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Conduction mechanism of barium titanate ceramics

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Abstract

Barium titanate ceramics are semiconductor devices presenting a highly non-linear resistivity vs. temperature characteristics (PTCR effect). Although it has been previously determined that this phenomenon can be described by a simple double depletion layer formed at the grain interfaces, details of some effects in these materials are not completely explained. In this work, the electrical properties of barium titanate ceramics above the Curie temperature are studied from the resistivity vs. temperature and dielectric constant vs. temperature at the grain boundaries. Experiments can be explained as the result of double Schottky barriers formed at the grain boundaries. These barriers are considered to have an exponential concentration of electrically donor active dopants.

Keywords: B. Grain boundaries; C. Electrical properties; D. Perovskites; E. PTC devices

1. Introduction

Barium titanate ($BaTiO_3$) exhibits a positive temperature coefficient of resistance (PTCR effect). This effect involves a substantial non-linear change of resistivity with temperature around the Curie temperature (T_C) [1]. It was determined that compositional modifications of Sr^{+2}, or Pb^{+2} for Ba^{+2} produce changes in the Curie point to higher or lower temperatures [2].

Several models have been developed to explain the PTCR effect [3,4]. However, it is mostly accepted that the barium titanate PTCR phenomenon is a grain boundary resistive effect [5,6]. These barriers are strongly influence by the details of sample preparation, specially the sintering and cooling atmospheres [7].

One of the most recognised theories to explain the electrical structure of the grain boundary is the Heywangy's model. The model is based on the formation of a potential barrier at the grain boundaries. This model has been extend by Jonker, who took into account of the influence of the polarisation on the resistivity below the Curie point [3]. Then, this model is termed the Heywang-Jonker model. It assumes the formation of a bidimensional layer along the grain boundaries of $BaTiO_3$, and this layer exhibits different electrical properties than those of the bulk phase [8,9]. This explanation is based on the presence of surface acceptor states at the grain boundaries, which cause a potential barrier as a result of the upward bending of the conduction band in the depletion layer.

According the Heywang model the barrier height is given by,

$$\phi(T) = e.N_e^2/(8.\varepsilon_0.\varepsilon_r.N) \quad (1)$$

where T is the absolute temperature (K), e the electronic charge, (ε_0 the permittivity of the free space, ε_r the relative permitivity of the $BaTiO_3$ within the grain boundary layer, N the donor concentration in the bulk and N_e the temperature dependent concentration of the occupied acceptor states. Based on the Fermi–Dirac statistics one may determine N_e by:

$$N_e = N_s/(1 + \exp(E_F + \phi(T) - E_s)/kT) \quad (2)$$

where $E_F = kT.\ln(N_C/N)$, N_s denote the density of acceptor-state, E_s the energy of the surface state in relation to the bottom of the conduction band, k the Boltzmann constant, T the temperature, E_F the Fermi level and N_C the conduction electrons $N_C = 1.56\times10^{22}$ cm^{-3} (equal to Ti density).

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The effective resistivity of the ceramics assumes the form

$$\rho = \rho_g[1 + (bkT/de\phi)\cdot\exp(e\phi/kT)] \quad (3)$$

where, $b = N_e/2N$ is the effective thickness of the grain boundary region, ρ_g is the grain resistivity. By using the following equations:

$$\varepsilon_m = \varepsilon_r(d/2b), \text{ and} \quad (4)$$

$$b = N_e/(2.N), \quad (5)$$

the barrier height is related with the measured dielectric constant according to:

$$e\phi = e.d.N_e/8.\varepsilon_0.\varepsilon_{m.} \quad (6)$$

where ε_m is the measured dielectric constant.

According to Jonker [10] the lowering of the barrier height below T_C is explained by assuming compensation of the surface layer along different directions of the ferroelectric domains at both sides of the grain boundary. The surface charge at the grain boundary layer is compensated by the charge related to the ferroelectric component.

