Electrical Properties of Bulk and Grain Boundaries in Donor Doped Barium Titanate Ceramics

W. Preis, A. Bürgermeister, and W. Sitte

Department of General, Analytical and
Physical Chemistry, University of Leoben,
Franz-Josef-Strasse 18, A-8700 Leoben, Austria

Donor doped (n-conducting) barium titanate, $BaTiO_3$, plays an import role in various electroceramic components, such as positive temperature coefficient (PTC) resistors. The electrical properties of these thermistors are mainly governed by the microstructure of the ceramics. It is thus inevitable to elucidate the contributions of both the bulk and the grain boundaries to the overall resistance of the ceramics in order to gain a better understanding of the prevailing conduction mechanism.

The resistivities of the bulk as well as the grain boundaries were determined on n-conducting $BaTiO_3$ ceramics doped with Y and Mn (donor doped with acceptor co-doping) by means of impedance spectroscopy as a function of temperature ranging from 25 to 400°C. The average grain sizes of the disk-shaped metallized samples were around 3 µm. The impedance spectra were analyzed by application of appropriate equivalent circuits. Whereas the bulk resistivity was found to be almost independent of temperature with typical values around 10 Ω cm, the grain boundary resistivity increased by several orders of magnitude when the temperature was raised through the ferroelectric-paraelectric phase transition temperature ($T_C \approx 90$ - 125°C), as can be seen in Fig. 1. The rapid increase of the sample resistance with temperature (PTC effect) is followed by an exponential decrease of the resistance above approximately 200°C (NTC behavior).

Besides the bulk and grain boundary resistivities the proper analysis of the impedance spectra allowed likewise the determination of the grain boundary capacitance as a function of temperature, see Fig. 2. Above the ferroelectric-paraelectric phase transition temperature (Curie point) the grain boundary capacitance obeys the Curie-Weiss law where the reciprocal relative permittivity varies linearly with temperature, i.e.

$$\varepsilon^{-1} \propto (T - \Theta) \tag{1}$$

with Θ being the Curie-Weiss temperature. The ferroelectric-paraelectric phase transition temperatures were confirmed by heat capacity measurements, employing differential scanning calorimetry (DSC).

The PTC effect can be interpreted in terms of a Schottky-barrier-model [1,2]. The electrons of the n-conducting bulk are trapped by acceptor states located at the grain boundary core. The negative net-charge of the grain boundary core is counterbalanced by adjacent depletion space charge zones. In the regime of linear response (small voltage drops across the boundary layers) the ratio between the grain boundary and the bulk resistance is related to [3,4]

$$R_{gb} / R_b \propto \frac{kT}{2e\phi_0} \exp\left(\frac{e\phi_0}{kT}\right) \tag{2}$$

where ϕ_0 corresponds to the potential barrier height. From Fig. 1 one can deduce that the calculated lines according to the Heywang model (Schottky-barrier-model) fit the experimental data satisfactorily. Optimized values for the temperature dependent energy level and the density of the acceptor type grain boundary states will be given.

Acknowledgements

The authors gratefully acknowledge financial support by the Materials Center Leoben (MCL).

References

[1] W. Heywang, J. Am. Ceram. Soc. 47 (1964) 484.
[2] G. H. Jonker, Solid State Electron. 7 (1964) 895.
[3] I. Denk, J. Claus, and J. Maier, J. Electrochem. Soc. 144 (1997) 3526.
[4] J. Fleig, S. Rodewald, and J. Maier, J. Appl. Phys. 87 (2000) 2372.

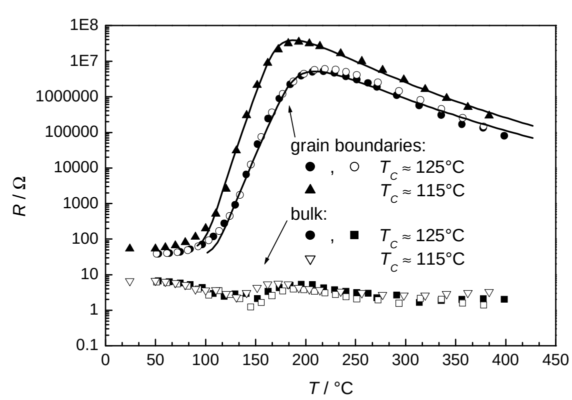

Fig. 1 Temperature dependence of bulk and grain boundary resistances of n-conducting $BaTiO_3$ ceramics with different Curie points (T_C). Sample dimensions: 2.2 mm thickness, 8.0 mm diameter. The solid lines have been calculated according to the Heywang model (Schottky-barrier-model).

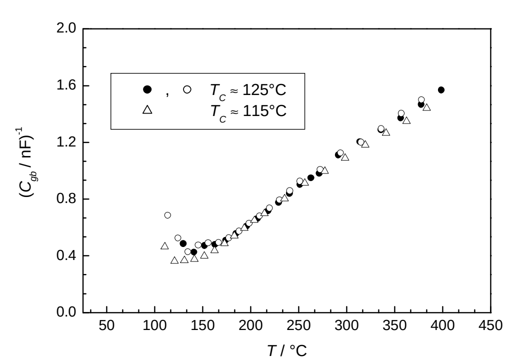

Fig. 2 Reciprocal grain boundary capacitance of n-conducting $BaTiO_3$ ceramics with different Curie points (T_C) plotted versus temperature. Sample dimensions: 2.2 mm thickness, 8.0 mm diameter.