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Preparation and characterization of $Bi_{4-x}Pr_xTi_3O_{12}$ solid solutions

The $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) solid solutions ($x = 0.05, 0.10, 0.15$) with small praseodymium content were prepared by solid-state method. Thermal, electric, and dielectric properties of BPT were studied. It was revealed that BPT titanates crystalize in an orthorhombic structure and exhibit p-type semiconductivity. Dielectric constant of BPT increased, Curie temperature (T_C), electrical conductivity and dielectric losses decreased, but lattice parameters and thermo-EMF coefficient remained practically unchanged with the increase of praseodymium content in layered $Bi_{4-x}Pr_xTi_3O_{12}$. It was determined that activation energy of direct current (DC) electrical conductivity and linear thermal expansion coefficient (LTEC) of BPT changes at ferroelectric (FE) → paraelectric (PE) phase transition. The activation energy and LTEC changed below and above T_C from 1.08–1.56 eV to 0.45–0.86 eV and from $(9.10–10.80) \cdot 10^{-6}$ K^{-1} to $(13.12–14.61) \cdot 10^{-6}$ K^{-1}, respectively. The AC electrical conductivity studies of BPT illustrated short-range order with ionic translations assisted by small-polaron hopping.

Keywords: layered bismuth titanates; dielectric constant; dielectric losses; electrical conductivity; thermo-EMF; thermal expansion.

Introduction

$Bi_4Ti_3O_{12}$ belongs to the Aurivillius phase family $Bi_2A_{n-1}B_nO_{3n+3}$, structure of which consists of alternated fluorite-like $[Bi_2O_2]^{2+}$ layeres and perovskite-like $[A_{n-1}B_nO_{3n+1}]^{2-}$ blocks, where n – number of octahedral layers in the perovskite-like block [1]. This triple-layered ($n = 3$) Aurivillius phase is ferroelectric with high Curie temperature ($T_C = 948$ K [2]). The possibility to preserve the ferroelectric properties within a wide temperature range lets us to consider layered bismuth titanate as a promising material for radio-, acusto-, and optoelectronics; and thus can be used for production of optical displays, piezoelectric transducers, filters, capacitors, and different types of memory devices. So, for example, as a material for non-volatile memory devices the lanthanum-substituted $Bi_{3.25}La_{0.75}Ti_3O_{12}$ bismuth titanate is proposed, functional characteristics of which are better than of traditional ferroelectrics, such as $PbTi_{1-x}Zr_xO_3$ or $SrBi_2Ta_2O_9$ [3].

Crystal structure, physico-chemical, and functional properties of the solid solutions $Bi_{4-x}Ln_xTi_3O_{12}$ (Ln = rare-earth element) were studied in a number of pa-

pers [1, 3–8]. In [4] it was found that partial substitution of Bi by La in $Bi_4Ti_3O_{12}$ leads to decrease of orthorhombic distortion degree of $Bi_{4-x}La_xTi_3O_{12}$ solid solutions at $x \leq 1.0$, and at $x > 1.0$ they had tetragonal structure and were paraelectrics. According to the [1, 4] results, at $x \leq 0.75$ La^{3+} ions substitute Bi^{3+} in perovskite-like $[Bi_2Ti_3O_{10}]^{2-}$ blocks, and at $x > 0.75$ they can substitute Bi^{3+} ions in fluorite-like $[Bi_2O_2]^{2+}$ layers too, so formula of $Bi_{4-x}La_xTi_3O_{12}$ solid solutions at $x \leq 0.75$ and $x > 0.75$ should be written as $[Bi_2O_2][Bi_{2-x}La_xTi_3O_{10}]$ and $[Bi_{2-y}La_yO_2]$ $[Bi_{2-x+y}La_{x-y}Ti_3O_{10}]$, respectively. Authors of [5] established that partial substitution of Bi with La or Ce in $Bi_4Ti_3O_{12}$ leads to the decrease of Curie temperature of ceramics (T_C values for $Bi_{3.5}La_{0.5}Ti_3O_{12}$ and $Bi_{3.5}Ce_{0.5}Ti_3O_{12}$ samples were 798 and 813 K, respectively, both being lower than T_C for $Bi_4Ti_3O_{12}$ phase). At the same time, La_2O_3 addition to the layered bismuth titanate improved its dielectric properties; by authors' opinion, it was caused by de-

