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DIELECTRIC PROPERTIES OF AURIVILLIUS PHASE $Bi_{10}Fe_6Ti_3O_{30}$ WITH A NANO-SIZED PSEUDO-PEROVSKITE BLOCKS

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Distinctive features of dielectric properties of a ceramic material based on Aurivillius phase $Bi_{10}Fe_6Ti_3O_{30}$ have been studied.

Keywords: ceramics, Aurivillius phases, dielectric properties.

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1. Introduction

In general, the structure of Aurivillius phases $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ can be regarded as alternating fluorite-like layers $F=\{(Bi_2O_2)^{2+}\}_\infty$ and pseudo-perovskite blocks $P=\{(Bi_{m+1}Fe_{m-3}Ti_3O_{3m+1})^{2-}\}_\infty$ consisting of m pseudo-perovskite layers [1, 2]. According to experimental data from papers [3-5], the number of octahedral layers in a pseudo-perovskite block of Aurivillius phases $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ may reach $m=9$, which corresponds to the compound $Bi_{10}Fe_6Ti_3O_{30}$. The thickness of the pseudo-perovskite block in this compound is $\sim$3.7 nm [3]. In this context, the Bi_2O_3-TiO_2-Fe_2O_3 system represents a unique object, since for the majority of layered pseudo-perovskite compounds, m cannot exceed 6 (E.g., see [6, 7]). The extremely high stability of compounds $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ with a great number of pseudo-perovskite layers in the structure was analyzed in papers [4, 5, 8].

Following the data of papers [9-11], Aurivillius phases Bi_2O_3-TiO_2-Fe_2O_3 possess multiferroic properties. Compounds $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ experience high-temperature phase conversion (Curie point) accompanied by transition from an orthorhombic structure to a tetragonal one [13-15], for $Bi_{10}Fe_6Ti_3O_{30}$, this occurs at 953 K [3, 16, 17].

Papers [3, 16] describe the preparation of $Bi_{10}Fe_6Ti_3O_{30}$ using solid-state chemical reactions. As shown in papers [4, 17], given the limiting value of m, multilayered Aurivillius phases will be in a state close to indifferent equilibrium. Such objects are of interest when regarded as transition nanostructures from a chemical compound to a heterogeneous system.

The study of the properties of Aurvillius phases with a great number of pseudo-like layers in the structure is of particular interest. The physical and chemical properties of compounds $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$, including $Bi_{10}Fe_6Ti_3O_{30}$, are described in papers [3-8, 16, 17]. Dielectric properties of some compounds $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ are described in papers [15, 18-23], however, only papers [24, 25] provide a system-oriented approach.

This paper aims to study the nature of the electric relaxation for a ceramic material $Bi_{10}Fe_6Ti_3O_{30}$ using electric modulus formalism for analyzing dielectric data. Combined with the data on composition and structure of the compound $Bi_{10}Fe_6Ti_3O_{30}$, the said research is required to forecast a possibility for preparing new multiferroic materials using that compound.

2. Experimental

For the synthesis of $Bi_{10}Fe_6Ti_3O_{30}$, solid-state chemical reactions were employed. The purity of initial reagents Bi_2O_3, TiO_2 and Fe_2O_3 was 99.9% or higher. Papers [3, 26] describe the procedure in detail. Phase state was studied using the X-ray diffractometry (XRD) employing XRD-7000 Shimadzu. The elemental composition of the samples was determined by the energy dispersive X-ray microanalysis (FEI Quanta 200 SEM with the EDAX attachment).

Electrical measurements were taken for samples in tablet form, 7 mm in diameter, 3 mm thick, with platinum electrodes on the end face. Investigation was carried out in the open air using RCL-meter Fluke PM6063 (USA), within the temperature range 70–470°C, in the range f 10 kHz to 1MHz. Temperature was regulated using a tube furnace SNOL (Latvia) containing a double-pin cell with a sample. Toward that end, resistance R, module Z, and impedance phase shift angle φ were measured, and these values subsequently served as a basis for the determination of real and imaginary parts of the complex electrical module $\overline{M}$, complex specific conductivity $\overline{\sigma}$, complex dielectric permeability $\overline{\varepsilon}$ and loss-angle tangent $tg\varphi=\varepsilon''/\varepsilon'$ according to the following ratios:

