

# BaTiO<sub>3</sub>-based positive temperature coefficient of resistivity ceramics with low resistivities prepared by the oxalate method

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Positive temperature coefficient of resistivity (PTCR) ceramics with low resistivities at room temperature were obtained by using oxalate-derived barium titanate powders. The average room-temperature resistivity of the PTCR ceramics was 4 Ω cm, and the magnitude of their PTCR jump was around four orders with a voltage proof of more than 50 V mm<sup>-1</sup>. These PTCR properties are significantly influenced by the calcination temperature of the starting materials and by the resultant properties of the ceramic bodies. The microstructure of such-PTCR ceramics with a low room-temperature resistivity produced in this study was found to be rather heterogeneous. Complex impedance measurements revealed that the resistivity of the present PTCR materials was determined predominantly by the grain-boundary resistance even at room temperature.

## 1. Introduction

Since the positive temperature coefficient of resistivity (PTCR) effect was found by Haayman *et al.* [1], many investigations have been performed with respect to the semiconductive mechanism and the resistivity anomalous mechanism of PTCR ceramics. In addition, a number of applications have been made by using this unique property [2]. Examples of applications include heaters and thermal sensors in the early days, and more recently, overcurrent regulators of low-power circuits. PTCR ceramics which have low resistivity at room temperature could be potential candidates for overcurrent regulators of low-power circuits.

It is well-known that the PTCR effects of semiconducting barium titanate ceramics are affected by their preparation conditions: source materials, additional elements, sintering processes, etc. Semiconducting barium titanate ceramics are conventionally prepared by using semiconducting barium titanate powders as starting materials, which are produced by the solid-state reaction of BaCO<sub>3</sub> and TiO<sub>2</sub> [3, 4]. A few papers have reported that some semiconducting barium

titanate ceramics were obtained by using barium titanate powders prepared from barium titanyl oxalate [5, 6]. PTCR ceramics treated in these reports, however, showed resistivities of more than 10 Ω cm [7], and few papers discussed the resistivities for bulk and grain boundaries separately [8].

The present work was concerned with BaTiO<sub>3</sub>-based PTCR ceramics with low resistivity (4 Ω cm) at room temperature and with a PTCR jump of about four orders of magnitude, which were produced by using oxalate-derived pure barium titanate as starting materials. The influence of the microstructure on the electrical characteristics has been discussed on the basis of observation of the microstructure by a scanning electron microscope (SEM) and a transmission electron microscope (TEM) and measurement of the impedance at various frequencies.

## 2. Experimental procedure

### 2.1. Materials and sample preparation

Barium titanate powders (> 99.9%; Central Glass Co. Ltd) as starting materials, were prepared by

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calcination of barium titanate, BaTiO<sub>3</sub> (C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, produced by the Clabaugh method [9], at various temperatures (750–1100 °C) in air. Strontium titanate powders (> 99.9%; Central Glass Co. Ltd) were prepared from strontium titanate oxalate at 800 °C in air. Calcium titanate powders were prepared by solid-state reaction of calcium carbonate (> 99.9%; Central Glass Co. Ltd) and titanium oxide (> 99.9%; Toho Titanium Co. Ltd) at 1100 °C in air. Lead titanate powders were prepared by solid-state reaction of lead oxide (> 99.5%; Mitsui Metal Industry Co. Ltd) and titanium oxide at 850 °C in air.

The particle sizes of barium titanate powders prepared at various temperatures were estimated from BET values. X-ray powder diffraction patterns of these powders were measured by using an X-ray diffractometer (Rigaku; RINT-1000, CuK<sub>α</sub>).

The starting materials were mixed in a ball mill (250 ml). The composition was described by the formula Ba<sub>0.675</sub>Sr<sub>0.045</sub>Ca<sub>0.125</sub>Pb<sub>0.155</sub>TiO<sub>3</sub> (Curie point ~150 °C) with a small amount of added lanthanum SiO<sub>2</sub>, and manganese. The mixed powders with binder (PVA 0.5 wt %) were pressed into pellets (25 mm diameter, 2.5 mm thick) whose average green density was 2.7 g cm<sup>-3</sup>. The sintering of the pellets was performed at 1300 °C in air. The combination of heating-cooling rate and hold time was either 300 °C h<sup>-1</sup>, 0.5 h or 200 °C h<sup>-1</sup>, 1.0 h, which was controlled by a programmable furnace. The average size of the ceramic pellets after sintering was 19 mm diameter and 1.9 mm thick.

