

Dielectric Properties of $\text{Bi}_4(\text{Ti},\text{Nb},\text{Mn})_3\text{O}_{12}$ Titanates

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Abstract The $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ($x = 0.05, 0.10, 0.15$) solid solutions have been synthesized by means of solid state reactions method, their crystal structure, microstructure, electrical and dielectric properties within wide interval of temperatures and frequencies have been investigated. It is found that the $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ titanates crystallize in an orthorhombic structure and are *p*-type semiconductors, which sinterability and dielectric constant increase, but grain size and thermo-EMF coefficients decrease at partial substitution of titanium by niobium and manganese. It is established that ceramics is electrically homogeneous and relaxation processes in it are non-Debye-like, and values of activation energy of relaxation obtained from results of impedance and modulus spectroscopy are in a good agreement.

Keywords Layered Bismuth Titanate, Solid Solutions, Electrical Conductivity, Thermo-EMF, Dielectric Constant, Dielectric Losses, Impedance Spectroscopy, Modulus Spectroscopy

1. Introduction

Layered bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ belongs to the Aurivillius phase family $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$, whose structure consist of alternated fluorite-like $[\text{Bi}_2\text{O}_2]^{2+}$ layers and perovskite-like $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ blocks, where *n* is a number of octahedral layers in the perovskite-like block [1]. A-positions with cubeoctahedral environment (CN = 12) in the $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ blocks occupy the low-charged large cations ($\text{Na}^+, \text{Sr}^{2+}, \text{Bi}^{3+}$ etc), and B-positions inside oxygen octahedrals (CN = 6) occupy the high-charged small cations ($\text{Ti}^{4+}, \text{Nb}^{5+}, \text{W}^{6+}$ etc.).

Triple-layered ($n = 3$) Aurivillius phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is ferroelectric with high Curie temperature ($T_C = 948$ K [2]), which lets us to consider this phase and its derivatives as promising materials for radio-, acusto- and optoelectronics, which may be used for production of optical displays, piezoelectric transducers, filters, condensers, and different type of memory devices. So, for example, as material for non-volatile memory devices the

lanthanum-substituted $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ solid solution was proposed, whose functional characteristics were essentially better that of such traditional ferroelectrics as $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ or $\text{SrBi}_2\text{Ta}_2\text{O}_9$ [3].

It is known, that physicochemical and functional properties of ceramics based on the layered bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ may be improved by means of partial substitution of different cations in its structure, in particular, of Ti^{4+} ions in the perovskite-like $[\text{Bi}_2\text{Ti}_3\text{O}_9]^{2-}$ blocks, which was studied in a number of works [4–9].

So, it was found, that introduction of MnO_2 into $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ led to the increasing of size of the grains of $\text{Bi}_{3.25}\text{La}_{0.25}\text{Ti}_{3-x}\text{Mn}_x\text{O}_{12}$ ceramics, increasing of its electrical resistivity and dielectric constant [4]. Authors of [5] had obtained ferroelectric ceramics with composition $\text{Bi}_4\text{Ti}_2\text{Nb}_{0.5}\text{Fe}_{0.5}\text{O}_{12}$ having $T_C = 903$ K and studied its electrical and dielectric properties. According to [6], in $\text{Bi}_4\text{Ti}_{3-x}\text{Cr}_x\text{O}_{12}$ solid solutions the phase transition from ferroelectric to paraelectric phase took place near 933 K, and exchange interactions in them had antiferromagnetic character. In the work [7] the effect of substitution of titanium by iron on the dielectric properties of $\text{Bi}_4\text{Ti}_{3-x}\text{Fe}_x\text{O}_{12}$ solid solutions had been investigated.

In the [8] it was found that doping of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by tungsten oxide WO_3 led to the sharp decreasing of electrical conductivity of formed $\text{Bi}_4(\text{Ti},\text{W})_3\text{O}_{12}$ ceramics. According to the [9], the partial substitution of titanium by niobium and cobalt in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ lead to the increase of the unit cell volume of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Co}_x\text{O}_{12}$, and to the decrease of their dielectric constant and dielectric losses, and do not affect practically on the value of their linear thermal expansion coefficient. The results of [10] shows, that partial simultaneous substitution of titanium by niobium and iron in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ led to the reduction of grains size, Curie temperature, dielectric constant and dielectric losses of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ solid solutions, and did not affect practically their sinterability, lattice constants, and thermo-EMF coefficient. Electrical resistivity of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ ceramics was determined by grains electrical resistivity, and relaxation processes in it were of a non-Debye type.

In this work the effect of simultaneous substitution of titanium in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by niobium and manganese on the

crystal structure, microstructure, electrical conductivity, thermo-EMF, dielectric constant and dielectric losses of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ($x \leq 3.75$ mol.%) had been studied.