$$\overline{M} = i\omega\varepsilon_0\frac{S}{l}\overline{Z} = M' + jM'', \tag{1}$$

$$\overline{\sigma} = \frac{l}{S}\overline{Z}^{-1} = \sigma' + j\sigma'', \tag{2}$$

$$\overline{\varepsilon} = \frac{1}{j\varepsilon_0\omega}\cdot\frac{l}{S}\overline{Z}^{-1} = \varepsilon' - j\varepsilon'', \tag{3}$$

where M' and M'' are real and imaginary constituents of $\overline{M}$; σ' and σ'' are real and imaginary constituents of $\overline{\varepsilon}$; $\omega = 2\pi f$ is circular frequency, ε_0 is vacuum dielectric permeability, S and l are the sample area and thickness, correspondingly. The measuring procedure is described in papers [24, 25].

3. Results and discussion

Fig. 1 a, b present an X-ray diffraction pattern and a microstructure of a $Bi_{10}Fe_6Ti_3O_{30}$ sample, correspondingly. The data obtained testify to a single phase of the tested material and to good agreement between real chemical composition and stoichiometric one. At room temperature, Aurivillius phase has a rhombic elementary cell (space group $D_{4h}{}^{17}$-14/mmm), with parameters a=4.7 Å, b=5.2 Å, c=81.8 Å.

The dielectric properties of $Bi_{10}Fe_6Ti_3O_{30}$ were studied using electric modulus formalism. Such an approach is informative for studying volumetric response from ceramic materials in a case when increased conductivity of a sample complicates analysis of dielectric relaxation processes [27, 28]. As shown in papers [24, 25], Aurivillius phases' conductivity will increase with an increase in the number of pseudo-perovskite layers in the structure.

Fig. 2 shows typical frequency dependencies for the overall specific electric conductivity $\sigma_{ac}(f)$ for $Bi_{10}Fe_6Ti_3O_{30}$ at different temperatures. This behavior reflects the interrelation between the relaxation process in charge carriers and conductivity in grain volume. The nature of the curves $\sigma_{ac}(f)$ corresponds to the "universal dynamic response" [29]:

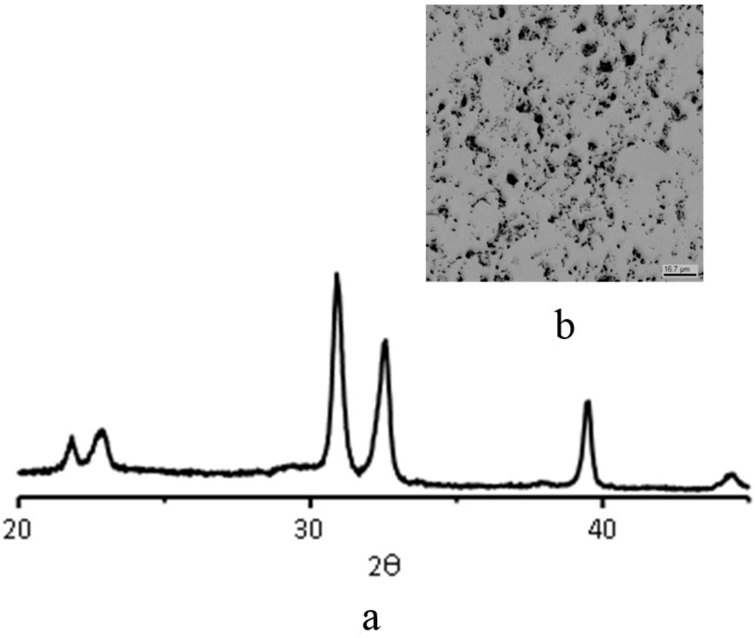

FIG. 1. X-ray diffractograms (λ= 1.54056 Å) (a) and electron micrographs (b) for $Bi_{10}Fe_6Ti_3O_{30}$

$$\sigma(f) = \sigma_{dc} + Af^{\alpha}, \tag{4}$$

where σ_{dc} – direct current specific conductivity, A– pre-exponential factor, f – frequency, α – an index denoting the degree of interrelation between charge carriers and crystal lattice ($0<\alpha<1$).