The ceramic samples produced using barium titanate powders which were prepared at 800 and 1100 °C from oxalate are referred to here as samples A and B, respectively.

## 2.2. Electrical measurements

An In–Ga alloy was rubbed on both surfaces of the sample pellet as electrodes to provide ohmic contacts. D.c. resistivities of the specimens were measured by a two-probe method at room temperature (25 °C) up to 350 °C. The measurement was made every 5 °C by a programmable thermostatic air bath.

The complex impedance measurements of specimens were made over the frequency range from 5 Hz–13 MHz at room temperature by using an impedance analyser (YHP; 4192ALF) with correction for the inductance of the measurement leads at every frequency. For impedance measurements, the ceramic pellets were cut into rectangular chips (about 2 mm × 3 mm, 5 mm in length). Silver electrodes were plated on both surfaces of the chip, on to which two leads were soldered.

## 2.3. Observation of microstructures

The microstructures of the ceramic bodies were observed by using a scanning electron microscope (SEM; Jeol, JSM-T200) and a transmission electron microscope (TEM; Jeol, JEM-2000FX).

## 3. Results and discussion

### 3.1. Characterization of starting materials

Fig. 1 shows BET and average particle sizes (calculated from BET values by assuming a spherical particle shape) of barium titanate powders calcined at various temperatures. BET of barium titanate powders tends to decrease with increase in calcination temperature of oxalate. In other words, the average particle size increases with increase in calcination temperature.

The X-ray diffraction patterns of barium titanate powders are shown in Fig. 2. Barium titanate powders prepared at 800 °C (Fig. 2b) shows a pseudo-cubic structure in which the reflections 002 and 200 cannot be resolved into two peaks. On the other hand, barium titanate powders prepared at 1100 °C (Fig. 2a) show a tetragonal structure whose reflections 002 and 200 can be resolved into two peaks. This structure change depends on the particle size (surface effect).

### 3.2. Electrical properties

Fig. 3 shows the resistivity–temperature curves for samples A and B. The resistivity of sample A at room temperature is lower than that of sample B. The magnitude of the PTCR jump of sample A, however, is larger than that of sample B.

The resistivity at room temperature, the resistivity–temperature coefficient and the voltage proof of the PTCR ceramics are plotted versus preparation temperature of barium titanate powders as a starting

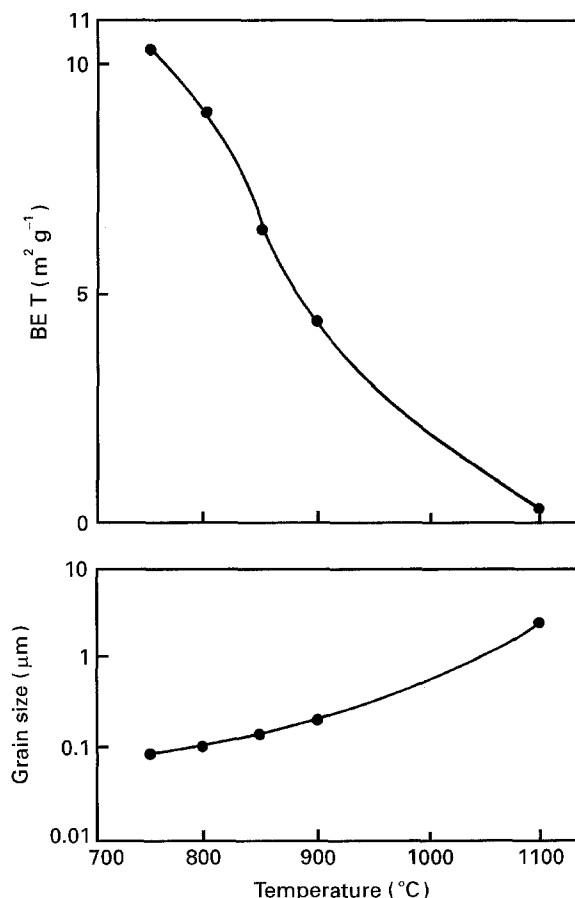


Figure 1 BET and average particle size of oxalate-derived barium titanate powders prepared at various calcination temperatures.