2. Materials and Methods

Ceramic samples of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ($x = 0.00, 0.05, 0.10, 0.15$) titanates were synthesized using solid-state reactions method from mixtures of Bi_2O_3 , TiO_2 , Nb_2O_5 , and Mn_2O_3 powders (chemically pure qualification) taken in appropriate stoichiometric relations in air within temperature interval of 923–1223 K during 17 hours with some intermediate regrindings according to methods described in detail in [9, 10].

Identification of the samples and determination of their lattice constants was performed using X-ray diffraction analysis (XRD) (Bruker D8 XRD Advance diffractometer, $\text{CuK}\alpha$ -radiation, Ni-filter) and IR absorption spectroscopy (IR Fourier-spectrometer Nexus of ThermoNicolet). Porosity (Π) of the samples was calculated as $\Pi = (1 - (\rho/\rho_{\text{XRD}})) \cdot 100\%$, where ρ is bulk density, which was determined from the mass and dimensions of the samples; ρ_{XRD} – X-ray density. Microstructure and chemical composition of ceramics were studied using scanning electron microscope JSM–5610 LV equipped with chemical analysis system EDX JED–220.

Dielectric measurements were carried out in the temperature range 300–1100 K for frequencies between 10^2 – 10^6 Hz using imittance meter E7–25. DC electrical conductivity and thermo-EMF of sintered ceramics was studied within 480–1100 K and 780–1100 K respectively

according to the methods described in [11]. Values of activation energy of DC electrical conductivity (E_A) and thermo-EMF (E_S) of the samples were determined from linear parts of $\ln(\sigma_{\text{DC}}T) = f(1/T)$ and $S = f(1/T)$ dependences respectively. All measurements were performed in air.

3. Results and Their Discussion

According to the results of EDX analysis, within their accuracy, the chemical composition of the samples was coincided to the presumable. After final stage of the synthesis all the $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ samples were monophasic within XRD reliability (Figure 1, *a*) and crystallized in an orthorhombic structure like parent compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (SG *B2cb* [8]).

Lattice constants of $\text{Bi}_4\text{TiO}_{12}$ ($a = 5.406(10)$ Å, $b = 5.422(7)$ Å, and $c = 32.75(4)$ Å), were in a close agreement with an earlier studies: 5.444(1), 5.413(1), and 32.858(1) Å [8], 5.4403, 5.4175, and 32.7862 Å [12]. Lattice constants of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ solid solutions were close to the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ones (Table 1), which is in well agreement with the fact that sizes of substituting and substituted ions are close to each other (for CN = 6 according to [13] Ti^{4+} , Nb^{5+} , and Mn^{3+} ionic radii are equal to 0.605, 0.640, and 0.580 Å respectively). Unit cell of the $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ solid solutions was slightly elongated in the c direction (c/\sqrt{ab}) ratio increased) at partial substitution of titanium by niobium and manganese (Table 1). Note that similar effect was obtained by us earlier also for $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Co}_x\text{O}_{12}$ [9] and $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ solid solutions [10].

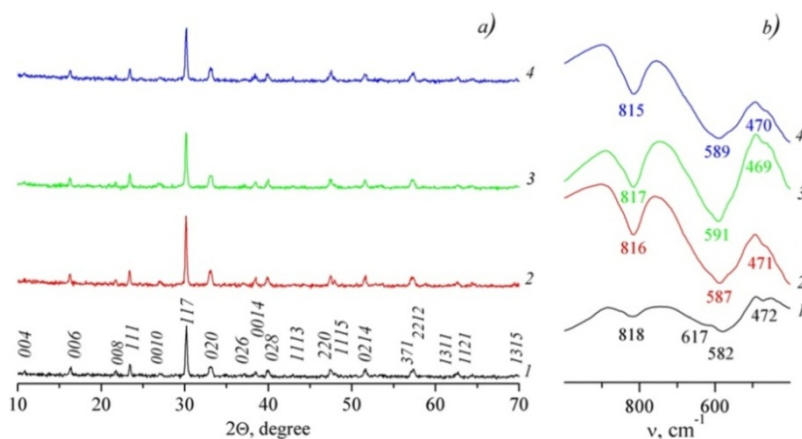


Figure 1. X-ray powder diffractograms ($\text{CuK}\alpha$ -radiation) (*a*) and IR-absorption spectra (*b*) of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ samples: $x = 0$ (1), 0.05 (2), 0.10 (3), and 0.15 (4)

Table 1. Lattice constants, X-ray density (ρ_{XRD}), bulk density (ρ), and porosity (Π) of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ titanates

x	a , Å	b , Å	c , Å	c/\sqrt{ab}	V , Å ³	ρ_{XRD} , g/cm ³	ρ , g/cm ³	Π , %
0.00	5.406±0.010	5.422±0.007	32.75±0.04	6.049	959.8±3.9	8.11	4.80	41
0.05	5.407±0.009	5.416±0.007	32.77±0.04	6.055	959.8±4.0	8.13	5.10	37
0.10	5.409±0.009	5.416±0.007	32.79±0.04	6.058	960.4±4.1	8.14	5.51	32
0.15	5.395±0.010	5.415±0.007	32.79±0.04	6.067	957.9±3.9	8.18	5.73	30

