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CHARACTERIZATION OF PTC EFFECT IN BATIO$_3$-CERAMICS AS A SPECIAL PHASE TRANSITION – FRACTAL APPROACH

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Abstract. *The applications of $BaTiO_3$-ceramics are very important and constantly increasing nowadays. In that sense, we analyzed some phenomena related to inter-granular effects. We used experimental data based on Murata powders and processing technology. Our original contribution to Heywang-Jonker-Daniels inter-granular capacity model is based on thermodynamic fractal analysis applied on phase transition in ceramic structures. In this case, PTCR effect has a diffuse first-order phase transition character in a modified Landau theory-fractal approach. Its basic properties are considered. This is an original contribution as a bridge between theoretical aspects of $BaTiO_3$-ceramics and experimental results.*

Key words: *PTCR effect, $BaTiO_3$-ceramics, Heywang-Jonker-Daneils model, fractal correction, phase transition*

1. INTRODUCTION

The positive temperature coefficient of electrical resistivity (PTCR or PTC) effect, in this case, is a jump in the resistivity of many orders of magnitude in a certain temperature range of the poly-crystalline semiconducting *n*-doped $BaTiO_3$ across the Curie point ($T_0 \sim 130^oC$), respectively, in the paraelectric-ferroelectric phase transition (tetragonal-cubic structural change) (see [1-4]). For NTC materials, the temperature coefficient of electrical resistivity has a negative value. The PTC phenomena are usually strongly associated with the grain-boundary phenomenon and, by themselves, represent the electric semiconductor-insulator transition, which will be preliminarily shown in this text. A typical material with PTCR properties is a $BaTiO_3$-ceramic doped with 0.5 x10^{-2} mol $Nb^{3+}$of or Sn^{3+} [1]. In the

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PTC markets, there is an enormous number of devices based on the PTCR effect. For example, those could be chemical sensors, heaters, and current limiters.

Sintering in an oxygen atmosphere affects not only the two-layer electrical potential barrier height, but also the grain boundaries resistance and capacitance. Due to adsorbed gases variations at the grain boundaries this effect appears. Sintering under these atmospheric conditions, results in increasing the number of oxygen acceptors and resistance in the grain boundary. The PTC effect in $BaTiO_3$, as a complex phenomenon, according to available literature, involves more general features (Nowotny and Rekas [5], Mitić [6]).

In short, the most important causes that lead to the PTC effect are the donor concentration – the charge carrier concentration – N_d, the acceptor state density at the grain boundaries – N_s, and the depth of acceptor level – the energy gap between the energy levels of the acceptor states – E_s. In addition to these variables, but less important, are the indirect causes such as porosity, mean grain size (~ 10 μm), abnormal grain growth, preparative conditions, and composition, etc.

The most important model to be considered here is the Heywang model based on statistical thermodynamic methods - Heywang [7,8], as well as its modifications, the Jonker [9], Daniels [10], and Mitić-Kocić fractal approach [11,12]. Nonetheless, other models are also known; for example [6], Lewis and Catlow for Ti acceptors, Saburi models of variable valences of Ti^{4+} ions etc.

In this paper, based on the theory of phase transitions [13-16], especially Mott's electric insulator-conductor phase transitions [17], and, on the basis of the above, supported by the experiment, a simple model of the Landau-type Joule heating of this diffuse phase transition for the PTC effect could be formulated.

The paper is organized in the following way: In Section 2, the basics of experimental design and theoretical models are described. Section 3 is the basic part of the work. This Section discusses the experimental results and formulates a preliminary model. The paper is concluded with Section 4.

2. EXPERIMENT

2.1. Experimental details

The samples used for analysis in this paper were obtained using the solid-state sintering method [6]. As the starting material, high purity, commercial $BaTiO_3$ Murata powder (99.9% purity, mean grain size <2μm) was used. The starting powder was mixed into a mill with balls and isopropyl alcohol. In the mixture, organic binders were added, and homogenization was performed for 48 hours. This powder was dried and granulated at a standard vibrating sieve – Fritch Pulverissete 5. Then, the powder is pressed into tablets at a pressure of 86 MPa. After pressing, the samples were sintered at 1190ºC for 1 and 2h.

