

FERROELECTRIC-SEMICONDUCTIVE PROPERTIES OF BaTiO₃ - BASED PTCR CERAMICS

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The interrelated semiconductor and ferroelectric properties of n-doped BaTiO₃ ceramics were considered for describing their electrical properties in a large range of temperatures. A double barrier Schottky model (Heywang-Jonker) combined with the Landau-Devonshire model were used in order to explain the ferroelectric-semiconductor properties of n-doped BaTiO₃ ceramics with PTCR characteristics. The resistivity-temperature R(T) dependencies were simulated for various model parameters, in the whole range of temperatures, including the ferro-para phase transition. A limited range of the donor concentration and of the surface state density for the semiconductive behaviour at room temperature was obtained from the model, similar as in experiments. The results obtained for different model parameters were discussed in connection with the composition and processing parameters of BaTiO₃-based PTCR materials.

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1. Introduction

The electrical properties of BaTiO₃ (BT) ceramic are determined by the type and concentration of the dopants and by the processing conditions as well. Undoped BT is a high insulator material, but doped with donors it turns in semiconductor at room temperature and shows an anomalous electrical resistivity jump by several orders of magnitude at the Curie temperature, known as Positive Temperature Coefficient of Resistivity (PTCR) [1]. This effect is due to the interrelated semiconductive and ferroelectric properties of this material. The general accepted model that describes this behavior, proposed by Heywang [2], considers the composition and electrical inhomogeneity of the grain bulk and grain boundary (GB) that give rise to potential barriers between the individual crystallites of the ceramic body, that are temperature-dependent through the permittivity $\epsilon(T)$. This theory explained the Resistivity-Temperature R(T) dependencies of n-doped BT ceramics, only in the paraelectric phase. Some fits using the results of Landau-Devonshire (LD) theory [3] were done by Wang and Umeya [4] in order to estimate the effective capacitance and resistance of the BT sample.

In order to obtain the Resistivity-Temperature dependences of the n-doped BT materials in the whole range of temperatures, we used in the present work the Heywang model, in which the ferroelectric behavior is described in the frame of the LD theory of ferroelectricity [3].

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2. Theory

The variation of the potential barrier at the ceramic grain boundary with the coordinates (x_i) is a solution of Poisson equation:

$$\Delta V(x_i, T) = \rho(x_i, T) / \epsilon_0 \epsilon(x_i, T), \quad (1)$$

where $\epsilon(x_i, T)$ is the nonlinear dielectric constant, the charge density is: $\rho(x_i, T) = -eN_D(x_i, T)$ and N_D is the density of donors inside the grain. The electric field across the grains is dependent on the potential barrier, according to the equation: $\bar{E}(x_i, T) = -\text{grad}V(x_i, T)$. For solving the above coupled non-linear equations, explicite dependencies for $\epsilon(x_i, T)$ have to be proposed, using empirical formula or phenomenologic relations derived from the models describing the ferroelectric lattice. In the present paper, we used both types of relations in order to simulate the PTCR characteristics and to discuss the role of the model parameters. In the frame of LD theory, the ferroelectric lattice of BT is described by its free energy at zero stress as a power series of polarization:

$$F = \frac{\beta}{2}(T - T_0)P^2 - \frac{\gamma}{4}P^4 + \frac{\delta}{6}P^6 + \dots, \quad (2)$$

where β , γ and δ are the LD parameters of the system. The temperature dependence of the permittivity is:

$$\epsilon(T) = \epsilon_0 \left(\beta(T - T_0) - 3\gamma P^2(T) + 5\delta P^4(T) \right)^{-1}, \quad (3)$$

where the spontaneous polarization is temperature-dependent according to the relation:

$$P(T) = \pm \frac{\gamma}{2\delta} \sqrt{1 + \sqrt{1 - \frac{4\beta\delta}{\gamma^2}(T - T_0)}}. \quad (4)$$

in which the ferroelectric lattice is considered as homogeneous. The behaviour of the free-electrons subsystem is described by the Heywang theory [2], in which the grain of the n-doped BT polycrystalline ceramics consists of two distinct regions with different electrical properties: a low conductivity and low permittivity bulk (B) and a high permittivity ferroelectric grain boundary (GB). The discrete surface states created at the GBs act as electron traps that repel free electrons from the GB into the bulk, resulting in the formation of a depletion layer. The charge exchange necessary to equilibrate the Fermi level creates a Schottky barrier between GB and the two adjacent bulks, with the potential:

$$V_0 = \frac{eN_s^2(T)}{8\epsilon_0\epsilon(T)N_d(T)}, \quad (5)$$

where N_s is the density of trapped electrons, N_d is the donor concentration, E_s is the energy of the surface states, E_F is the Fermi level energy, k is the Boltzmann constant and e is the electron charge.

