

Specific Features of Charge Relaxation in the Solid Solution of Barium Titanate Stannate in the Presence of a Constant Electric Field

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Abstract—The electric properties of ceramic barium titanate stannate modified with chromium oxide are examined via impedance spectroscopy at frequencies ranging from 100 Hz to 1 MHz and in the temperature interval of 300–550 K. In order to reveal specific electrophysical features of polycrystalline samples that contain crystallites (interior regions of grains) and grain boundaries, a constant electric field that facilitates the accumulation of spatial charge near structural inhomogeneities is applied to the electrodes. The experimental results are interpreted using the Maxwell–Wagner double-layer capacitor model and the Schottky barrier model.

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INTRODUCTION

Electroceramics in the form of solid solutions based on barium titanate attract much attention owing to the stability of their parameters over a wide range of temperatures and the possibility of adjusting them. Such adjustment is performed by changing the microstructure, shifting the phase transition temperature (for different ratios of initial components), varying the resistivity (introducing doping impurities), and so on. Solid solutions of barium titanate stannate, which are now being studied extensively as an alternative to lead-containing ceramic materials for a variety of applications in electronics, are a promising compositions [1].

EXPERIMENTAL

Samples of $\text{Ba}(\text{Ti}_{0.95}\text{Sn}_{0.05})\text{O}_3$ composition, prepared in accordance with ordinary ceramic processing technology, were used in this work. To produce semi-conducting samples, 0.2 wt % chromium oxide was added to the initial mixture. Electrodes were deposited by baking on silver paste; in the range of voltages applied to the samples, the obtained contacts were close to ohmic. The electric properties of the samples, shaped as tablets 10 mm in diameter and 0.6 mm thick, were studied using a WK 4270 LCR meter and a Keithley 6517A electrometer in the temperature range of 300–550 K. The amplitude of the test harmonic signal was 0.2 V, and the frequency ($\omega/2\pi$) was varied from 100 Hz to 1 MHz. The electrometer's measuring voltage was 1 V.

RESULTS AND DISCUSSION

It is known that the Curie point shifts toward lower temperatures upon the partial substitution of Ti^{4+} ions with Sn^{4+} ions. The Curie point for the studied composition (determined from the maximum of the temperature dependence of permittivity) corresponded to a temperature of 360 K.

The electric properties of such polycrystalline objects as ceramics are often examined using the brick wall model. A simplified equivalent circuit diagram of the sample can be presented as a series combination of two RC segments (a capacitor and an active resistance connected in parallel; see Fig. 1), like a Maxwell–Wagner double-layer capacitor. One segment (R_B-C_B) characterizes the dielectric response of the bulk of a crystallite (grain), and the other one ($R_{GB}-C_{GB}$) represents the boundary regions. The energy barrier at contact near-surface crystallite layers can be presented in a first approximation as a double Schottky barrier. This approach was described in detail in [2].

Let us first examine the experimental temperature dependence of electric conductivity of the sample σ in Arrhenius coordinates (Fig. 2). Two regions can be distinguished: ferroelectric phase region (I) and paraelectric region (II). With DC conductivity $\log \sigma$ (curve 1 in Fig. 2), the values fall throughout region I and drop sharply near the phase transition temperature. An increase in $\log \sigma$, which is typical of semiconductor materials, is seen in the paraelectric phase. This increase is represented by a linear segment with an activation energy of 1.23 eV. The dashed segment of this curve represents the predicted behavior of σ in the

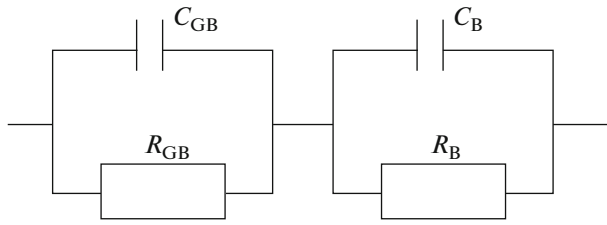


Fig. 1. Equivalent circuit of the ceramic sample. C_{GB} , R_{GB} and C_B , R_B are the electric capacitance and the resistance of grain boundaries and the bulk of grains, respectively.

corresponding temperature interval (the measured resistance values lay outside the measuring range of our instrument). AC conductivity σ was determined from the scalar impedance (Z) and the angle of phase shift between the current and voltage (φ) with allowance for the parallel equivalent circuit:

$$\sigma = A \cos \varphi / Z, \quad (1)$$

where A is the geometric factor.