Electrical characteristics in the function of temperature were measured with Hewlett Packard 4276A LCZ meter. The measuring electrical resistance was at the constant voltage U=250V. In continuation, our method, with the use of mathematical-physical tools, was applied to pure $BaTiO_3$.

2.2. Theoretical models of the PTC effect and electrical properties of $BaTiO_3$- ceramics

Heywang assumed in [7,8] model with a two-dimensional layer with grain boundaries and active acceptor states. These acceptors attract electrons from the bulk, resulting in an electron-depletion double-layer electric-potential barrier of Schottky type with thickness of *b* (see Fig. 1),

$$b = \frac{N_S}{2N_d} \tag{1}$$

The temperature dependence of the acceptor state density, $Ns=Ns(T)$, (T-temperature), for N_{s0} – the total number of acceptor states is described by:

$$N_S = \frac{N_{S0}}{1+\exp\dfrac{(E_F + e\phi_0 - E_S)}{kT}}, \tag{2}$$

where E_S is the energy of acceptor states, e – elementary charge, k is the Boltzmann constant, and, for N_C – the effective density of the states in the conduction band, E_F is the Fermi energy which equals

$$E_F = kT\ln\frac{N_C}{N_d}. \tag{3}$$

The depletion layer formula in a grain boundary electric potential barrier φ_0 is:

$$\phi_0 = \frac{eN_S^2(T)}{8\varepsilon_0\varepsilon_r(T)N_d}, \tag{4}$$

where, ε_0 – vacuum permittivity, $\varepsilon_r=\varepsilon_r(T)$ s the relative permittivity of the grain boundary region. Permittivity ε_r follows the Curie-Weiss law:

$$\varepsilon_r = \frac{C}{T - T_0}, \tag{5}$$

where C is the Curie-Weiss constant.

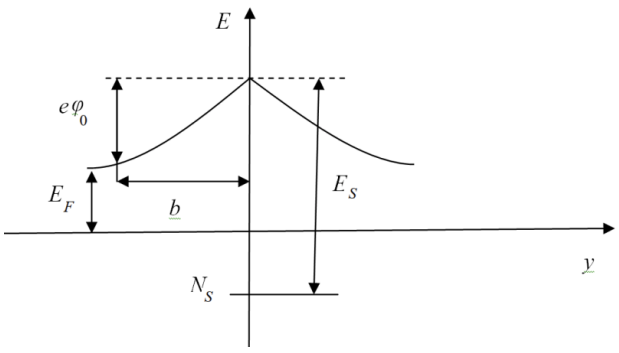

Fig. 1 Double Schottky barrier at the grain boundary caused by a two-dimensional acceptor layers with the grain boundary. After Heywang 1961, 1964 [7,8]

At $T=T_0$, for the Fermi energy level E_F, the acceptor levels are well below and filled so that $Ns=Ns_0$. Due to the decrease in permittivity with increasing temperature in the grain boundary region – the phase transition of $BaTiO_3$ ceramics from ferroelectric to paraelectric above the Curie temperature T_0, potential φ_0 increases proportionally with the temperature as expressed in equations (4) and (5) (see Fig. 2).

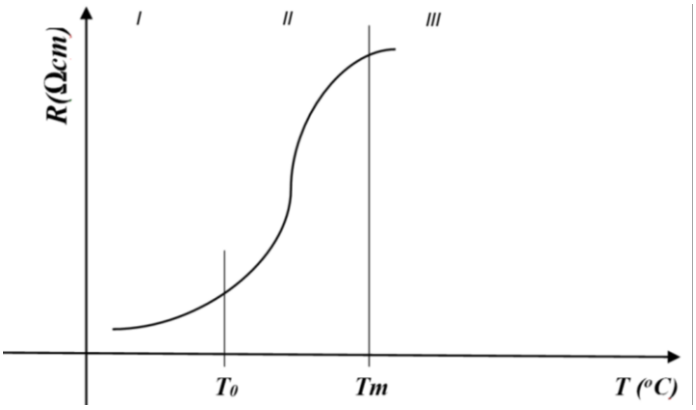

Fig. 2 A typical sketch graph characteristic of the PTC effect. The characterized temperature region or PTC ceramics: *I* – semiconductor region; *II* – transition region; and *III* – insulator region. The maximum resistivity is obtained at temperature T_m

