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Anomalous behaviour of dynamic electrical conductivity in semiconductor ferroelectric ceramics near the phase transition temperature

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Abstract

The article presents the results of a study of the electrical properties of semiconductor perovskite ceramics based on a solid solution of barium-strontium titanate with the addition of the rare earth element of cerium with the initial formula $Ba_{1-x-y}Sr_xCe_yTiO_3$ ($x = 0.05$, $y = 0.003$). A scanning electron microscope was used to obtain images of the sample surfaces and the elemental composition data. The measurements were performed by impedance spectroscopy in the temperature range of 348–385 K in the frequency range of 10^2 – 10^6 Hz using an LCR metre. It was found that there is an anomalous behaviour in the dynamic electrical conductivity of the samples in the temperature range close to the ferroelectric-paraelectric phase transition. This is expressed by a decrease in the value of the real part of the dynamic conductivity with an increase in frequency. An analysis of the simplified equivalent circuit of the intergranular barrier showed that this anomaly can be explained by introducing an inductive element into the circuit. This element can be considered a “negative capacitance element”. Following the results of the study, a conclusion was made about the generalised character of the phenomenon.

Keywords: Semiconductor ceramics, Impedance spectroscopy, Negative capacitance effect, Posistor

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1. Introduction

The study of barium-strontium titanate (BST) ceramics with rare earth elements has attracted the attention of researchers for many years [1–4]. Such interest is due to the fact that above the Curie temperature, there is a sharp increase in sample resistance, i.e. there is an effect of positive temperature coefficient resistance (PTCR), which enables the extensive practical use of the material. The mechanism of this effect has not been fully understood yet. Various models have been proposed, but the most widely recognised was the Heywang model [5], in which the temperature behaviour of doped titanates is attributed to phenomena occurring at the grain boundaries. The idea of the model is that at the grain boundary (GB) there are acceptor states with trapped electrons. This leads to the formation of a barrier layer similar to the Schottky barrier. The transition from the ferroelectric phase to the paraelectric phase leads to an increase of the barrier height and as a consequence the PTCR effect.

At the same time, an anomalous behaviour of electric quantities (so called “negative capacitance effect”) is observed in some oxide heterostructures, Schottky diodes, and metal-dielectric (ferroelectric)-semiconductor structures (MIS structures). This shows as a change in the nature of a sample’s impedance from capacitive to inductive. The study of this effect can give way to new micro and nanoelectronic devices, in particular to an increase in the capacity superdense dynamic RAM systems [6–17]. Since the negative capacitance effect can be found in heterophase structures, it is reasonable to assume that it is associated with phenomena at interphase boundaries of a different nature: at the grain boundaries in polycrystals, the barriers in the semiconductor diodes, at the metal-semiconductor or semiconductor-insulator barriers in MIS-structures.

Therefore, the aim of this work was to study the negative capacitance effect within the radio range of the test signal frequency at the Schottky barriers which are formed in the grain boundaries of posistor ceramics.

2. Experimental

Ceramic samples with the initial formula $\text{Ba}_{1-x-y}\text{Sr}_x\text{Ce}_y\text{TiO}_3$ ($x = 0.05$, $y = 0.003$) in the form

of tablets 10 mm in diameter and 1 mm thick were prepared by the technology of solid-phase pressing for posistors [18]. Trivalent cerium ions penetrate into the perovskite lattice and substitute divalent barium ions, which leads to the formation of semiconductor ceramics with an electronic type of conductivity, i.e. the following reaction takes place:



Following the preparation of samples, a microscopic examination of their morphology and elemental composition was conducted using a JEOL JSM 6380LV scanning electron microscope. Fig. 1 shows a micrograph of the mechanically chipped surfaces of the BST ceramics, which allows thoroughly analysing the shape and size of the crystallites, as well as the intercrystalline space. By the nature of the mechanical chipping it is obvious that the microcrystalline ceramic structure is fairly homogeneous and the size of most grains varies between 5 and 8 μm . The elemental analysis showed that the ratio between the sum of the N_{Ba} and strontium atom concentrations and the concentration of titanium atoms $\frac{N_{\text{Ba}} + N_{\text{Sr}} + N_{\text{Ce}}}{N_{\text{Ti}}} = 0.96$ corresponds (within the measurement accuracy) to the initial composition.

