Origin of Appearance of PTCR Properties in Bi-Sr-Ti-O System

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(Bi_{0.85}Sr_{0.15})₄(Ti_{0.95}Nb_{0.05})₃O₁₂ shows a large positive temperature coefficient of resistivity (PTCR) properties of almost 4 orders of magnitude at about 543K. This temperature does not correspond to the Curie point of Bi₄Ti₃O₁₂, but to the melting point of Bi metal. The microstructure of samples with or without showing PTCR properties observed by optical microscopy, showed the presence of Bi metal distributed in matrix. The various resistivity-temperature characteristics were obtained by controlling the distribution Bi metals in the matrix. Therefore, the new appearance of PTCR properties in Bi-Sr-Ti-O system would be related with the melting and solidification of Bi metal which is finely distributed in samples and isolated for each other. The equivalent electrical circuit for the samples were determined by complex impedance and modulus analysis. A model of this appearance of PTCR properties is proposed from these results as follows; Electrical current would flow in Bi metal at lower temperatures, but would not flow at higher temperatures. The resistivity of the sample at higher temperatures would be determined by matrix. Another RC component which acts only in the vicinity of PTCR temperature was also observed. This component may be due to the interface of Bi metals and the matrix.

Keywords: positive temperature coefficient of resistivity (PTCR) properties, bismuth-strontium-titanate-oxygen system, impedance and modulus analysis, equivalent electrical circuit, new mechanism of PTCR properties

I. Introduction

It is well known that semiconducting BaTiO₃ ceramics show PTCR (Positive Temperature Coefficient of Resistivity) properties above the Curie temperature (T_c = 393K). PTC materials are used for many applications as self-regulating heating elements and current limiters for electric applications.

The PTCR property is believed to be attributed to the grain boundary potential barrier, proposed by Heywang⁽¹⁾⁽²⁾, and subsequently modified by Jonker⁽³⁾. The Heywang model explains the drastic change in resistivity as existing due to the potential barriers at the grain boundaries. The potential barriers are caused by the acceptor-type interface between ferroelectric-ferroelectric boundaries.

Previously, we observed PTCR properties at about 543K in Sr- and Nb- doped Bi₄Ti₃O₁₂ ceramics fired in Ar atmosphere⁽⁴⁾. Bi₄Ti₃O₁₂ is a ferroelectric material with Curie point of 948K⁽⁵⁾. The temperature at which PTCR properties appeared does not correspond to this Curie point of Bi₄Ti₃O₁₂. Heywang's models fail to explain the appearance of PTCR properties in this system. Since sintering atmosphere is Ar, Bi metals are found to be distributed in samples. Because the melting point of Bi metal is 544.4K, which corresponds to the temperature of appearance of PTCR properties, the mechanism of PTCR properties may be related with melting and solidification of Bi metal. Then, the purpose of the present

study is to investigate the origin of appearance of PTCR properties in Bi-Sr-Ti-O ceramics, in preparing the various morphology of the microstructures with or without PTCR properties.

Hodge et al. proposed that combined analysis using both the complex impedance and the complex modulus formalisms had certain advantages over the conventional methods to determine the equivalent electrical circuit for polycrystalline materials⁽⁶⁾. Using this technique, The equivalent circuit for the PTCR materials is tried to be established in this system. Then the model of the mechanism of PTCR properties in Bi-Sr-Ti-O system will be proposed.

II. Experimental Procedure

The specimens were prepared from 99.9%Bi₂O₃, 99.9%SrCO₃, 99.9%TiO₂, and 99.9%Nb₂O₅ as the doping element. The nominal composition of the specimens is (Bi_{0.85}Sr_{0.15})₄(Ti_{0.95}Nb_{0.05})₃O₁₂. After mixing the weighed powders in ethyl-alcohol, the mixed powders were calcined at 1023K for 3h to produce the doped Bi₄Ti₃O₁₂. The calcined powders were pressed into disks of 10 mm in diameter with 10 mm thick. The compacted powder was sintered at 1373K to 1423K for 2h in Ar atmosphere. In order to prepare the various morphologies of the microstructures, compacting and sintering conditions were altered as shown in Table 1. It is found that the distribution and the size of Bi metal embedded in the matrix are sensitive to reducing atmosphere during sintering, since Bi easily volatilizes from samples. To prevent Bi from volatilization, samples B and C were enclosed with

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Table 1. Preparation conditions of samples

Sample	Compacting pressure	Sintering condition
A	141MPa	1373K, 2h
B	141MPa	1423K, 2h
C	71MPa	1423K, 2h
D	141MPa	1398K, 2h

Fig. 1. Resistivity-temperature characteristics of $(\text{Bi}_{0.85}\text{Sr}_{0.15})_4(\text{Ti}_{0.95}\text{Nb}_{0.05})_3\text{O}_{12}$

Fig. 2 The resistivity-temperature characteristic of Bi metal

Bi metal powder in a crucible during sintering.