The evolution of the built-in barrier potential V_0 with temperature is described by the equation:

$$V_0 = \frac{eN_s^2(T)}{2\epsilon_0\epsilon(T)N_d(T)} \frac{1}{\left[1 + \frac{N_c}{N_d(T)} \exp\left(\frac{eV_0 - E_0}{kT}\right) \right]^2}, \quad (6)$$

where N_c is the density of electrons in the conduction band. Using the potential $V_0(T)$, the bulk and GB resistivities are calculated respectively, according to the equations:

$$R_{\text{bulk}}(T) = \frac{1}{2e^2\mu N_d(T)b(T)}, \quad \frac{R_{\text{GB}}(T)}{R_{\text{bulk}}(T)} = 1 + 2b(T)z \frac{kT}{eV_0(T)} \exp\left(\frac{eV_0(T)}{kT}\right), \quad (7)$$

where $b(T)$ is the depletion layer width that is temperature-dependent, z is the density of GBs on the unit length and μ is the electron mobility. If the carrier concentration and the surface state density are constant, the resistivity of the sample can be calculated according to the approximative relation, as:

$$R(T) \propto A \exp(eV_0 / kT), \quad (8)$$

where A is a constant almost independent on temperature [4-5]. In case that spatial effects are considered, for the one-dimensional model $V_0 = V_0(x, T)$, in which x is the coordinate across the grain boundary, the average resistivity is obtained as:

$$\bar{R}(T) = \int R(x, T) dx / \int dx \quad (9)$$

We used for simulations eqs. (1)-(9), with LD parameters for pure BT ceramic: $T_0=393\text{K}$, $\beta=4.5 \times 10^5 \text{m/F}$, $\gamma=2.6 \times 10^9 \text{m}^5/\text{F/C}^2$, and $\delta=-4.7 \times 10^{10} \text{m}^9/\text{F/C}^4$ [6]. The parameters used by Heywang for the PTCR data of Sb-BT ceramics: $E_s=0.9\text{eV}$, $\mu=0.5\text{cm}^2/\text{Vs}$, $N_c=1.1 \times 10^{22}\text{cm}^{-3}$, $N_d=2 \times 10^{19}\text{cm}^{-3}$, $N_s \cong 10^{14}\text{cm}^{-2}$ were considered for reference [7-8].

3. Results

3.1 The role of the ferroelectric lattice on the PTCR behaviour

We used the described approach to simulate different possible experimental situations. For example, in case of some BT-based solid solutions that show a suppressed $\epsilon(T)$ dependence in the ferroelectric phase and a modified Curie-Weiss law in the paraelectric phase, within GB region where the built-in potential barrier is high, the dielectric constant is diminished by comparison to the bulk (Fig. 1). We considered the potential as parabolic, partially screened in the bulk and dependent on the spatial coordinates and temperature. The computed resistivity $R(x, T)$ is shown in Fig. 2. The PTCR jump at the transition temperature (around 400K) is observed both in the bulk and in the grain boundary region, but with different intensity. The values of the resistivity itself and of the PTCR jump are higher in the grain boundary region ($x=0$), confirming the hypothesis that PTCR is indeed a grain boundary phenomena. The average values of the grain boundary and bulk resistivity after integration over spatial coordinate, can also be calculated, for different values of the model parameters.

