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Analysis of conductivity and PTCR effect in Er-doped $BaTiO_3$ ceramics

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Abstract

Barium titanate ceramics with different Er additions in the range from 0.25 to 8 at.% were prepared by a solid state route. Several values of the nominal Ba/Ti ratio were considered according to different potential incorporation mechanisms of the dopant. PTCR effect was detected also for high Er content and for different nominal incorporation mechanisms. Impedance Spectroscopy and I–V measurements in the temperature range from 20 to 200 °C were used to verify the Double Depletion Layer model over the whole temperature range. First results of Differential Analysis of Impedance data are presented.

Keywords: $BaTiO_3$ and titanates; Impedance; PTC devices

1. Introduction

The Positive Temperature Coefficient of Resistivity (PTCR) effect is a jump in the resistivity of a few orders around an onset temperature T_0 (Fig. 1). It is observed in polycrystalline semiconducting *n*-doped $BaTiO_3$ (BT) across the Curie temperature (T_c) of the ferroelectric-paraelectric transition and it is strongly related to grain boundary phenomena.[1] A large number of devices based on the PTCR effect, like heaters, current limiters and chemical sensors exist and are produced both in the form of a bulk ceramic and film.[2–4] In spite of the wide diffusion of PTCs, several fundamental aspects, still unclear, are responsible for the lack of standardisation in the preparation methods used by different manufacturers and limit the development of new applications for such devices (e.g. embedding in printed circuits). In order to obtain semiconducting ceramics with PTCR behaviour, light doping (0.1–0.5 at.%) with elements substituting at the Ba or Ti site is required, associated to the formation of electrons as charge compensation defects. The ionic radius of the substituting element is the parameter which mainly determines the incorporation site, i.e. large ions like La^{3+} (1.15 Å) replace Ba^{2+} (1.35 Å), while small ions like Nb^{5+} (0.64 Å) replace Ti^{4+} (0.68 Å). Ions with intermediate size like Er^{3+} (0.96 Å) can be accommodated in both sites and with different mechanisms of charge defect compensation, depending on the stoichiometry of hosting structure.[5]

The most widely accepted model of the PTCR effect, due to Heywang and Jonker (HJ),[6,7] is based on the existence of Schottky potential barriers caused by electron acceptor states at grain boundaries. This theory successfully explains the increasing part of the resistivity in the paraelectric phase, but it is unable to explain the screening of the potential taking place for $T < T_0$, i.e. when the BT structure is in the ferroelectric state, as well as the non-linearity of the I–V characteristic close to the maximum of resistivity.[8,9] For practical purposes, a simultaneous description of the whole $R(T)$ curve is required, in order to identify the best material's properties and optimal processing conditions for the PTCR effect. Taking into account the interrelation between the conductive and ferroelectric properties of BT ceramics,

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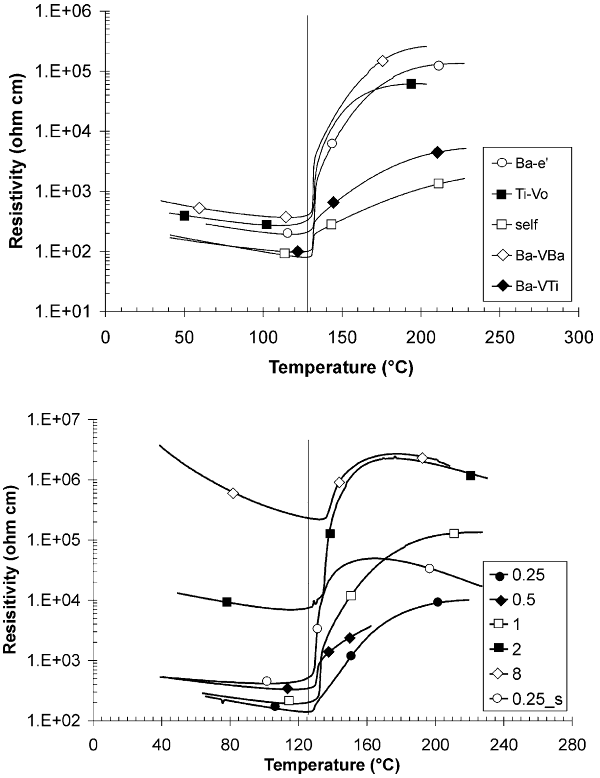

Fig. 1. Resistivity vs. temperature curves for various Er-doped $BaTiO_3$ ceramics: the upper part refers to samples with 1 at.% of Er and different stoichiometries, the lower part is relative to samples doped with mechanism (i.) and with different Er amounts.

a theoretical approach was recently developed[10] which extends the HJ theory also to the ferroelectric phase. Here we report the PTCR behaviour of Er-doped BT ceramics in a wide range of compositions and the analysis of d.c. and a.c. conductivity of selected samples in the frame of such extended HJ theory. In addition, preliminary results about the Differential Impedance Analysis (DIA) of impedance spectroscopy measurements of Er-doped $BaTiO_3$ are reported.