Electrical measurements were performed in the frequency range of 10^2 – 10^6 Hz and the temperature range of 348–385 K by impedance spectroscopy using a WK 4270 LCR metre. In-

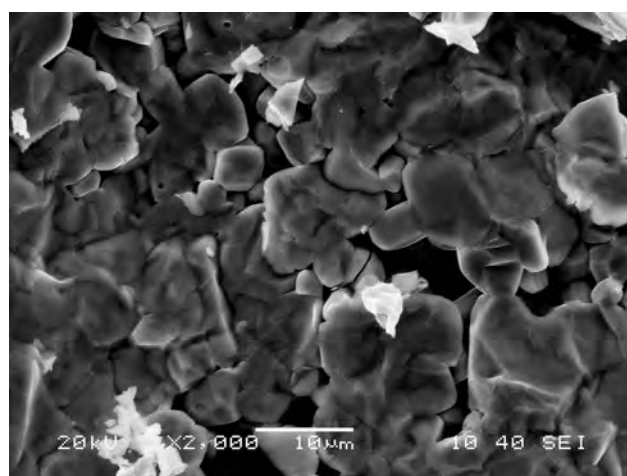


Fig. 1. Electron microscope image of the ceramic grains

Ga electrodes were previously deposited on the sample surfaces. It was found that for a temperature range of 293–348 K the contact resistance is negligible compared to the resistance of the sample.

The test signal amplitude was 0.3 V, the sample temperature was recorded with a thermocouple with an accuracy of ± 1 °C.

The indications of the LCR metre allowed determining the sample impedance module and the phase angle displacement between current and voltage. The dynamic conductivity Y was calculated from the impedance Z data using following formulas:

$$Y = \text{Re}Y + i\text{Im}Y = \frac{1}{Z}; Z = z \cos \varphi - iz \sin \varphi,$$

where Y and Z are complex values, z is the impedance module, φ is the phase angle displacement between current and voltage, i is an imaginary number.

3. Results and discussion

Fig. 2 shows the frequency dependence of the real part of the complex conductivity at various temperatures. In the range of high temperatures, the conductivity monotonously grows as, according to [5], there is an increase in the height of the potential barrier due to a decrease in

values of the dielectric permittivity near the grain boundaries (Fig. 2a). However, in the temperature range below the phase transition when the PTCR effect is slightly manifested, the behaviour is atypical: with an increase in frequency the conductivity first decreases and then increases, i.e. frequency dependencies show the minimum conductivity (Fig. 2b). Such behaviour may be due to the presence of the inductive circuit element or the “negative capacitance” effect. Structures, in which this effect was detected, have one thing in common: inertial conductivity whose mechanism can have its own peculiarities in each particular case.

We are not talking here about a real effect of the self-induced electromotive force, i.e. such an effect should be enhanced with an increase in frequency, while in the studied samples it is observed in the low-frequency region. However, the inductance can be considered as an inertial factor caused by the presence of a “delayed barrier” at grain boundaries as proposed in [19].

Let’s consider a simplified equivalent circuit (Fig. 3) of the grain boundary (GB) where one $R-L$ link reflects the Joule energy dissipation and the inertance of the charge carriers, and the other $R-C$ link considers the displacement current and dielectric losses of bound carrier oscillations in the space charge region (SCR).