Four absorption bands occurring at 815–818 cm^{-1} (ν_1), 617 cm^{-1} (ν_2) (only for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase), 582–589 cm^{-1} (ν_3), and 469–472 cm^{-1} (ν_4) were observed in the absorption spectra of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ powders (Figure 1, *b*). According to [5, 13], these bands corresponded to the stretching (ν_1 – ν_3) and bending (ν_4) vibrations of Bi–O (ν_1 and ν_4) and Ti–O (ν_2 – within *ab*-plane, ν_3 – along *c*-axis) bonds respectively. The ν_1 , and ν_4 peaks positions did not change practically at partial substitution of titanium by niobium and manganese in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, but ν_3 peak position shifted to the larger values at *x* increasing so partial replacement of Ti^{4+} by Nb^{5+} and Mn^{3+} in layered bismuth titanate lead to the shortening of Ti–O bonds along *c*-axis of its crystal structure.

The values of porosity of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ sintered ceramics varied within 30–37%, were smaller than for unsubstituted bismuth titanate (41%), and decreased at *x* increase. Based on this fact, we can conclude, that addition of niobium and manganese oxides to the layered bismuth titanate improves its sinterability. The results of this work are in a good agreement with the data [10], where it was found that dual doping of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by Nb_2O_5 and Co_3O_4 improved the sinterability of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Co}_x\text{O}_{12}$ solid solutions [10].

The sintered $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics presented grains with plate-like morphology and average grain size about 1–3 μm (measured along the larger dimensions of platelets), which did not depend practically on the substitution degree of Ti by Nb and Mn (Figure 2) and were essentially less than for pristine $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (15–30 μm). The aspect ratio (length/thickness) of the sintered grains seemed to be the same for all samples.

Our results are in contrary with the data of [4], in which it was found that partial substitution of Ti by Mn in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ leads to the increase of grain sizes of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{3-x}\text{Mn}_x\text{O}_{12}$ ceramics. The cause of this may be due to the fact that in our work $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was doped not

only by Mn_2O_3 , but also by Nb_2O_5 , so, the shrinking of grain sizes of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ solid solutions may be caused by the presence in them of both substituents, Nb^{5+} , and Mn^{3+} . Note that in [10] it was found that dual substitution of Ti by Nb and Fe in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ also lead to the essential decreasing of the grain sizes of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ ceramics in comparison to the unsubstituted $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase.

$\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ compounds were *p*-type semiconductors (Figure 3), which coincided with previous literature data [14–16], according to them electrical conductivity of layered bismuth titanate increased with temperature increasing, and values of thermo-EMF coefficient of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase at high temperatures were positive [15, 16]. Seebeck's coefficient values of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ solid solution were essentially less than for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (Figure 3, *b*). In [9, 10] it was found that values of thermo-EMF coefficient of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Co}_x\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ solid solutions were close to the ones for unsubstituted bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. So, strong decrease of Seebeck's coefficient of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ in comparison with parent $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is due to the introduction in it manganese ions instead titanium ones. The similar results were obtained in [11] where it was established that values of thermo-EMF coefficient of perovskite BiFeO_3 sharply decreased at dual substitution in it of Bi by Nd and of Fe by Mn.

The values of DC electrical conductivity of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ solid solution in ferroelectric (FE) region were larger than for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, but in paraelectric region (PE) they were less or close to the values of electrical conductivity of unsubstituted bismuth titanate (Figure 3, *a*).

The values of apparent activation energy of DC electrical conductivity of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ in PE region were equal to 0.86(2), 1.81(5), 1.37(4), and 0.80(3) eV for *x* = 0, 0.05, 0.10, and 0.15 respectively.

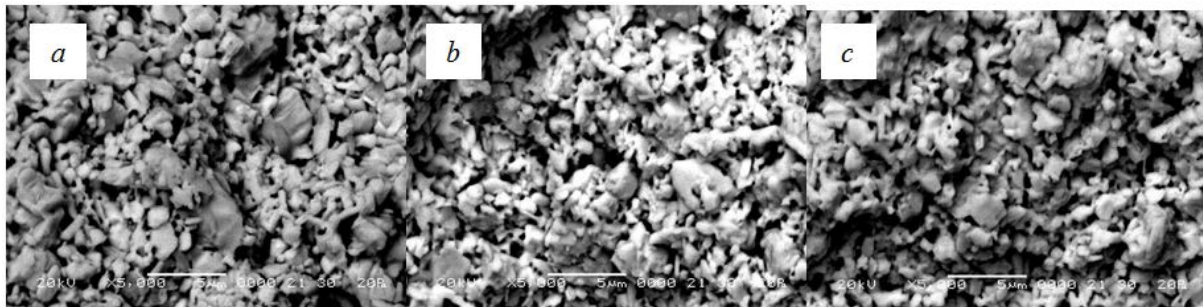


Figure 2. Electron micrographs of surfaces of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics: *x* = 0.05 (*a*), 0.10 (*b*), and 0.15 (*c*).