2. Experimental

Powders of Er-doped $BaTiO_3$ were prepared by the solid state route. Proper amounts of $BaCO_3$, TiO_2 and $Er(NO_3)_3$ were mixed by wet ball milling and reacted at 1100 °C for 4 h to prepare the following nominal compositions, each corresponding to a different incorporation mechanism:

1. $Ba_{(1-y)}Er_yTiO_3$, Ba substitution, electron compensation,
2. $Ba_{(1-y)}Er_yTi_{(1-y/4)}O_3$, Ba substitution, Ti vacancies compensation,
3. $Ba_{(1-(3/2)y)}Er_yTiO_3$, Ba substitution, Ba vacancies compensation,
4. $Ba_{(1-y/2)}Er_yTi_{(1-y/2)}O_3$, Ba and Ti substitution, self compensation,
5. $BaEr_yTi_{(1-y)}O_{(3-y/2)}$, Ti substitution, O vacancies compensation.

The amount of Er ranged between 0.25 and 8 at.% ($0.0025<y<0.08$). After cold pressing at 150 MPa, powders were fired in Pt crucibles at 1450 °C for 24 h in air and cooled down at 10 °C/min. One sample with $y=0.0025$ was also cooled down at a lower rate (3 °C/min) to change the degree of reoxidation of grain boundaries. Grain size of sintered ceramics was evaluated by the intercept method on SEM images (LEO 1450vp). Resistivity vs. temperature curves were measured by the application of a steady voltage (1 V) across disk-shaped samples 1 mm thick with Ag–Pd electrodes and recording the current (Electrometer, Keithley 617). I–V curves were collected at different temperatures by the same equipment. The electrical impedance was measured as a function of frequency (FRA, Solartron SI1260) in the range 10^{-1}–10^6 Hz and at various temperatures. Experimental data were analysed by both the ideal circuits method and DIA.[11,12] An ideal circuit made of a resistance (R_{bulk}) in series with an R-C.P.E. parallel element (representing the grain boundary) was used to fit spectra by means of a non-linear least-squares procedure[13] and to extract the frequency independent parameters (dielectric constant and resistivity of bulk and grain boundary regions).

3. Results and discussion

A PTCR effect was detected for all nominal incorporation mechanisms up to 1 at.% of Er, while in the case of composition (i). (Ba substitution, electron compensation) the range extended to 8 at.% (Fig. 1). This is a clear indication that, for limited Er additions (<1 at.%), nominal compensation mechanisms (ii)–(v). did not actually take place or some other reaction contributed to the generation of conduction electrons. One possible explanation is the hypothesis of Morrison et al.[14] about the creation of electrons mainly by oxygen loss from the $BaTiO_3$ lattice at high temperature. This mechanism could also be significantly active for the nominal composition (i.) and explains the relatively low resistivities found even for high concentrations of Er. It is worth noting that the onset temperature (130–135 °C) is higher than the T_c of pure $BaTiO_3$. This is a quite unusual result, but is consistent with previous observations[5] of an increase in the tetragonality of Er-doped $BaTiO_3$ at room temperature with respect to pure $BaTiO_3$. Therefore, electrical measurements and structural analysis indicate that a stabilisation of the ferroelectric phase is occurring when up to 1 at.% of Er is incorporated in $BaTiO_3$. Several models have been proposed to describe electric conduction across the grain boundary barrier[8,15] and account for the non-linear dependence of current density on applied field. Deviations from Ohm's law are commonly expressed by the α parameter in the phenomenological relation:

$$\ln I = \beta + \alpha \ln V \tag{1}$$

where I is the current density and V is the voltage applied to the sample. For PTCR ceramics, values of α between 2 (Child's law) and 15 have been reported,[9] while theoretical estimations of that parameter remain below 6.[15] In our samples the deviation from linearity above T_0 was quite low ($\alpha \leqslant 2$) and almost independent from temperature, while a marked temperature dependence was shown by the β parameter in the ohmic region of the curves. In the limit of low voltage, the HJ formula for diffusion type conduction across the grain boundary can be simplified as:

$$\ln j = -\frac{\phi_0}{kT} + \ln\frac{\phi_0}{kT} + \ln\frac{n_D \mu e}{z_0} + \ln V_{gb} \tag{2}$$

