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Effects of O_2 and N_2 atmospheres on the PTCR characteristics of Y-doped PTCR $BaTiO_3$ ceramics

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The positive temperature coefficient of resistivity (PTCR) materials in the perovskite-type ferroelectric consist of semiconducting barium titanate and its solid solutions with strontium titanate and lead titanate [1–6]. The PTCR $BaTiO_3$ ceramics sintered in air or oxidizing atmosphere exhibit an anomalous increase in electrical resistivity near the ferroelectric Curie temperature (~120 °C) [7–11]. PTCR characteristics of the semiconducting $BaTiO_3$ ceramics originate from the existence of an electrical potential barrier arising from the presence of a two-dimensional surface layer of acceptor state, e.g., segregated acceptor ions or adsorbed oxygen at the grain boundaries [8, 9, 12, 13]. PTCR characteristics of the semiconducting $BaTiO_3$ ceramics, annealed under vacuum or in reducing gas atmospheres, undergo changes that critically reduce the magnitude of the resistivity jump [14].

Porous PTCR $BaTiO_3$ ceramics has been reported to exhibit large PTCR effects [15–18]. Oxygen can adsorb at the grain boundaries because of the presence of pores in the porous ceramics, which are more favorable to form surface acceptor states compared with ordinary dense ceramics [19]. In this study, the porous PTCR $BaTiO_3$ ceramics are prepared by adding polyethylene glycol (PEG; 20 wt%). The aim of this study is to investigate the effect of measuring atmosphere (O_2, N_2) on the PTCR characteristics of the porous PTCR $BaTiO_3$ ceramics and to confirm the role of oxygen on the grain boundaries in origin of the PTCR characteristics of the porous ceramics.

High-purity PTCR $BaTiO_3$ ceramic powder was utilized in this study (Toho Titanium Co. Ltd, Japan). The powder was commercially obtained as $BaTiO_3$ powder containing $SrTiO_3$ (19.2 mol%) and Y_2O_3 (0.2 mol%). The powder is referred to as Y-doped $BaTiO_3$. The mean particle size and ferroelectric Curie temperature of the powder were 0.7 μm and 61 °C, respectively. The PEG (powder form, mean particle size: 50 μm, Shinyo Pure Chemicals Co. Ltd, Japan) of 20 wt% was added to the Y-doped $BaTiO_3$ powder and then mixed in a mortar for 1 h. The mixture was compacted by die-pressing at a pressure of 40 MPa to prepare the green compacts ($15 \times 12 \times 7$ mm^3). The green compacts were sintered at 1350 °C for 1 h in air.

The microstructure of the Y-doped $BaTiO_3$ ceramics was analyzed by scanning electron microscopy (SEM). The average grain size of the ceramics was estimated by the line-intersecting method. During heating and cooling cycles in the temperature range of 25 to 300 °C, the electrical resistance was measured with a digital multimeter under O_2 and N_2 atmospheres, and under N_2 followed by O_2 atmosphere.

Fig. 1 shows a SEM micrograph of the fractured Y-doped $BaTiO_3$ surfaces. It was found that the Y-doped $BaTiO_3$ ceramics containing PEG of 20 wt% had a high porosity (25.2%) and fine grain size (5.1 μm). The porous ceramic is advantageous to oxidize grain boundaries and to produce surface acceptor states [19]. The Y-doped $BaTiO_3$ ceramics was heated from 25 to 300 °C followed by cooling from 300 to 25 °C, in order to investigate how the adsorption or desorption of oxygen at the grain boundaries affects the magnitude of the PTCR effect during heating and cooling cycles.

Figs 2 and 3 show the electrical resistivities of the porous ceramics measured in O_2 and N_2 atmospheres, respectively, during heating and cooling cycles. The PTCR characteristics up to ~150 °C under O_2 and N_2 atmospheres are nearly same during heating, whereas those at high temperatures (>150 °C) are sensitive to the atmosphere. In O_2 atmosphere, the resistivity of the porous ceramics during cooling is slightly higher than that during heating cycle. This is due to a small increase in potential barrier because of a small decrease in the number of conduction electrons, owing to the adsorption of oxygen at the grain boundaries [20]. In N_2 atmosphere, the PTCR characteristics of the porous ceramics during cooling cycle are quite different from that during heating cycle. The resistivity of the porous ceramics during cooling is much lower than that during heating [21]. The magnitude of PTCR jump in the porous ceramics during cooling is low in comparison to

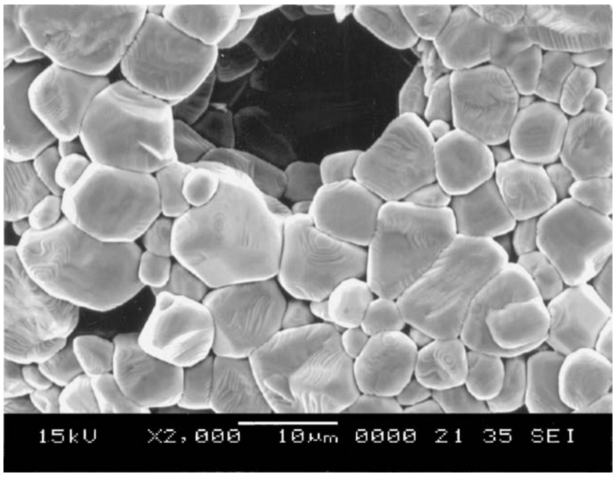

Figure 1 SEM micrograph of the fractured Y-doped $BaTiO_3$ surfaces.

