

## Effect of re-oxidation firing on PTCR properties of Sm-doped barium titanate ceramics

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The effect of reduction and re-oxidation firing on the PTCR properties of Sm-doped barium titanate ceramics was investigated for the application in multilayered PTC thermistors. The lattice parameters  $a$ , and  $c$  decreases monotonically with increasing oxygen concentration in the re-oxidation atmosphere, which seems to be related with an electrostatic Coulomb interaction between an oxygen vacancy and the nearest other atoms. With an increase in the oxygen concentration, the resistivity at room temperature and the magnitude of the resistivity jump as a function of temperature increased in the region of oxygen concentrations of 0-10%. However, the resistivity at room temperature and the magnitude of the resistivity jump is nearly constant and saturated in the region of oxygen concentrations of 10-20%. This phenomenon is considered to be related with the variation of oxygen and barium-vacancy concentrations near grain boundaries.

**Key words:** PTC, re-oxidation, resistivity, jump characteristics, and oxygen content.

### Introduction

Ceramics with a positive temperature coefficient of resistance (PTCR) [1, 2] based on barium titanate ( $\text{BaTiO}_3$ ) are important functional materials that have found various applications such as in thermal sensors, self-regulating heaters and over-current protecting devices [3, 4]. Recently, there have been many studies to improve the safety and reliability of electronic circuits and devices that are essential requirements for their applications. A PTC thermistor protects a circuit through increases of the resistance value by self-heating occurring from an overcurrent. If the cause of the over-current disappears, the resistance value will decrease to a low value (normal state). So, the component can be used repeatedly. The resistance value in the normal state should be low in order to reduce power consumption or signal attenuation. However, most PTC ceramic thermistors are in a bulk shape having only surface electrodes, which limits a lower resistance and miniaturization of PTC ceramic thermistors. PTC thermistors with a multilayer structure have been studied to solve the above problems [5, 6]. As the firing temperature of  $\text{BaTiO}_3$ -based PTC is near 1300 °C, if a multilayer PTC thermistor is fired in an ambient atmosphere, the inner metal electrode will oxidize and the PTC properties will disappear. Therefore, multilayer PTC thermistors must be fired in a reducing atmosphere to protect the metal electrode from oxidation. Ni as the inner electrode is usually used from a consideration of Ohmic contact between Ni and ceramic body.

Undoped  $\text{BaTiO}_3$  ceramics are an insulators due to their large band gap ( $> 3$  eV), which, however, can be reduced to a much lower value by introducing small amounts of trivalent ions (such as La, Y, Sm, etc) in the Ba-sites to produce n-type semiconduction [7]. Such a semiconducting system exhibits an anomalous increase in the resistivity with temperature near the ferroelectric Curie temperature ( $T_c$ ). This anomalous increase of resistance as a function of temperature is the jump characteristic of a PTCR. Similarly, pentavalent dopants (Sb, Nb, Ta) can also produce semiconducting ceramics by substitution at Ti-lattice sites. Some transition metal ions (Mn, Fe, V) have been shown to enhance the PTCR effect [8]. As  $\text{BaTiO}_3$  is the major ingredient in the composition and the dopant concentrations are very low, the purity level of the starting materials must be controlled precisely.

Some theoretical models have been suggested to explain the anomalous increase in the resistivity. So far, the most acceptable explanation for the PTC phenomenon was originally proposed by Heywang [7] and it was later modified by Jonker [8]. This model is based on the presence of grain boundary depletion layers consisting of two-dimensional surface acceptor states, where absorbed oxygen atoms or segregated acceptor ions are present as impurities. These surface acceptor states take up conduction electrons from the neighborhood and a negative charged boundary layer is formed followed by a positive space charge forming a symmetrical potential barrier. This theory successfully describes the anomalous resistivity at high temperatures above the Curie temperature,  $T_c$ , but it is unable to explain the decrease of potential barrier in the ferroelectric region ( $T < T_c$ ). Taking into account the interrelation between the conductive and ferroelectric properties of  $\text{BaTiO}_3$  ceramics, a theoretical approach was recently developed which extends

