

Electrical Characteristics of (BaSr)TiO₃-based PTCR Devices under the Electric Field

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ABSTRACT

Semiconducting (Ba · Sr)TiO₃ ceramic device, which shows the PTCR effect, has been usually used as a current limiter. In this case, the device should endure the condition under the high electric field. In this study, the dynamic electrical properties of the PTCR device under high voltage has been evaluated. Two different formulated powders were used and the sintered bodies exhibited the different grain size and porosity. The wide range of characterization such as complex impedance spectroscopy, microstructure, I-V characteristics and voltage dependence of resistivity of the samples were performed. The PTCR effect of the specimen containing coarse grains was very sensitively dependent on the AC electric field, showing that it was inversely proportional to the grain boundary potential barrier. The withstanding voltage was proportional to the potential barrier of grain boundary.

Key words : PTCR effect, BaTiO₃, Electric field, Withstanding voltage

1. Introduction

The semiconducting BaTiO₃-PTCR(Positive Temperature Coefficient of Resistivity) ceramics are widely used as temperature sensors, self regulating heaters, over-current and over-temperature protectors, motor starters and degaussers due to their special R-T, I-V and I-t characteristics. The PTCR effect is known to be originated by the electrical back-to-back double Schottky barrier^{1,2)} at grain boundary due to the decrease of permittivity by the phase transition of BaTiO₃ ceramics from ferroelectric to paraelectric above the Curie temperature.³⁾

It is known that the slope and the maximum value of the resistance jump in the PTCR device greatly depend on an applied electric field. This voltage dependence of the PTCR effect, in particular under high voltage, is an important factor to be considered in circuit designing for electrical goods. This is because even if a PTCR device showed high resistance at small signal, the resistance could be greatly decreased at large signal. Moreover, in the case of degaussing circuit, low resistance, high withstanding voltage and gradual attenuation current slope of the PTCR device are required because the technical trends in color TV and monitor prefer high definition and wide screen. However, most of the previous studies on PTCR effect have been focused on the development of materials having higher resistance jump by controlling additives and sintering conditions.^{4,6)} This is why the static electrical properties at low electric voltage have been mostly reported so far. As the technical trends

are changing, the dynamic electrical properties of PTCR device under high voltage became more influential than ever.

In this study, the voltage dependence of the PTCR effect has been examined using commercial formulated powders. The grain and grain boundary resistance of the samples are measured by the complex impedance spectroscopy method. The AC and DC electric field was applied to the samples to evaluate the voltage dependence of the PTCR effect, and the results were analysed with respect to microstructure of the samples.

2. Experimental

Two commercial grades of formulated powders of PT (Toho Co., Japan, grade# 0510) and PH2 (Hayashi Co., Japan, grade# B-06) for the PTCR device were sintered at different conditions, as shown in Table 1, in order to make the low resistance samples. The compositions of PT and PH2 powders were (Ba_{0.746}Sr_{0.25}Y_{0.004})TiO₃ and (Ba_{0.726}Sr_{0.2}Ca_{0.07}Y_{0.004})TiO₃, respectively. 1 mol% of excess TiO₂ and 1 wt% of SiO₂ were added to increase sinterability and 0.05 mol% MnCO₃ was also added to increase PTCR jump.^{4,13)}

The green pellets were sintered then electroded with Ni non-electrolytic plating for an ohmic contact and Ag silk-printing was followed. The final dimensions of the sintered samples were 14 mm in diameter and 2.5 mm in thickness. The samples were polished for an observation of microstructure. Porosity was figured out by the point counting method using an image analyzing system. Grain size measurement of thermally etched specimen was performed by line intercept method.⁷⁾

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Table 1. Initial Powder Characteristics and their Sintering Conditions

Sample	Tap density; N=0 (g/cm ³)	Forming density (g/cm ³)	Heating rate (°C/hr)	Sintering temperature (°C)	Soaking time (min.)	Cooling rate (°C/hr)
PT	1.3 ± 0.1	3.2 ± 0.05	200	1320	120	60
PH2	1.6 ± 0.1	3.1 ± 0.04	200	1330	120	100

The complex impedance spectroscopy method⁸⁾ was employed for the measurement of grain and grain boundary resistance, respectively, using a LF Impedance Analyzer (HP4192A) from 5 Hz to 13 MHz. The voltage dependence of the PTCR effect was analysed under the AC and DC fields, respectively. The voltage dependence of resistance and the withstanding voltage were measured by a digital oscilloscope (Tektronix TDS410A) and a multimeter (Advantest TR6846).

