# The positive temperature coefficient of resistivity of lanthanum-doped $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics as a function of barium excess

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It has been known since 1955 that semiconducting barium titanate exhibits a positive temperature coefficient of electrical resistivity (PTCR) near the ferroelectric Curie temperature. PTCR ceramics were used to fabricate a liquid level sensor [1], thermal controller, current limiter, current stabilizer, temperature compensator, television degausser, etc. [2, 3]. In spite of the marvellous development in the application of PTCR ceramics, many things about the PTCR effect still remain to be clarified, such as the shape of the resistivity–temperature characteristics below the Curie point, the grain size dependence of the effect, the exact role of transition elements normally used for enhancing it, etc. [4]. Kuwabara [5] has shown that the stoichiometry of the starting barium titanate powders (excess $TiO_2$ or BaO) was very important in producing small grain-sized ceramics which can exhibit large PTCR effects. However, only a qualitative microstructural description was provided to interpret effect of grain size on the PTCR effect. In the present study, a more quantitative investigation of the microstructural influence on the PTCR effect in lanthanum-doped $Ba_{0.8}Sr_{0.2}TiO_3$ with different amounts of BaO excess is reported.

Commercially obtained $BaTiO_3$ (HPBT-1, Fuji Titanium Industry Co. Ltd, Japan) was mixed with the required amount of $Sr(OH)_2 \cdot 8H_2O$ and $La(NO_3)_2 \cdot 6H_2O$ and different amounts of $BaCO_3$ to produce a low Curie temperature of semiconducting barium titanate powders with different BaO excesses. The raw material mixtures were mechanically milled in deionized water. The milled slurry was dried and calcined at 1100° C for 1 h. The calcined powders were then ball milled, dried again and sieved through a 140 mesh screen to produce the starting semiconducting powders with compositions of $Ba_{0.8}Sr_{0.2}TiO_3$ + 0.2 mol % $La_2O_3$ + $x$ mol % BaO ($x$ = 0, 1, 1.5, 2, 2.73 and 3.5). Disks were pressed and sintered at 1400° C for 1 h in a programmable furnace. A cooling rate of 150° C h$^{-1}$ was used in this study. These disks, after sintering, were about 8.8 mm in diameter and 2 mm in thickness. The average intercept length of the grains was determined by lineal analysis of the as-sintered specimens' surfaces observed by scanning electron microscopy (SEM).

The resistance–temperature characteristics were measured by using a two-probe method with an indium–gallium (60:40) electrode applied to the opposite faces of the fired disks. A voltage of 1 V was applied to specimens.

The addition of BaO at least up to 3.5 mol % seems to favour the PTCR effect, as shown in Fig. 1. It shows that an abrupt increase in the maximum to minimum ratio of resistivity as the amount of BaO added reaches 2 mol %. These data correlate well with direct microscopic observation (Fig. 2) and grain size measurement (Fig. 3). When the average grain size decreased from 2.73 μm (1.5 mol % BaO excess) to 1.23 μm (3.5 mol % BaO excess), the maximum to minimum ratio of resistivity increased from 1.7 to 5, but all the relevant samples had almost the same relative sintered densities (Fig. 4) which have also been found to significantly affect the magnitude of the effect [6]. A phase diagram for the $BaO–TiO_2$ system reported by Rase and Roy [7] has shown that a second phase, $Ba_2TiO_4$, appeared for the BaO excess $BaTiO_3$ samples. The presence of $Ba_2TiO_4$ as a second phase for samples containing $\geqslant 0.1$ mol % excess BaO has been further confirmed by direct microscopical examination [8]. This second phase which was expected to form in our BaO-excess samples would play an important role in grain inhibition. The effect of the addition of small amounts of BaO on grain growth is evident from the SEM photographs (Fig. 2).

