Dielectric Properties of Bi₄(TiₓNbₓMnx)₃O₁₂ Titanates

Andrei Klyndyuk*, Ekaterina Chizhova

Department of Physical, Colloid and Analytical Chemistry, Belarusian State Technological University, Belarus Republic

Abstract The Bi₄Tiₓ₂NbₓMnxO₁₂ (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 Bi₄Tiₓ₂NbₓMnxO₁₂ 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 non-Debye-like, and values of activation energy of relaxation processes in it were of a non-Debye type.

Nonetheless, it was found, that introduction of MnO₂ into Bi₁₂₃-Lax₄Ti₃O₁₂ led to the increasing of size of the grains of Bi₁₂₃-Lax₄Ti₃-xFeO₁₂ ceramics was determined by grains electrical resistivity, and relaxation processes in it were of a non-Debye like type.

In the [8] it was found that doping of Bi₄Ti₃O₁₂ by tungsten oxide WO₃ led to the sharp decreasing of electrical conductivity of formed Bi₄(Ti,W)₃O₁₂ ceramics. According to the [9], the partial substitution of titanium by niobium and cobalt in Bi₄Ti₃O₁₂ lead to the increase of the unit cell volume of Bi₄Ti₃-xNbₓFeO₁₂, 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 Bi₄Ti₃O₁₂ led to the reduction of grains size, Curie temperature, dielectric constant and dielectric losses of Bi₄Ti₃-xNbₓFeO₁₂ solid solutions, and did not affect practically on their sinterability, lattice constants, and thermo-EMF coefficient. Electrical resistivity of Bi₄Ti₃-xNbₓFeO₁₂ 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 Bi₄Ti₃O₁₂ by niobium and manganese on the

Keywords Layered Bismuth Titanate, Solid Solutions, Electrical Conductivity, Thermo-EMF, Dielectric Constant, Dielectric Losses, Impedance Spectroscopy, Modulus Spectroscopy
crystal structure, microstructure, electrical conductivity, thermo-EMF, dielectric constant and dielectric losses of Bi₄Ti₃₋₂NbₓMnₓO₁₂ (x ≤ 3.75 mol.%) had been studied.

2. Materials and Methods

Ceramic samples of Bi₄Ti₃₋₂NbₓMnₓO₁₂ (x = 0.00, 0.05, 0.10, 0.15) titanates were synthesized using solid-state reactions method from mixtures of Bi₂O₃, TiO₂, Nb₂O₅, and MnO₂ 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 crystal structure, microstructure, electrical conductivity, thermo-EMF, dielectric constant and dielectric losses of Bi₄Ti₃₋₂NbₓMnₓO₁₂ (x ≤ 3.75 mol.%) had been studied.

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 Bi₄Ti₃₋₂NbₓMnₓO₁₂ samples were monophasic within XRD reliability (Figure 1, a) and crystallized in an orthorhombic structure like parent compound Bi₄Ti₃O₁₂ (SG B2cb [8]).

Lattice constants of Bi₄Ti₃O₁₂ (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 Bi₄Ti₃₋₂NbₓMnₓO₁₂ solid solutions were close to the Bi₄Ti₃O₁₂ 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] Ti⁵⁺, Nb⁵⁺, and Mn³⁺ ionic radii are equal to 0.605, 0.640, and 0.580 Å respectively). Unit cell of the Bi₄Ti₃₋₂NbₓMnₓO₁₂ solid solutions was slightly elongated in the c direction (c/√(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 Bi₄Ti₃₋₂NbₓCoₓO₁₂ [9] and Bi₄Ti₃₋₂NbₓFeₓO₁₂ solid solutions [10].

![Figure 1. X-ray powder diffractograms (CuKα-radiation) (a) and IR-absorption spectra (b) of Bi₄Ti₃₋₂NbₓMnₓO₁₂ samples: x = 0 (1), 0.05 (2), 0.10 (3), and 0.15 (4)](image)

| x     | a, Å  | b, Å  | c, Å  | c/√(ab) | V, Å³  | ρₓRD, g/cm³ | ρ, g/cm³ | 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\(^{-1}\) (\(v_1\)), 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\(_{3–x}\)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 \(v_4\) peaks positions did not change practically at partial substitution of titanium by niobium and manganese oxides to the 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\(_{3–x}\)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\(_{3–x}\)Nb\(_x\)Co\(_x\)O\(_{12}\) solid solutions [10].

The sintered Bi\(_4\)Ti\(_{3–x}\)Nb\(_x\)Mn\(_x\)O\(_{12}\) ceramics presented grains with plate-like morphology and average grain size about 1–3 \(\mu\)m (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 \(\mu\)m). 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\(_{3–x}\)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\(_{3–x}\)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\(_{3–x}\)Nb\(_x\)Fe\(_x\)O\(_{12}\) ceramics in comparison to the unsubstituted Bi\(_4\)Ti\(_3\)O\(_{12}\) phase.