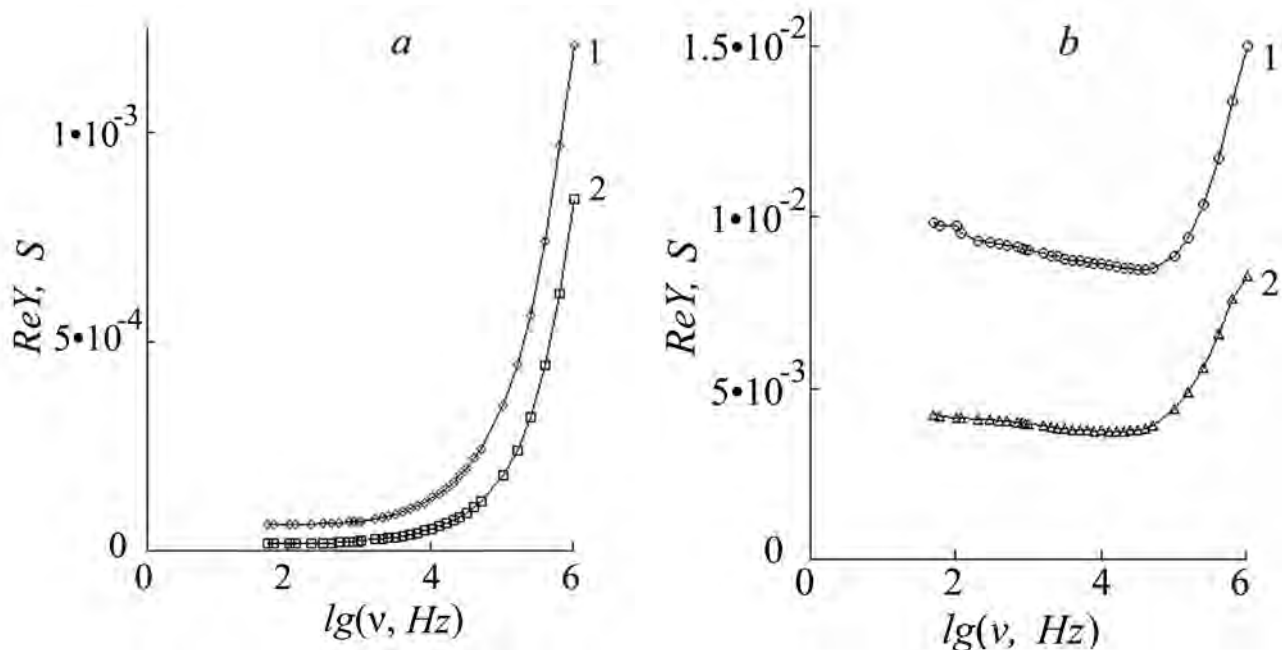


Fig. 2. Frequency dependence of the real part of the complex conductivity at different temperatures: a – curve 1 at $t = 75$ °C, curve 2 at $t = 81$ °C; b – curve 1 at $t = 103$ °C, curve 2 at $t = 102$ °C

Let Y_1 and Y_2 be admittance of the first and second link, respectively (see Fig. 3). Then admittance of the whole chain is $Y = Y_1 + Y_2$. As $Y = 1/Z$, then:

$$Y_1 = \frac{1}{Z_1} = \frac{1}{R_1 + i\omega L} = \frac{R_1}{R_1^2 + (\omega L)^2} - i \frac{\omega L}{R_1^2 + (\omega L)^2};$$

$$Y_2 = \frac{1}{Z_2} = \frac{1}{R_2 - \frac{i}{\omega C}} = \frac{R_2}{R_2^2 + \frac{1}{(\omega C)^2}} + i \frac{1}{R_2^2 + \frac{1}{(\omega C)^2}};$$

$$\text{Re}(Y_1) = \frac{R_1}{R_1^2 + (\omega L)^2}; \text{Re}(Y_2) = \frac{R_2}{R_2^2 + \frac{1}{(\omega C)^2}};$$

$$\text{Re}Y = \text{Re}(Y_1) + \text{Re}(Y_2).$$

where $\omega = 2\pi\nu$ is the cyclic frequency.

Fig. 4 shows the frequency dependences of real admittance components for each link and the whole chain. It is obvious that $\text{Re}Y$ in the range of $10^2 - 10^3$ Hz decreases and then increases with an increase in frequency. Thus, even a simplified circuit with an inductive element allows qualitatively interpreting the results of the experiment.

[20] proposed a method for presenting experimental data for a particular frequency band using CY – diagrams, where C and Y are real components of electric capacity and conductivity, respectively. Such an approach allows identifying the characteristic features of equivalent circuits with the inductance and capacitance elements.