where j and V_{gb} are current density and applied voltage drop across the grain boundary, ϕ_0 is the voltage barrier at grain boundary without external field, μ is the electron mobility, n_D is the donor concentration in the bulk and z_0 is the depletion layer width. Combining (1) and (2), an expression for the β parameter is obtained:

$$\beta = \beta(T) + \beta_0 = -\frac{\phi_0}{kT} + \ln\frac{\phi_0}{kT} + \ln\frac{n_D \mu e}{z_0} \tag{3}$$

where the dependence on temperature is mainly given by the function $\ln(x) - x$, with $x = \phi_0/kT$. Fig. 2 shows the $\beta(T)$ values calculated for two samples with nominal composition $Ba_{(1-y)}Er_yTiO_3$ and $y = 0.025$ (sample A) and $y = 0.08$ (sample B) at various temperatures in the range 40–200 °C, compared with the theoretical expression (3). The potential barrier ϕ_0 at grain boundary was estimated for each temperature by fitting the impedance spectroscopy data and using the extended HJ model, as described elsewhere.[10] This represents, in the ohmic regime, a validation of the method used to calculate d.c. properties by means of a.c. measurements and can be considered a demonstration of the validity of the Double Depletion Layer theory over the whole temperature range. Another confirmation of this model is the possibility to reproduce the temperature dependence of the resistivity both in the ferro and in the paraeletric phase: Fig. 3 shows an example of the improvement to the Heywang model obtained taking into account a partial screening of the grain boundary potential barrier by spontaneous polarisation for $T < T_c$. Good agreement can be found for samples with markedly different PTCR characteristics as those reported in Fig. 1.

A different approach to the analysis of IS data is represented by the Differential Analysis (DIA)[11,12] where information is extracted directly from experimental data, without assuming any preliminary working hypothesis, i.e. limited number of time constants or, equivalently, ideal circuits. This could be particularly beneficial for a deeper insight in the PTCR phenomenon, which is connected to the complicated structure and properties occurring at the grain boundary. The DIA is based on the local scanning analysis: a simple first order inertial system extended by an additive term is applied for a local estimator, called a local operating model (LOM). Structure of LOM is represented by a resistance R_o connected in series to a parallel R–C.

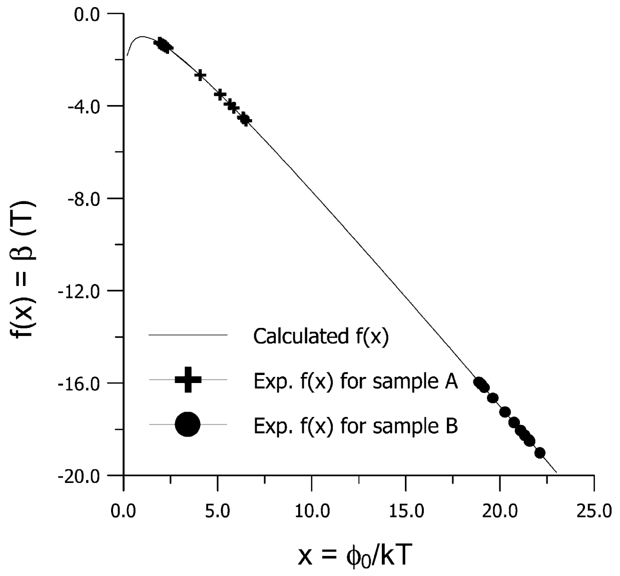

Fig. 2. The β (T) parameter estimated for samples of nominal composition $Ba_{(1-y)}Er_yTiO_3$ with $y = 0.0025$ (sample A) and $y = 0.08$ (sample B) at different temperatures in the range 40–200 °C.

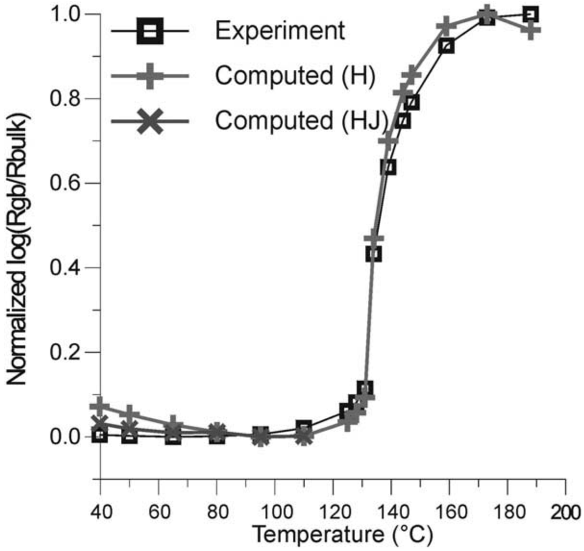

Fig. 3. Comparison among calculated and experimental resistivities for a sample of nominal composition $Ba_{(1-y)}Er_yTiO_3$ with $y = 0.0025$. Theoretical points are computed either using a low-temperature screening factor (HJ) or without any screening (H).