For Aurivillius phases, this type of $\sigma_{ac}(f)$ dependency characterizes slow relaxation mechanisms for polarization and polaron "hopping" movement [20], for which a hop frequency (f_p) between self-localization states corresponds to the change in the slope of $\sigma_{ac}(f)$ curves, it being <100 kHz at temperatures < 400°C. As the temperature rises, the curves enter a plateau phase.

Fig. 3 a, b represent frequency dependencies between a real (ε') and imaginary (ε") constituent parts of complex dielectric permeability of the compound $Bi_{10}Fe_6Ti_3O_{30}$ at different temperatures. The ε',ε"(f) dependencies are given as smooth curves with a single peak at temperatures $\geqslant$370°C, and with different dispersion in areas of low and high frequencies, increasing with increased temperature. Peaks of curves ε', ε"(f) for temperatures exceeding 370°C are apparently beyond the frequency range of measurements. In the low frequency range, ε' values are reasonably high, while they sharply decrease when frequencies exceed 100 kHz. The ε"(f) dependency is of a similar nature, however, at lower frequencies (< 100 kHz), its value is an order of magnitude greater, which points to conductivity contribution towards direct current [27, 31]. Within the low frequency range, a rise in temperature will cause extreme dispersion of dielectric permeability determined by the presence of thermally activated charges (e.g. volume charge, charged defects, etc.) [9].

Dielectric losses within the temperature range under consideration are relatively insignificant (loss tangent is $tg\varphi=\varepsilon''/\varepsilon'$ <0.15). Frequency dependencies of $tg\varphi(f)$ are characterized by dispersion within the low frequency range, they sharply decrease at higher frequencies (Fig. 3c). Increased $tg\varphi$ values in the low frequency range testify to the presence

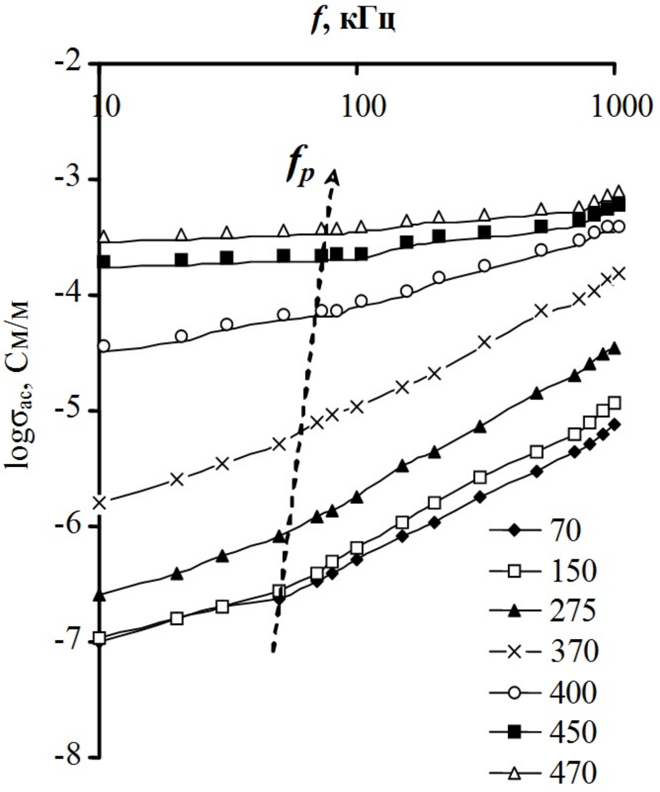

FIG. 2. Frequency dependence of the ac-conductivity $Bi_{10}Fe_6Ti_3O_{30}$

of direct current electric conductivity (σ_{dc}) [31]. Dielectric losses will increase as temperature rises, which, apparently, are determined by recrystallization processes in the sample volume, or by reduced oxygen vacancies.