At a frequency of 100 Hz (curve 2), $\log \sigma$ in region I increases linearly and slowly with an activation energy of 0.22 eV. An order-of-magnitude reduction, which changes to linear growth with an activation energy of 0.60 eV, is observed in the paraelectric phase near the Curie point. Application of constant shifting field $E_{\text{shift}} = 46 \text{ V cm}^{-1}$ leads to substantial changes (curve 4): the activation energy in region I is reduced to 0.10 eV, and the $\log \sigma$ values grow somewhat; the $\log \sigma$ decay in region II covers a wider temperature interval and changes to $\log \sigma$ growth (as a result, σ approaches the values of DC conductivity). At a frequency of 10^5 Hz (curve 3), $\log \sigma$ behaves much like it did at 100 Hz (curve 2), but the activation energy in region I is lower (0.15 eV), and the reduction in region II is less steep and covers a much wider temperature interval. The application of the shifting field (curve 5) alters the shape of the curve only at $T > 455 \text{ K}$ and results in a reduction in σ .

The behavior of all curves in Fig. 2 near the Curie point, where the curves decay, can be explained by the well-known effect of the positive temperature coefficient of resistance (PTCR), also called the posistor effect. It is known that posistor ceramics are produced by introducing a certain amount of a needed additive into an initial mixture to make the material semiconducting. For example, if a divalent barium ion is replaced with a trivalent metal ion in the bulk of a crystallite, a fixed positively charged defect (donor) and a weakly bound electron are produced as a result. However, barium vacancies, which act as acceptors, can form (primarily at grain boundaries) during annealing in air under atmospheric pressure and at high tem-

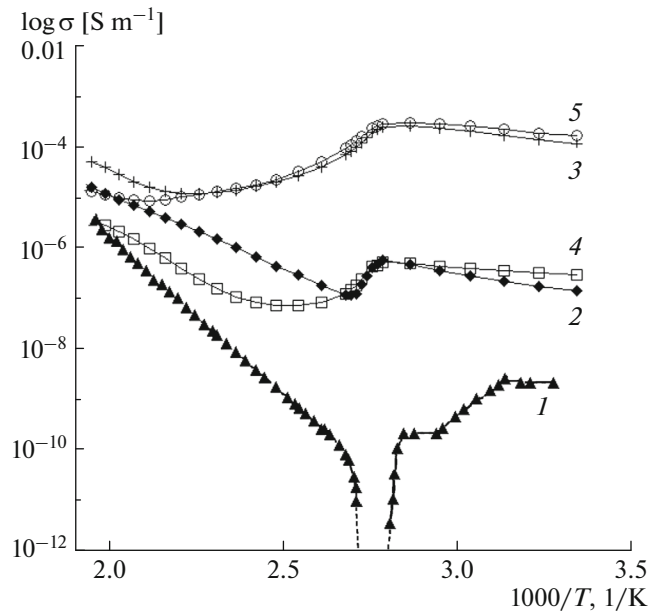
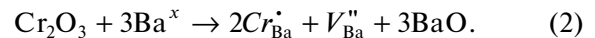


Fig. 2. Temperature dependences of electric conductivity of the sample in Arrhenius coordinates: (1) DC measurements; (2 and 3) measurements at frequencies of 100 Hz and 100 kHz with no shifting field; and (4 and 5) measurements at the same frequencies with a shifting field.

peratures. The following reaction (in Kröger–Vink notation) then occurs:



Cation barium vacancies serve as electron traps in this case, thus enhancing the Schottky-type potential barrier at grain boundaries [3]. On the other hand, the low activation energy in the ferroelectric phase can be attributed to the effect of spontaneous polarization, which produces strong electric fields that reduce contact resistance at grain boundaries. All of the above agrees with the Heywang–Jonker model for the PTCR effect [4].

It should be noted that E_{shift} produces opposite effects in regions I and II: it enhances σ in the ferroelectric phase and reduces σ in the paraelectric one. At the same time, the field has no effect in the range of temperatures where PTCR is observed.

The dielectric characteristics of samples are presented in Fig. 3. It follows from Fig. 3a that ϵ' had no noticeable frequency dispersion in the ferroelectric phase. Such behavior is typical of the bulk of grains in which the oscillations of domain boundaries (the region of dispersion of which is well above 1 MHz) make the primary contribution to the real part of permittivity. When $T > 500 \text{ K}$, an increase in ϵ' was observed at low frequencies. This is common for perovskites [5] and is associated with the motion of charged particles and defects (primarily oxygen vacan-

