Dielectric Properties of Bi₄(TiₓNbₓMnᵧ)₃O₁₂ Titanates

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Abstract The Bi₄Ti₃₋₂ₓNbₓMnₓO₁₂ (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 Bi₄Ti₃₋₂ₓNbₓMnₓO₁₂ 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 Bi₄Ti₃O₁₂ belongs to the Aurivillius phase family Bi₂Aₓ₋₁BₓO₃₋₁₋₂, whose structure consist of alternated fluorite-like [Bi₂O₃]²⁻ layers and perovskite-like [Aₓ₋₁BₓO₃₋₁₋₂]²⁻ blocks, where n is a number of octahedral layers in the perovskite-like block [1]. A-positions with cubic-octahedral environment (CN = 12) in the [Aₓ₋₁BₓO₃₋₁₋₂]²⁻ blocks occupy the low-charged large cations (Na⁺, Sr²⁺, Bi³⁺ etc), and B-positions inside oxygen octahedrals (CN = 6) occupy the high-charged small cations (Ti⁴⁺, Nb⁵⁺, W⁶⁺ etc.).

Triple-layered (n = 3) Aurivillius phase Bi₄Ti₃O₁₂ is ferroelectric with high Curie temperature (TC = 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, condensors, and different type of memory devices. So, for example, as material for non-volatile memory devices the lanthanum-substituted Bi₃.₅₅Laₐ₋₃.₅₃Ti₃O₁₂ solid solution was proposed, whose functional characteristics were essentially better that of such traditional ferroelectrics as PbTi₁₋ₓZrₓO₃ or SrBi₂Ta₂O₉ [3].

It is known, that physicochemical and functional properties of ceramics based on the layered bismuth titanate Bi₄Ti₃O₁₂ may be improved by means of partial substitution of different cations in its structure, in particular, of Ti⁴⁺ ions in the perovskite-like [Bi₂Ti₃O₉]²⁻ blocks, which was studied in a number of works [4–9].

So, it was found, that introduction of MnO₂ into Bi₃₋₂₋ₓLaₓ₋₃₋₂₋ₓ₋₁₋ₓ₋₃₋ₓ₋₁₋ₓ₋₁₋ₓ₋₃₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋¹₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋¹₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋ₓ₋₁₋x—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.
crystal structure, microstructure, electrical conductivity, thermo-EMF, dielectric constant and dielectric losses of $\text{Bi}_4\text{Ti}_3\text{Nb}_x\text{Mn}_x\text{O}_{12}$ ($x \leq 3.75 \text{ mol.\%}$) 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 $\text{Bi}_2\text{O}_3$, $\text{TiO}_2$, $\text{Nb}_2\text{O}_5$, and $\text{Mn}_2\text{O}_3$ powders (chemically pure qualification) taken in appropriate stoichiometric relations in air within temperature interval of $923–1223 \text{ K}$ 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, CuK$_\alpha$-radiation, Ni-filter) and IR absorption spectroscopy (IR Fourier-spectrometer Nexus of ThermoNicolet). Porosity ($\Pi$) of the samples was calculated as $\Pi = (1 - (\rho/\rho_{\text{XRD}})) \times 100\%$, where $\rho$ is bulk density, which was determined from the mass and dimensions of the samples; $\rho_{\text{XRD}}$ – 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 $300–1100 \text{ K}$ for frequencies between $10^2–10^6 \text{ Hz}$ using immitance meter E7–25. DC electrical conductivity and thermo-EMF of sintered ceramics was studied within $480–1100 \text{ K}$ and $780–1100 \text{ K}$ respectively according to the methods described in [11]. Values of activation energy of DC electrical conductivity ($E_d$) and thermo-EMF ($E_x$) 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 monophase 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 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($a = 5.406(10) \text{ Å}$, $b = 5.422(7) \text{ Å}$, and $c = 32.75(4) \text{ Å}$), were in a close agreement with an earlier studies: $5.444(1), 5.413(1),$ and $32.858(1) \text{ Å}$ [8], $5.4403, 5.4175,$ and $32.7862 \text{ Å}$ [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 $\text{CN} = 6$ according to [13] $\text{Ti}^{4+}$, $\text{Nb}^{5+}$, and $\text{Mn}^{3+}$ ionic radii are equal to $0.605, 0.640,$ and $0.580 \text{ Å}$ 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](image.png)

