Abstract
Electrical anisotropy of single-crystal \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \) and \( \text{BaBi}_4 \text{Ti}_4 \text{O}_{15} \) was investigated and compared with the properties of polycrystalline ones. It was observed that the dielectric permittivity perpendicular to the \( c \)-axis was much higher than that in the \( c \)-axis direction and showed the strong low-frequency dispersive behavior. Also, the conductivity perpendicular to the \( c \)-axis showed the higher value than that parallel to the \( c \)-axis. From the estimated activation energy, it is thought that \( \text{Bi}_2 \text{O}_2 \) layer acts as a barrier against the charge transport.

1. Introduction
Several layer-type bismuth compounds, which have ferroelectric properties, were discovered by B. Aurivillius in 1950\(^1\). This group of ferroelectric compound is very interesting structurally. It has alternating \( \text{Bi}_2 \text{O}_2 \) layers, which have rock salt structure, and perovskite-like \( \text{A}_{n-1} \text{B}_n \text{O}_{3n+1} \) blocks in their crystal structures (Fig. 1) and is expected to have the electrical anisotropy.

In this investigation, the measurements of the dielectric permittivity and DC conductivity were carried out on single- and polycrystalline \( \text{Bi}_4 \text{Ti}_3 \text{O}_{12} \) and \( \text{BaBi}_4 \text{Ti}_4 \text{O}_{15} \) and the doping effects of Nb(5+) on Ti (4+) site for polycrystal were examined.
2. Experimental Procedure

Transparent, thin plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystal was obtained by flux method using $\text{Bi}_2\text{O}_3$ as a flux. The growth method proposed by Van Uitert was modified by keeping a vertical temperature gradient suggested by Morrison etc$^2$. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ single crystal, as it melts congruently at 1150°C, was grown by melting at 1250°C and slow cooling (cooling rate: 4°C/h) with the vertical temperature gradient of 20-30°C/cm. The obtained single crystals were annealed and slowly cooled in order to eliminate twin, and polished carefully. The obtained single crystals were characterized by Laue camera and X-ray diffractometer. The polycrystalline samples were prepared by the ordinary method. The dopants of Nb(5+) etc. were doped in the polycrystalline sample up to 5.0 at.%. The dielectric properties were measured in the frequency range of 1 kHz to 10 MHz and the DC conductivity was measured for single- and polycrystalline samples electroded with Pt or ohmic Ag(In/Ga).

3. Results and Discussion

(1) Dielectric measurements

Fig. 2 shows the frequency dependence of the dielectric permittivity at room temperature for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$. The values of the dielectric permittivity perpendicular to the c-axis were about 2 times for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and about 5 times for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ higher than those parallel to the c-axis and showed frequency dependence. On the other hand, the dielectric permittivity parallel to the c-axis shows the weak frequency dependence. The polycrystals showed the intermediate behavior. The difference in the anisotropy between $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ can be attributed to the difference in the spontaneous polarization component; there is no c-axis component of spontaneous polarization in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, while $4\mu\text{C/cm}^2$ in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Temperature dependence of the dielectric permittivity for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ revealed a sharp peak at the Curie temperature of 676°C and a broad, anomalous peak at low temperature in the range of 500-600°C, as reported by Fouskova etc$^3$. This anomalous peak showed a strong low-frequency dispersion. In preliminary experiments, using with Pt electrode always revealed two anomalous peaks below the Curie temperature, which show the strong low-frequency dispersion, at low temperature near 300°C and in the range of 500-600°C. The peak near the lower temperature of 300°C was disappeared by using ohmic Ag(In/Ga). So, it is thought Pt
electrode is non-ohmic. On the other hand, the peak in the range of 500-600°C was independent on the electrode materials and the peak temperature was changed slightly run by run. The origin of the anomalous peak near 500°C has not been explained yet, but it is considered to be caused by intrinsic charge polarization. The dielectric permittivity of Bi$_4$Ti$_3$O$_{12}$ single crystal sample always gave a very sharp increase at the Curie temperature, especially in the perpendicular direction to the c-axis as indicated in Fig.3. The behavior of the dielectric permittivity vs. temperature for the polycrystal revealed the intermediate character of those perpendicular and parallel to the c-axis of single crystal, and also showed the low-frequency dispersion. The temperature dependence of the dielectric permittivity for BaBi$_4$Ti$_4$O$_{15}$, as illustrated in Fig.4, showed more broad peak at the Curie temperature of 395°C than that of Bi$_4$Ti$_3$O$_{12}$ and there was a frequency dependence of Curie temperature for both of single- and polycrystal. The observed behavior is explained by the possible ordering of Bi and Ba ions in the two types of B sites in the pseudo-perovskite blocks.

(2) DC conductivity measurements

Fig.5 and 6 compare the temperature dependence of DC conductivity for single- and polycrystalline Bi$_4$Ti$_3$O$_{12}$ and BaBi$_4$Ti$_4$O$_{15}$, respectively. It is evident that the conductivity parallel to the c-axis is lower than that perpendicular to the c-axis. The activation energies parallel to the c-axis, which is estimated from the slope, gave slightly higher values than that perpendicular to the c-axis. The activation energies parallel to the c-axis are the same as 1.1eV for both of Bi$_4$Ti$_3$O$_{12}$ and BaBi$_4$Ti$_4$O$_{15}$. These facts indicate that Bi$_2$O$_2$ layer acts as a barrier against charge transport.

4. Summary

Single- and polycrystalline Bi$_4$Ti$_3$O$_{12}$ and BaBi$_4$Ti$_4$O$_{15}$ were prepared and their electrical anisotropy in the dielectric and conducting properties were compared. The dielectric permittivity and conductivity was larger in the direction perpendicular to the c-axis. The anisotropy in the conductivity and the activation energy suggests that Bi$_2$O$_2$ layer acts as a barrier against charge transport.

References

1. B. Aurivillius, Arkiv Kemi 1, 463, 499 (1949); 2, 519 (1950); 5, 39 (1952)
Fig. 2 Frequency dependence of dielectric constant for single- and polycrystalline Bi$_4$Ti$_3$O$_{12}$ and BaBi$_4$Ti$_4$O$_{15}$ at room temperature.

Fig. 3 Temperature dependence of the dielectric permittivity of single- and polycrystalline Bi$_4$Ti$_3$O$_{12}$ (measured at 1MHz).

Fig. 4 Temperature dependence of the dielectric permittivity of single- and polycrystalline BaBi$_4$Ti$_4$O$_{15}$ (measured at 1MHz).

Fig. 5 Temperature dependence of the conductivity for single- and polycrystalline Bi$_4$Ti$_3$O$_{12}$.

Fig. 6 Temperature dependence of the conductivity for single- and polycrystalline BaBi$_4$Ti$_4$O$_{15}$.