In the region *II*, the dependence $R = R(T)$ is considered to be of the exponential type. The resistivity of the $BaTiO_3$-samples, R, is related to the Schottky potential barrier, as in equation, where R_0 is a constant:

$$R = R_0 \exp \frac{e\varphi_0}{kT}. \tag{6}$$

Heywang's model was not able to explain the PTC behavior below T_0 accurately. Jonker model ([9]) assumed that, as a result of strong electric fields around grain boundaries, the electric permittivity for a ferroelectric state is smaller than that assumed by Heywang. Lowering of the surface potential barrier is explained as the effect of compensation the surface charges with different directions of the ferroelectric domains on both sides. The total resistance of a material is described by the equation:

$$R = R_0\left(1+\frac{zbkT}{e\varphi_0}\exp\frac{e\varphi_0}{kT}\right). \tag{7}$$

Where z is the number of grains per cm. Based on Daniels type of models [10], the thickness of cation vacancy (oxygen, titan or, for Daniels model – barium vacancies) in sintered donor-doped $BaTiO_3$ grains, rich insulating layers can be up to 3 μm. With fine-grain $BaTiO_3$ samples, cation vacancy layers act as the acceptor state dominating the electric structures in the grains and these conditions resulting in the global insulation profile.

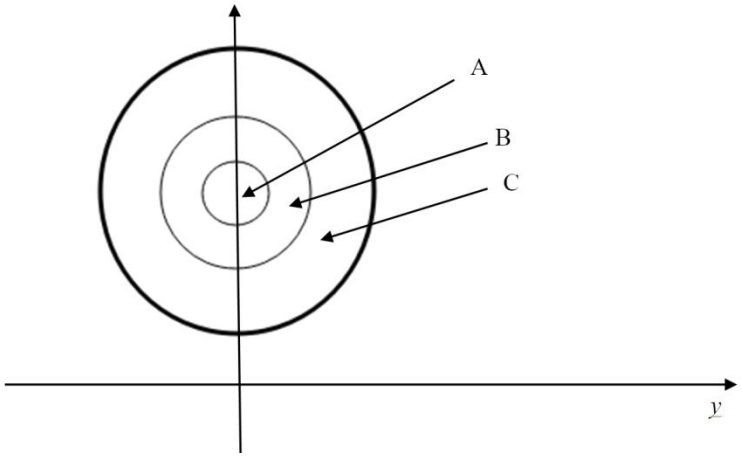

Fig. 3 Schematic picture of one ceramic grain in polycrystalline $BaTiO_3$ above Curie temperature T_0: A. Tetragonal type $BaTiO_3$ crystal region; B. Area with gradient of tetragonality; C. Cubic type $BaTiO_3$ crystal region. Roughly, in the region C located insulating grain boundary layer (here is the place of the nonzero Schottky potential barrier), A+B area bulk is characterized as *n*-type semiconductor, Nowotny and Rekas 1991 [5]

The PTC effect dependence, above the Curie temperature, on the grain size considered with influence the structural gradient across the $BaTiO_3$ grain [5]. According to them, below T_0 the tetragonal structure is stable only in the crystalline bulk phase. In the outer part of the grain forms, there is a low dimensional layer predominantly of the cubic structure. This circumstance results in the formation of the tetragonality gradient between the two structures (Fig. 3), [5]. Between the bulk and the insulating grain, this develops a boundary layer as an electrical potential barrier, resulting in a high electrical resistivity. Below T_0, the barrier significantly decreases as a result of high permittivity [7,8] or electrical polarization compensation effect produced ([9]) or due to the influence the presence of cation vacancies [10]. In further research into the PTC effect, new ideas emerged. For example, considering the fractality of grain or pore shapes, that is, electron trajectories in $BaTiO_3$-ceramics.