In this work the electrical properies of the barium titanate PTCR ceramics are studied using the resistivity vs. temperature and the dielectric constant vs. temperature curves. Experimental data can be reproduced using the Heywang–Jonker model and a modified model.

2. Experimental

The resistance of a commercial PTC (Philips PH 97224, 0.992 cm diameter and 0.268 cm thick) was measured with an electrometer (Keithley 614). The ac impedance measurements were performed in a Hewlett Packard (PH 4284A LCR analyser), using zero dc-applied voltage, amplitude of 1 V and a frequency of 1 KHz. All the electrical properties were measured by using the two-probe method from 20 to 210°C in air. The heating was performed with a furnace. The sample was held at the desired temperature for enough time to equilibrate with the temperature reading before each test was carried out. The impedance versus frequency was measured from 20 Hz to 1 MHz at room temperature to obtain the sample grain resistivity. Since features for thermistors of the same type present varying characteristics, the same thermistor was used for a complete set of measurements.

The measured dielectric constant was obtained from the capacitance measured according to,

$$\varepsilon_m = C.t/(\varepsilon_{0.}S) \quad (7)$$

where C is the capacitance measured, t the thickness of the sample, S the area of the electrode.

3. Results and discussion

The resistivity vs. temperature and dielectric constant vs. temperature are shown in Figs. 1 and 2, respectively. From Fig. 1 the resistivity maximum and its temperature can be obtained ($\rho_{max} = 4.8\ 10^7\ \Omega$ cm and $T_{max} = 143$°C). On the other hand, from the Fig. 2 the Curie temperature can be obtained ($T_C = 75$°C). In order to propose a model, which reproduces the experimental data some parameters should be evaluated, as discussed below.

The room temperature measurements of capacitance with the frequency were carried out on the same sample. The real and the imaginary parts of the impedance at each frequency were calculated, and the results were plotted in the form of complex impedance diagrams. Such plots permit the separation of the grain resistivity (ρ_g) from the grain boundary layer resistance. The obtained results showed that the grain resistivity was $\rho_g = 10\ \Omega$ cm. From studies using Scanning Electron Microscopy a grain size of about 2 μm was determined. The charge concentration (N) was obtained using the equation $N = (\mu.e.\rho_g)^{-1}$ where, μ is the electron mobility (0.5 cm^2 V^{-1} s^{-1}), e the electronic charge and ρ_g the grain resistivity. According this value the charge carrier concentration was $N = 1.25\times10^{18}$ cm^{-3}.

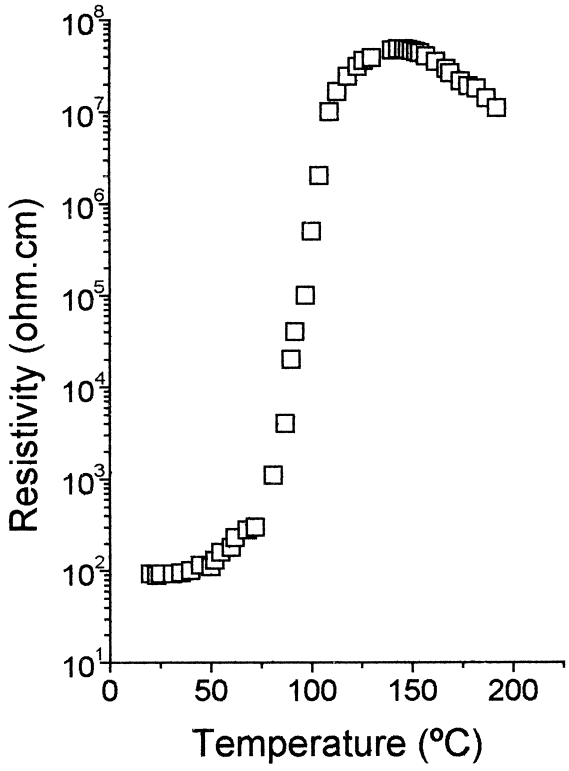

Fig. 1. Resistivity vs. temperature curve.