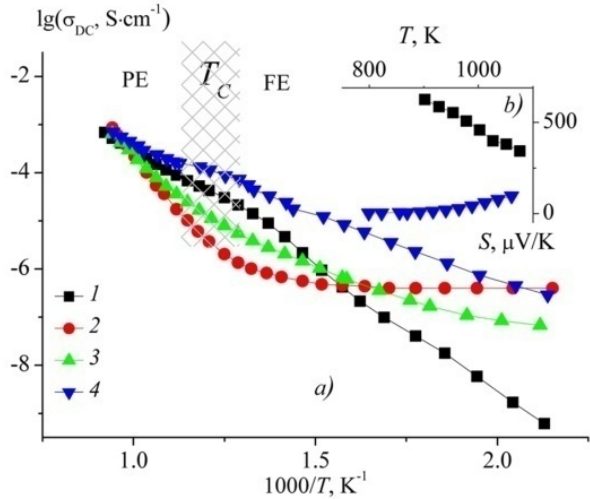


Figure 3. Dependences of DC electrical conductivity (a) and thermo-EMF coefficient (b) of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ samples vs temperature: $x = 0$ (1), 0.05 (2), 0.10 (3), and 0.15 (4).

The values of dielectric constant of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics increased with increase in temperature and at dual substitution of Ti^{4+} by Nb^{5+} and Mn^{3+} (Figure 4, a, c), and the sharp maximum, corresponding to the ferroelectric to paraelectric phase transition, was observed on the $\varepsilon = f(T)$ dependences for the samples studied. The Curie temperature value (T_C) was equal to 972.5, 987.3, 963.4, and 933.9 K for the samples with $x = 0, 0.05, 0.10,$ and 0.15 respectively, and, in the whole, decreased at x increasing. Decreasing of T_C of layered bismuth titanate at partial substitution in it of titanium by niobium and manganese, observed in this work, are in a good accordance with the results of works [5–7, 9, 10], in which the similar effect was detected on $\text{Bi}_4\text{Ti}_2\text{Nb}_{0.5}\text{Fe}_{0.5}\text{O}_{12}$ [5], $\text{Bi}_4\text{Ti}_{3-x}\text{Cr}_x\text{O}_{12}$ [6], $\text{Bi}_4\text{Ti}_{3-x}\text{Fe}_x\text{O}_{12}$

[7], $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Co}_x\text{O}_{12}$ [9], and $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Fe}_x\text{O}_{12}$ solid solutions [10].

Dielectric losses of investigated samples increased with increase in temperature and decreased at dual substitution of Ti^{4+} by Nb^{5+} and Mn^{3+} (except $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ solid solution which dielectric losses were maximal among the samples studied) (Figure 4, b, d). On the $\text{tg}\delta = f(T)$ dependences two anomalous regions were observed near 600–700 K and 940–970 K. The second anomaly is connected to the FE→PE phase transition, but the first one probably belongs to the oxygen vacancies movement out (migration) of domain walls [17]. The similar trends of $\sigma = f(T)$ and $\text{tg}\delta = f(T)$ dependences for $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics (Figures 3, a, 4, b) let us conclude that dielectric losses in these materials are due to the conduction of the samples, but relaxation losses, connected to the dipole polarization, are very small.

The values of Curie temperature of the samples slightly varied at varying of frequency (Figure 5, a), which indicates that $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ phases were not normal ferroelectrics [5]. When the testing frequency increased from $2 \cdot 10^2$ Hz to $5 \cdot 10^5$ Hz, the dielectric constant and dielectric losses of ceramics studied decreased substantially (Figure 5), as a result of the suppression of relaxing polarization at high frequencies.

The frequency dependences of AC electrical conductivity of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ at various temperatures consisted of two parts: the frequency independent plateau at low frequencies which was attributed to the long-range translational motion of ions contributing to DC conductivity (σ_{DC}) [7, 18], and nonlinearly increasing part at high frequencies ($>10^5$ Hz), which showed ν^n dependence corresponding to the short-range translation ion hopping [5, 18].