Benoit Mandelbrot [18] systematically introduced fractal geometry during six decades of the last century. In this context, for a practical approach for describing complex non-Euclidean curves and shapes, see [19]. Some examples of the application of fractal geometry are given by Gouyet [20]. Objects in the fractal geometry, among other things, are characterized by a unique number – the Hausdorff fractal dimension DH_f. The basic relation for it is $DH_f > DT$, where DT is the topological dimension. The Mitić-Kocić hypothesis is that the $BaTiO_3$–ceramics working temperature must be influenced by these three fractality factors. According to them, the correction of "theoretic" temperature T is:

$$T_f = \alpha_f T, \tag{8}$$

with fractal corrective factor α_f. These three factors α_S, α_P, α_M – in that order, surface, pores, and particle (electron) movement (Brownian motion) fractal parts, participate (see [11,12]) as follows:

$$\alpha_f = \Phi(\alpha_S, \alpha_P, \alpha_M), \tag{9}$$

where, Φ is some function. In the paper Mitic et al. [11], showed the contours of many ceramic grains to be fractal curves with $1.5 < DH_f < 2$. For theoretical elaboration on α_M see [21]. In this context, proposed by Uchino and Nomura [22], the diffuse phase transformation of relative permittivity ε_r at T_{max} the equation

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{r\max}} = \frac{(T - T_{\max})^{\gamma}}{C'}, \tag{10}$$

C' is a Curie-like constant, and γ is the critical exponent. Exponent $\gamma \in [1,2]$, γ = 1,2, in order for a sharp phase transformation and for strong diffuse phase transition. For single crystal $BaTiO_3$, γ is 1.08. In the modified $BaTiO_3$-ceramics it can progressively increase up to 2 (see [12]). The connection of the mentioned phase transitions with the fractal structure of ceramics is known in the literature. Therefore, it also affects the conductive properties of $BaTiO_3$ ceramics. The PTC effect could, for the above, be considered as a kind of conditional, diffuse phase transition. However, the thermodynamic equation of the state of clean-phase transition in this context is not determined. In this paper, based on the theory of phase transitions (see [13-16]), especially Mott's electric insulator-conductor phase transitions [17], and on the basis of the above, supported by the experiment, a simple model of Landau-type Joule heating of this diffuse phase transition could be formulated. The reasons for using the word "diffuse", in relation to this phase transition, are due to the mechanism of its manifestation, but also to the theoretical method by which it is examined.

From the standard modern point of view, phase transitions and critical phenomena are essentially quantum-statistical phenomena, although they can very often be treated thermodynamically [4],[13-16]. Phase transitions in the case of electrical conductivity of the conductor (usually, metal)-insulator type can be considered, roughly, from more aspects [17], [20]: strictly correlated systems (e.g. the Mott phase transition [17]), disorder, frustration, and fractals [20]. The Mott phase transition, which has a behavior similar to the NTC effect (see [23]), in principle, cannot be applied to $BaTiO_3$-ceramics or analogous materials due to the absence of structural details.

The basic restrictions for the classification of simple insulators or conductors and "weak" external fields is Ohm's law between the current density j_α and the applied electrical field E_β, [17] ($\alpha, \beta = 1, \ldots, d$; d is the dimension of the system):

$$j_\alpha(\mathbf{q}, \omega) = \sum\nolimits_\beta \sigma_{\alpha\beta}(\mathbf{q}, \omega) E_\beta(\mathbf{q}, \omega). \tag{11}$$

If linear response theory is applied, then the conductivity tensor is $\sigma_{\alpha\beta}(\mathbf{q}, \omega)$ derived from an equilibrium current-current correlation function. For an insulator, at zero temperature, the static electrical conductivity vanishes (Re {. . .}: real part):

$$\sigma_{\alpha\beta}^{DC}(T \to 0) = \lim\nolimits_{T,\omega,|\mathbf{q}|\to 0} \mathrm{Re}(\sigma_{\alpha\beta}(\mathbf{q}, \omega)) = 0. \tag{12}$$

For an ideal metal-conductor, the behavior of this tensor is (e as the elementary charge and n/m^* as the ratio between the charge carrier concentration and the effective mass):

$$\mathrm{Re}(\sigma_{\alpha\beta}(\mathbf{q}; \omega, T \to 0)) = \frac{\pi e^2 n}{m^*} \delta_{\alpha\beta} \delta(\omega). \tag{13}$$

Results reported by Limelette et al., 2003 [24] for Mott metal-nonmetal (here, metal-dielectric) transition report conductivity measurements of Cr-doped V_2O_3, determined critical thermodynamic relations associated with the equation of state and corresponding exponents. The universal scaling function associated with the equation of state, for conductivity σ, pressure P, and temperature T, of the following type: $\sigma=\sigma$ (P, T), is investigated in detail. The universal properties of a liquid-gas transition are established.