For electrical measurements, In-Ga (40:60) alloy was painted on the polished surfaces of the samples to provide ohmic contacts. The resistivity-temperature characteristics were measured by D.C. two-probe method using computer-controlled D.C. powersupply/monitor (Advantest TR6143), in the range of room temperature to 623K at a heating rate of 0.083K/sec (5K/min).

A computer-controlled impedance analyzer (HP 4192A) was used for A.C. impedance measurements over the frequency range of 5Hz to 13MHz. Firstly, the frequency dependences of complex impedances are measured at each temperature. Then complex modulus are calculated from these results.

The microstructure of the samples has been observed by the optical microscopy. The appeared phases of the samples

were identified by X-ray diffraction powder techniques using CuK_α radiation, and by the electron probe microanalysis (Shimazu EPMA).

III. Results and Discussion

1. Resistivity-temperature characteristics

Fig. 1 shows the resistivity-temperature characteristics of specimens prepared by the conditions shown in Table 1. Sample B shows the typical PTCR curve appeared in this system. The resistivity increases rapidly at about 543K on heating, by about 4 orders of magnitude, (from $\sim 1 \Omega \text{ m}$ to $> 10^4 \Omega \text{ m}$), and at higher temperatures, the resistivity decreases with increasing temperature. On cooling, the resistivity shows sharp decrease at about 503K, which is different temperature from one on heating.

The samples A, C, D show no PTCR properties. In particular, two extreme examples of A and D are important. The resistivity of sample A is the highest at room temperature, and decreases with increasing temperature. This negative temperature coefficient of resistivity (NTCR) is nearly equal to one for sample B at higher temperatures over 503K. On the other hand, sample D has the lowest resistivity, and its characteristic is similar to that of the Bi metal as shown in Fig. 2. The samples C has intermediate characteristics between sample B and D. The sample C shows the knick at 543K where Bi metals start to melt.

The resistivity-temperature characteristics observed in this study will be classified into following three categories; (1) NTCR properties with higher resistivities (sample A) (2) sharp PTCR properties (sample B) (3) Bi metal-like resistivity-temperature characteristics with low resistivities (sample C, D)

2. Microstructures

The microstructures in cross-section near the surface of the samples A, B and D are observed as shown in Fig. 3 (a), (b), and (c), respectively. The phase with bright contrast was identified as Bi metal by EPMA. The matrix with dark contrast is identified as $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ by XRD as shown in Fig. 4. In the microstructure of sample A (Fig. 3 (a)) with NTCR properties, the Bi phases are almost spherical and isolated from each other. The sizes of Bi phases are about $1 \sim 5 \mu \text{ m}$, and the distances between Bi phases are about $5 \sim 10 \mu \text{ m}$. In the microstructure of sample B (Fig. 3(b)) with PTCR properties, Bi metals are more distributed near the surface. The conductivity can be detectable only in this Bi rich region near the surface. The corresponding microstructures near the surface of sample B were enlarged as shown in Fig. 5 (a). Bi metals are isolated from each other and embedded within dense matrix. There forms few network of Bi metal. The sizes of Bi metals are about $10 \mu \text{ m}$, and the distances of Bi phases are about $10 \sim 20 \mu \text{ m}$. In the microstructure of sample D (Fig. 3 (c)) with Bi metal-like resistivity-temperature characteristics, there are some networks of Bi metal near the surface of the sample as

Fig. 3. Optical micrograph in cross-section near the surface of (a) sample A with NTCR properties (b) sample B with PTCR properties (c) sample D with Bi metal-like resistivity-temperature characteristics

shown in Fig. 5 (b). Because of firing at high temperature, the vaporization of Bi metal is accelerated during firing, and makes the matrix porous.

Typical resistivity-temperature characteristics mentioned above are related to the distribution of Bi metals.

The small volume fraction of Bi metal in sample A with NTCR properties is due to the insufficiently reducing atmosphere during firing. The absence of Bi rich region brings high resistivities ($> 10^5 \Omega \text{ m}$) of sample A. The NTCR property of sample A is responsible for matrix of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$.

Low resistivities ($\sim 10^1 \Omega \text{ m}$) at lower temperatures in sample B with PTCR properties are related with the presence of Bi rich region. The electrical current may flow preferentially along Bi phases at these temperatures. On the other hand, since the negative temperature coefficient of resistivity at higher temperatures in this sample approximately corresponds to that of sample A, the electrical current may not flow along Bi phases, but only through the matrix.

Sample D shows some networks of Bi metal, which create the electrical short circuit along Bi phase, resulting in disappearance of PTCR properties.