To analyze relaxation processes of the electric field, the frequency dependencies of the imaginary part of the electric module $M"(f)$ was examined (Fig. 4a). At the temperatures specified, for dependencies $M"(f)$, single peaks of the same height are recorded, which differ in the position with respect to the frequency axis. Their nature points to a single relaxation process in the sample volume and for an increase in electric conductivity with temperature rise. This is also proved by the nature of diagram $M"$–M' (Fig. 4b), represented by semi-circles centered on the X-axis, which agrees with Debye relaxation [29]. As the temperature rises, peaks of the curves $M"(f)$ will shift to higher frequencies. The frequency range below the peak will determine the range where the charge carriers are mobile at long distances, while the frequency range above the peak means that the carriers are in a "trap", in a potential pit, with mobility at short distances preserved. The frequency range, where peaks are recorded on the curves $M"(f)$ are characterized by a change in the movement of charge carriers from long to short distances. In this case, the asymmetry of the peak, denoting relaxation processes with different time responses, is not observed [32].

According to the position of the high-frequency peak on the $M"(f)$ curves, the relaxation time of dielectric polarization, $\tau_M = \frac{1}{2\pi f_m}$, was determined, with temperature dependence following the Arrhenius law:

$$\tau_M = \tau_0 \exp\left(\frac{\Delta E_M}{kT}\right), \tag{5}$$

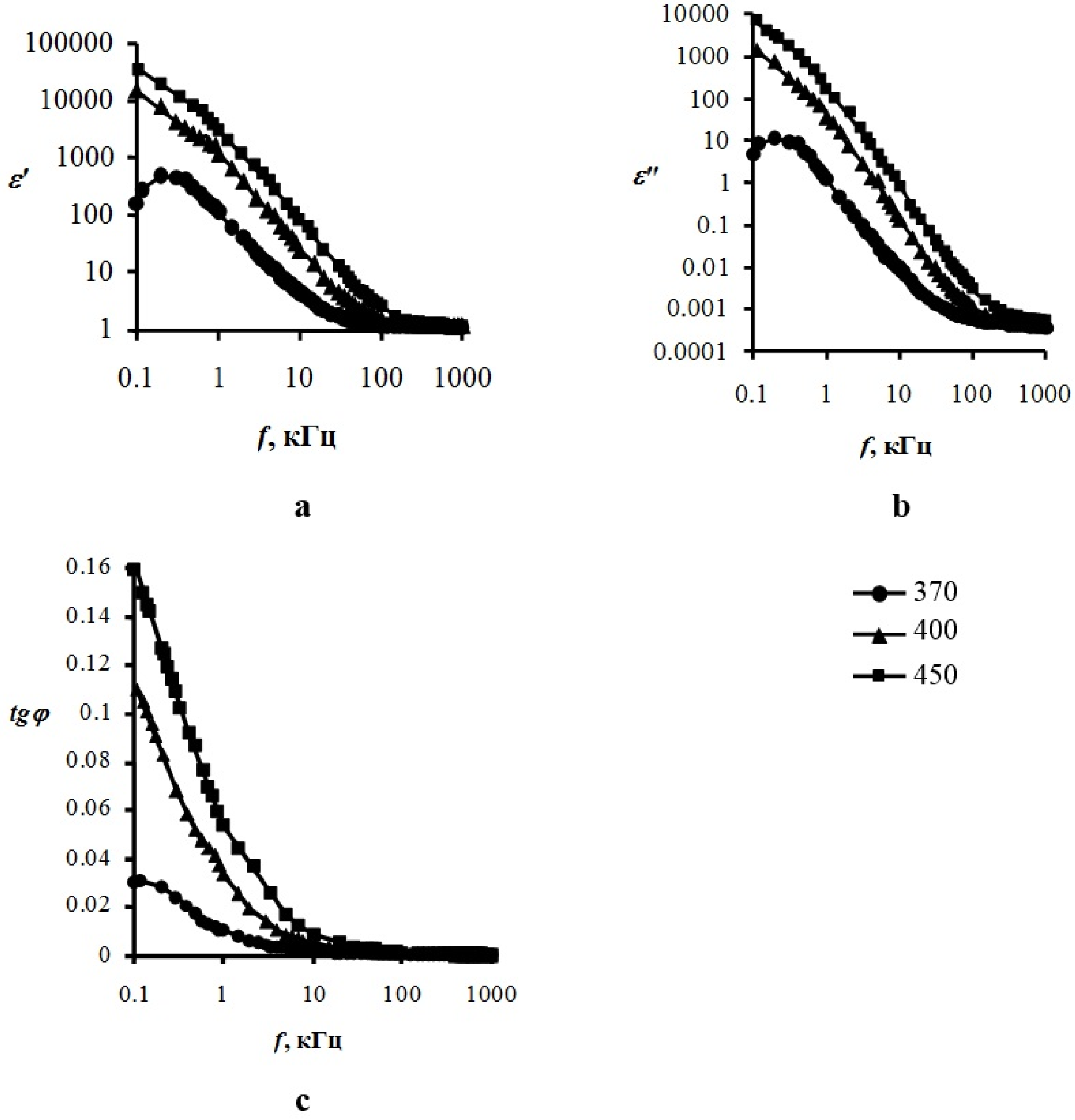

FIG. 3. Frequency dependence of the real, ε' (a) and imaginary, ε"(b) parts of the dielectric permittivity (a, b) and dielectric, $tg\varphi$, for $Bi_{10}Fe_6Ti_3O_{30}$, measured at various temperatures

