Microstructure–PTCR Property Relationships in PbTiO$_3$–TiO$_2$ Ceramics

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Niobium doped PbTiO$_3$–TiO$_2$ ceramics show PTCR properties at the Curie temperature of PbTiO$_3$ (490°C). This paper describes the relationships between PTCR characteristics and the microstructure of PbTiO$_3$–TiO$_2$ ceramics. PTCR properties depend on the firing conditions that vary the microstructure of PbTiO$_3$–TiO$_2$ ceramics. The PTCR properties disappear when TiO$_2$ grains are connected each other from one end of the sample to the other. The resistivity–temperature characteristics of the interface between PbTiO$_3$ and TiO$_2$ grains are directly measured. It is found that PTCR characteristics are originated at the interface between PbTiO$_3$ and TiO$_2$ grains. On the basis of this idea, a new type of PTCR PbTiO$_3$–TiO$_2$ ceramics with the boundary layer structure is proposed.

KEY WORDS: PbTiO$_3$–TiO$_2$ ceramics; interface boundary; electron microscopy; electric property; PTCR.

1. Introduction

It is well known that semiconducting BaTiO$_3$ ceramics show the Positive Temperature Coefficient of Resistivity (PTCR) properties above the Curie temperature ($T_c=120°C$). PTCR materials are mainly used for self-regulating heating elements and many other electronic parts. In order to expand their high temperature applications, PTCR materials with high Curie temperature have been demanded. PTCR materials of (Ba$_{0.8}$Sr$_{0.2}$)TiO$_3$ with the Curie temperature of 300°C are produced in manufacturing scale up to now. Recently, it was reported that Nb-doped PbTiO$_3$–TiO$_2$ composite ceramics showed PTCR properties at the Curie temperature of PbTiO$_3$ (490°C), which is the highest temperature among those of available PTCR materials. The Curie temperature of this system is controlled by the addition of SrTiO$_3$ and CaTiO$_3$.

Fig. 1 shows PTCR characteristics of the reported PbTiO$_3$–TiO$_2$ ceramics in comparison with those of BaTiO$_3$. SrTiO$_3$ addition decreases the Curie temperature of PbTiO$_3$–TiO$_2$ system as well as improves the stability. The resistivity in PbTiO$_3$–TiO$_2$ system at room temperature decreases with increasing TiO$_2$ content. The appearance of PTCR properties in this system depends on the firing conditions. The PTCR properties disappear in raising the firing temperature or in increasing the firing time. The microstructure of PbTiO$_3$–TiO$_2$ ceramics consists of fine grain PbTiO$_3$ and TiO$_2$ phases. This means that the origin of PTCR properties of PbTiO$_3$–TiO$_2$ ceramics is different from that of semiconducting BaTiO$_3$ ceramics. The origin of PTCR properties in BaTiO$_3$ ceramics is at the grain boundaries of BaTiO$_3$, which is the interface between the ferroelectric–ferroelectric grains. But in PbTiO$_3$–TiO$_2$ ceramics, it can be considered that PTCR properties are originated from the interface between the ferroelectric PbTiO$_3$ and non-ferroelectric TiO$_2$ phases.

![Fig. 1](image-url)
The purposes of the present studies are,
1) to clarify the relationships between PTCR properties and the microstructures in PbTiO$_3$–TiO$_2$ ceramics, and
2) to make clear the origin of PTCR properties in PbTiO$_3$–TiO$_2$ ceramics by directly measuring the electrical resistivity–temperature characteristics between PbTiO$_2$ and TiO$_2$ grains.

It is well known that ZnO varistors and boundary layer (BL) capacitors are designed in utilizing the grain boundary of the ceramics. On the basis of this findings, a new PbTiO$_3$–TiO$_2$ PTCR ceramic with BL structure is proposed.