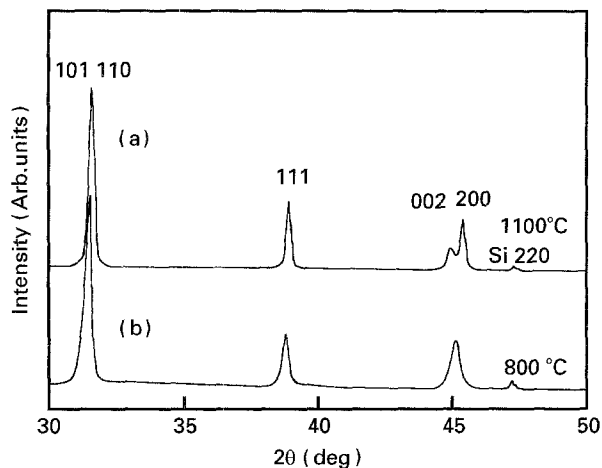


Figure 2 X-ray diffraction patterns ( $\text{CuK}\alpha$ ) of barium titanate powders prepared at (a) 1100°C and (b) 800°C. Pattern (a) represents tetragonal structure, and (b) represents pseudo-cubic structure.

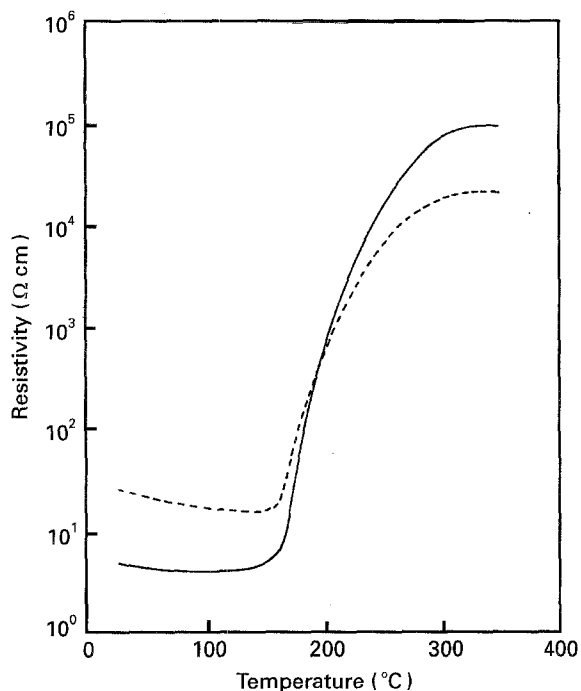


Figure 3 Typical resistivity-temperature curves of the PTZR ceramics (—) for sample A, (---) sample B. The ceramic samples were produced under sintering conditions of  $1300^\circ\text{C h}^{-1}$ ,  $200^\circ\text{C h}^{-1}$ .

material, in Fig. 4. The resistivity-temperature coefficient, ( $\alpha$ ), which coincides with the magnitude of the PTZR jump, is defined as

$$\alpha = \frac{2.303 \times \log(R_b/R_a)}{T_b - T_a} \times 100 (\% \text{ } ^\circ\text{C}^{-1}) \quad (1)$$

where  $R_a$  ( $\Omega\text{ cm}$ ) is twice the resistivity value at room temperature,  $T_a$  ( $^\circ\text{C}$ ) is the temperature where the resistivity is  $R_a$ ,  $T_b$  ( $^\circ\text{C}$ ) is  $T_a + 50$ ,  $R_b$  ( $\Omega\text{ cm}$ ) is the resistivity at  $T_b$ . The high preparation temperature of barium titanate powders as a starting material resulted in high resistivity of the PTZR ceramics at room temperature. The resistivity-temperature coefficient and the voltage proof increased with increasing preparation temperature of barium titanate powders up to