where τ_M is relaxation time in the grain volume determined by the peak of the curves *M"(f)*, τ_0 is a pre-exponential factor, E_M is energy of activation of the charge carriers in the grain volume determined by the curve slope τ_M(1/T), k is Boltzmann constant, and T is absolute temperature.

The relaxation time τ within the temperature range under consideration ranged from $5 \cdot 10^{-4}$–$1 \cdot 10^{-3}$ s. The activation energy E_M of the charge carriers in the grain volume, estimated by ratio (5), was 0.8±0.1 eV, which is a typical value for compounds of Aurivillius phases type [18-25], with electric conductivity determined, primarily, by oxygen vacancy movement. The presence of oxygen vacancies in the structure of bismuth-containing Aurivillius phases is caused by the partial evaporation of Bi^{3+} ions under the high synthetic temperatures of these materials. This contributes to the overall electric conductivity, along

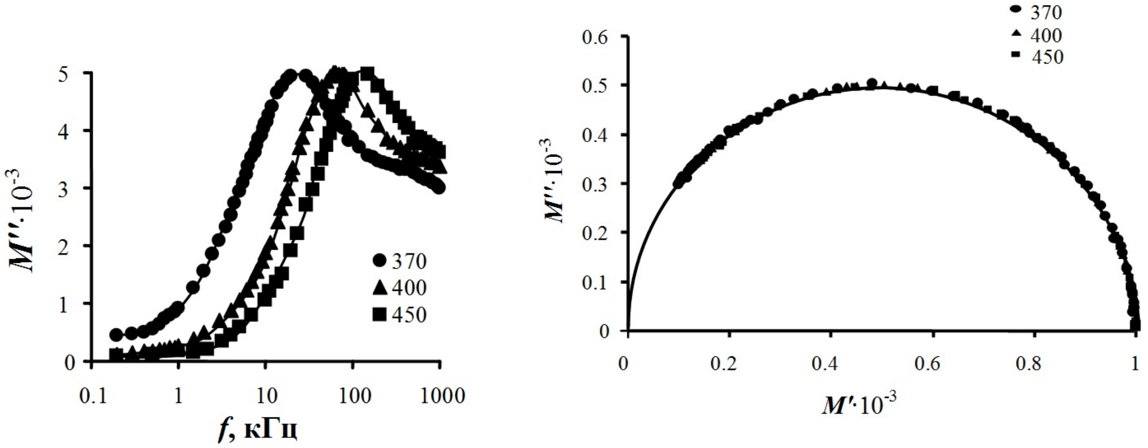

FIG. 4. Frequency dependence of the imaginary part of the electric modulus, M" (a), and the *M"–M'* diagram (b) for $Bi_{10}Fe_6Ti_3O_{30}$ measured at various temperatures

with the phenomenon of hopping polarons between the Fe^{3+}–O–Fe^{2+} positions at elevated temperatures [3, 26].

4. Conclusion

Based on the Aurivillius phase $Bi_{10}Fe_6Ti_3O_{30}$, distinctive features of dielectric behavior of a ceramic material prepared using solid-state chemical reactions have been studied. The presence of a single process of Debye-type dielectric relaxation in a bulk sample (E_M=0.8±0.1 eV) has been shown.

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