2. Experimental Procedures

2.1. Sample Preparations

The specimens were prepared from 99.89 % PbO and 99.7 % TiO$_2$ with 99.89 % Nb$_2$O$_5$ as the doping element. The nominal compositions of the specimens are

$$\text{Pb(Tio.998Nbo.002)O}_3-30\text{mol}\% (\text{Ti}_4\text{o.998Nb}_4\text{o.002})\text{O}_3$$

The weighed powders were mixed and calcined at 600°C for 3 h. The calcined powders were ground in a wet mill and pressed into disks of 10 mm in diameter with 10 mm thick. The green compacts are put in the Al$_2$O$_3$ crucible with (PbCO$_3$)$_2$Pb(OH)$_2$$\cdot$3ZrO$_2$ for creating PbO atmosphere. They were then sintered at 1025~1075°C for 2 h in Ar atmosphere.

The origin of the appearance of PTCR properties is directly studied by measuring the electrical resistivity between PbTiO$_3$ and TiO$_2$ grains. This experiments require the large grain size of PbTiO$_3$ and TiO$_2$ grains about 1 mm, for bonding the electrical wire. The large grains of PbTiO$_3$ and TiO$_2$ were prepared by mixing the sintered blocks of 0.6 mol% Nb doped TiO$_2$ 1 mm in diameter and calcined PbTiO$_3$–10mol%TiO$_2$ powders, and then follow by sintering at 1200°C for 2~3 h in Ar. The sintered body consisted of large PbTiO$_3$ grains with about 1 mm in diameter, and polycrystalline TiO$_2$ blocks.

2.2. Resistivity Measurements and Microstructure Observations

The microstructures of the sintered samples were observed by using transmission electron microscopy. The microstructural constituent was analyzed with Energy Dispersion X-ray (EDX) microanalysis. Thin foil specimens were prepared by ion–beam milling.

Using two prove method, the resistivity of samples was measured from room temperature to 600°C on heating at a rate of 3°C/min in air. In–Ga alloys were used for the electrodes, which were covered with stainless steel sheets. The resistivity–temperature characteristics of the PbTiO$_3$–TiO$_2$ interface were directly measured by welding a fine Pt electrode wire on the surface of each grain. The Pt wire was fine enough to contact only one PbTiO$_3$ grain.

3. Results and Discussion

3.1. Microstructures and PTCR Properties

Fig. 2 exhibits the resistivity–temperature characteristics of PbTiO$_3$–30mol%TiO$_2$ ceramics sintered at 1000~1075°C for 2 h. The specimens sintered at 1000~1025°C provide the PTCR characteristics, but ones sintered above 1050°C do not. This suggests that the sintering temperatures required to reveal PTCR properties are below 1025°C.

Fig. 3 shows the transmission electron micrographs of PbTiO$_3$–30mol%TiO$_2$ samples sintered at 1025°C for 2 h, which yielded PTCR properties. Fig. 3(a) indicates that TiO$_2$ grains appearing as bright image were surrounded by dark PbTiO$_3$ grains. The dark field micrograph imaged with PbTiO$_3$ diffracted beam clearly reveals this morphology as shown in Fig. 3(b).

On the other hand, the transmission electron micrograph of PbTiO$_3$–30mol%TiO$_2$ ceramics sintered at 1075°C, which did not show PTCR properties, is shown in Fig. 4. TiO$_2$ grains appear to be linked together. This morphology is different from one shown in Fig. 3. This suggests that the formation of the linked TiO$_2$ grains could cause electrons to flow in the low-resistivity circuits of TiO$_2$ grains, resulting in vanishing PTCR properties. Judging from the micrographs of Figs. 3 and 4, the appearance or disappearance of PTCR properties is related to the morphology of the microstructure as schematically illustrated in Fig. 5. When TiO$_2$ grains are surrounded by the PbTiO$_3$ phase in Fig. 5(a), PTCR properties appear. But raising the sintering temperatures or prolonging the sintering time causes the formation of linked TiO$_2$ grains. Once TiO$_2$ grains grow and link together from one end of the sample to
Fig. 3. Transmission electron micrographs of PbTiO₃-30mol\% TiO₂ ceramics sintered at 1 025°C for 2 h, which yielded PTCR properties.

Fig. 4. Transmission electron micrograph of PbTiO₃-30mol\% TiO₂ ceramics sintered at 1 075°C for 2 h, which gives non-PTCR properties.