$BaTiO_3$ -ceramics and their dielectric properties, partly in contrast to single-crystal theory (see Wang 2010 et al. [25], and their dependence $\varepsilon_r = \varepsilon_r$ (P, T)) – the pure thermodynamic approach, the situation is more complicated. Within the linear Heywang-Jonker – Daniels theory using the fractal approach, for constant state parameters, exists this relation $\varepsilon_r(\omega)$-1 = $\sigma(\omega)/i\omega\varepsilon_0$. From the semiconductor-dielectric diffuse phase transition point of view, all of these can lead to a new, conductive phase transformation, which could be the best candidate for the PTCR effect understanding and explanation.

3. Results and Discussion

In this section, considering the foundation of the thermodynamic PTCR effect. It represents a continuation of the research of the Landau's thermodynamic theory presented by Wang 2010 et al. [25]. Haywang's model, etc., is microscopic and yet semi-qualitative, and, in some segments, explanatory. It does not foresee the possibility, either quantitatively or qualitatively, that this is, from a theoretical point of view, a phase transition. More precisely, therefore, it is a phase transition and not a PTCR effect. The effect, in this context, physically, is characterized by a single phase (for example, the Meissner effect exists in a superconducting phase).

Similar to non-diffuse first-order phase transition in dielectrics under a hydrostatic pressure, within the Landau-Devonshire model, the following correction of the Gibbs free energy originating from the electric current density is in the form of:

$$G(T, j) = G_0 + a_j (T - T_{p0}) j^2 + B_j j^4 + D_j j^6, \tag{14}$$

Where G_0 – Landau-Devonshire potential, B_j<0, D_j>0, $T_p=T_{p0}+B_j^2/(4a_jD_j)$-transition temperature (see [4], [15], [16], [25]). If the external electric field E is a constant ($\sigma=j/E$), the temperature dependence of σ in a first-order phase transition is given in the Fig. 4.

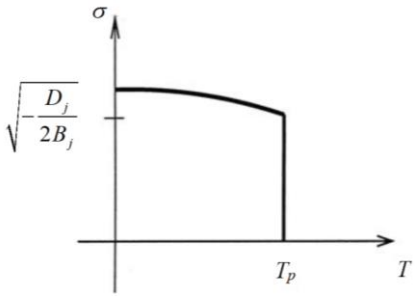

Fig. 4 The temperature dependence of electrical conductivity σ in a first-order phase transition, as an explanation of the non-diffusion part of the PTC effect, similar to Schwabl 2006 [15]

In [6], for undoped atmospherically reduced $BaTiO_{3-x}$, after the fluorination process, a significant PTC effect was manifested. Experimental results and the graphs, logarithms of the specific electrical resistivity R (Ω cm) as a function of temperature T, for sintering times 1, 2, and 3 h, are given in that paper. For further analysis, in the case of atmospheric pressure, more acceptable is a dependence conductivity function $\sigma = \sigma(T)$, ($\sigma = 1/R$) as Fig. 5.