The effect of the BaO addition on PTCR is quantitatively described in terms of inhibition of grain growth. However, the fact that barium titanate ceramics with Ba-rich compositions can exhibit large PTCR effects may be contrary to the model proposed by Daniels *et al.* [9], in which the existence of barium vacancies near the grain boundaries was assumed to be inevitable for the occurrence of the PTCR effect. On the other hand, Heywang [10] explained the PTCR characteristics in terms of the temperature dependent Schottky-type grain boundary potential barrier.
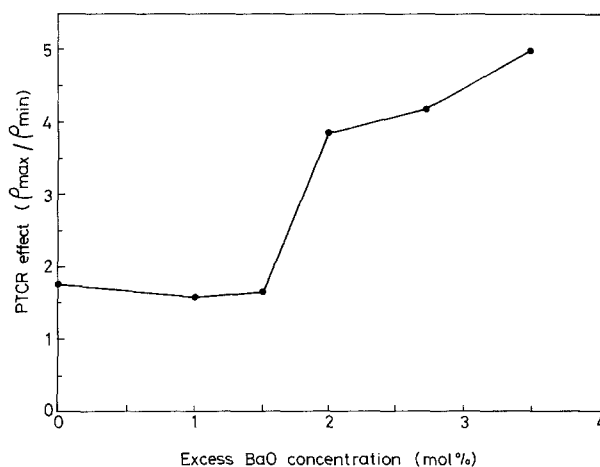


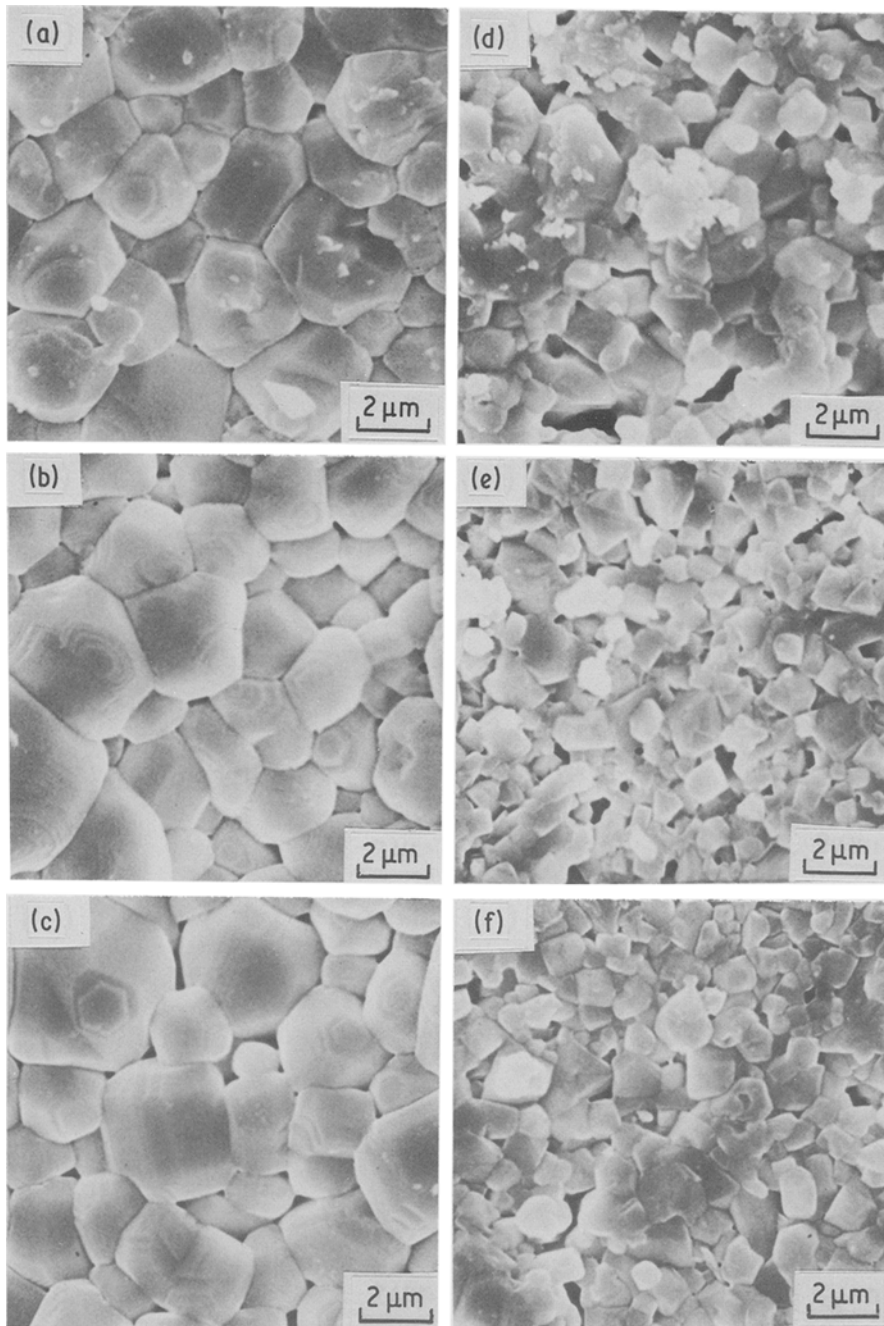Figure 1 PTCR effect as a function of excess BaO added to samples.