The procedure of the DIA includes a scanning with the LOM through the whole frequency range, applying a very narrow observation window—few, or even one point. This procedure ensures determination of the LOM parameter's estimates ($\hat{P}_{LOM}$). Usually it is applied in the following form, known as temporal analysis:

$$\lg\hat{P}_{\mathrm{LOM}} \Rightarrow f(\tau) \tag{4}$$

where $\tau = -\log\,\omega$ Eq. (4) can also be described in a spectral form, where the spectral line position determines the value of the parameter's estimate, while its intensity is determined by the frequency range where this value has approximately constant behaviour. An example of DIA is given in Fig. 4, where the temporal plots of the R parameter suggest that impedance diagrams are not completely described by the two time-constants model, even when a C.P.E. is used for the capacitance. In particular, three critical temperatures can be identified, the first (T_{C1}) corresponding to the beginning of transformation from a tetragonal ferroelectric structure to a cubic paraelectric one. The "fuzzy" behaviour of R in the low frequency region can be ascribed to a reorganisation of ferroelectric domains under the perturbation signal. At T_{C2} only positive values of R are obtained, indicating that the effect of the ferroelectric polarisation disappears, while at T_{C3} the system can be described with just one time-constant process. The spectral maxima in the spectral plots of resistance (R_{m}) well reproduce the general PTC behaviour reported in Figs. 1 and 3.

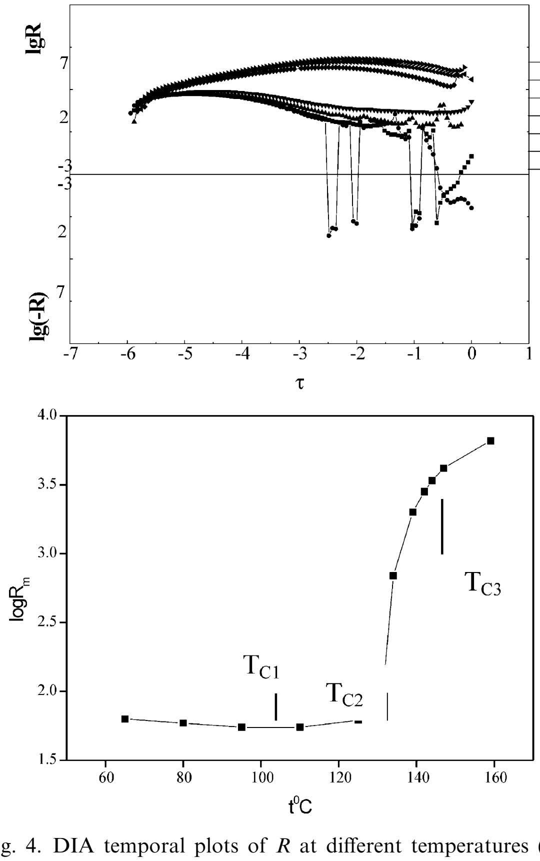

Fig. 4. DIA temporal plots of R at different temperatures (up) and development with temperature of R_{m} (down). The sample is the same of Fig. 3.

4. Conclusions

Barium titanate ceramics with different Er additions in the range from 0.25 to 8 at.% were prepared according to different potential incorporation mechanisms of the dopant. A PTCR effect is observed for Er concentration below 1 at.% also when the nominal compensation mechanism does not involve electrons production. The best resistivity jump was obtained for the composition $\mathrm{Ba}_{(1-y)}\mathrm{Er}_y\mathrm{TiO}_3$ with $y = 0.01$. The T_{c} of doped compositions slightly increases with respect to pure BaTiO_3 and is related to an increase in the tetragonality of the lattice. The Double Barrier Shottky theory has been applied to model the PTCR effect in Er-doped BT ceramics, by considering both ferroelectric and semiconducting properties. Using input parameters determined from IS measurements the model describes satisfactory both para and ferroelectric phases for different amounts of dopant. We believe that this approach can be useful for both the rationalisation of experimental data and the processing optimisation of PTCR ceramics. A phenomenological description of processes contributing to the PTCR effect was also given by the Differential Analysis of Impedance.

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