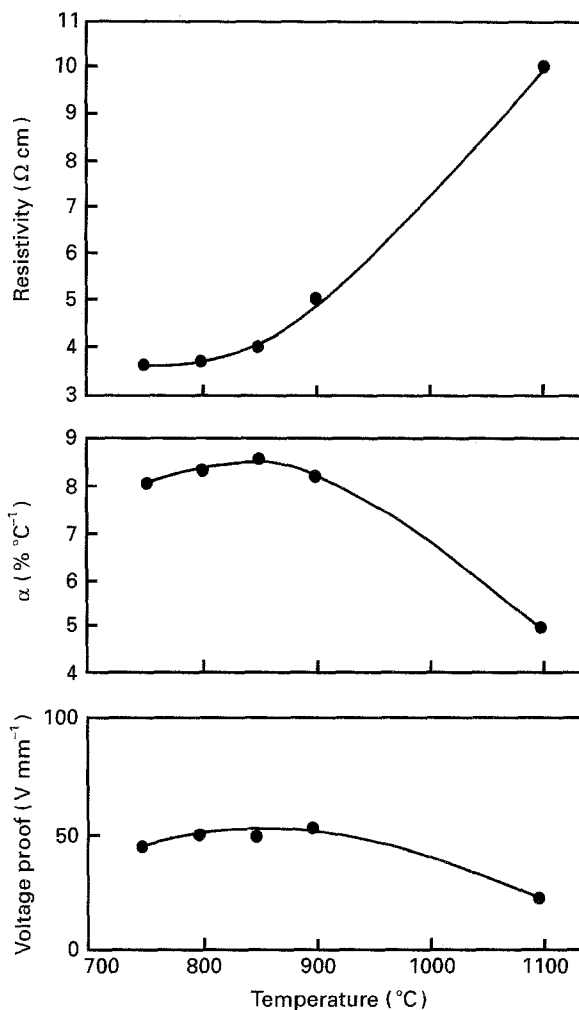


Figure 4 Resistivity, magnitude of the PTZR effect,  $\alpha$ , and voltage proof of the PTZR ceramics plotted against calcination temperature of the starting materials. The ceramics were sintered in air at  $1300^\circ\text{C}$ , and the heating and cooling rate was controlled at  $300^\circ\text{C h}^{-1}$ .

$900^\circ\text{C}$ , but then decreased rapidly above this temperature. In previous papers, ordinary PTZR ceramic materials with low resistivities showed a small PTZR jump and low voltage proof. Note that the PTZR ceramics (sample A) exhibited a large PTZR jump and a high voltage proof in spite of having low resistivity at room temperature. This property will facilitate the application of these PTZR ceramics to some devices in the near future.

### 3.3. Microstructure of the PTZR ceramics

The relative density of sample A was 90%, while that of sample B varied over the range 80%–85%, which was calculated assuming that the ideal density of the ceramic body was  $6.04 \text{ g cm}^{-3}$ .

Fig. 5 shows scanning electron micrographs of as-sintered surfaces and thermally etched surfaces (after polishing of the surface and heat treatment at  $1220^\circ\text{C}$ ) of the ceramic bodies; Fig. 6 shows transmission electron micrographs. The microstructure of the PTZR ceramic bodies is affected by the calcination temperature of barium titanate powders as starting materials. The ceramic body of sample A is constituted by

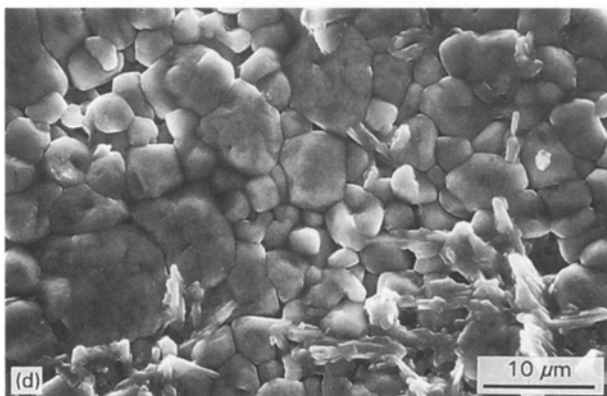
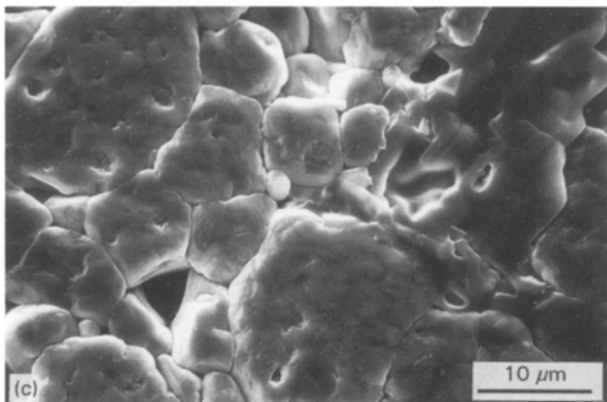
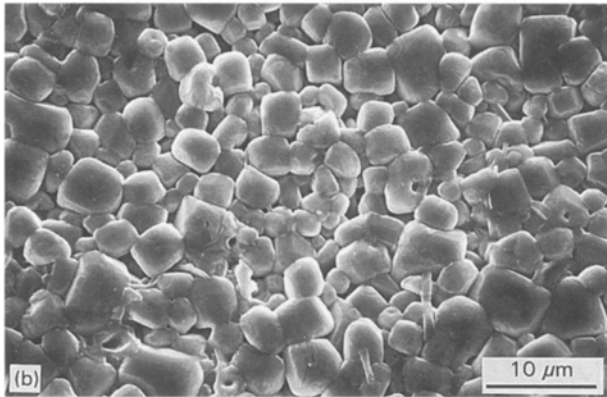
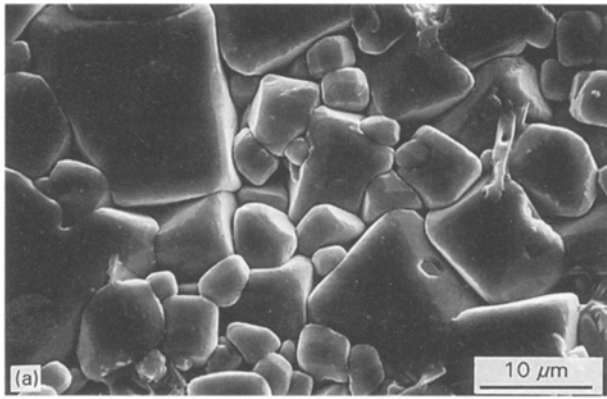


