An Anomalous Electric Property Found in Grain and at the Grain Boundary of the Barium Titanate Ceramic Doped with Bismuth

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It has been reported[1-3] that the resistivity of the polycrystalline barium titanate ceramic doped with bismuth increased anomalously above its Curie point. It is generally considered that this increase is due to the existence of a particular barrier at the grain boundary of the ceramic. However, the experimental results obtained with a single crystal do not seem to support this view. For example, Brown and Taylar[4] recently indicated that the single crystal of barium titanate doped with niobium prepared by the zone-melting process showed the same anomaly. Also, Kawabe and Inuishi[5] reported that a similar increase in resistivity could be found in the semiconductor obtained by reducing the barium titanate single crystal with hydrogen.

These results may suggest that the polycrystalline and single crystals of this ceramic have different electric properties.

A large-grained ceramic with an anomalous increase in resistivity was prepared, and the potential changes in the grain and at the grain boundary were studied (see Fig. 1).

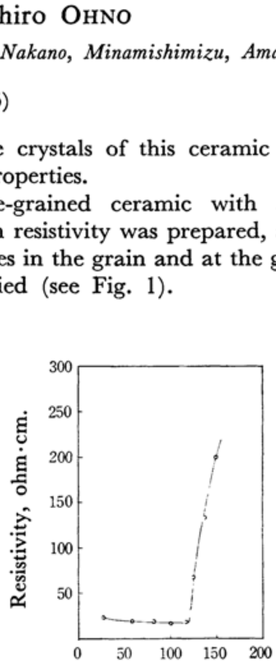

Fig. 1. Resistivity-temperature dependence of specimens used this experiment.

1) H. A. Sauer and S. S. Flaschen, Proc. Electron. Com. Sym. 7th, Washington D. C. May, 1956.
2) O. Suburi, *J. Phys. Soc. Japan*, **14**, 1159 (1959).
3) W. Heywang, *Solid State Electron*, **3**, 51 (1961).
4) F. Brown and C. E. Taylor, *J. Appl. Phys.*, **35**, 2554 (1964).
5) K. Kawabe and Y. Inuishi, *Japanese J. Appl. Phys.*, **2**, 590 (1963).

Experimental

Specimens of barium titanate ceramic doped with bismuth were prepared from barium titanyl oxalate[6] as the starting substance. This powder was mixed with 0.1 mol.% bismuth sesquioxide using a ball mill and was calcined at 1000°C in air. It was then pressed into disks 50 mm. in diameter and 3 mm. thick and was sintered at 1400°C in air. The mean grain diameter was found under a macroscope to be about 500 μ. This was cut into plates 1 mm. thick, 20 mm. long and 5 mm. wide, pasted into glass plates, lapped to a thickness below 300 μ in order to obtain a single grain layer, and etched in order to make it possible to see the grain boundary. The electrodes were made at both sides of the specimen by utilizing the special nickel plating shown in Fig. 2.

The potential change produced in the specimen was measured by the two-points method using a sharp-headed probe made of tungsten wire 0.3 mm. in diameter. The head was wet with liquid indium-mercury alloy[7] in order to obtain an ohmic contact.

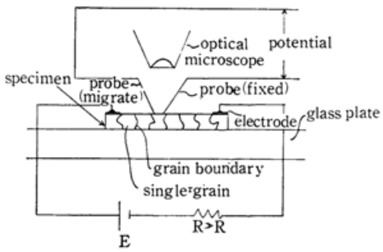

Fig. 2. Scheme of specimen and measure method.

Results and Discussion

Figure 3 shows the variation in the electrical potential between two probes. The one was fixed at the side of the specimen, while the other was moved on the surface on the grain. A large potential difference was always observed across the grain boundary. This shows that a barrier exists at the grain boundary, but its magnitude is different according to the specimen. This may indicate that the amount of barrier existing at the grain boundary varies and that the property of this barrier may be affected by the grain.

It is clear that the grain boundaries of the barium titanate ceramic doped with bismuth have a particular potential barrier. However, it is not clear whether the height of this potential barrier depends on the temperature above the Curie point. Therefore, the temperature-dependence of the potential drop should be measured. For this purpose, the resistivity of the grain was measured at various temperatures. The specimen was heated and its temperature was measured by a 0.1 mm.-in-diameter copper-constantan thermocouple pasted on the glass plate attached to the specimen.

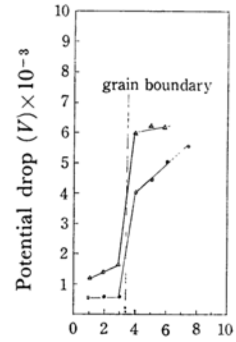

Fig. 3. Potential drop variation in case that crossed a grain boundary.

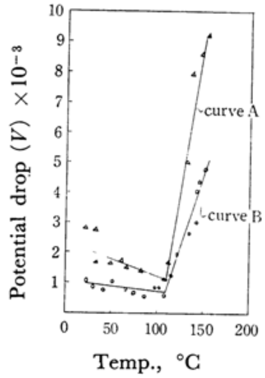

Fig. 4. Potential drop-temperatures dependence of the inside of grain.

Curve A Curve B

Fig. 5. Measured grains correspond with Curves A and B.

The potential change was found to be at about 110°C (see Figs. 4 and 5). In Fig. 4, the anomalous increase in resistivity in the grain is shown. This suggests that the anomalous increase of resistivity can not be attributed only to the barrier at the grain boundary. However, it was not possible to determine separately the temperature-dependent resistivity in the grain and that due to the barrier existing at the grain boundary.

The results obtained from this experiment may be summarized as follows: (1) A particular barrier causing a large potential change would exist at the grain boundary of the barium titanate ceramic doped with bismuth. (2) An anomalous increase in resistivity was observed in the grain of the barium titanate ceramic doped with bismuth, but it is

6) W. S. Clabaugh, E. M. Swiggard and R. Gilchrist, *J. Res. Natl. Bur. Stands.*, **56**, 286 (1956).
7) S. S. Flaschen and L. G. von Uitert, *J. Appl. Phys.*, **27**, 190 (1956).

not clear whether the mechanism of the increase of the resistivity of this material is to be attributed to the barrier at the grain boundary or to that in the grain.

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