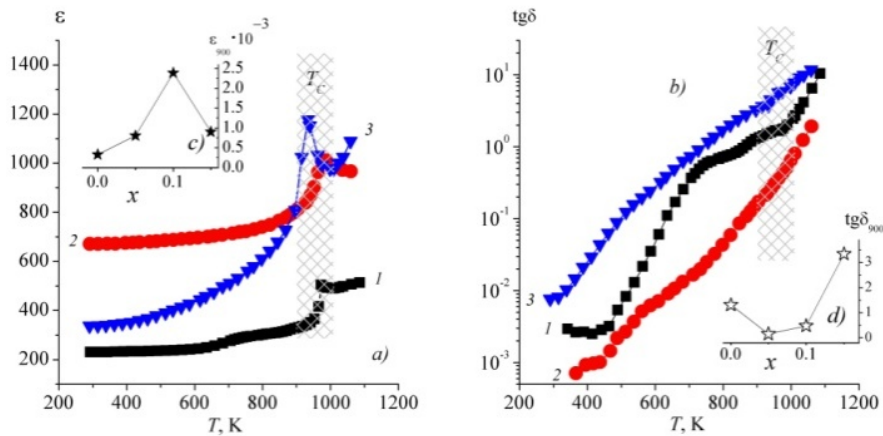


Figure 4. Temperature (a, b) and concentration (c, d) dependences of dielectric constant (a, c), and dielectric losses (b, d) of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics ($\nu = 10^5$ Hz): $x = 0$ (1), 0.05 (2), and 0.15 (3).

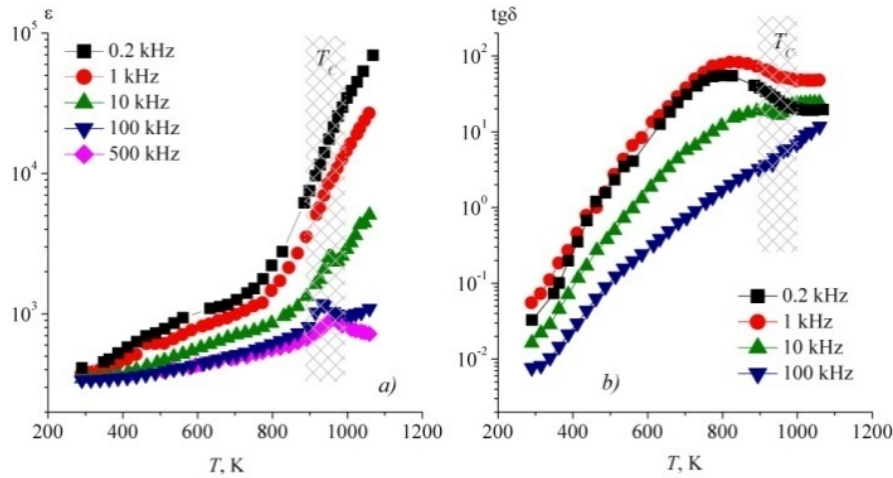


Figure 5. Temperature dependences of dielectric constant (a), and dielectric losses (b) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ at different frequencies.

The frequency dependent AC electrical conductivity of $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ceramics at all temperatures obeyed Jonscher's power law $\sigma(\nu) = \sigma(0) + A\nu^n$, where $\sigma(\nu)$ is the total conductivity, $\sigma(0)$ is the DC conductivity, A is the temperature-dependent constant which determines the strength of polarizability, and exponent n represents the degree of interaction between the mobile ions and the lattice around them [17, 19]. The values of n were less than one which indicates that charge carriers motions was translational [18]. The character of $n = f(T)$ dependence shows hopping mechanism of charge carriers [17, 19]. For a small polaron hopping, n increases with increase in temperature, while for a large polaron hopping, n decreases with increase in temperature. The values of n were less than one and increased below 823 K and decreased above 823 K, hence we concluded that AC electrical conductivity arised mainly due to the short-range order translation hopping assisted by small polaron ($T < 823$ K) and large polaron ($T > 823$ K) hopping mechanism.

On the complex impedance plots ($Z'' = f(Z')$) dependences, or Nyquist plots) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics measured at different temperatures (Figure 6) only one semicircle present in the high-frequency region, which indicates that electrical resistivity of the ceramics is mainly determined by the electrical resistivity of the grains (R_g), and the contribution of the grain boundaries (R_{gb}) or electrode contacts (R_{ei}) is negligible [20]. A decrease in the size of semicircles (R_g values) at temperature gaining indicated that the electrical conductivity of ceramics was thermally activated and had a semiconducting character.

The temperature dependence of the electrical resistivity of grains (Figure 6) was governed by Arrhenius equation $R_g = A \cdot \exp(E_A/RT)$ and the activation energy of the intragranular (bulk) electrical conductivity of ceramics (E_A), determined from the $\ln R_g = f(1/T)$ dependence was equal to 0.526 ± 0.032 eV.