Figure 5 Scanning electron micrographs of (a, b) as-sintered surfaces and (c, d) thermally etched surfaces of the PTCR ceramic bodies: (a, c) sample A, (b, d) sample B.

heterogeneous grains whose sizes are 10–20 μm and 1–5 μm. Spaces between the large grains (> 10 μm) in the ceramics are filled with small grains. Sample B, however, is constituted by homogeneous grains whose average size is about 5 μm.

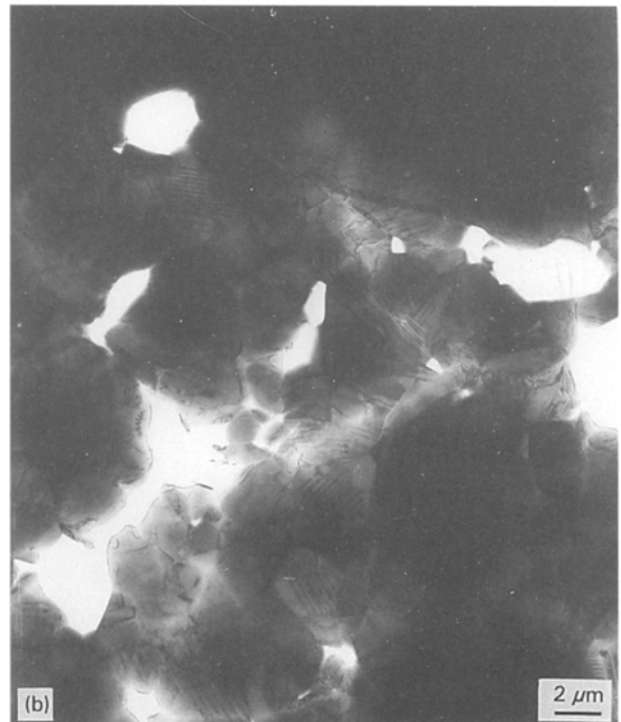
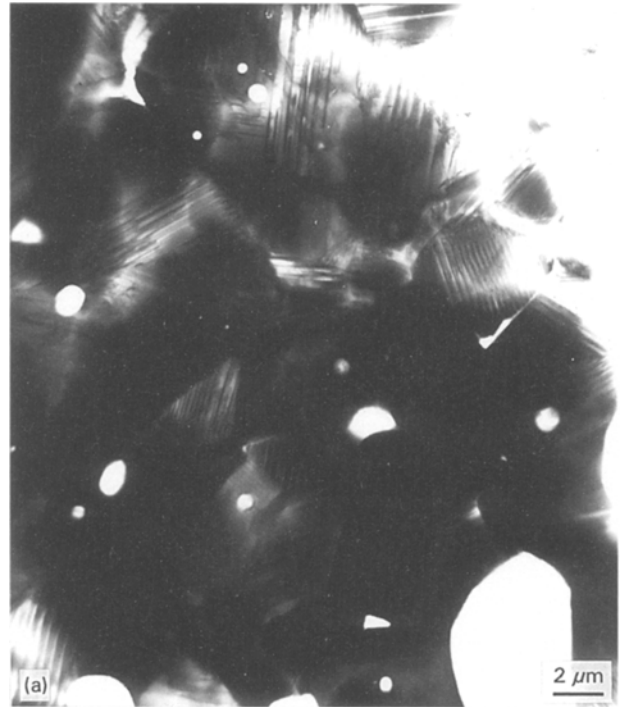