creasing of oxygen vacancy concentration in ceramics. Partial substitution of Bi with Nd in $Bi_4Ti_3O_{12}$ leads to the decrease of Curie temperature, dielectric losses, and electrical conductivity of $Bi_{4-x}Nd_xTi_3O_{12}$ ceramic; and impoves its polarization properties because of reduction of bismuth and oxygen vacancy concentrations [7]. In [8] the $Bi_{4-y}Tb_yTi_3O_{12}$ phase formation in the powder mixtures of Bi_2O_3, Tb_4O_7, and TiO_2 was investigated. It was found that partial replacing of Bi by Tb results in shrinking of unit cell of $Bi_{4-y}Tb_yTi_3O_{12}$ solid solutions, decrease of orthorhombic distortion degree of their crystal lattice, and, as a consequence, leads to the decrease of temperature of FE → PE (ferroelectric → paraelectric) phase transition (up to ≈28 K for $y = 0.4$).

In this work the results of investigation of crystal structure, thermal, electric, and dielectric properties of ceramic samples of $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) solid solutions with small praseodymium oxide content ($x \leq 3.75$ mol.%) are presented.

Experimental

$Bi_{4-x}Pr_xTi_3O_{12}$ ($x = 0.00, 0.05, 0.10, 0.15$) ceramic samples were prepared by solid-state reactions method from mixtures of Bi_2O_3 (99.0%), Pr_6O_{11} (99.0%), and TiO_2 (99.5%) powders taken in appropriate stoichiometric ratios. Precursor mixtures were calcuned in air within temperature interval of 923–1223 K for 17 hours with some intermediate regrindings, according to procedure described in details in [6].

Identification of the samples was performed using X-ray diffraction analysis (XRD) (Bruker D8 XRD Advance diffractometer, Cu Kα radiation) and IR absorption spectroscopy (IR Fourier-spectrometer Nexus of ThermoNicolet).

Relative density (ρ_{rel}) of the samples was calculated as

$$\rho_{rel} = (\rho_{app}/\rho_{XRD}) \cdot 100\%, \quad (1)$$

where ρ_{app} – apparent density, determined from the mass and dimensions of the samples; ρ_{XRD} – X-ray density.

Thermal expansion of the samples was studied using DIL 402 PC (Netzsch) dilatometer within 290–1130 K with heating-cooling rate of 1–5 K/min. Dielectric measurements were carried out in the temperature range 300–1090 K for frequencies between 100 Hz and 1 MHz using immittance meter E7-25. DC electrical conductitivy and thermo-EMF of sintered ceramics were studied within the temperature ranges of 470–1090 K and 780–1090 K,

respectively, according to the procedure described elsewhere [9]. Values of linear thermal expansion coefficient (LTEC, α) and activation energy of DC electrical conductivity (E_A) of the samples were determined from linear parts of $\Delta l/l_0 = f(T)$, and $\lg\sigma_{DC} = f(1/T)$ dependences, respectively. All measurements were performed in air.

Results and discussion

All $Bi_{4-x}Pr_xTi_3O_{12}$ samples after final stage of annealing were found single phase within XRD reliability (Fig. 1), and crystallized in orthorhombic structure like parent compound $Bi_4Ti_3O_{12}$ (space group $B2cb$) [10]. Lattice constants of Bi_4TiO_{12} ($a = 5.449(9)$ Å, $b = 5.422(9)$ Å, and $c = 32.85(4)$ Å) were in a close agreement with an earlier studies: 5.444(1), 5.413(1), and 32.858(1) Å [10], 5.4403, 5.4175, and 32.7862 Å [11], and 5.4438(1), 5.4105(1), and 32.8226(5) Å [8]. Lattice constants of $Bi_{4-x}Pr_xTi_3O_{12}$ solid solutions were close to the $Bi_4Ti_3O_{12}$ ones (for example, for $Bi_{3.90}Pr_{0.10}Ti_3O_{12}$ $a = 5.449(7)$ Å, $b = 5.420(9)$ Å, and $c = 32.80(3)$ Å), which agrees with the fact that sizes of substituting and substituted ions are close to each other (for C.N. = 6 according to [12] Bi^{3+} and Pr^{3+} ionic radii are 1.11 and 1.013 Å, respectively).