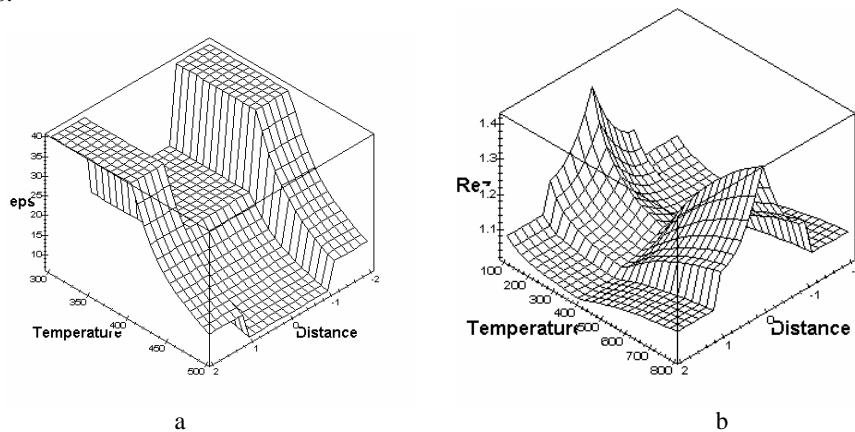


Fig. 1 Simulated coordinate and temperature dependencies of the: (a) Dielectric constant $\epsilon(x, T)$, (b) Resistivity $R(x, T)$. The distance x is considered across the boundary between the adjacent grains.

3.2 The role of the free electron sub-system on the PTCR behaviour

In Fig. 2, the computed logarithm of the relative density, $\log(R_{GB}/R_{bulk})$ is depicted, for the indicated values of the model parameters [8]. The model correctly describes that the PTCR anomaly takes place exactly at the Curie-Weiss temperature T_0 , that coincides or is very close to the temperature where the minimum value of the resistivity R_{min} is obtained. Looking to the Fig. 2, we can see that the approximation (8), used for many PTCR materials in literature [1-2], results indeed from the exact calculations of $R(T)$ dependencies obtained within the present theoretical approach. We mention that the approximation is valid only in a limited domain of temperatures included in the range (T_0, T_{max}) , where the dependence of the dielectric constant with temperature following the Curie-Weiss law impose the main trend of the $R(T)$ behaviour, since all the other parameters are practically constant. Consequently, a linear dependence of the logarithm of resistivity with temperature is obtained only in this limited range of temperatures.

The role of the Heywang model parameters [2] on the PTCR characteristics were also analysed. The results of our simulations based on the eq. (5)-(7) are presented in Figs. 3-7. Starting with the dielectric constant dependence on temperature as computed from the LD theory, we solved numerically the eq. (6) in order to find the barrier potential $V_0(T)$ and using it in (7), we calculated the bulk and GB resistivity.

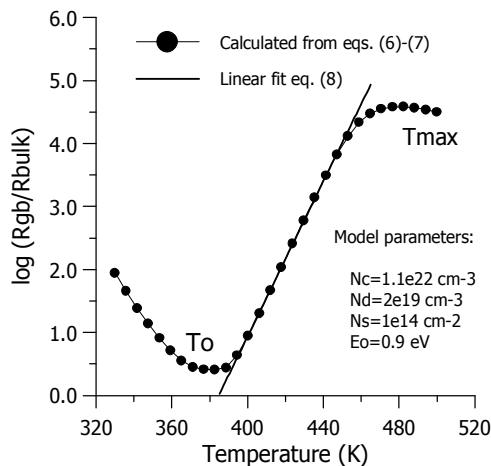


Fig. 2. Simulated PTCR curves for the indicated model parameters [8] and the linear fit eq. (8).

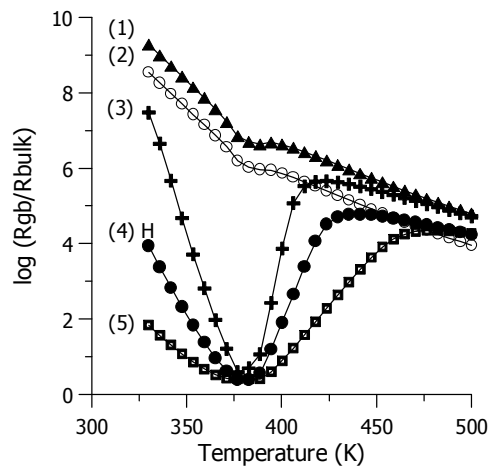


Fig. 3 The role of the donor concentration on the PTCR characteristics.

The role of the donor concentration on the PTCR curves is illustrated in Fig. 3, for the values: (1) $N_d=2 \times 10^{15} \text{ cm}^{-3}$, (2) $N_d=5 \times 10^{18} \text{ cm}^{-3}$, (3) $N_d=1 \times 10^{19} \text{ cm}^{-3}$, (4) $N_d=2 \times 10^{19} \text{ cm}^{-3}$, (5) $N_d=8 \times 10^{19} \text{ cm}^{-3}$, all the other parameters being the same as originally proposed by Heywang [7-8]. The $R(T)$ dependencies are affected by this parameter in whole the range of temperatures, giving rise to different values of resistivity at the room temperature, different NTCR in the ferroelectric phase and different PTCR behaviour (with various slopes and maximum value of the resistivity R_{max}). PTCR jumps of various orders in magnitude (2-6) can be obtained from the model for various donor concentrations. In case of Heywang value of $N_d=2 \times 10^{19} \text{ cm}^{-3}$, an increasing of the resistivity of 4 orders in magnitude was obtained (curve 4 in Fig. 3).