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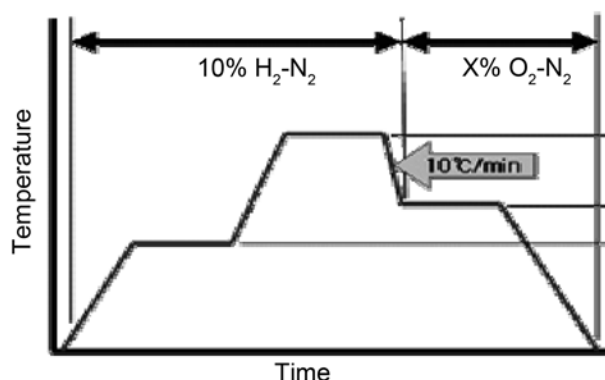


Fig. 1. Firing profile for reduction and re-oxidation.

the Heywang and Jonker model to the ferroelectric phase.

In the present study, the effect of reduction and re-oxidation firing on the PTCR properties of Sm-doped barium titanate ceramics was studied for the application as multilayered PTC thermistors.

## Experimental

The material compositions of PTCR ceramics used in this study are  $(\text{Ba}_{0.997}\text{Sm}_{0.003})\text{TiO}_3 + 0.2 \text{ mol}\% \text{ BaO} + 0.05 \text{ mol}\% \text{ MnO} + 6 \text{ mol}\% \text{ BN}$ . The method of sample preparation is as follows. In advance,  $\text{BaTiO}_3$  powder was prepared by means of a calcination ( $1150^\circ\text{C}$ , 2 h) process with the mixed powders of  $\text{BaCO}_3$  and  $\text{TiO}_2$ . Then,  $\text{BaTiO}_3$ ,  $\text{Sm}_2\text{O}_3$  (Aldrich, 99.9%),  $\text{MnCO}_3$ , and BN were mixed by wet ball-milling for 24 h in water with zirconia balls. The mixed powders were pressed into disks 8.5 mm in diameter and 1 to 2 mm in thickness under  $100 \text{ kgf/cm}^2$ .

The disk samples were fired according to the firing profile shown in Fig. 1. For binder removal, the samples were heated at a rate of  $2 \text{ K}\cdot\text{minute}^{-1}$  and held at  $600^\circ\text{C}$  for 2 h. The samples were heated at a rate of  $5 \text{ K}\cdot\text{minute}^{-1}$  and fired in a reducing atmosphere at  $1200^\circ\text{C}$  for 2 h. To obtain a reducing atmosphere, a reducing gas of  $\text{H}_2$  and a carrier gas of  $\text{N}_2$  were used and the concentration of oxygen was  $10^{-11}$ - $10^{-12}$  in the region of reduction firing. After reduction firing, the samples were cooled to  $800 \text{ K}\cdot\text{minute}^{-1}$  at a rate of  $10^\circ\text{C}/\text{min}$ . and re-oxidized for 2 h. Re-oxidizing gases were  $\text{N}_2$  and  $\text{O}_2$  and various re-oxidation conditions of 0, 10, and 20% were used. After that, the samples were cooled to room temperature at a rate of  $4 \text{ K}\cdot\text{minute}^{-1}$ .

Phase information from polished surface of sintered samples was made at room temperature using an X-ray diffraction technique (XRD), using  $\text{CuK}\alpha$  radiation (Rigaku). The lattice parameters were calculated using a least square method. The density and porosity of the sintered disks were measured using the Archimedes method. The thermally-etched surfaces of the fired samples were observed using a scanning electron microscope (SEM) in order to investigate the microstructure. The sintered samples were given electrodes by rubbing In-Ga alloy on the surfaces. The electrical resistivity was measured as a function of temperature

using a digital multi-meter (Agilent, 34970A) in a temperature programmable box chamber at a heating rate of  $10 \text{ K}\cdot\text{minute}^{-1}$ .