It should be noted that 0014 reflection in the $Bi_{4-x}Pr_xTi_3O_{12}$ diffractograms was the most intensive, in contrast with 117 peak for $Bi_4Ti_3O_{12}$. Other 00l peaks had higher intensity as well (I_{006}/I_{117} ratio was equal to 0.6, 1.7, 3.0, and 2.8 for x = 0.00, 0.05, 0.10, and 0.15, respectively). This fact shows that partial substitution of Bi with Pr in $Bi_4Ti_3O_{12}$ leads to the texturing of the samples. The nature of this phenomenon is not clear yet and will be studied in the future.

Three absorption bands occurring at 810–818 cm^{-1} (ν_1), 573–582 cm^{-1} (ν_2), and 474 cm^{-1} (ν_3) were observed in the absorption spectra of $Bi_{4-x}Pr_xTi_3O_{12}$ powders. According to [7, 11], these bands correspond to the stretching (ν_1 and ν_2) and bending (ν_3) vibrations of Bi–O (ν_1 and ν_3) and Ti–O (ν_2) bonds, respectively. The peak positions did not change with x increasing, so partial replacing of Bi by Pr in layered $Bi_4Ti_3O_{12}$ did not affect practically the metal-oxygen interactions in its crystal structure.

The relative density values for $Bi_{4-x}Pr_xTi_3O_{12}$ ceramics varied within 77–80% and increased with x, being essentially larger than for unsubstituted bismuth titanate (60%). These results show that addition of praseodymium oxide to the layered bismuth titanate improves its sinterability. Note that according to the literature data [6, 7] addition of lanthanum or neodymium oxides to the $Bi_4Ti_3O_{12}$, on the contrary, had lowered its sinterability.

On the temperature dependences of relative elongation an inflection point near 940–970 K was observed (Fig. 2). It is related to the FE → PE phase transition [8] and is accompanied by the increase of LTEC values of the samples (Table 1).
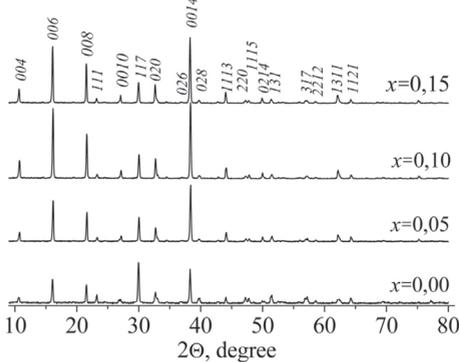

Fig. 1. X-ray powder diffractograms (Cu Kα radiation) of $Bi_{4-x}Pr_xTi_3O_{12}$ solid solutions

An inflection point, which was determined as an intersection of linear parts of $\Delta l/l_0 = f(T)$ dependences at low (FE region) and high temperatures (PE region), corresponds to the Curie temperature and decreases with x (Fig. 2, inset). It is in a good agreement with the literature data, according to which substitution of Bi with Ln in $Bi_4Ti_3O_{12}$ leads to lowering of its Curie temperature [4–8].