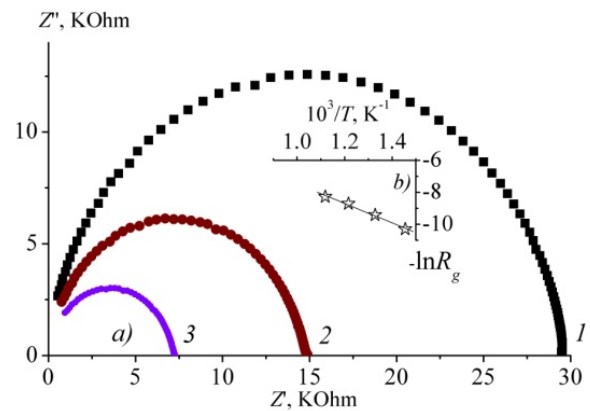


Figure 6. Complex impedance plots ($Z'' = f(Z')$) for the $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics at different temperatures: 687 K (1), 753 K (2), and 823 K (3). Inset shows Arrhenius plots of grain (volume) conductivity (R_g) $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics.

Frequency dependencies of imaginary part of impedance (Z'') of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ solid solution at different temperatures are presented in the Figure 7. As can be seen, on the $Z'' = f(\nu)$ dependencies there was only one maximum, which values decreased at temperature increasing, position shifted to the higher frequencies, but the shape remained practically unchanged.

The obtained features indicate the occurrence of thermally activated relaxation processes in the ceramics with only single value of relaxation time, that is, the relaxation processes in $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ possess, probably, the Debye character [18]. The intensity of maximum on the $Z'' = f(\nu)$ dependencies of the ceramics studied strongly decreased at temperature increase, indicating that temperature dependence of the relaxation time of Arrhenius type. The value of activation energy of relaxation processes obtained from the $\ln \tau_{Z''} = f(1/T)$ dependence, where $\tau_{Z''}$ is the relaxation time, determined from the position of the maximum on the $Z'' = f(\nu)$ dependence, (Figure 7, inset), was equal to 0.440 ± 0.028 eV.

The presence of only one peak in the frequency dependences of the imaginary part of impedance indicates that the relaxation response of ceramics is determined mainly by the contribution of its intragranular regions [18].

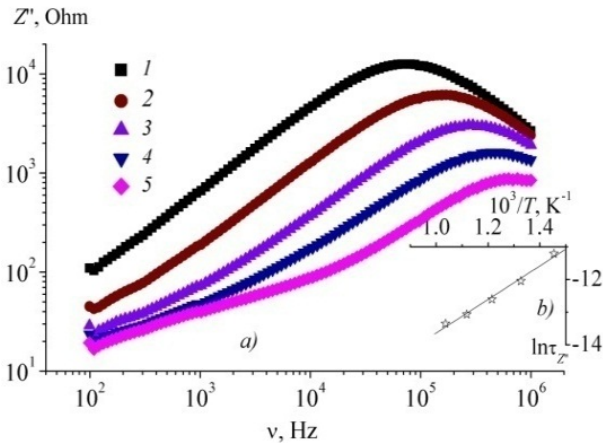


Figure 7. Frequency dependences of imaginary part of impedance (Z'') of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics at different temperatures: 687 K (1), 753 K (2), 823 K (3), 894 K (4), and 965 K (5). Inset shows Arrhenius plots of relaxation time ($\tau_{Z''}$) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics.

On the Figure 8 the frequency dependences of imaginary part of electrical modulus (M'') of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics are shown at which only a single peak was observed at different temperatures. The frequency range below the peak determines the region in which the charge carriers are able to move over long distances, and the frequency range above the peak corresponds to the situation where the charge carriers are confined to the walls of potential well and are capable of moving only over short distances [20]. At temperature gaining the peak on the $M'' = f(\nu)$ dependencies shifts towards higher frequencies, which implies that dielectric relaxation in $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ is thermally activated. A slight asymmetry of the M'' peaks is observed and the magnitude of the width of the peaks at their half-maxima is larger than ideal Debye response (1.14 decades), which shows that relaxation processes in the ceramics are, probably, of non-Debye type [20, 21]. The low values of M'' at low frequencies indicate that contribution of electrode processes in the polarization of material is negligible. The value of activation energy of relaxation determined from the $\ln \tau_{M''} = f(1/T)$ dependence, where $\tau_{M''}$ is the relaxation time obtained from the position of peak on the $M'' = f(\nu)$ dependencies (Figure 8, inset), was equal to 0.509 ± 0.020 eV, which, within the error of measurements and calculations, coincides with the value of activation energy of relaxation, found from the results of impedance spectroscopy, and also with the activation energy of bulk (intragranular) conductivity of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics, which indicates that charge carriers in the processes of relaxation overcome the same energy barrier.