The voltage dependence of resistance was defined as *K* from the Eq. 1. According to Ohm's law, the *K* should be 1. However, because of the voltage dependence of resistance in the PTCR samples, the *K* is usually less than 1.

$$I = \frac{V}{K \cdot R_{PTCR}} \tag{1}$$

where, *K* : Voltage dependence constant, *I* : Current (A), *V* : Voltage (V) and *R*_{PTCR} : Resistance of PTCR device (ohm).

3. Results and Discussion

The sintered density, porosity and mean grain size of the PTCR samples manufactured by the PT and PH2 formulated powders are represented in Table 2, and their microstructures are shown in Fig. 1. The PT samples show higher sintered density around 95.3 ± 0.08% and smaller grain size around 7.1 ± 1.4 μm than that of the PH2 samples. Because large grains form large intergranular pores in the microstructure,⁹⁾ the tendency that a sample composed of large grains represents low density are well matched. The PT samples revealed more irregular grain size distribution

Table 2. Sintering Characteristics of Samples

Sample	Sintered density (g/cm ³)	Porosity (%)	Average grain size (μm)
PT	5.59 ± 0.06	5 ± 1	7.1 ± 1.4
PH2	5.52 ± 0.08	11 ± 2	11.0 ± 0.6

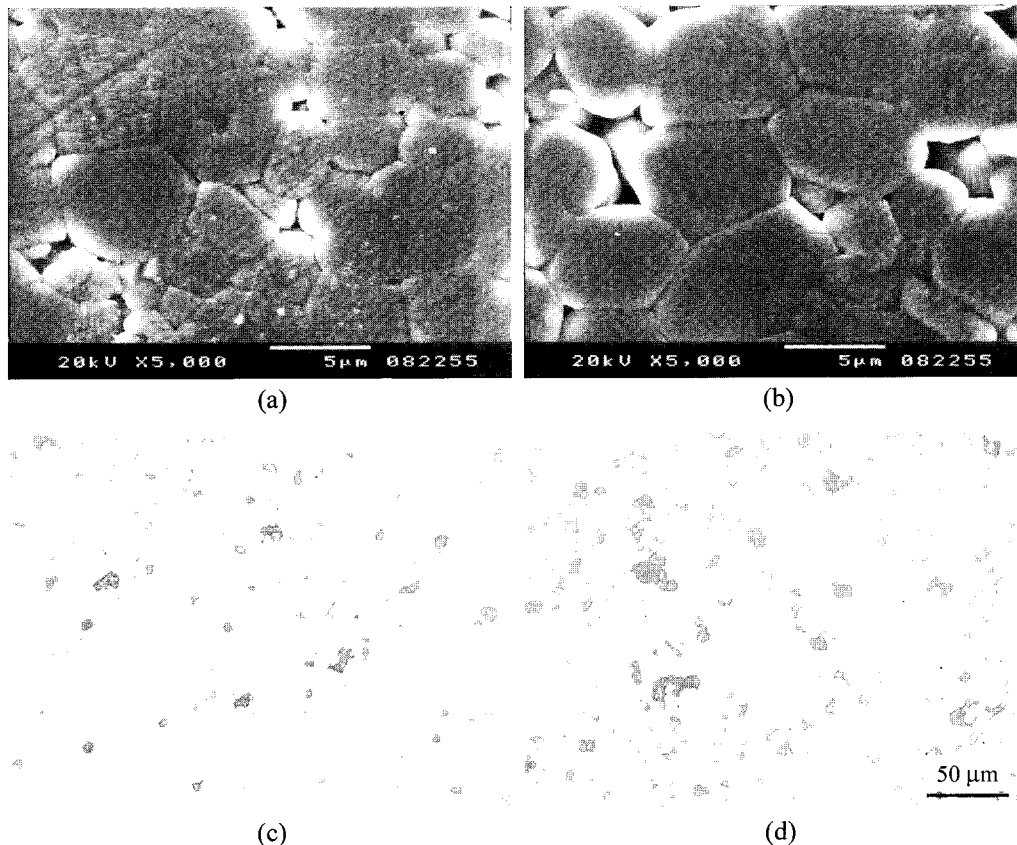


Fig. 1. Microstructures of thermally etched samples, (a) PT and (b) PH2 and polished specimen, (c) PT and (d) PH2.