The LTEC values of $Bi_{4-x}Pr_xTi_3O_{12}$ titanates in FE state decreased, but in PE state increased with x (Table 1). The LTEC values in PE state can be explained by anharmonicity of metal-oxygen vibrations in disordered cationic sublattice of Pr^{3+}-substituted bismuth titanate $Bi_{4-x}Pr_xTi_3O_{12}$. The LTEC values in FE state could be caused either by increase of dipole-dipole interactions or by decrease of oxygen and bismuth vacancy concentrations in the BPT. The first explanation is in contrast with the fact that T_C of $Bi_{4-x}Pr_xTi_3O_{12}$ solid solutions decreases with x. So, the decrease of LTEC values of BPT ceramics in FE region is due to the decrease of the vacancy concentration in it [3].

$Bi_{4-x}Pr_xTi_3O_{12}$ compounds are p-type semiconductors (Fig. 3), which confirms previous data [7, 14]. According to [7, 14] electrical conductivity of layered bismuth titanate increases with temperature [7,14] and thermo-EMF coefficient of $Bi_4Ti_3O_{12}$ phase at high temperatures

is positive [14]. Seebeck coefficient values of BPT ceramics were close to each other (Fig. 3b), which corresponds to the isovalent character of substitution of Bi with Pr. But DC electrical conductivity of the samples decreased with x (Fig. 3a) due to the defect concentration decrease as was mentioned above. Near T_C there is a change in the slope of linear sections at the Arrhenius plots $\lg\sigma_{DC} = f(1/T)$. Values of activation energy of the samples' DC electrical conductivity in PE region are essentially less than in FE one (Table 1). Similar results were obtained in [15] for $Bi_4Ti_2Nb_{0.5}Fe_{0.5}O_{12}$ ceramics, activation energy values of which were equal to 1.21 eV and 0.50 eV below and above T_C, respectively (AC, $\omega = 10^5$ Hz). Partial substitution of Bi with Pr in $Bi_4Ti_3O_{12}$ increases E_A of BPT in FE state and low-
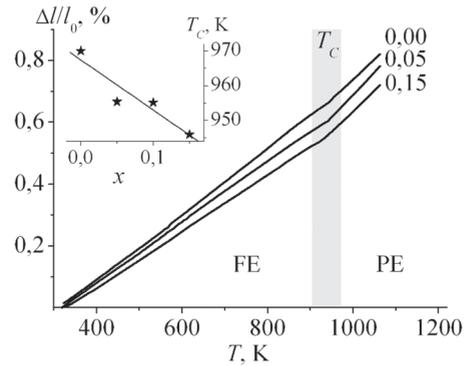

Fig. 2. Temperature dependences of relative elongation of $Bi_{4-x}Pr_xTi_3O_{12}$ sintered ceramics. Inset shows concentration dependences of T_C

Table 1

Values of apparent activation energy of DC electrical conductivity (E_A) and linear thermal expansion coefficient (α) of $Bi_{4-x}Pr_xTi_3O_{12}$ titanates

x	E_A, eV		$\alpha\cdot10^6$, K^{-1}	
	FE	PE	FE	PE
0.00	1.08±0.02	0.86±0.02	10.80±0.06	13.12±0.02
0.05	1.24±0.01	0.46±0.02	09.62±0.01	14.61±0.02
0.10	1.23±0.02	0.45±0.01	09.31±0.01	13.53±0.01
0.15	1.56±0.04	0.49±0.01	09.10±0.01	13.48±0.01

ers it in PE state (Table 1). Note that E_A value of layered bismuth titanate below T_C obtained in this work coincides with the data given in [14]: 1.0 eV for $Bi_4Ti_3O_{12}$ ceramics.