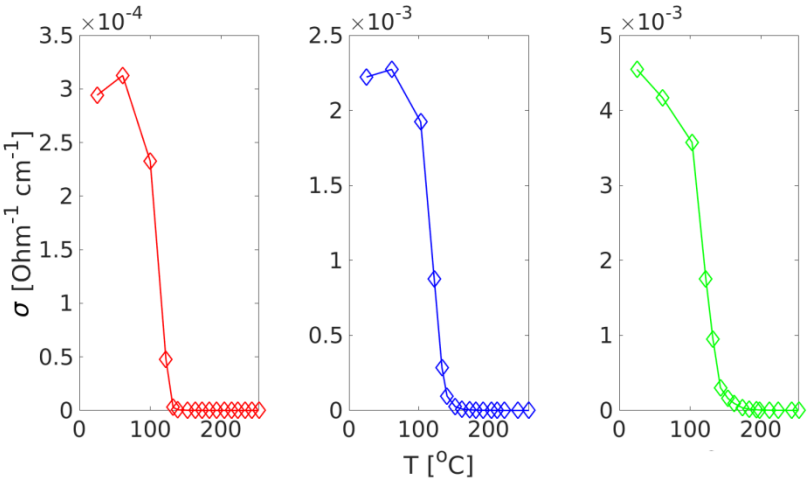

Fig. 5 PTC effect for undoped $BaTiO_{3-x}$ after fluorination process, semiconductor-insulator relative phase transition, specific electrical resistivity R, conductivity function $\sigma = \sigma(T) = 1/R$, T is temperature. From left to right, sintering time, in order: 1, 2, and 3h; Mitić, 2001 [6]

In the thermodynamic theory of phase transitions, various thermodynamic potentials are considered, such as free energy as a function of characteristic parameters. $BaTiO_3$ grains are characterized by the dependence of Gibbs free energy on polarization and strain [25], [26]. As a result, in particular, a known dependence $\varepsilon_r = \varepsilon_r(p,T)$ is obtained. For $BaTiO_3$ ceramics, this may have a very small effect, due to the described general conditions of the PTC effect. The idea of the paper is to start from macroscopic electro-thermal effects in the case of transport processes in a constant applied electric field E, for external atmospheric pressure unchangeable and fixed measurement time interval and volume of specimens – t, V. Joule's law in differential form for metals is known:

$$\frac{d^2Q}{dtdV} = \mathbf{j}\cdot\mathbf{E}. \tag{15}$$

Q is the Joule heat. For $BaTiO_3$ ceramics, generalized Ohm's law $j = \sigma_\alpha E^\alpha$ ($1 \le \alpha < 15$, [27]) is considered. It will be considered as $\alpha = 1$. Then, it is valid that:

$$\frac{d^2Q}{dtdV} = \sigma E^2 \sim \sigma, \tag{16}$$

or:

$$Q = Vt\sigma \sim \sigma. \tag{17}$$

In this context, the following physical quantities (due to the constancy of the pressure, a label is introduced $Q=Q_p$, see [13]) are important the most:

$$\frac{d\sigma}{dT} \sim \frac{dQ_p}{dT} = c_p, \tag{18}$$

c_p is the molar heat capacity and the molar entropy:

$$\int \frac{d\sigma}{T} \sim S_e = \int \frac{dQ_p}{T}. \tag{19}$$

If the chemical potential $\mu=0$, for the Gibbs potential $G=G(T, p)$, the following thermodynamic relations are known:

$$S_e = -\left(\frac{\partial G}{\partial T}\right)_p \tag{20}$$

and

$$c_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p. \tag{21}$$

By definition, a first-order phase transition has a finite discontinuity in the first derivative by temperature of the Gibbs potential $G(T, P)$ and a divergence in the second derivative, [13,15].

If numerically differentiated by the temperature, the data $\sigma = \sigma(T)$ in Fig. 6 presents dependency $(d\sigma/dT)(T)$ which is obtained as shown in Fig. 7.

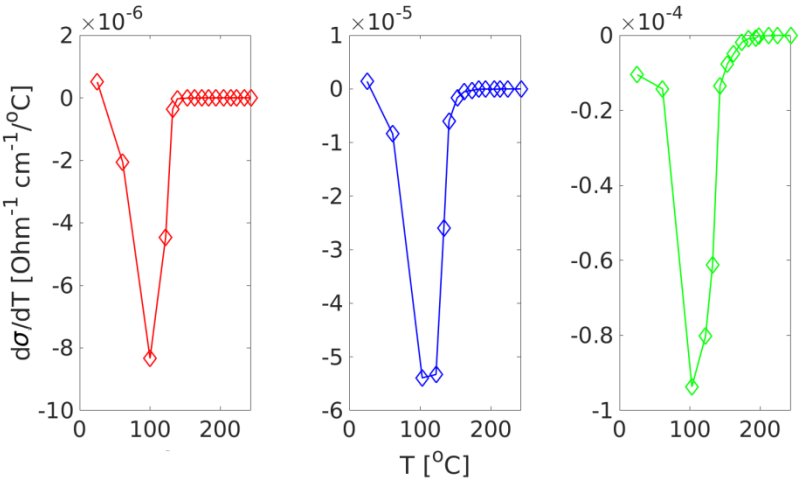

Fig. 6 Numerically differentiated curves $\sigma = \sigma(T)$ presented in Fig. 5. The temperature corresponding to the minimum of the curve is T_p