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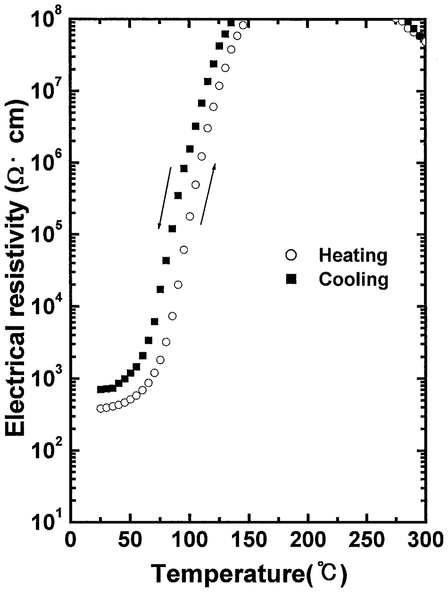

Figure 2 Electrical resistivities of the Y-doped $BaTiO_3$ ceramics measured during heating and cooling in O_2 atmosphere.

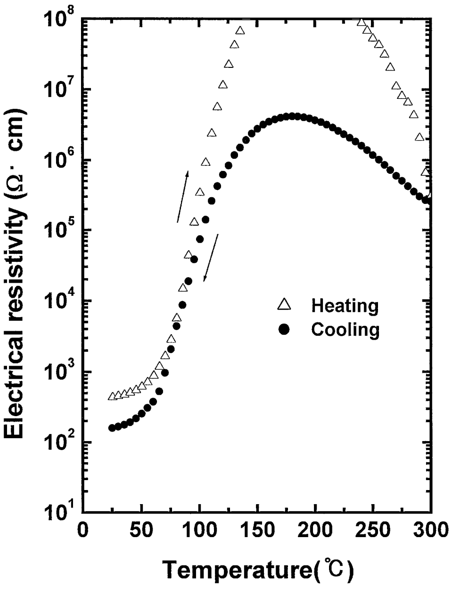

Figure 3 Electrical resistivities of the Y-doped $BaTiO_3$ ceramics measured during heating and cooling in N_2 atmosphere.

that during heating. The temperature corresponding to maximum resistivity during cooling is shifted to lower temperature.

Fig. 4 shows the electrical resistivity of the porous ceramics during heating and cooling cycles, when the atmosphere was changed from the reducing N_2 to O_2 atmosphere. It is confirmed that the low-temperature resistivity of the porous ceramics is found to be lowered during cooling after heating in N_2 atmosphere, and the resistivity is raised again by exposing to O_2 atmosphere. From this result, it is found that oxygen is adsorbed at the grain boundaries during heating in O_2 atmosphere, thus annihilating the oxygen vacancies created during N_2 reduction and significantly increasing the grain boundary resistance. These results confirm that the PTCR properties are strongly affected by chemisorbed oxygen at the grain boundaries and are recovered as the atmosphere is changed from reducing to oxidizing. The present study strongly supports the validity of the Heywang model [8, 12, 13].

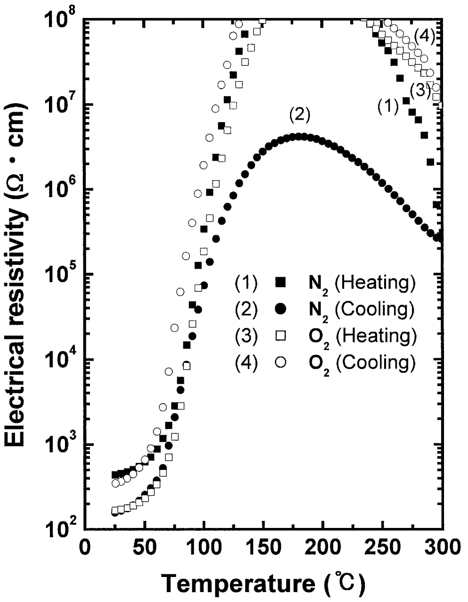

Figure 4 Electrical resistivity as a function of temperature of the Y-doped $BaTiO_3$ ceramics during heating and cooling. Atmosphere was changed from the reducing N_2 (■, ●) to O_2 (■, ●) atmosphere.

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