Similar PTCR curves as resulted for various donor concentrations were obtained for different surface state densities, as following: (1) $N_s=1.34 \times 10^{18} \text{ cm}^{-2}$, (2) $N_s=2 \times 10^{18} \text{ cm}^{-2}$, (3) $N_s=3 \times 10^{18} \text{ cm}^{-2}$, (4) $N_s=4 \times 10^{18} \text{ cm}^{-2}$, (5) $N_s=10^{21} \text{ cm}^{-2}$. The other parameters have the values originally proposed by Heywang [7-8]. The corresponding $R(T)$ dependencies are depicted in Fig. 4. This parameter affects the $R(T)$ curves in whole the range of temperatures. A strong NTCR effect is present in the ferroelectric phase for all the values of N_s . An increase of 4 orders in magnitude of the room temperature resistivity is achieved when the surface state density is ranging from $N_s=2 \times 10^{18} \text{ cm}^{-2}$ to $N_s=3 \times 10^{18} \text{ cm}^{-2}$ and only an increase of less than one order is obtained between $N_s=3 \times 10^{18} \text{ cm}^{-2}$ and

$N_s=4\times 10^{18}$ cm⁻². The high temperature resistivity tends to similar values for a surface state density $N_s<4\times 10^{18}$ cm⁻².

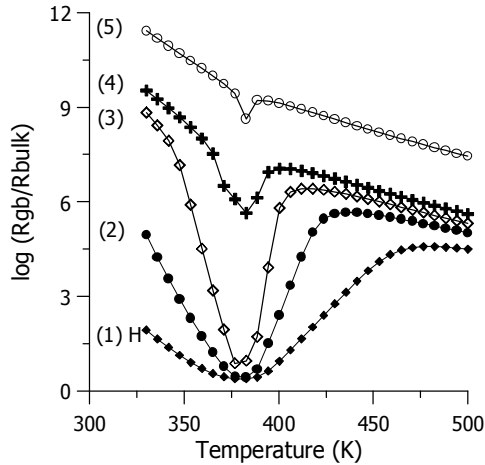


Fig. 4 The role of the surface state density on the PTCR behaviour.

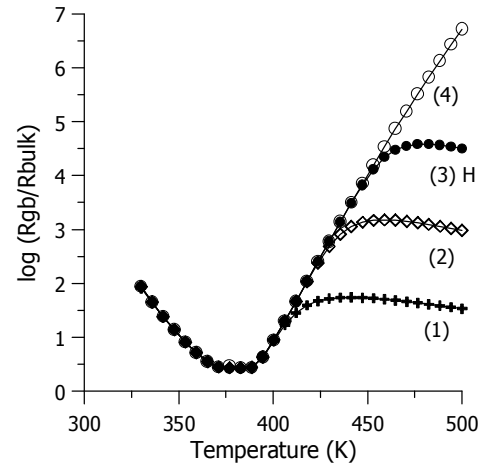


Fig. 5 The role of the surface state energies on the PTCR characteristics.

The influence of the surface state energy on the logarithmic $R(T)$ dependencies are shown in Fig. 5, for E_s having the values: (1) $E_0=0.5$ eV, (2) $E_0=0.7$ eV, (3) $E_0=0.9$ eV and (4) $E_0=1.4$ eV. The slope of the PTCR curves, the resistivity in whole the ferroelectric region and the minimum value of the resistivity R_{\min} are not affected by this parameter. Instead, it determines the maximum value of the resistivity R_{\max} and the temperature corresponding to this maximum (T_{\max}), giving indications about the total PTCR jump of the resistivity. The thermal energy corresponding to the maximum resistivity, kT_{\max} , where the depopulation of electron traps starts to take place, is commonly used in literature [1-2] as an estimation of the surface state energy. According to the dependence of kT_{\max} as a function of the surface state energy obtained from the present theoretical approach (that is not a linear one, as shown in Fig. 6), we can see that the approximation $E_s \approx kT_{\max}$ is a rough approximation valid only for low values of the surface state energy. For instance, according to our calculations, for $E_0=0.4$ eV, the corresponding thermal energy is $kT_{\max}=0.375$ eV, but the value $E_0=1$ eV is more than 50% underestimated by the corresponding thermal energy that is of 0.42 eV).