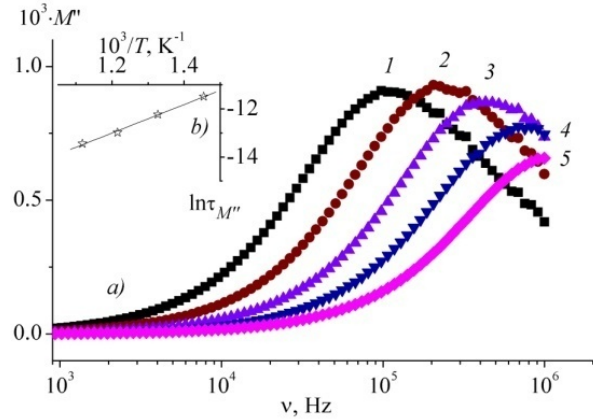


Figure 8. Frequency dependences of imaginary part of electrical modulus (M'') of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics at different temperatures: 687 K (1), 753 K (2), 823 K (3), 894 K (4), and 965 K (5). Inset shows Arrhenius plots of relaxation time ($\tau_{M''}$) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics.

The frequency dependences of normalized imaginary parts of impedance (Z''/Z''_{max}) and electrical modulus (M''/M''_{max}) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ sintered ceramics are presented in the Figure 9. The maxima on the $Z''/Z''_{max} = f(\nu)$ and $M''/M''_{max} = f(\nu)$ dependencies at different temperatures are not coincided which indicates that relaxation processes in it at this temperatures are non-Debye type and the relaxation in the ceramics is due to the short-range movement of charge carriers [22].

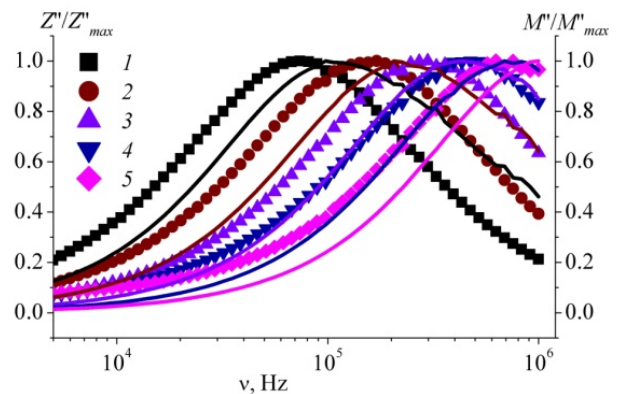


Figure 9. Frequency dependences of normalized peaks Z''/Z''_{max} (symbols) and M''/M''_{max} (lines) of $\text{Bi}_4\text{Ti}_{2.7}\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ ceramics at different temperatures: 687 K (1), 753 K (2), 823 K (3), 894 K (4), and 965 K (5).

4. Conclusions

The $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ solid solutions with small substitution degree of titanium by niobium and manganese ($x = 0.05, 0.10, 0.15$) have been synthesized using conventional solid state reactions method, their crystal structure, microstructure, electrical and dielectric properties within wide interval of temperatures and frequencies have been investigated.

It was found that the $\text{Bi}_4\text{Ti}_{3-2x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ titanates crystallized in an orthorhombic structure and were *p*-type semiconductors, which sinterability and dielectric constant increase, but grain size and thermo-EMF coefficient decrease at dual substitution of titanium by niobium and manganese. It was established that ceramics is electrically homogeneous and relaxation processes in it are non-Debye-like, and values of activation energy of relaxation obtained from results of impedance and modulus spectroscopy are in a good agreement. From the analysis of frequency dependencies of AC electrical conductivity of the samples it had been determined that AC electrical conductivity arised mainly due to the short-range order translation hopping assisted by small polaron (at low temperatures) and large polaron (at high temperatures) hopping mechanism.

Abbreviations

EMF electromotiv eforce
 CN coordination number
 SG space group
 FE ferroelectric
 PE paraelectric
 DC direct current
 AC alternate current