*Figure 2* Scanning electron micrographs of as-sintered surfaces of BaO excess samples. Excess BaO concentrations are (a) 0 mol % (b) 1 mol % (c) 1.5 mol % (d) 2 mol % (e) 2.73 mol % (f) 3.5 mol %.
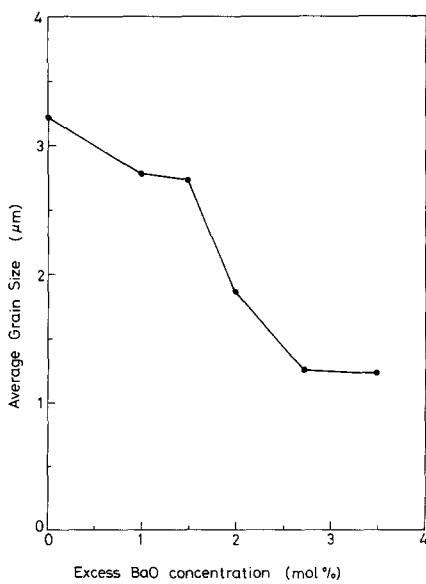


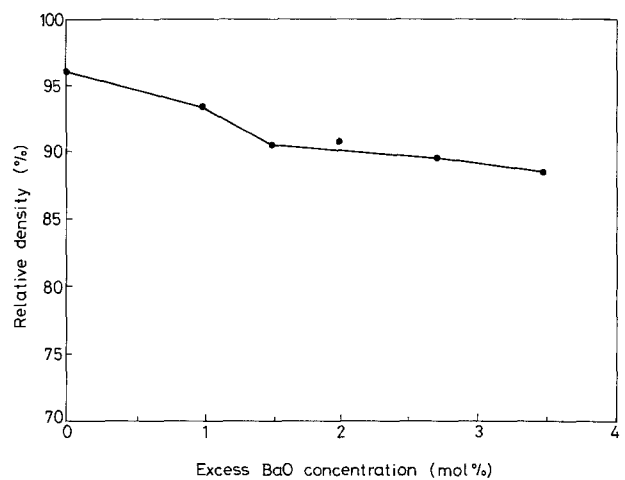*Figure 3* Average grain size as a function of excess BaO added to samples.



*Figure 4* Relative sintered density as a function of excess BaO added to samples.

Whether or not the varying amounts of second phase obtained from excess BaO influence the physical nature of the grain boundary potential barrier and thus affect the PTCR effect, may also need to be considered. To investigate this possibility, more experimental work is necessary on grain boundary analysis.

## References.

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