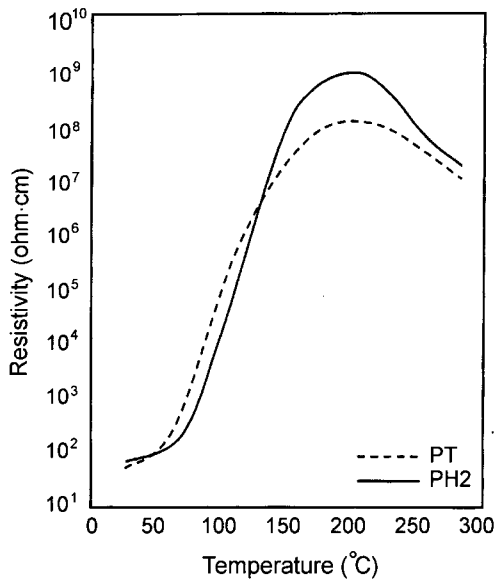


Fig. 2. Resistivity-temperature characteristics of PT and PH2 samples.

than that of the PH2.

Resistivity-temperature curve shown in Fig. 2 revealed a typical PTCR effect. The room temperature resistivity of the samples was in the range of 50~70 Ω · cm. The Curie temperature of the PT and PH2 samples was 55°C and 60°C, respectively. It is well known that the Sr substitution in Ba site shifts down the Curie temperature of BaTiO₃ ceramics.¹⁰ Therefore, this must be caused due to the different content of Sr in the PT and PH2 composition; namely the PT sample contains more Sr elements than the PH2 sample does. The PTCR jump of PH2 sample was reached up to 10⁹ Ω · cm above Curie temperature, which is higher than that of the PT. It is because pores act as fast diffusion path of oxygen for oxidizing the grain boundaries, PTCR effect enhanced by the creation of cation vacancies near grain boundaries, which plays a role of acceptor.¹¹ Another notable thing is that the slope of the PTCR curve above Curie temperature for the PH2 sample is quite steep.

Fig. 3 shows the complex impedance pattern of each samples. The dimension of the samples was uniformly adjusted

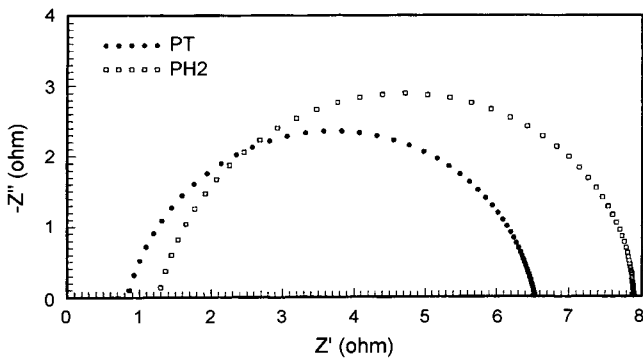


Fig. 3. Complex impedance spectra of PT and PH2 samples.

before the measurement. The grain resistance of the PH2 sample is slightly higher than that of the PT and the grain boundary resistance of the PH2 is much higher than that of the PT. It is well known in PTCR samples that the grain boundary resistance dominate the whole resistance of the sample, and this phenomenon is consistent with room temperature resistivity of the samples shown in Fig. 2. It is reported that the grain boundary resistance is directly related with acceptor state density at grain boundaries, which is considered to be segregated acceptor ions^{12,13} or adsorbed oxygen.¹⁴ This behavior seems to be caused by compensation of acceptors at grain boundaries by the difference of normal component of spontaneous polarization between two adjacent grains.¹⁵ From the maximum resistivity and slope of resistivity jump in Fig. 2, the acceptor state density of the PH2 sample at grain boundaries is believed higher than that of the PT sample. Higher grain boundary resistance measured by the complex impedance spectroscopy supports this phenomena.

