured the complex dielectric permittivities at several

frequencies. They found an anomalous peak along the b axis and two peaks along the c axis, besides a peak at T_c . The magnitudes of these peaks were strongly temperature dependent, and the temperature where the peaks appear increased slightly with frequency. Because of the strong low-frequency dispersive behaviour of these peaks, they considered the origin of these anomalies to be a space charge generated in the crystal or at its surface.

Newnham *et al.*⁹⁾ predicted that CBOL with an odd value of n would have one phase transition. According to their prediction, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with $n=3$ cannot have two transitions. The present study was undertaken in order to obtain more information on the properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and to clarify the origin of the dielectric anomalies. Single crystals of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ were investigated by dielectric measurement, optical transmission spectrum and temperature dependence of resistance.

§2. Experimental Procedure

In making sample crystals, the starting materials of Bi_2O_3 (Iwaki Pharmacy Co., Ltd.), TiO_2 (Toho Titanium Industry) and BaTiO_3 (Fuji Titanium Inc.) were of 77.7% purity. The single crystals of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ used in this experiment were grown by the flux method using the technique developed by Morrison *et al.*¹⁰⁾ Transparent thin single crystals with sizes up to about $10 \times 10 \times 1$ mm were obtained. The

crystals had the (001)-dominant face morphology. Single crystals of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ were grown by the Czochralski method from a molten mixture of Bi_2O_3 , TiO_2 and BaTiO_3 with stoichiometric composition using the technique mentioned by Takusagawa *et al.*¹¹⁾ The boule was about 7 mm in diameter and 60 mm in length. It was cut so as to obtain a single crystal specimen measuring $5 \times 3 \times 0.2$ mm.

The temperature dependence of the dielectric permittivity and the resistivity of the specimens were observed between -50°C and 600°C . Two sample containers were used, and a cylindrical furnace 50 mm in diameter with a temperature regulator for high temperatures, and another temperature-controlled chamber were used between -50°C and 50°C . The dielectric measurement was limited to a maximum temperature of about 600°C because of the instability of the In–Ga alloy electrodes at high temperatures and because of the extremely high dielectric loss of the material.

An automatic AC bridge (Yokogawa, Hewlett & Packard [YHP] 4262A LCR meter) was used to measure the complex dielectric permittivity; the conventional four-terminal method was used. The bridge was operated at 120 Hz, 1 kHz and 10 kHz with a measuring voltage of 1 V. A high-resistance meter (YHP 2329A) was used to measure the resistance in the range between 10^{11} and $10^7 \Omega$ with various applied voltages of 10, 25, 50, 100, and 250 V. A precision digital meter (YHP 2501) was used to measure relatively low resistances of the order of 10^7 to $10^5 \Omega$ with a fixed applied voltage of 1 V. The two-terminal method was used in measuring the resistances. The gold electrodes on the specimens were deposited by sputtering. Each measurement was performed after a long decay time of up to about thirty minutes of the absorption current in the samples.

A Hitachi recording spectrometer, model EPS-3T, was used for measuring the optical transmission spectrum, and the specimens were kept at room temperature during this measurement.

§3. Experimental Results

3.1 Dielectric properties

Both ohmic and non-ohmic contacts of the electrodes to the crystal were studied. As shown in Fig. 1, the I – V curve with In–Ga

alloy electrodes is ohmic, while that obtained with Au electrodes is non-ohmic. Figure 2 shows the dielectric loss parallel to the c axis measured at 1 kHz and 10 kHz for both In–Ga electrodes and Au electrodes. As shown in the figure, a small hump in the loss at 1 kHz is observed at -30°C in the specimen with Au electrodes, whereas the specimen with In–Ga electrodes does not show such a hump. It is therefore considered that this hump is due to surface charge accumulated in the non-ohmic surface barrier.