## Results and Discussions

The phase information of samples re-oxidized at different concentrations of oxygen, as examined by X-ray diffraction, is shown in Fig. 2. It is obvious that the tetragonal barium titanate phase formed in all samples; peaks were identified on the basis of the Joint Committee on Powder Diffraction Standards (JCPDS) data.

Fig. 3 shows the variation of the room temperature lattice parameters ( $a$ , and  $c$ ) and the tetragonal distortion ( $c/a$ ) as a function of the concentration of oxygen in the region of re-oxidation. The lattice parameters were calculated from the (002) and (200) planes. The lattice parameters ( $a$ , and  $c$ ) as well as the tetragonal distortion ( $c/a$ ) decrease simultaneously with an increase in the concentration of oxygen. Defects and impurities can influence the lattice parameters distinctly. The dependence of the lattice parameter ( $a$ ,  $c$ ) on the concentration of oxygen is considered to be related with the variation of the Coulomb potential due to oxygen vacancies [11]. Fig. 4 shows the displacements of ions around a positively charged oxygen vacancy. The

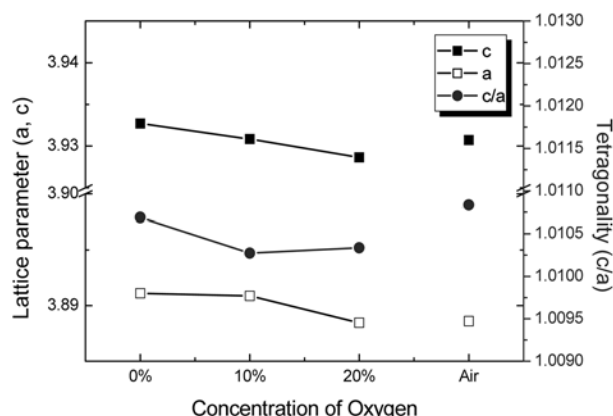


Fig. 2. X-ray diffraction patterns of samples re-oxidized at various oxygen concentrations.

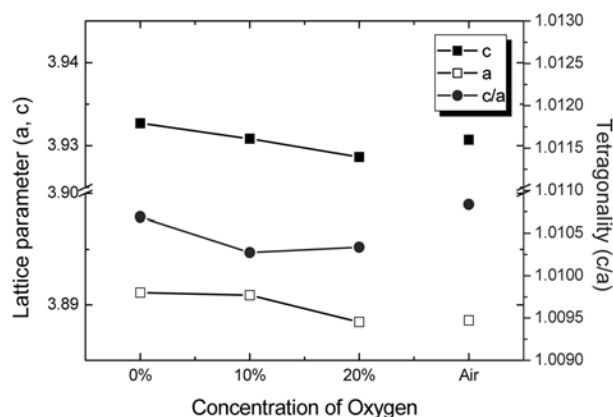


Fig. 3. Dependence of lattice parameters ( $a$ , and  $c$ ), and tetragonality ( $c/a$ ) on the oxygen concentration.

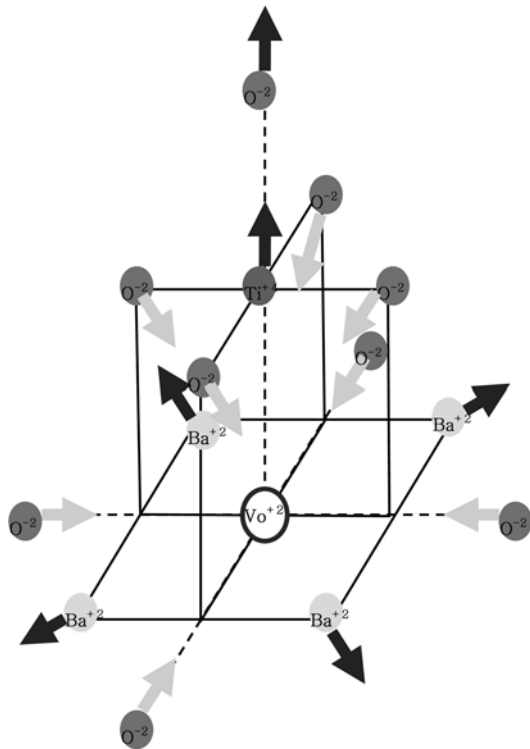


Fig. 4. Displacement of ions surrounding an oxygen vacancy.