In the temperature dependences of dielectric constant of $Bi_{4-x}Pr_xTi_3O_{12}$ titanates abrupt maxima near 930–940 K was observed (Fig. 4a). It was caused by FE → PE phase transition, and phase transition temperature (T_C) lowered with increasing praseodymium content in the samples (Fig. 4d) and was close to the T_C values deter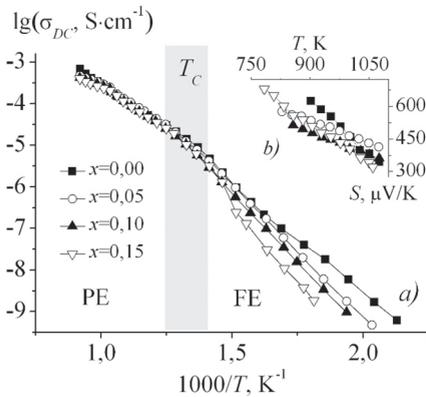mined from the $\Delta l/l_0 = f(T)$ dependences (Fig. 2, inset). Dielectric constant values of BPT ceramics increased with x, which was more prominent at high temperatures (Fig. 4a, c). Dielectric losses of investigated samples increased with temperature and decreased when Pr concentration (Fig. 4b, e). Besides, on the $tg\delta = f(T)$ dependences two anomalous regions were observed: near 760–820 K and 930–940 K. The second anomaly is related to the FE → PE phase transition, but the first one is probably due to the oxygen vacancy movement out (migration) of the domain walls [16].

The values of Curie temperature of the samples are frequency independent (Fig. 5a, b), which indicates that $Bi_{4-x}Pr_xTi_3O_{12}$ phases are normal ferroelectrics [15]. When the testing frequency increased from 100 Hz to 100 kHz, the dielectric constant and dielectric losses of BPT ceramics decreased substantially due to the suppression of relaxing polarization at high frequencies.

The dielectric constant of normal ferroelectrics follows the Curie–Weiss law

$$\varepsilon = C/(T - T_\Theta), \qquad (2)$$

where C is Curie–Weiss constant and T_Θ is Curie–Weiss temperature. The Curie–

Fig. 3. Dependences of DC electrical conductivity (*a*) and thermo-EMF coefficient (*b*) of $Bi_{4-x}Pr_xTi_3O_{12}$ samples vs temperature
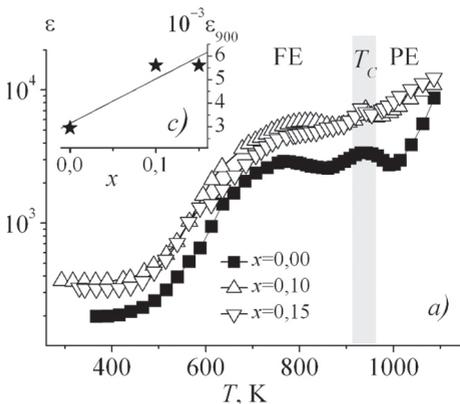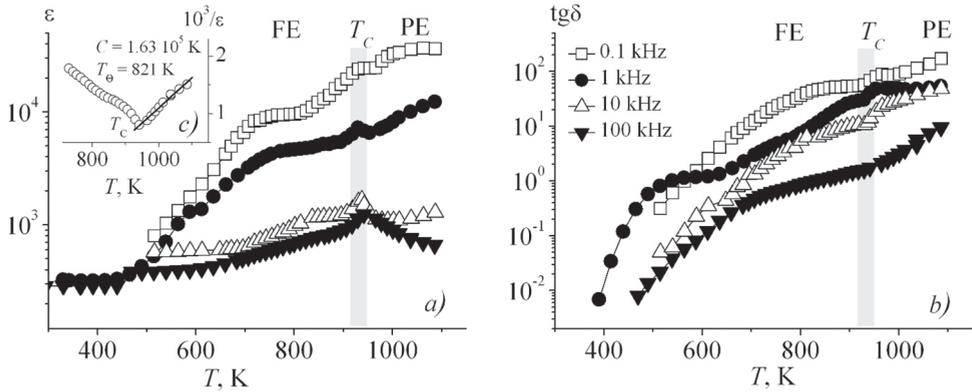

Fig. 4. Temperature (a, b) and concentration (c–e) dependences of dielectric constant (a, c), dielectric losses (b, e), and T_C (d) of $Bi_{4-x}Pr_xTi_3O_{12}$ ceramics (ω = 1 kHz)

Fig. 5. Temperature dependences of dielectric constant (a) and dielectric losses (b) of $Bi_{3.85}Pr_{0.15}Ti_3O_{12}$ at different frequencies. Inset (c) shows the inverse dielectric constant as a function of temperature at 100 kHz

Weiss plot for $Bi_{3.85}Pr_{0.15}Ti_3O_{12}$ phase at 100 kHz is shown in the Fig. 5c. The parameters obtained from the linear fit are $C = 1.63\times10^5$ K and $T_\Theta = 821$ K. The magnitude of Curie–Weiss constant is of the same order as of well-known displasive-type ferroelectrics, such as $BaTiO_3$ ($C = 1.7\cdot10^5$ K [15]).