Figures 3 and 4 show the real part, ϵ' , of the dielectric permittivity perpendicular ($\epsilon' \perp c$) and parallel ($\epsilon' // c$) to the c axis respectively, measured with the In–Ga alloy ohmic electrodes. Because of the irregular surfaces of the single crystals used, only the relative values of the dielectric permittivity are given; however the order of magnitudes of the dielectric permittivity thus obtained agrees with those formerly reported.^{6,7)} As shown in Fig. 3, the values ϵ' in $\epsilon' \perp c$ increase monotonically up to the Curie temperature, except for a small hump around 70°C . This dielectric dispersive behaviour in $\epsilon' \perp c$ seems similar to that observed in some glasses or in some materials with hopping conduction.^{12–14)} Fouscova & Cross⁷⁾ reported that the real part of the dielectric permittivity parallel to the b axis, $\epsilon' // b(\epsilon' \perp c)$, measured at 1 kHz showed a large peak around 500°C ; but no corresponding peak is found in the present experiment. This discrepancy is considered to be due solely to the difference in the nature of the electrical contact. On the other hand, the value of ϵ' in $\epsilon' // c$ shows a large peak around 500°C , which exactly corresponds to that observed by Fouscova & Cross,⁷⁾ but the small hump observed around 300°C in their ex-

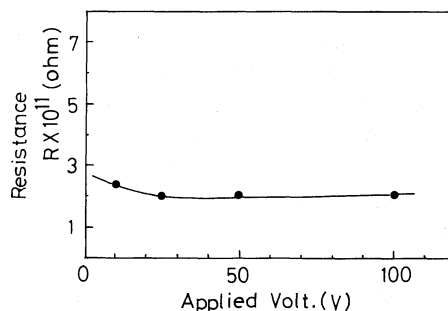


Fig. 1. Electrical resistance vs. applied voltage in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystal with In–Ga electrodes.

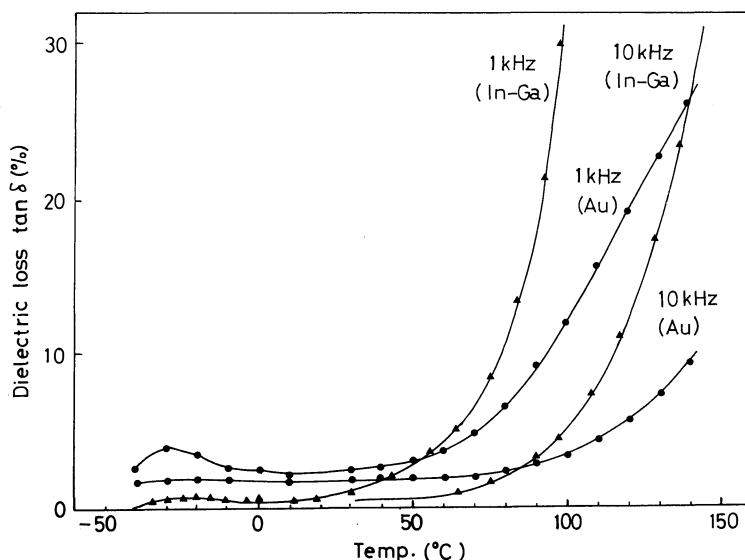


Fig. 2. Dielectric loss of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ parallel to c axis with In-Ga and Au electrodes at 1 kHz and 10 kHz.

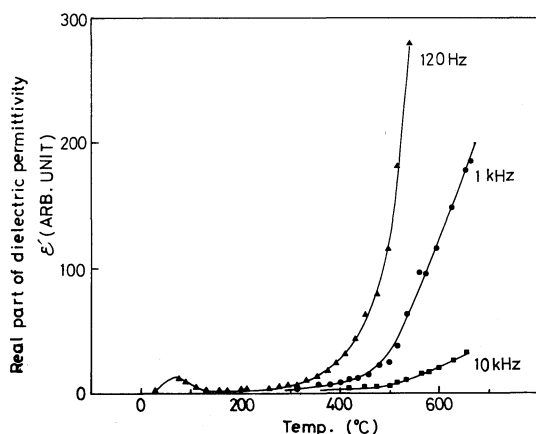


Fig. 3. Real part (ϵ') of the dielectric permittivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ perpendicular to c axis with ohmic electrodes of In-Ga alloy.