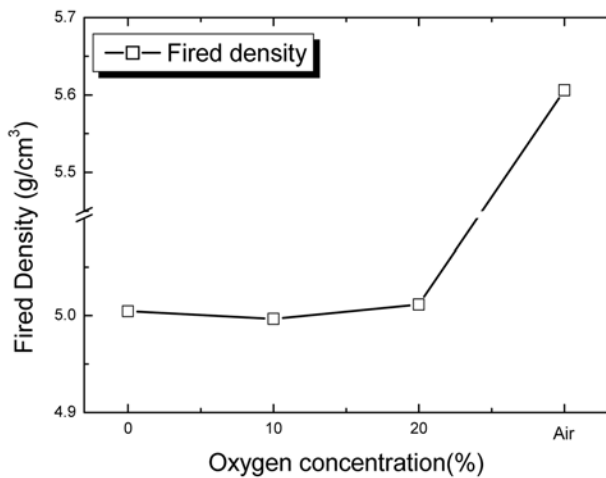


Fig. 5. Variation of fired density as a function of oxygen concentration.

nearest oxygen ions to the vacancy move toward the defect. On the other hand, the movements of positively charged Ti and Ba ions are outward with respect to the oxygen vacancy. Thus, the ionic displacements seem to be due to the electrostatic Coulomb interaction. The oxygen vacancy formed in the region of reduction firing expands the lattice as described above. With an increase in the concentration of oxygen in the region of re-oxidation, the concentration of oxygen vacancies decreases and the lattice shrinks due to the movements of positively charged Ti and Ba ions toward the negatively charged oxygen ion.

The density of samples re-oxidized at different concentrations of oxygen is shown in Fig. 5. Most of the samples except the sample fired in air have similar densities of 5.

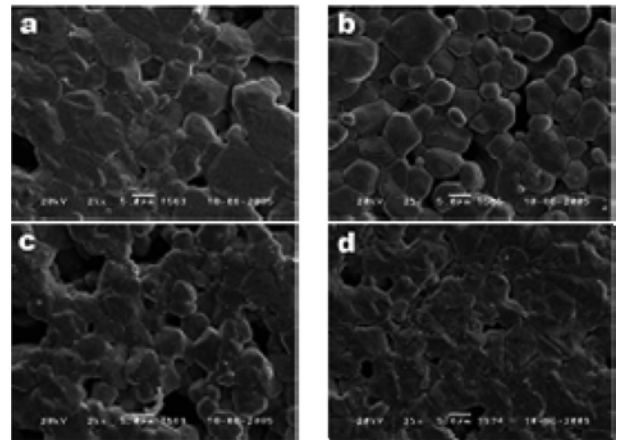


Fig. 6. Microstructures fired and reoxidized at different oxygen concentrations.