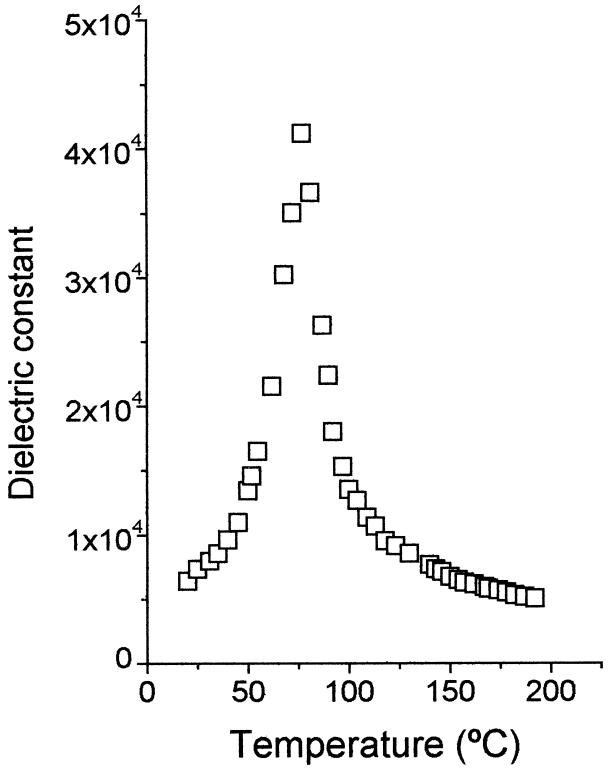

Fig. 2. Dielectric constant vs. temperature curve.

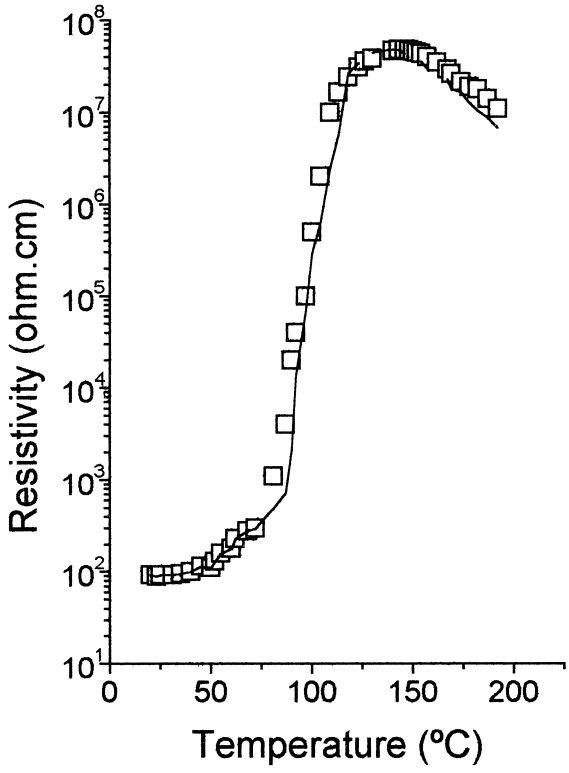

Fig. 3. Resistivity vs. temperature curve. As seen, a good fit cannot be obtained considering a constant donor concentration. (—) calculated, (□) measured.