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

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$c/\sqrt{(ab)}$</th>
<th>$V$, Å$^3$</th>
<th>$\rho_{\text{XRD}}$, g/cm$^3$</th>
<th>$\rho$, g/cm$^3$</th>
<th>$\Pi$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.406±0.010</td>
<td>5.422±0.007</td>
<td>32.75±0.04</td>
<td>6.049</td>
<td>959.8±3.9</td>
<td>8.11</td>
<td>4.80</td>
<td>41</td>
</tr>
<tr>
<td>0.05</td>
<td>5.407±0.009</td>
<td>5.416±0.007</td>
<td>32.77±0.04</td>
<td>6.055</td>
<td>959.8±4.0</td>
<td>8.13</td>
<td>5.10</td>
<td>37</td>
</tr>
<tr>
<td>0.10</td>
<td>5.409±0.009</td>
<td>5.416±0.007</td>
<td>32.79±0.04</td>
<td>6.058</td>
<td>960.4±4.1</td>
<td>8.14</td>
<td>5.51</td>
<td>32</td>
</tr>
<tr>
<td>0.15</td>
<td>5.395±0.010</td>
<td>5.415±0.007</td>
<td>32.79±0.04</td>
<td>6.067</td>
<td>957.9±3.9</td>
<td>8.18</td>
<td>5.73</td>
<td>30</td>
</tr>
</tbody>
</table>
Four absorption bands occurring at 815–818 cm$^{-1}$ ($v_1$), 617 cm$^{-1}$ ($v_2$) (only for Bi$_4$Ti$_3$O$_{12}$ phase), 582–589 cm$^{-1}$ ($v_3$), and 469–472 cm$^{-1}$ ($v_4$) were observed in the absorption spectra of Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$O$_{12}$ powders (Figure 1, b). According to [5, 13], these bands corresponded to the stretching ($v_1$–$v_3$) and bending ($v_4$) vibrations of Bi–O ($v_1$ and $v_4$) and Ti–O ($v_2$– within $ab$-plane, $v_3$ – along $c$-axis) bonds respectively. The $v_1$, and $v_4$ peak positions did not change practically at partial substitution of titanium by niobium and manganese in Bi$_4$Ti$_3$O$_{12}$, but $v_2$ 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 Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_3$O$_{12}$ by Nb$_2$O$_5$ and Co$_3$O$_4$ improved the sinterability of Bi$_{4}$Ti$_{3}$-2Nb$_{0.05}$Co$_{0.15}$O$_{12}$ solid solutions [10].

The sintered Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_3$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 Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ leads to the increase of grain sizes of Bi$_{3.25}$La$_{0.75}$Ti$_{1-x}$Mn$_x$O$_{12}$ ceramics. The cause of this may be due to the fact that in our work Bi$_4$Ti$_3$O$_{12}$ was doped not only by Mn$_2$O$_3$, but also by Nb$_2$O$_5$, so, the shrinking of grain sizes of Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_3$O$_{12}$ also lead to the essential decreasing of the grain sizes of Bi$_{4}$Ti$_{3-2x}$Nb$_x$Fe$_x$O$_{12}$ ceramics in comparison to the unsubstituted Bi$_4$Ti$_3$O$_{12}$ phase.

Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_3$O$_{12}$ phase at high temperatures were positive [15, 16]. Seebeck’s coefficient values of Bi$_{4}$Ti$_{3-2x}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ solid solution were essentially less than for Bi$_4$Ti$_3$O$_{12}$ (Figure 3, b). In [9, 10] it was found that values of thermo-EMF coefficient of Bi$_{4}$Ti$_{3-2x}$Nb$_x$Co$_x$O$_{12}$ and Bi$_{4}$Ti$_{3-2x}$Nb$_x$Fe$_x$O$_{12}$ solid solutions were close to the ones for unsubstituted bismuth titanate Bi$_4$Ti$_3$O$_{12}$. So, strong decrease of Seebeck’s coefficient of Bi$_{4}$Ti$_{3-2x}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ in comparison with parent Bi$_4$Ti$_3$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 Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$O$_{12}$ solid solution in ferroelectric (FE) region were larger than for Bi$_4$Ti$_3$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 Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$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](image_url)  
**Figure 2.** Electron micrographs of surfaces of Bi$_{4}$Ti$_{3-2x}$Nb$_x$Mn$_x$O$_{12}$ ceramics: $x = 0.05$ (a), 0.10 (b), and 0.15 (c).
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], $\text{Bi}_4\text{Ti}_3-\text{Cr}_x\text{O}_{12}$ [6], $\text{Bi}_4\text{Ti}_3-\text{Fe}_x\text{O}_{12}$ [7], $\text{Bi}_4\text{Ti}_3-2\text{Nb}_x\text{Co}_x\text{O}_{12}$ [9], and $\text{Bi}_4\text{Ti}_3-2\text{Nb}_x\text{Fe}_x\text{O}_{12}$ 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 $\text{Bi}_4\text{Ti}_2\text{Nb}_{0.15}\text{Mn}_{0.15}\text{O}_{12}$ solid solution which dielectric losses were maximal among the samples studied) (Figure 4, b, d). On the $\tan\delta = f(T)$ dependences two anomalous regions were observed near 600–700 K and 940–970 K. The second anomaly is connected to the FE$\rightarrow$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 $\tan\delta = f(T)$ dependences for $\text{Bi}_4\text{Ti}_3-2\text{Nb}_x\text{Mn}_x\text{O}_{12}$ 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 $\text{Bi}_4\text{Ti}_3-2\text{Nb}_x\text{Mn}_x\text{O}_{12}$ phases were not normal ferroelectrics [5]. When the testing frequency increased from $2\times10^2$ Hz to $5\times10^5$ 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 ($\sigma_{\text{DC}}$) [7, 18], and nonlinearly increasing part at high frequencies ($>10^5$ Hz), which showed $\nu^n$ dependence corresponding to the short-range translation ion hopping [5, 18].
The frequency dependent AC electrical conductivity of Bi$_4$Ti$_{3-2x}$Nb$_x$Mn$_x$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 carrier 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 arose 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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$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 ($R_{el}$) 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 $R_g = A\exp(E_a/RT)$ 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±0.032eV.

Frequency dependencies of imaginary part of impedance ($Z''$) of Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$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±0.028eV.
The presence of only one peak in the frequency dependence of the imaginary part of impedance indicates that the relaxation response of ceramics is determined mainly by the contribution of its intragranular regions [18].

On the Figure 8 the frequency dependencies of imaginary part of electrical modulus ($M''$) of Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ ceramics at different temperatures 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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$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 $\ln(\tau_{Z''}) = f(1/T)$ dependence, where $\tau_{Z''}$ 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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ ceramics, which indicates that charge carriers in the processes of relaxation overcome the same energy barrier.

Figure 7. Frequency dependences of imaginary part of impedance ($Z''$) of Bi$_4$Ti$_{1.27}$Nb$_{0.15}$Mn$_{0.15}$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 Bi$_4$Ti$_{1.27}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ ceramics.

Figure 8. Frequency dependences of imaginary part of electrical modulus ($M''$) of Bi$_4$Ti$_{1.27}$Nb$_{0.15}$Mn$_{0.15}$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 Bi$_4$Ti$_{1.27}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ ceramics.

The frequency dependencies of normalized imaginary parts of impedance ($Z''/Z''_{max}$) and electrical modulus ($M''/M''_{max}$) of Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$O$_{12}$ sintered ceramics are presented in 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 these 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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Mn$_{0.15}$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 Bi$_4$Ti$_{3.2}$Nb$_x$Mn$_x$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 Bi$_{4}$Ti$_{3}$–$x$Nb$_{x}$Mn$_{x}$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 temperatures it had been determined that AC electrical conductivity arises mainly due to the short-range order translation hopping assisted by small polaron (at low frequency dependencies of AC electrical conductivity of the 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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