The temperatures of the relative or diffuse phase transitions are T_{p1}=100.0 ^oC, T_{p2}=102.8^oC, and T_{p3}=102.8^oC. The sintering time does not significantly affect their value. The minimums on the curves in Fig.6 are not a divergence in infinite. The equation (18) shows that this is a diffuse jump in magnitude proportional to c_p. In order to show that this is indeed a diffuse first-order phase transition, it is necessary to obtain the dependence of entropy on temperature. Using the procedure of numerical integration and relation (19), Fig. 7 is obtained.

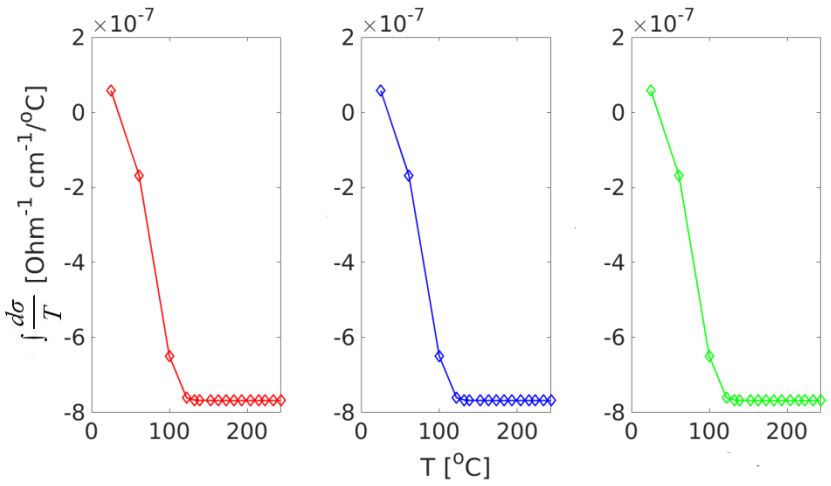

Fig. 7 Numerically integrated data from curves $\sigma = \sigma(T)$ in Fig. 5 using the equation (19). Entropy S_e has a diffuse finite jump

One way of considering this "diffusivity", based on degree laws, at this point, it is relevant, to consider the following relation:

$$\sigma_\alpha(T) = \sigma_\alpha(T_p) + |T - T_p|^{\alpha_{L,R}} . \tag{22}$$

Fitting experimental data to obtain, respectively (*L*-left, *R*-right), for α_L – 0.3054, 0.0210 and 0.5861, and, for α_R - 0.4314, 0.4567, and 0.4416. Then, the first derivation by temperature from a variable σ_α (T) determines the behavior around the phase transition point. These values suggest that there is scaling behavior in $BaTiO_3$ based on the relation of ceramic conductive properties. Electrical conductivity, in our preliminary model, around the temperature T_p, is α_L=0.5 and α_R=0. Statistical aspects for (22), in general, are given in [28]. However, it is necessary to discuss based on fractional-fractal Brownian motion [29]. There are also opportunities for further improvements. The evident diffusity of the transition can be interpreted by the geometric and velocity fractality, which is described by the equations (9) and (10). In particular, on the circumstances related to more general Gibbs free energy and entropy concepts (related to fractal dimension and entropy [30]), in addition to results related to various experiments, more analysis is necessary, based on the works [24] and [25]. The question arises, however, based on other thermodynamic phase transitions, such as the liquid-gas transition.

4. CONCLUSION

In this paper, preliminarily, the modified Landau theory of a diffuse first order phase transition was considered for a description of the PTCR effect in the specific case of $BaTiO_3$ ceramics. As a basis of it, the fractal Heywang-Jonker-Daniels model was considered. In addition to the basic thermodynamic relations, though slightly modified, the experimental results of the PTCR characteristic effect, for almost pure $BaTiO_3$-ceramics, were used.

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