Then, by fitting the maximum of resistivity values of N_s and E_s were obtained. The maximum was fitting with $N_s = 1.37 \times 10^{14}$ cm^{-2} and $E_s = 1.11$ eV. These values compared with the Heywang data are quite reasonable [3]. Then the resistivities above the Curie point were obtained by using the Eqs. (2), (3) and (6). An iterative method was used for the extraction of $\phi(T)$ and $N_e(T)$. A N_e is arbitrarily chosen, and then the barrier height from Eq. (6) is found. Then, N_e is calculated from Eq. (2). When, the N_e chosen and the N_e calculated converges to the same value resistivities are then calculated with the resulting values of barrier heights and N_e for temperatures above the Curie point [11,12]. At temperatures below the Curie point, the spontaneous polarisation present in the ferroelectric state should be taken into account for the explanation of the resistivity and the low permittivity. This can be done by reducing N_e with a suitable ΔN_e. N_e can be obtained from fitting the measured resistivity vs. temperature curves. Then, ΔN_e gives an estimate of the acceptor-state compensated by polarisation [12].

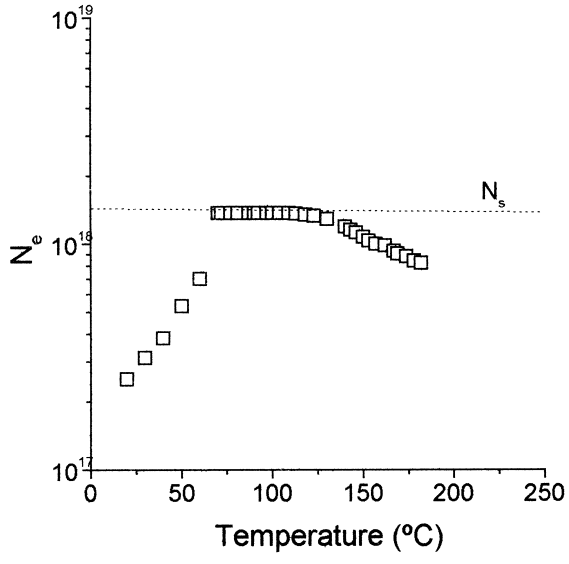

Fig. 4. Occupied acceptor-state density vs. temperature.

In Fig. 3 the measured resistivity vs. temperature and the calculated resistivity vs. temperature are shown. In Fig. 4 the occupied acceptor-state density N_e vs. temperature is shown. The difference between N_s and N_e at temperatures below T_C is due to the spontaneous polarization. This polarisation at the end of alternate domains at the grain boundary could neutralise the interfacial barrier; then, the low resistance before the anomalous jump is achieved by the reduced potential barrier as a result of partly compensated acceptor-state charges. At higher temperatures a depopulation of acceptor states produces a decrease of N_e [11]. In Fig. 5 the barrier height vs. temperature curves is shown. From this curve an important increase in the barrier

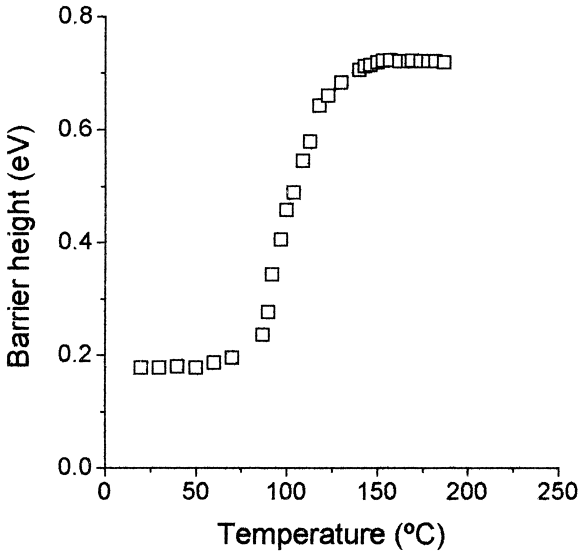

Fig. 5. Barrier height vs. temperature curve.

height above T_C is produced. At this temperature the spontaneous polarisation disappears and then, the barrier height increases.

From Fig. 3 the obtained fitting of the experimental curves is quite satisfactory. However, at temperatures above 150°C the model predicts lower resistivities than the experimental values. Therefore a more refined model was tested.