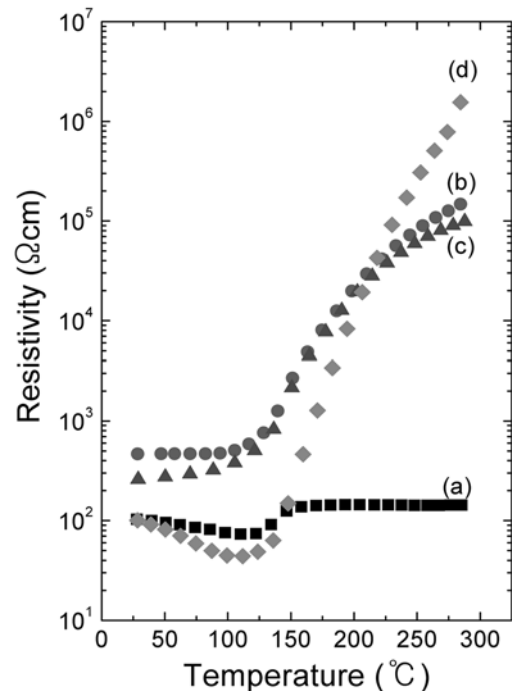
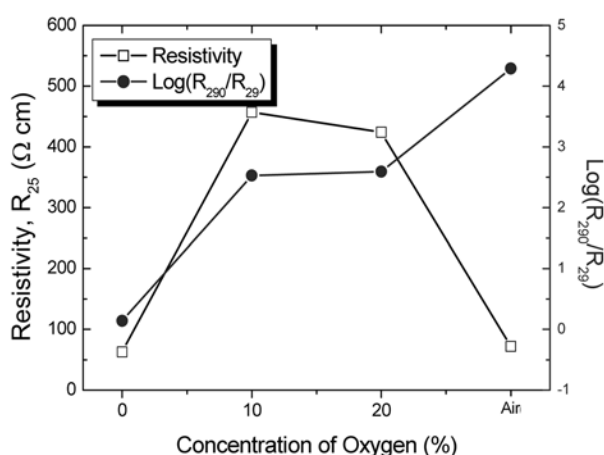


Fig. 7. Variation of resistivity as a function of temperature for PTC samples re-oxidized at various oxygen concentrations: (a) 0% O₂, 100% N₂, (b) 10% O₂, 90% N₂, (c) 20% O₂, 80% N₂ (d) air.

Fig. 6 shows the microstructures of samples re-oxidized at various concentrations of oxygen. Even if a noticeable difference in the grain size was not observed, the grain size decreased and became more uniform with an increase in the concentration of oxygen. The porosity is likely to have increased with an increase in the concentration of oxygen and irregular-shaped pores of various sizes are seen. The effect of re-oxidation on the grain size distribution is likely to be due to differences in the rates of grain growth. With an increase in the concentration of oxygen, the oxygen vacancies created during the reduction process diminish and uniform grain growth is thought to occur due to more random diffusion of Ba vacancies.

The effects of re-oxidation on the resistivity-temperature



**Fig. 8.** Resistivity of room temperature and jump characteristics as a function of oxygen concentration.

characteristics of the samples are demonstrated in Fig. 7. It is noticed that the jump characteristics of resistivity improves with an increase in the concentration of oxygen. Both oxygen and Ba vacancies are thought to be present in the reduced specimens. With an increase in the concentration of oxygen in the region of re-oxidation, the concentration of oxygen vacancies decreases very quickly and the dominant effect of the barium vacancies acting as acceptors, expands the insulating layer of the grain boundary region [12]. Therefore, the jump characteristics of resistivity will be expected to be increased, and this is indeed consistent with the experimental results as shown in Fig. 7.

The effects of re-oxidation on the resistivity and jump the characteristics of resistivity are shown in Fig. 8. It is noticed that the jump characteristics of resistivity increases monotonically with the concentration of oxygen. However, on moving from 0 to 10%, there was a slight increase in resistivity, and then the resistivity saturated. The saturation of the resistivity at 10% is considered to be related with the oxygen vacancies which create additional electrons.

## Conclusions

The effect of reduction and re-oxidation firing on the

PTCR properties of Sm-doped barium titanate ceramics was investigated for the application of multilayered PTC thermistor. The decrease of lattice parameters ( $a$ , and  $c$ ) with oxygen concentration in the re-oxidation atmosphere can be explained by the electrostatic Coulomb interaction between an oxygen vacancy and the other near atoms. The variation of the distribution of the grain size as a function of re-oxidation condition is considered to be related with the growth rate control by the concentrations of oxygen vacancies and barium vacancies. The resistivity at room temperature and the magnitude of the resistivity jump as a function of temperature increased in the region of oxygen concentrations of 0-10%. However, the resistivity at room temperature and the magnitude of the resistivity jump is nearly constant and saturated in the region of oxygen concentrations of 10-20%. This phenomenon is considered to be related with the variation of oxygen and barium vacancy concentrations near the grain boundaries.

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