Figure 6 Transmission electron micrographs of the PTCR ceramic bodies: (a) sample A, (b) sample B.

We have considered the relation between the starting materials (barium titanate) and the microstructure of the PTCR ceramics as follows. The particles of barium titanate powders with a high calcination temperature of oxalates can be called “rigid”: they are large in size and have high crystallinity. On the other hand, particles of barium titanate powders prepared at low temperature can be called “soft”: they are small in size and have low crystallinity. Because of a high reactivity of the “soft” powders, they grow so fast during sintering that the average grain size of the ceramics can become large. On the other hand, the

“rigid” starting material grow so slowly that the grain size can become small and homogeneous.

### 3.4. Contributions of microstructure of PTCR characteristics

The complex-plane impedance plots (Cole–Cole plots) of the PTCR ceramics specimens at room temperature are shown in Fig. 7. The fitting curves were extrapolated on the basis of the assumption that the line was completely circular and the centre of the circle did not always lie on the real axis. Fig. 8 explains an equivalent circuit for the PTCR ceramics.  $R_1$  represents the total resistance of the grains and  $R_2$  that of the grain boundaries.  $C_2$  is the total capacitance of the grain boundaries. The complex impedance,  $Z$ , is given by

$$Z = Z' + jZ'' \quad (2a)$$

$$Z' = R_1 + \frac{R_2}{1 + R_2^2 C_2^2 \omega^2} \quad (2b)$$

$$Z'' = -\frac{R_2 C_2 \omega}{1 + R_2^2 C_2^2 \omega^2} \quad (2c)$$

where  $Z'$  and  $Z''$  are real and imaginary parts of  $Z$ , respectively.  $\omega$  is the angular frequency.

On the basis of Equation 2, the resistance in the grains and that in the grain boundaries could be separated. The resistivities in grains of sample A (22  $\Omega$ ) and sample B ( $\sim 30 \Omega$ ) are not very different at room temperature, while the estimated resistance in grain boundaries of a sample A specimen is about 21  $\Omega$  and that of a sample B specimen is 320  $\Omega$ . As mentioned above, the average grain sizes of samples A and B are 10 and 5  $\mu\text{m}$ , respectively. According to this estimation, there are five hundred grain boundaries in a 5 mm length on a straight line for sample A, while

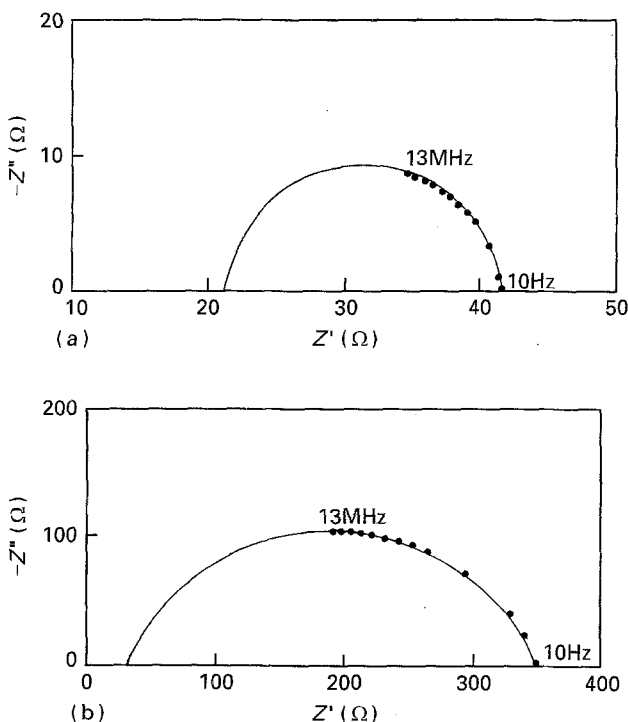


Figure 7 Impedance Cole–Cole plots of the PTCR ceramic specimens: (a) sample A, (b) sample B.  $Z = Z' + jZ''$ .