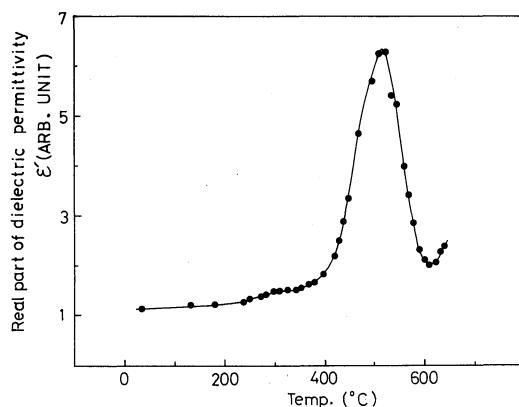


Fig. 4. Real part (ϵ') of dielectric permittivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ parallel to c axis at 1 kHz with ohmic electrodes of In-Ga alloy.

periment is not found in our experiment. Therefore, the small hump at about 300°C is considered to be due to surface charge.

Both $\epsilon' \perp c$ and $\epsilon' // c$ show a strong dispersion in the frequency range 120 Hz to 10 kHz, suggesting that the dielectric anomaly is caused by a characteristic relaxation time of the order of 10^{-2} to 10^{-3} s. The temperature dependence of the dispersion of the imaginary part, ϵ'' , of the dielectric permittivity is shown in Fig. 5.

3.2 Optical properties

The optical transmission spectrum of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ along the c axis observed at room tempera-

ture is shown in Fig. 6a. The transmission appears from about 380 nm to about 10000 nm. Therefore, the absorption edge of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is estimated to be about 380 nm (3.3 eV) and is found to be almost the same as that of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, as shown in Fig. 6b and c respectively. The band gap (E_g) of this material is about 3.3 eV as estimated from the observed absorption edge. The fact that the band gap energies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ and BaTiO_3 are almost the same (i.e., about 3.3 eV) indicates that the gaps are due to the common constituent TiO_6 .

3.3 Electrical resistivity

The temperature dependence of the resistivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was measured. The inverse temperature dependence of the resistance on a logarithmic scale is a straight line, as shown in Fig. 7, indicating that the carriers are thermally excited: a simple relation $\rho = \rho_0 \cdot \exp(E_a/2kT)$ is assumed, where E_a is the activation energy, ρ_0 a constant, and k Boltzmann's constant. The effect of non-ohmic contact (Au electrodes) is

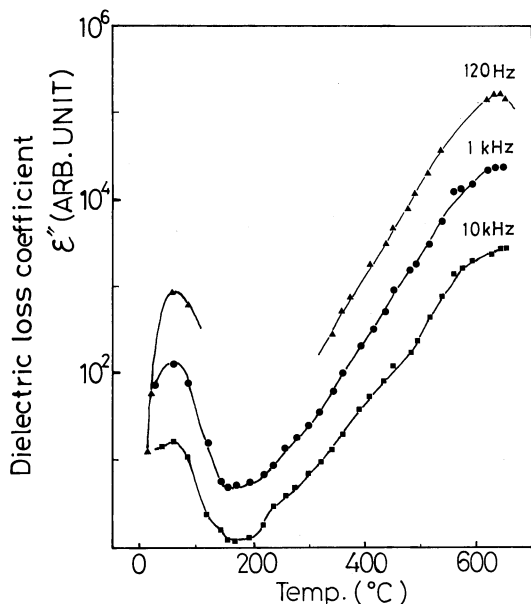


Fig. 5. Temperature dependence of dielectric loss coefficient (ϵ'') in $\epsilon'' \perp c$ with frequencies of 120 Hz, 1 kHz, and 10 kHz.

apparent, since the value of the resistance depends on the applied voltage, as shown in the figure. The activation energy perpendicular to the c axis is estimated to be 1.1 ± 0.2 eV, and is slightly smaller than the activation energy along