3. AC. impedance measurements

In order to further investigate the origin of PTCR properties in this system, impedance Z'' and modulus M'' spectroscopy for sample B with PTCR properties were measured as shown in Fig. 6. The corresponding electrically equivalent circuits are illustrated in Fig. 7.

At the room temperature, both impedance Z'' and modulus

Fig. 4 XRD pattern for $(\text{Bi}_{0.85}\text{Sr}_{0.15})_4(\text{Ti}_{0.95}\text{Nb}_{0.05})_3\text{O}_{12}$ sintered at 1423K for 2h

Fig. 5. Optical micrograph in Bi rich region of (a) sample B with PTCR properties (b) sample D with Bi metal-like resistivity-temperature characteristics

M'' spectroscopy show a peak at the higher frequency than 13 MHz. The corresponding RC component is approximately calculated at about $600 \Omega \times 20 \text{ pF}$.

In the vicinity of 513K where the resistivity shows the sharp increase, a remarkable change was observed. While impedance Z'' shows only one peak at about 500Hz, modulus M'' shows three distinguishable RC components, which are shown as R_1C_1 , R_2C_2 , R_3C_3 , respectively in Fig. 7 (b). They are roughly estimated at about $10^7 \Omega \times 40 \text{ pF}$, $3000 \Omega \times 60 \text{ pF}$, $200 \Omega \times 50 \text{ pF}$. R_1C_1 appears from 493K where the resistivity starts to show the PTCR properties, and becomes higher rapidly up to 523K. This component is responsible for the high resistivity. R_2C_2 was observed from 493K to 523K where R_1 is increasing. This component would play an important role to cause PTCR properties in this system. R_3C_3 corresponds to the RC component which is observed at lower temperatures (Fig. 7 (a)). The modulus M'' peak height of R_3C_3 decreases in these temperatures, which means the volume fraction of R_3C_3 component decreases if the volume capacitance of this component is assumed to be almost constant. On the other hand, the modulus M'' peak height of R_1C_1 increase at these temperatures, which means the volume fraction of R_1C_1 increases.

At higher temperatures, only R_1C_1 component is detectable as shown in Fig. 7 (c).

4. Origin of appearance of PTCR properties

The origin of appearance of PTCR properties in this system is schematically illustrated in Fig. 8.

(1) At lower temperatures, the electrical current will flow

Fig. 6. Impedance Z'' and modulus M'' spectroscopic plots against frequency for sample B with PTCR properties at 297K~623K

along Bi metal, where R_3C_3 will be originated from the matrix between Bi phases, as shown in Fig. 8 (a).

(2) In the vicinity of PTCR temperature, some kinds of the barrier (R_2C_2) such as Schottky-type potential barrier or the electrical double layer will be formed at the interface between Bi metal and the matrix as shown in Fig. 8 (b), in preventing the electrical current from flowing along Bi metals. This may be caused by the reason that the Bi metal is known to shrink by about 3% at the melting point. The barrier at the interface may be originated from the disconnection of Bi metals from the matrix because of the shrinkage of Bi molten metal. In these temperature ranges, the volume fraction of R_1C_1 increases, while that of R_3C_3 decreases.

(3) At higher temperatures, the electrical current entirely does not flow along the Bi metals but through the matrix (R_1C_1), since the barrier at the interface will considerably increase.

IV. Conclusions

$(\text{Bi}_{0.85}\text{Sr}_{0.15})_4(\text{Ti}_{0.95}\text{Nb}_{0.05})_3\text{O}_{12}$ shows a large PTCR properties of almost 4 orders of magnitude at about 543K.

(1) Various resistivity-temperature characteristics are related to the morphology of the microstructures. The sample with PTCR properties consists of the microstructure such that Bi metals are isolated from each other and embedded within dense matrix, in forming few network of Bi metal. Once network of Bi metals is formed, PTCR properties disappear.

(2) Three distinguishable RC components observed by

Fig. 7. The corresponding equivalent electrical circuit for sample B with PTCR properties at 297K~623K

Fig. 8. The model of origin of appearance of PTCR properties

impedance and modulus analysis. R_1C_1 are interpreted as the matrix of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$. This component is responsible for high resistivities at higher temperatures. R_2C_2 is active only in the vicinity of PTCR temperature. R_3C_3 will be originated from the matrix between Bi phases. This component is detectable at lower temperatures.

(3) New mechanism of PTCR properties is suggested as follows; At the lower temperatures, the electrical current flows along Bi metals and resistivities are low. At higher temperatures, the electrical current does not flow along Bi metals but only through the matrix, and the resistivity increases rapidly. The occurrence of two kinds of electrical circuits dependency on the temperatures, will be due to some kinds of barrier formed at the interface between Bi metal and the matrix.

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