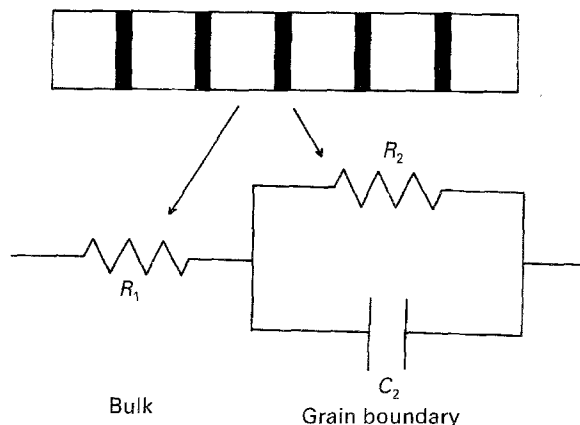


Figure 8 Equivalent circuit for complex impedance measurements of PTCR ceramics.  $R_1$ ,  $R_2$  and  $C_2$  represent total resistance of the grain bulk, that of the grain boundaries and the total capacitance of the grain boundaries, respectively.

there are a thousand boundaries in the same length for sample B. The resistance of one grain boundary for sample A is 0.04  $\Omega$  (21/500) and that for sample B is 0.32  $\Omega$  (320/1000). Although the lack of information about the thickness of the grain boundary made direct estimation of the resistivities ( $\Omega\text{cm}$ ) impossible, the total resistance at one grain boundary could be compared using the above estimation.

The capacitances of the grain boundary are 420 and 38 nF for samples A and B, respectively. These are calculated on the basis of Equation 2 by using the estimated  $Z'$  value at 13 MHz and the extrapolated  $R_1$  and  $R_2$  values. The relaxation time for both samples is of the same order ( $\sim 10$  ps). The difference in the resistance and the capacitance of the grain boundary between the two samples can be explained only by the difference in the thickness of the grain boundary. The Cole–Cole plot (Fig. 7), however, is quite different for the two samples; the plot for sample A forms a perfect circular arc and the centre is on the real axis, which suggests a single relaxation. On the other hand, the plot for sample B is heavily depressed and the centre of the circle is not on the real axis, which suggests a multiple relaxation. From these results, it is concluded that the grain boundaries in sample A are constituted by only one phase in spite of its heterogeneous microstructure, while those in sample B are constituted by heterogeneous phases. The difference in electrical properties between the two samples is mainly caused by the differences in the grain boundaries.

The heterogeneous phase in sample B described above might be caused by the contamination of  $\text{ZrO}_2$  from  $\text{ZrO}_2$  balls used for the ball milling. 1400 and 2500 p.p.m. contaminated  $\text{ZrO}_2$  were detected for samples A and B, respectively. These may affect the PTCR effect. Further study on the grain boundary of the ceramics is now under way in which not only the impurity effect but also the impedance measurement above the Curie point will be investigated.

### 4. Conclusion

The PTCR ceramics whose resistivities were 4  $\Omega\text{cm}$  at room temperature were obtained by using

oxalate-derived barium titanate powders as the starting material. In spite of such low resistivity at room temperature, the magnitude of the PTCR jump was larger and the voltage proof was higher compared with those of the PTCR ceramics published in previous papers.

These characteristics were influenced by their microstructure, particularly the properties of the grain boundaries, which were estimated by the complex impedance measurement. The grain boundary of the PTCR ceramics obtained by using the "soft" barium titanate powders prepared at lower calcination temperature (800 °C), were composed of homogeneous phases in spite of the heterogeneous microstructures of the ceramic bodies. On the other hand, the "rigid" barium titanate powders prepared at higher calcination temperature (1100 °C) produced ceramics having heterogeneous grain boundaries. The ceramics prepared from the "soft" barium titanate had lower resistivity, larger magnitude of PTCR effect and higher voltage proof than those of ceramics prepared from

the "rigid" barium titanate. Further discussion about these phenomena will be made in the future.

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*Received 17 May 1994*

*and accepted 20 January 1995*