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Microstructure and the PTCR Effect of Semiconducting Barium Titanate Ceramics

Makoto KUWABARA and Hiroaki YANAGIDA

Kyushu Institute of Technology, Tobata, Kitakyushu, 804
Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, 113

The PTCR (positive temperature coefficient of resistivity) effect is one of the most eminent properties in polycrystalline ferroelectrics, which has appeared only in semiconducting barium titanate ceramics. It is known that the existence of grain boundary is inevitably necessary for the PTCR effect, and this effect is associated with the ferroelectric phase transformation of barium titanate. The problem relating to the microstructural dependence of the PTCR effect has, however, been left open.

This paper is concerned with an extremely large PTCR effect of more than 7 orders of magnitude observed in incompletely densified semiconducting barium titanate ceramics having small grain sizes in the range of 2 to 5 μm, and also with the microstructural dependence of the large PTCR effect.

Semiconducting barium titanate ceramic bodies were prepared under a strictly controlled condition using a commercial barium titanyl oxalate $BaTiO(C_2O_4)_2 \cdot 4H_2O$ powder as a starting material and reagent-grade Sb_2O_3 as a dopant. The mixed powder was pressed into pellets at various pressures and then fired at 1350°C for 2 hours in air. Successive cooling rate is very important to develop the PTCR effect, and it was here chosen at 100°C/h. The relative densities of present PTCR bodies ranged from 60 to 93%, where a special effort was made to range them as wide as possible to examine in detail the structural dependence of the PTCR effect. All the present PTCR materials were prepared to have the same composition described by the formula $Ba_{0.998}Sb_{0.002}TiO_3$.

A certain comparison may be made between the two ceramic microstructures shown in Fig. 1, in which the photograph (A) shows the microstructure of a ceramic body prepared in the present study and (B) shows that of a

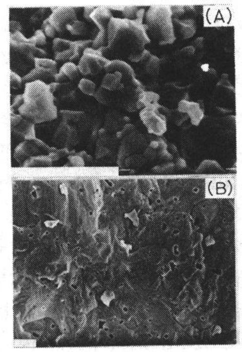

Fig. 1. A typical grain structure of the present PTCR materials (A), and that of normal PTCR materials with small PTCR effects (B). Bars = 10 μm.

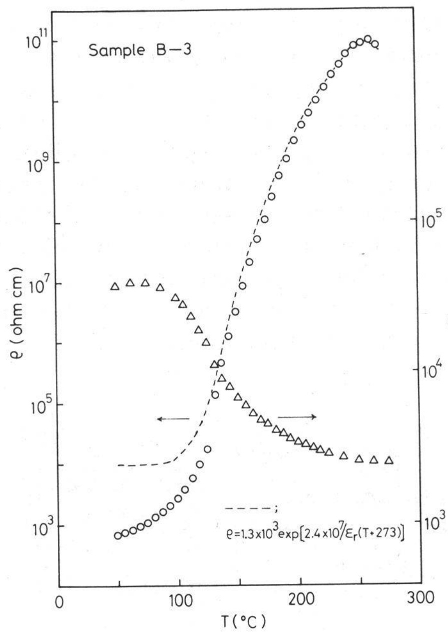

Fig. 2. Resistivity and dielectric constant plotted as a function of temperature for one of the present specimens.

ceramic with a small PTCR effect (2 orders of magnitude). Electrical measurements revealed that the temperature dependence of dielectric constants of the present specimens closely followed the Curie-Weiss law above the Curie point, and a good agreement between the PTCR effect calculated, on the basis of Heywang's model,[1] and the observed one was obtained as shown in Fig. 2. This strongly supports the notion that Heywang's model would be the most feasible one to describe the PTCR mechanism basically. However, further consideration based on Heywang's model should be needed to interpret the microstructural dependence of the PTCR effect and the mechanism of such a large PTCR effect as mentioned above.

Reference

1) W. Heywang: J. Am. Ceram. Soc. **47** (1964) 484.