The frequency dependences of AC electrical conductivity of $Bi_{3.85}Pr_{0.15}Ti_3O_{12}$ at various temperatures are given in Fig. 6. The frequency independent plateau at low frequencies is attributed to the long-range translational motion of ions contributing to DC conductivity (σ_{DC}) [17, 18]. At high frequencies ($>10^4$ Hz) the AC electrical conductivity shows ω^n dependence which corresponds to the short-range transla-tion ion hopping [15, 18].

The frequency dependent AC electri-cal conductivity of BPT ceramics obeys Jonscher's power law [19] at all tempera-tures

$$\sigma(\omega) = \sigma(0) + A\omega^n, \qquad (3)$$

where $\sigma(\omega)$ is the total conductivity, $\sigma(0)$ is the DC conductivity, A is the temper-ature-dependent constant which deter-mines the strength of polarizability, and n represents the degree of interaction

between the mobile ions and the lattice around them [15, 19]. The values of n are less than one, which indicates that motion of charge carriers is translational [18, 20]. The shape of n vs. T dependence suggests hopping mechanisms of charge carriers [18, 19]. In case of small-polaron hop-ping, n increases with temperature, while for a large polaron hopping, n decreases with temperature. As shown in inset of Fig. 6, the values of n are less than 1 and are found to increase with temperature;
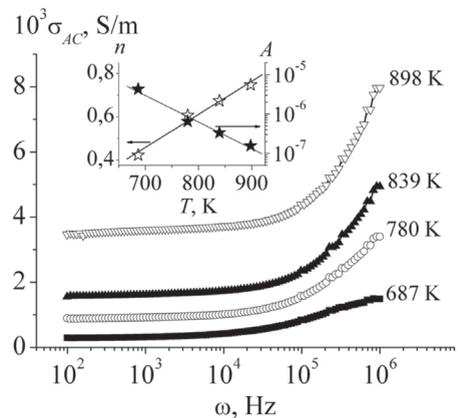

Fig. 6. Frequency dependences of AC electrical conductivity of $Bi_{3.85}Pr_{0.15}Ti_3O_{12}$ at different temperatures. Inset shows the variation of Jonscher's power law parameters (n, A) as a function of temperature

hence we conclude that AC electrical conductivity arises mainly due to the short-range order translation hopping assisted by small-polaron hopping mechanism.

Conclusions

The $Bi_{4-x}Pr_xTi_3O_{12}$ solid solutions ($x = 0.05$, 0.10, 0.15) with small substitution degree were synthesized and their thermal expansion, DC and AC electrical conductivity, dielectric constant and dielectric losses were measured. The samples crystallized in orthorhombic structure and possessed p-type semiconductive and normal ferroelectric properties. Lattice constants and thermo-EMF coefficient of BPT were practically composition independent, but Curie temperature, electrical conductivity and dielectric losses decreased with x. Activation energy of DC electrical conductivity and linear thermal expansion coefficient of $Bi_{4-x}Pr_xTi_3O_{12}$ changed at the temperature of ferroelectric to paraelectric phase transition, and their values were 1.08–1.56 eV and 0.45–0.86 eV, and $(9.10–10.80)\cdot10^{-6}$ K^{-1} and $(13.12–14.61)\cdot10^{-6}$ K^{-1} below and above Curie temperature, respectively. AC electrical conductivity investigations illustrate short-range order ionic translation hopping assisted by small-polaron hopping mechanism.

Acknowledgements

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