Therefore, the calculated logarithm of the maximum relative resistivity shows a perfect linear dependence *versus* the surface state energy E_0 , as presented in Fig. 7. This dependence obtained from the model prove the essential role of the surface state energy in establishing the maximum value of the resistivity and finally the total PTCR jump for a given sample.

In conclusion, the influence of the model parameters on the characteristics of the PTCR effect can be summarised as following: (a) the temperature corresponding to the minimum resistivity is approximate equal to the critical temperature of the ferro-para phase transition and it is determined only by the ferroelectric lattice imposed through the composition of sample; (b) the resistivity at the room temperature is determined mainly by the donor concentration and less by the surface state density; (c) the minimum value of the resistivity is determined by the effective donor concentration; (e) the slope of the temperature dependencies of $\log(R_{GB}/R_{bulk})$ are determined mainly by the donor concentration and by the surface state density; (f) the maximum value of the resistivity and the temperature corresponding to this maximum are influenced by the donor density, but determined essentially by the surface state energy.

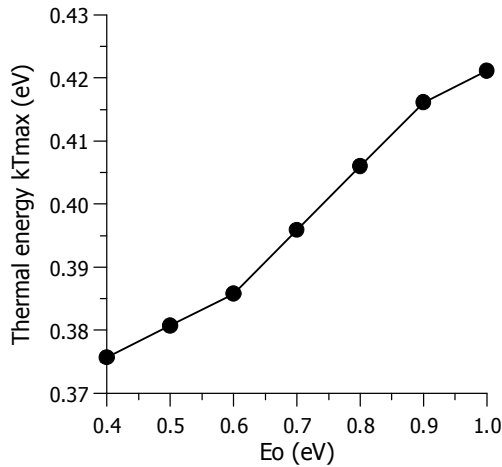


Fig. 6 The maximum thermal energy vs. the surface state energy, E_0 .

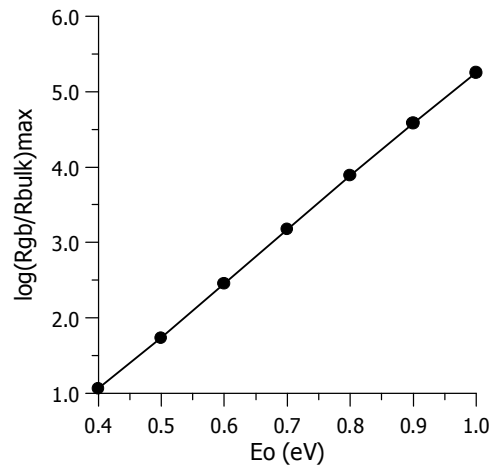


Fig. 7 The maximum value of the logarithm of resistivity vs. the surface state energy, E_0 .

4. Conclusions

The double depletion layer model (Heywang-Jonker) and the Landau-Devonshire theory of ferroelectricity were used together in order to describe the connected ferroelectric and semiconductive properties of BT-based PTCR materials. The resistivity-temperature dependencies were described successfully by the present approach in the whole range of temperature, including the ferro-para phase transition. The role of the donor concentration, of the density of surface states and of the trap energy on the PTCR behaviour and parameters were discussed.

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References

- [1] J. Nowotny, M. Rekas, *Ceramics International* **17**, 227 (1991).
- [2] W. Heywang, *Ferroelectrics* **49**, 3 (1983).
- [3] A. F. Devonshire, H. H. Wills, *Adv. Phys.* **3**[10], 85 (1954).
- [4] D. Y. Wang, K. Umeya, *J. Am. Ceram. Soc.* **73**, 669 (1990); **73**, 1574 (1990); **74**, 280 (1991).
- [5] J. Nowotny, M. Rekas, *Ceramics International* **17**, 227 (1991).
- [6] Y. Yano, K. Iijima, Y. Daitoh, T. Terashima, Y. Bando, Y. Watanabe, H. Kasatani, H. Terauchi, *J. Appl. Phys.* **76**, 7833 (1994).
- [7] W. Heywang, *Solid State Electron.* **3**, 51 (1961).
- [8] W. Heywang, *J. Am. Ceram. Soc.* **47**, 484 (1964).