$BaTiO_3$ thermistors are sintered at high temperatures and then cooled slowly to room temperature. Then, a non-uniform defect concentration during the cooling process is established because of time-dependent diffusion phenomena. Since the diffusion coefficient decreases with temperature, the defect concentrations become frozen with an inhomogeneous distribution at room temperature. The main result would be that defect concentrations are lower near the surface than in the bulk of the grain. Although several functions for the profile shape of the dopant concentration could be adopted, we chosen the following function:

$$N(x) = N_1 + N_2 \exp(-x/\lambda) \tag{8}$$

where $N_1 + N_2$ is the donor concentration in the bulk of the grain and λ is a parameter. Parameters N_2 and λ determine the donor concentration profile close to the intergrain and thus the width and steepness of the barriers. A new iterative process was carried out in all the temperature range. The calculated resistivities are shown in Fig. 6. From this figure a good fitting above the temperature of maximum resistivity was achieved. However, at lower temperatures the fitting fails.

The explanation for these findings can be related to the ferroelectric–paraelectric transition and to the barrier shape effect. At temperatures between the Curie point and the temperature of resistivity maximum, the

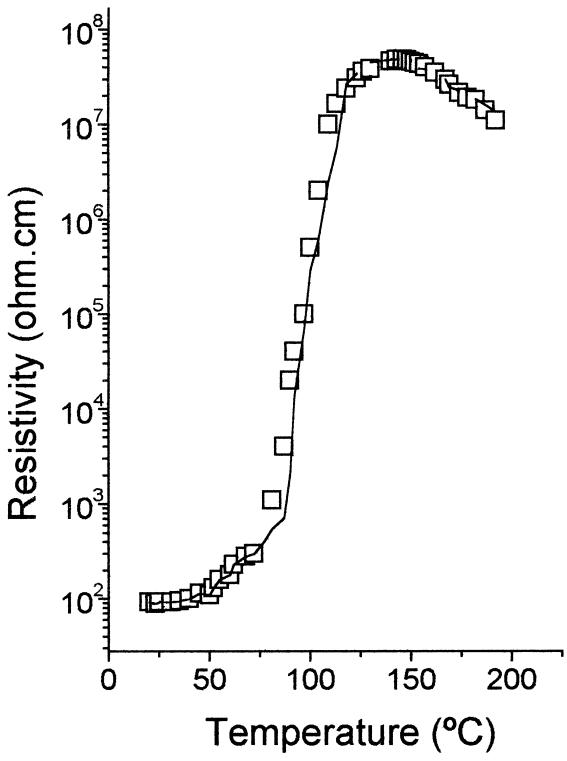

Fig. 6. Resistivity vs. temperature curve. (—) calculated, (□) measured.

ferroelectric–paraelectric transition is produced. In this step the conduction mechanism is governed by this phase transition, and as a consequence, the exact donor profile does not have a relevant effect. Then, a simple model with a constant donor concentration reproduces the experimental data. However, when the temperature increases, the sample is in the paraelectric state and the intergranular barrier control the conduction process. In this case the exact barrier shape should be taken into account. Then the second model with a profile of donor concentration presents a good fitting.

4. Conclusions

From the experimental results we can conclude that:

a. At temperatures below the Curie point the spontaneous polarisation present in the ferroelectric state produces a variation in the occupied acceptor-state density.
b. At temperatures between the Curie temperature and the temperature of resistivity maximum, the ferroelectric to paraelectric transition is the major contribution to the increase in the resistivity.
c. At temperatures higher than the temperature of resistivity maximum, the sample is in paraelectric state. In this state, the resistivity decreases when

the temperature increases. In this case the barrier shape has more important consequences.

Therefore, when the experimental data are reproduced, two modifications in the Heywang's model need to be considered. On of these changes is the use of an exponential donor concentration at temperatures above the temperature of resistivity maximum. On the other hand, a variation in the occupied acceptor-state density at temperatures below the Curie point needs to be kept in mind.

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