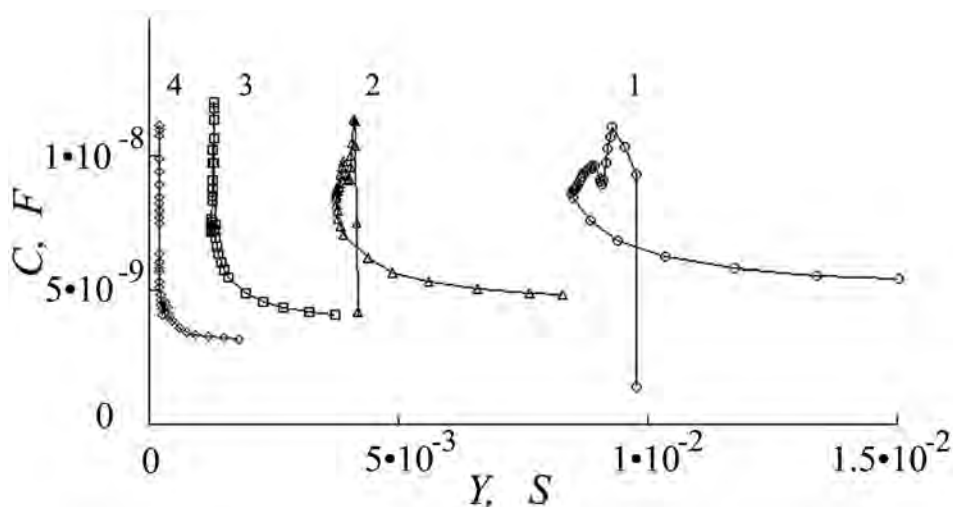


Fig 5. Capacity dependence on conductivity at different temperatures (in °C) 1 – 75; 2 – 81; 3 – 87; 4 – 97

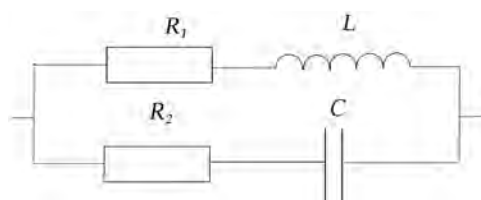


Fig 3. Simplified equivalent circuit of the grain boundary

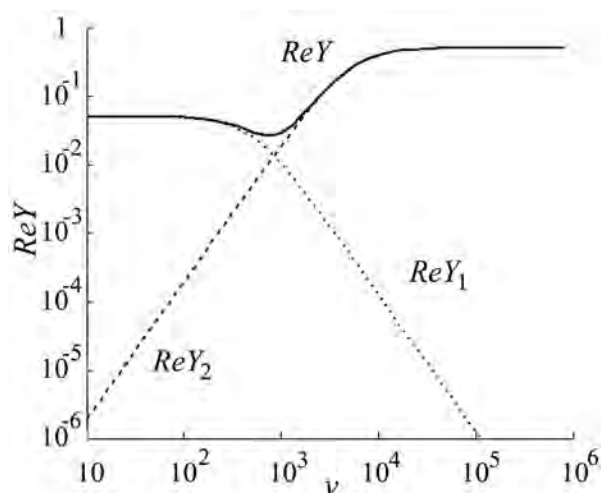


Fig 4. Frequency dependences of real admittance components for each link and the whole chain. The calculations are performed using the MathCAD package at the following values of parameters (in measurement units) $R_1 = 20, R_2 = 2, C = 10^{-4}, L = 4 \cdot 10^{-2}$

The results obtained for coordinates CY are shown in Fig. 5. It is seen that with an increase in temperature the shape of the curves is changed from the characteristic loops to a nearly vertical dip. Curves 1 and 2 exactly correspond to the theoretical calculations with regard to the

equivalent circuit with an inductive element, obtained in [21].

4. Conclusions

The experiments showed that a ceramic posistor based on a solid solution of barium-strontium titanate with the addition of cerium (0.3 at%) demonstrates an anomalous behaviour of the dynamic conductance. The analysis of the simplified circuit of the grain boundary indicates a manifestation of the negative capacitance effect. Considering the fact that this effect occurs both in devices with p - n transitions and in semiconductor ceramic samples of different compositions, we can assume that it is connected to processes of charge carrier capture in the energy barrier areas, and is possibly of a generalised character.

Contribution of the authors

A. M. Solodukha – research concept, results analysis, text editing. G. S. Grigoryan – conducting research, methodology development, writing of text, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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