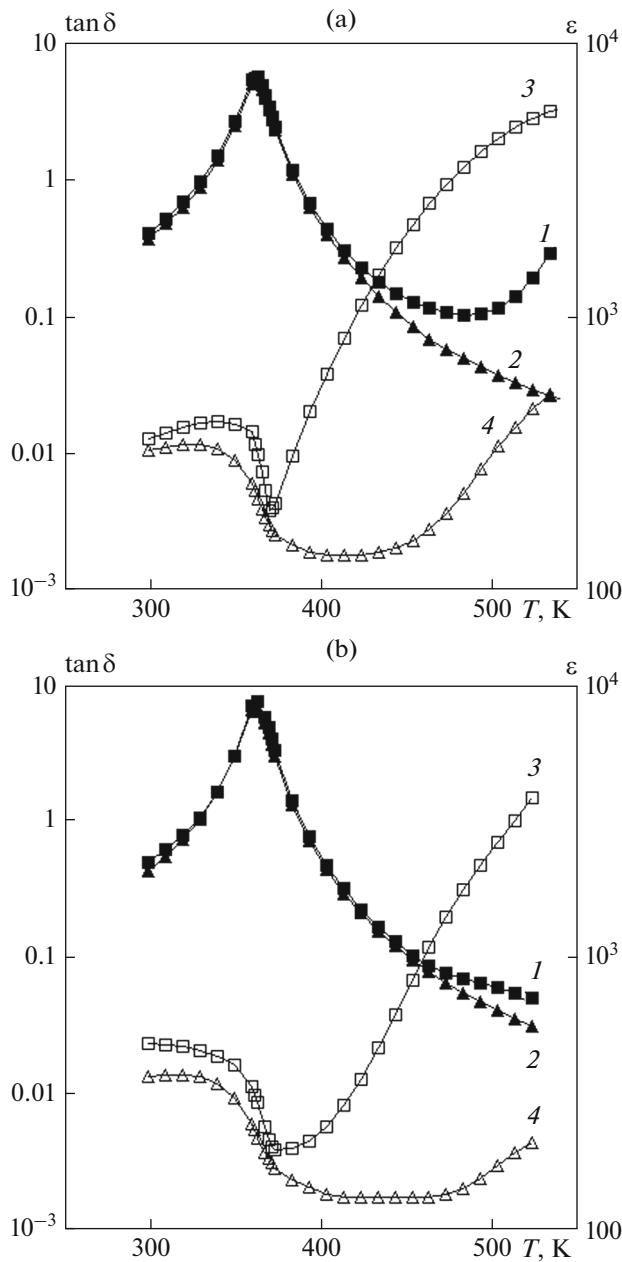


Fig. 3. Temperature dependences of the real part of permittivity ϵ' and dielectric loss tangent $\tan\delta$ (a) without and (b) with a shifting field: ϵ' (1 and 2) and $\tan\delta$ (3 and 4) at frequencies of 100 Hz (1 and 3) and 100 kHz (2 and 4).

cies) that form the relaxing spatial charge [6]. As for the dielectric loss tangent, weak dispersion in region I changes to strong (approximately two orders of magnitude) dispersion in region II, and low-frequency energy losses dominate.

The shifting field lowers the values of ϵ' and $\tan\delta$ (Fig. 3b). The strongest change in ϵ' is observed in region II at low frequencies, while $\tan\delta$ changes in the same region at both low and high frequencies.

It is convenient to use the electrical module (M) representation in further analyzing the effect of E_{shift} on relaxation processes, since the ϵ -representation provides, in accordance with the Maxwell–Wagner double-layer capacitor model, a mixed expression for the relaxation time: with certain simplifications [2], $\tau_{\text{MW}} = R_{\text{B}}C_{\text{GB}}$. This expression features the parameters of both the bulk of a grain and the grain boundaries. The M representation allows us to separate the response of grains from that of boundaries. With the equivalent circuit shown in Fig. 1, we can obtain the following expression for the imaginary part of the electrical module at a fixed temperature [3]:

$$M'' = \frac{C_0}{C_{\text{GB}}} \left[\frac{\omega R_{\text{GB}} C_{\text{GB}}}{1 + (\omega R_{\text{GB}} C_{\text{GB}})^2} \right] + \frac{C_0}{C_{\text{B}}} \left[\frac{\omega R_{\text{B}} C_{\text{B}}}{1 + (\omega R_{\text{B}} C_{\text{B}})^2} \right], \quad (3)$$

where C_0 is the geometric capacity of the sample.

The M'' maximum condition (at $\omega\tau = 1$) for each element of the circuit is $\omega\tau_{\text{GB}} = 1$ and $\omega\tau_{\text{B}} = 1$, where $\tau_{\text{GB}} = R_{\text{GB}}C_{\text{GB}}$ and $\tau_{\text{B}} = R_{\text{B}}C_{\text{B}}$. With ceramics, the general rule is $\tau_{\text{GB}} > \tau_{\text{B}}$.