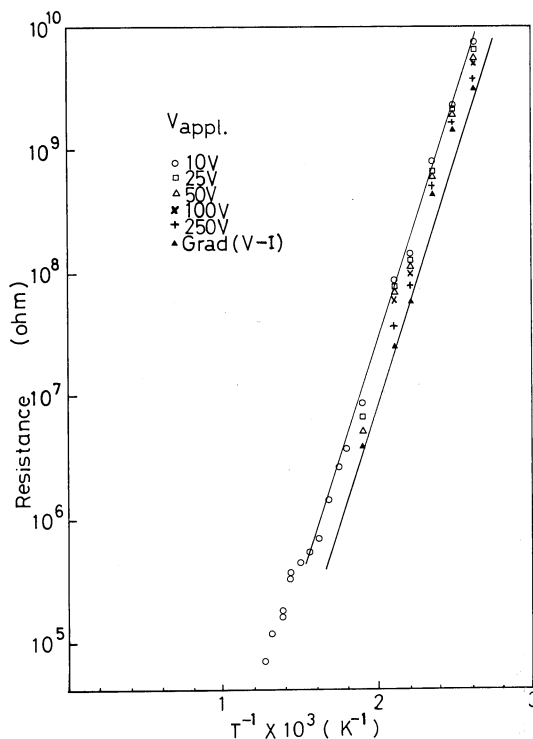


Fig. 7. Inverse temperature dependence of electrical resistance on logarithmic scale of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ perpendicular to c axis. Grad ($V-I$) is the extrapolated approximate value of the resistance at $V \rightarrow \infty$.

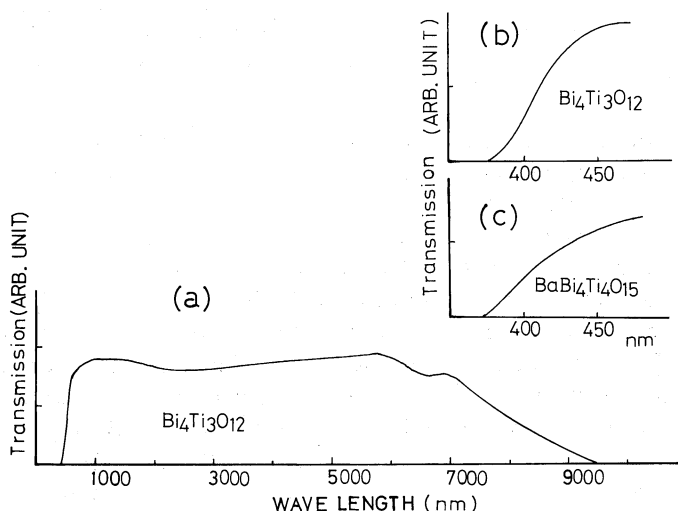


Fig. 6. Optical transmission spectra of single crystals along c axis observed at room temperature: a. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, b. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, c. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$.

the c axis, which is estimated to be 1.3 ± 0.2 eV. This seems to suggest the existence of a Bi_2O_2 layer which acts as a barrier against charge carriers. The activation energies E_a , estimated from the temperature dependence of the resistance, are less than half of the value of E_g (3.3 eV) expected from the optical fundamental absorption edge (Fig. 6(a)). This discrepancy in the values of E_a and E_g suggests that the carriers for E_a are impurities and vacancies.

§4. Discussion

In this experiment, it is found that the dielectric anomaly in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ below $T_c^{6,7)}$ is more or less affected by the electrical contact between the electrodes and the specimen, and that some of the anomalous dielectric permittivity previously observed by Fouscova and Cross⁷⁾ was undetectable in our measurement with the electrodes making ohmic contact with the specimen. From this fact, the results of Fouscova and Cross⁷⁾ apparently include a contribution from surface charge accumulated in the non-ohmic barrier at the interface with the electrode. It is interesting that the contribution from the surface charge causes a hump in $\epsilon' \perp c$ around 300°C. The large peak in ϵ''/c around 500°C is considered to be caused by intrinsic charge polarization, because the peak can still be seen in the measurement with ohmic contact. It is known that in the case of glass or amorphous materials, a hopping charge causes a low-frequency dielectric dispersion of the Debye type, similar to those observed in our experiment. In $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ only the tendencies of the frequency dependence of $\epsilon \perp c$ (for complex ϵ' , ϵ'') seem to agree with the dielectric dispersion given by Debye's dielectric relaxation equation. However, the behaviour of the dielectric dispersion observed in this experiment cannot be explained quantitatively by that equation. The dielectric peak at 500°C is considered to be due to induced polarization of the electron cloud across the potential barrier of the Bi_2O_2 layer.

§5. Conclusion

It is concluded that the dielectric anomalies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ observed previously^{5,7)} (at 300°C and 500°C) do not originate from any phase transition nor from any impurity or contamination. Surface charge at the non-ohmic contact (for the 300°C peak) and polarization of an electron cloud across the potential barrier of the Bi_2O_2 layer (for the 500°C peak) cause the dielectric peak in ϵ' .

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