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REFERENCES

- [1] N.C. Hyatt, J.A. Hriljac, T.P. Comyn, Cation disorder in $\text{Bi}_2\text{Ln}_2\text{Ti}_3\text{O}_{12}$ Aurivillius phases ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$ and Sm), *Mat. Res. Bull.*, Vol.38, 837–846, 2003.
- [2] J.F. Scott, C.A. Araujo, Ferroelectric memories, *Science*, Vol. 246, No. 4936, 1400–1405, 1989.
- [3] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Lanthanum-substituted bismuth titanate for use in non-volatile memories, *Nature*, Vol.401, 682–684, 1999.
- [4] P. Siriprapa, A. Watcharapasorn, S. Jiansirisomboon, Effects of Mn-dopant on phase, microstructure and electrical properties in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics, *Ceram. Int.*, Vol. 39, S355–S358, 2013.
- [5] S. Kumar, K.B.R. Varma, Structural and dielectric properties of $\text{Bi}_4\text{Ti}_2\text{Nb}_{0.5}\text{Fe}_{0.5}\text{O}_{12}$ ceramics, *Solid State Commun.*, Vol. 146, 137–142, 2008.
- [6] M.S. Koroleva, I.V. Piir, V.E. Grass, B.A. Belyi, D.A. Korolev, N.V. Chezhina, Synthesis and Properties of Chromium-Containing Bismuth Titanate Solid Solutions with the Layered Perovskite Type Structure, *Proc. Komi Sci. Centre of Ural Branch of Rus. Acad. Sci.*, Iss. 1(9), 24–28, 2012 [in Russian].
- [7] M.S. Shashkov, O.V. Malyshkina, I.V. Piir, M.S. Koroleva, Dielectric properties of iron-containing bismuth titanate solid solutions with a layer perovskite structure, *Physics of the Solid State*, Vol. 57, Iss. 3, 506–509, 2015.
- [8] M. Villegas, T. Jardiel, A.C. Caballero, J.F. Fernandez, Electrical Properties of Bismuth Titanate Based Ceramics with Secondary Phases, *J Electroceram.*, Vol. 13, 543–548, 2004.
- [9] A.I. Klyndyuk, E.A. Chizhova, A.A. Glinskaya, Synthesis and properties of niobium-, cobalt-substituted solid solutions of bismuth titanate with layered perovskite structure, *Proc. Nation. Acad. Sci. of Belarus. Chem. ser.*, Vol. 54, No 2, 154–160, 2018 [in Russian].
- [10] A.I. Klyndyuk, E.A. Chizhova, Thermal expansion, electrotransport and dielectrical properties of $\text{Bi}_4(\text{Ti}, \text{Nb}, \text{Fe})_3\text{O}_{12}$ solid solutions, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, To be published [in Russian].
- [11] A.I. Klyndyuk, E.A. Chizhova, Structure, Thermal Expansion, and Electrical Properties of $\text{BiFeO}_3\text{-NdMnO}_3$ Solid Solutions, *Inorg. Mater*, Vol. 51, No. 3, 272–277, 2015.
- [12] B.D. Stojanović, A.Z. Simoes, C.O. Paiva-Santos, C. Quinelato, E. Longo, J.A. Varela, Effect of processing route on the phase formation and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics, *Ceram Int.*, Vol. 32, 707–712, 2006.
- [13] R.D. Shannon, C.T. Prewitt, Revised values of effective ionic radii, *Acta Cryst. B.*, Vol. 25, Part 5, 946–960, 1969.
- [14] Y.M. Kan, G.J. Zhang, P.L. Wang, Y.B. Cheng, Preparation and properties of neodymium-modified bismuth titanate ceramics, *J. Eur. Ceram. Soc.*, Vol. 28, 1641–1647, 2008.
- [15] S.K. Kim, M. Miyayama, H. Yanagida, Electrical anisotropy and a plausible explanation for dielectric anomaly of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystal, *Mat. Res. Bull.*, Vol. 31, No. 1, 121–131, 1996.
- [16] A.I. Klyndyuk, E.A. Chizhova, A.I. Poznyak, Preparation and characterization of $\text{Bi}_{4-x}\text{Pr}_x\text{Ti}_3\text{O}_{12}$ solid solutions, *Chimica Techno Acta*, Vol. 4, No. 4, 211–217, 2017.
- [17] B. Jimenez, R. Jimenez, A. Castro, P. Millan, L. Pardo, Dielectric and mechanoelastic relaxations due to point defects in layered bismuth titanate ceramics, *J Phys: Condens Matter*, Vol. 13, No. 33, 7315–7326, 2001.
- [18] S. Kumari, N. Ortega, A. Kumar, S.P. Pavunny, J.W. Hubbard, C. Runaldi, G. Srinivasan, J.F. Scott, R.S. Katiyar, Dielectric anomalies due to grain boundary conduction in chemically substituted BiFeO_3 , *J. Appl. Phys.*, Vol. 117, 114102, 2015.
- [19] A.K. Jonscher, The ‘universal’ dielectric response, *Nature*, Vol. 267, 673–9, 1977.
- [20] M.J. Miah, A.K.M. Akhter Hossain, Magnetic, Dielectric and Complex Impedance Properties of $x\text{Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3\text{-(1-x)BiFe}_{0.9}\text{Gd}_{0.1}\text{O}_3$ Multiferroic Ceramics, *Acta Metal Sin. (Engl. Lett.)*, Vol. 29, Iss. 6, 505–517, 2016.
- [21] M.S. Koroleva, I.V. Piir, E.I. Istomina, Synthesis, structure

and electrical properties of Mg-, Ni-codoped bismuth niobates, *Chimica Techno Acta*, Vol. 4, No. 4, 231–241, 2017.

- [22] J.-W. Liu, D.-Y. Lu, X.-Y. Yu, Q.-L. Liu, Q. Tao, H. Change, P.-W. Zhu, Dielectric Properties of Eu-Doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ with Different Compensation Mechanisms, *Acta Metal. Sin. (Engl. Lett.)*, Vol. 30, Iss. 2, 97–103, 2017.