Fig. 4 (a) and (b) show the voltage dependence constant *K*

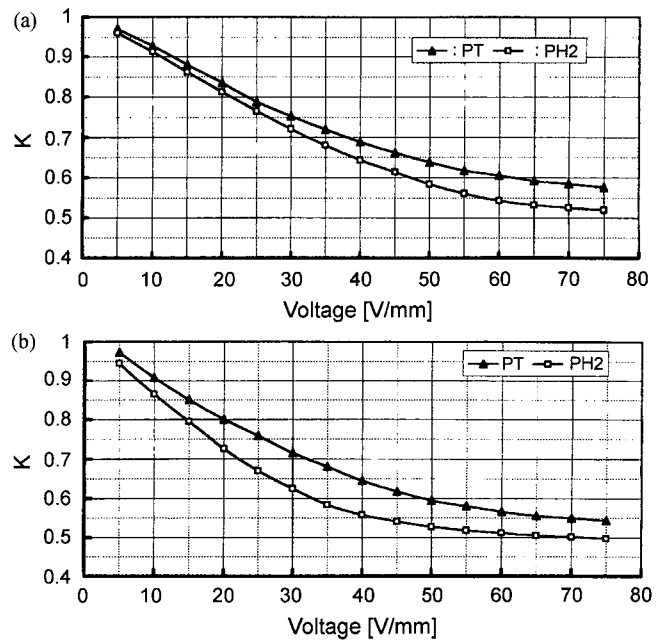


Fig. 4. Voltage dependence of resistance of PT and PH2 samples under (a) DC and (b) AC electric field.

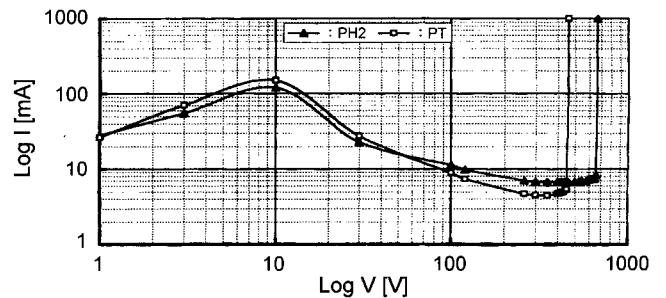


Fig. 5. I-V characteristics of PT and PH2 samples.

Table 3. Electrical Properties of the (BaSr)TiO₃-based PTCR Ceramics

Sample	Resistance (Ω)		Ts ($^{\circ}$ C)	Jump ($\times 10^6$)	Withstanding voltage (V)	Barrier height (eV)
	Grain	Grain boundary				
PT	0.67	5.70	55	2.05	450	0.71
PH2	0.83	6.63	60	15.55	650	0.74

as a function of applied voltage (electric field) to the samples. Both of DC and AC voltage were applied respectively. The K value under the DC electric field was higher than AC. It is believed due to the fact that the maximum AC voltage is $\sqrt{2}$ times higher than the root mean square value. For the application of the PTCR device under high electric field, higher K value is preferred. Regardless of DC and AC, K decreased as the applied voltage increased, and K is almost saturated above 60~70 V/mm. The PH2 sample, which has higher maximum resistivity, showed more sensitive response of K .

I-V behavior of the PT and PH2 samples was examined in order to find out the relationship between voltage dependence of resistance and withstanding voltage (breakdown voltage), and the results are shown in Fig. 5. The withstanding voltages of samples for the PT and PH2 were 450 V and 650 V, respectively (Table 3). A sample composed of fine grains has more grain boundaries in an unit volume than a sample composed of coarse grains. In this case, it is expected that the withstanding voltage of fine-grained sample will be higher than that of coarse-grained because fine-grained sample possesses more grain boundaries to overcome. However, even though the average grain size and the porosity of the PH2 sample are larger than that of the PT sample, the PH2 sample showed higher withstanding voltage. The calculated potential barrier heights¹⁶⁾ of the PT and PH2 samples from the slope of resistivity jump using the Arrhenius equation in the region of 200~300 $^{\circ}$ C were 0.71 eV and 0.74 eV, respectively. It is well known that the PTCR effect of semiconductive BaTiO₃ ceramics sensitively influenced by donor concentration, acceptor state density, and depth of acceptor level, each of which indirectly affected by processing parameters such as sintering temperature, sintering atmosphere, cooling rates, porosity, grain size, etc.¹⁷⁾ However, from the I-V characteristics, it is thought that the withstanding voltage depends mostly on the potential barrier height, which is closely related to the acceptor state density at grain boundaries.

4. Conclusion

The sample with higher porosity resulted in better the PTCR performance due to the easier and faster access of oxygen into the interior of sample, which oxidized grain boundaries. The complex impedance spectroscopy analysis for the sample with higher porosity showed higher grain boundary resistivity which supports the grain boundary oxidation. The voltage dependence of resistance K is decreased

as the electric field increased. Around 60-70 V/mm of electric field, K decreased to 0.5, which signifies that the resistivity of PTCR device fell 50%.

Withstanding voltage of the sample was proportional to the potential barrier, which is directly related to the acceptor state density at grain boundaries. Therefore, grain size and porosity control is believed a way to engineer the voltage dependence of PTCR effect as well as withstanding voltage of PTCR device for the application under high electric fields.

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