The following relations can be derived from the above formulas:

$$M''_{\text{GBmax}} = \frac{C_0}{2C_{\text{GB}}} \quad \text{and} \quad M''_{\text{Bmax}} = \frac{C_0}{2C_{\text{B}}}. \quad (4)$$

Since the effect of the shifting field is strongest at low frequencies, it is of interest to examine the temperature dependence of the imaginary part of the electrical module in this region of frequencies (Fig. 4). The M'' maximum is seen clearly. It shifts toward higher temperatures as the measuring signal frequency is increased, which is typical of Debye-type relaxation characterized by the familiar formula

$$\tau_r = \tau_0 \exp\left(\frac{U}{kT}\right), \quad (5)$$

where τ_r is the relaxation time, τ_0 is the preexponential factor, U is the activation energy, k is the Boltzmann constant, and T is absolute temperature.

This maximum must be associated with the equivalent circuit element that characterizes the response of grain boundaries: $\tau_r = \tau_{\text{GB}}$. This shift allows us to determine activation energy U using the formula

$$U = \frac{k \left(\ln \frac{\tau_{r1}}{\tau_{r2}} \right) T_1 T_2}{T_2 - T_1}, \quad (6)$$

where τ_{r1} and τ_{r2} are the relaxation times for temperatures T_1 and T_2 , respectively.

In this case, $U = 1.12$ eV. This value is close to the activation energy of DC conductivity and agrees with the data from [5]. It is therefore likely that a unified

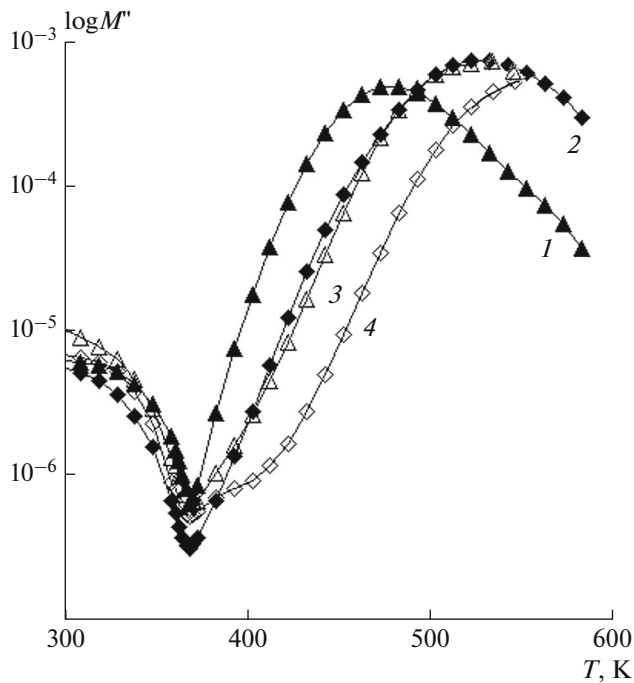


Fig. 4. Temperature dependence of the imaginary part of electrical module M'' measured at frequencies of 100 Hz and 100 kHz (1 and 2) with no shifting field and at the same frequencies (3 and 4) with a shifting field.

mechanism for conductivity and relaxation, which manifests itself in the region of grain boundaries, is present in both cases.

The shifting field shifts the maximum toward higher temperatures and raises its amplitude (see Fig. 4). Shift τ_r is characterized by the following formula from [7]:

$$\tau_r = \tau_0 \exp(-kV), \quad (7)$$

where V is voltage and k is the influence factor. The amplitude increases owing to a reduction in C_{GB} (see formula (4)), which is in line with the behavior of a Schottky barrier.

CONCLUSIONS

Our experimental data suggest that a shifting field interacting with spontaneous polarization facilitates the motion of charge carriers through a potential barrier near grain boundaries at relatively low temperatures (region I). The field has almost no effect in the domain of the influence of the posistor effect, since the potential barrier height is controlled by the variation in ϵ' (according to the Heywang model [3, 4]), which is determined by lattice vibrations. However, as the temperature is raised further and the mobility of charges associated with structure defects is increased, the effect of E_{shift} gets stronger.

With ceramic barium titanate stannate, the relatively weak constant shifting field manifests itself most vividly in the ferroelectric phase, in phenomena associated with oscillations of spatial charge near grain boundaries. The field limits the charge mobility and thus reduces the values of dielectric parameters and the AC conductivity. Additional impedance studies with the response of the bulk of grains distinguished from that of their near-boundary regions are needed in order to perform a more complete quantitative evaluation.

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