Bi\(_4\)Ti\(_{3–x}\)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\(_{3–x}\)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\(_{3–x}\)Nb\(_x\)Co\(_x\)O\(_{12}\) and Bi\(_4\)Ti\(_{3–x}\)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\(_{3–x}\)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 partial substitution in it of Bi by Nd and of Fe by Mn.

The values of DC electrical conductivity of Bi\(_4\)Ti\(_{3–x}\)Nb\(_x\)Mn\(_x\)O\(_{12}\) compounds were larger than for Bi\(_4\)Ti\(_3\)O\(_{12}\) in 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\(_{3–x}\)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. Electron micrographs of surfaces of Bi\(_4\)Ti\(_{3–x}\)Nb\(_x\)Mn\(_x\)O\(_{12}\) ceramics: \(x\) = 0.05 (a), 0.10 (b), and 0.15 (c).
Dielectric Properties of Bi$_4$(Ti,Nb,Mn)$_3$O$_{12}$ Titanates

The values of dielectric constant of Bi$_4$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_{2.7}$Nb$_{0.15}$Fe$_{0.15}$O$_{12}$ [5], Bi$_4$Ti$_{3-x}$Cr$_x$O$_{12}$ [6], Bi$_4$Ti$_{3-2x}$Co$_x$O$_{12}$ [7], Bi$_4$Ti$_{3-2x}$Nb$_x$Co$_x$O$_{12}$ [9], and Bi$_4$Ti$_{3-2x}$Nb$_x$Fe$_x$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 Bi$_4$Ti$_{1.8}$Nb$_{0.15}$Mn$_{0.15}$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→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 Bi$_4$Ti$_{3-2x}$Nb$_x$Mn$_x$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 Bi$_4$Ti$_{3-2x}$Nb$_x$Mn$_x$O$_{12}$ phases were not normal ferroelectrics [5]. When the testing frequency increased from $2 \cdot 10^2$ Hz to $5 \cdot 10^4$ 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 Bi$_4$Ti$_{1.8}$Nb$_{0.15}$Mn$_{0.15}$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 ($\sigma_{DC}$) [7, 18], and nonlinearly increasing part at high frequencies ($>10^5$ Hz), which showed $\nu^\nu$ 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 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 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 $\ln R_g = f(1/T)$ dependence, where $\tau$ 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 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].

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 $\ln(\nu) = f(1/T)$ dependence, where $\nu_{fr}$ 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.

4. Conclusions

The Bi$_4$Ti$_3$$_{2,5}$Nb$_{0.5}$Mn$_{0.5}$O$_{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 $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{Mn}_x\text{O}_{12}$ 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 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

Acknowledgements

This work was carried out in the frame of SPSI «Physical materials science, new materials and technologies» (subprogram «Materials science and materials technologies», task 1.17).

REFERENCES

[1] N.C. Hyatt, J.A. Hriljac, T.P. Comyn, Cation disorder in $\text{Bi}_3\text{Ln}_2\text{Ti}_3\text{O}_{12}$ Aurivillius phases ($\text{Ln} = \text{La—Pr, Nd and Sm}$), 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. Sirirapapa, A. Watcharapason, 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 $\text{Bi}_4\text{Ti}_3\text{Nb}_0.5\text{Fe}_0.5\text{O}_{12}$ ceramics, Solid State Commun., Vol. 146, 137–142, 2008.
[6] M.S. Koroleva, I.V. Piir, V.E. Grass, B.A. Beliy, D.A. Korolev, N.V. Chezhina, Synthesis and Properties of Chromium-Containing Bismuth Titanate Solid Solutions with the Layered Perovskite Type Structure, Proc. Kom. Sci. Centre of Ural Branch of Rus. Acad. Sci., Iss. 1(9), 24–28, 2012 [in Russian].
[7] M.S. Shashkov, O.V. Malyskhina, 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. Jardel, 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 BiFeO$_3$–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. Pozynak, Preparation and characterization of $\text{Bi}_4\text{Pr}_x\text{Ti}_3\text{O}_{12}$ 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. Pavuny, J.W. Hubbard, C. Rundali, 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 $\text{xBiFeO}_3\text{Sr}_0.05\text{TiO}_3-(1-x)\text{BiFeO}_3\text{Gd}_0.4\text{O}_3$ 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 CaCu3Ti4O12 with Different Compensation Mechanisms, Acta Metal. Sin. (Engl. Lett.), Vol. 30, Iss. 2, 97–103, 2017.