Fig. 5. Schematic illustration of the microstructures which yield (a) PTCR or (b) non-PTCR properties.

3.2. Origin of PTCR Properties

Referring the morphology of the microstructure in Fig. 3, it is expected that PTCR properties occur at the interface between PbTiO₃ and TiO₂ grains, as well as at the PbTiO₃-PbTiO₃ grain boundary. In order to further confirm the origin of PTCR properties, the resistivity-temperature characteristics of PbTiO₃-TiO₂ interface in the sample are directly measured as shown in Fig. 6. Fig. 7 shows the resistivity-characteristics measured between PbTiO₃ and TiO₂ grains, and between TiO₂ grains. PbTiO₃-TiO₂ interfaces exhibit PTCR properties at about 490°C, which is the Curie temperature of PbTiO₃. This observation is the first evidence in demonstration that PTCR properties originate from the interface of the ferroelectric (PbTiO₃) and the non-ferroelectric (TiO₂) materials. But no PTCR properties are observed at the TiO₂-TiO₂ interfaces.

3.3. BL PTCR Ceramics

Based on this observation, a new idea of PTCR ceramics with a boundary layer structure is proposed as follows; since PTCR properties occur at the interface between PbTiO₃ and TiO₂ grains, it is expected that the TiO₂ ceramics surrounded by the thin boundary layer of PbTiO₃ phases would enable to show PTCR properties. Therefore, the possibility of the formation of PbTiO₃-TiO₂ PTCR ceramics with such boundary layer structure is studied.

The boundary layer of PbTiO₃ around TiO₂ is formed by the same method used for the developments of BaTiO₃ boundary layer capacitor. Because PbO is formed by the reaction; PbO+TiO₂ → PbTiO₃, PbO coated on the surface of Nb-doped TiO₂ sample diffuses into TiO₂ bodies through grain boundaries, particularly above 883°C at which PbO
becomes liquid. As a result, PbTiO$_3$ could be formed along the grain boundaries of TiO$_2$ grains. The resistivity–temperature properties of TiO$_2$ sintered bodies with or without coating of PbO on the surface, are shown in Fig. 8. Niobium-doped TiO$_2$ samples, sintered at 1200°C for 2 h, exhibit no PTCR properties and show NTCR characteristics. But the PbO-coated samples show weak PTCR properties at 490°C.

Fig. 9 shows the corresponding electron micrographs of PbO-coated samples, (a) bright field and
4. Conclusions

The present paper describes the relationship of the microstructure and PTCR properties. The following conclusions were obtained.

(1) PTCR properties occur at the interface of ferroelectric (PbTiO₃) and non-ferroelectric (TiO₂) grains.

(2) PTCR properties in PbTiO₃–TiO₂ ceramics disappear when TiO₂ phases are linked together and form the electrical short circuit.

(3) The boundary layer (BL) type PbTiO₃–TiO₂ ceramics show PTCR properties at 490°C. They are formed by annealing the sintered TiO₂ bodies with the PbO painted on the surface. TEM analysis confirmed the existence of PbTiO₃ along the grain boundary of TiO₂ grains.

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REFERENCES

1) O. Saburi: J. Phy. Soc. Jpn., 14 (1959), 1159; J. Am. Ceram. Soc., 44 (1961), 54.
2) M. Okada, T. Iijima and M. Homma: Ceramic Microstructure '86, "Role of Interface", ed. by A. Pask and A.G. Evans, Plenum Publishing, (1988), 697.
3) M. Okada, T. Iijima and M. Homma: Sintering '87, ed. by S. Somiya, Elsevier Applied Sci. Pub., London, (1988), 884.
4) H. Nemoto and I. Oda: J. Am. Ceram. Soc., 63 (1980), 398.
5) S. Waku: J. Inst. Elect. Comm. Engrs, Jpn., 49 (1966), 37.
6) P. A. Marshall, Jr. W. R. Buessem and K. Forland: Am. Ceram. Soc. Bull., 42 (1963), 219.
7) D. E. Rase, B. Jaife, W. R. Cook and H. Yaffe: Piezoelectric Ceramics, Academic Press, London/New York, (1971), 117.