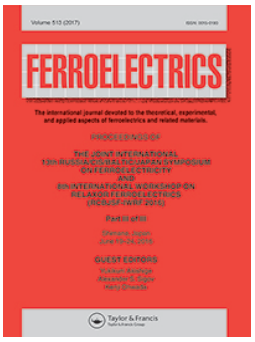

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Phase formation, structure, and dielectric properties of $(Na_{0.5}Bi_{0.5})TiO_3 – BaTiO_3 – Bi(Mg_{0.5}Ti_{0.5})O_3$ ceramics

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Phase formation, structure, and dielectric properties of $(Na_{0.5}Bi_{0.5})TiO_3$ – $BaTiO_3$ – $Bi(Mg_{0.5}Ti_{0.5})O_3$ ceramics

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ABSTRACT

Influence of $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) on phase formation, unit cell parameters, microstructure, dielectric and ferroelectric properties of solid solutions close to the Morphotropic Phase Boundary in the $(Na_{0.5}Bi_{0.5})TiO_3$ – $BaTiO_3$ system has been studied. The formation of samples with pure perovskite structure, characterized by increase in the unit cell parameters, and slight increase in the T_m value stimulated by BMT addition have been revealed. It was proved that modification of compositions by BMT additives leads to improvement of dielectric parameters.

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KEYWORDS
$(Na_{0.5}Bi_{0.5})TiO_3$; $BaTiO_3$; $Bi(Mg_{0.5}Ti_{0.5})O_3$; MPB; ceramics; perovskite structure; microstructure; ferroelectric phase transitions; relaxor properties

Introduction

$PbZr_xTi_{1-x}O_3$ (PZT)-based and other lead containing piezoelectric materials are widely used in various applications. Increasing concern about environment stimulated great scientific efforts aimed to development of new ecologically friendly lead free piezoelectric materials [1–8]. However, properties of new lead free materials can not compete with those of the lead-containing ones still. Ceramic solid solutions with perovskite-type structure based on bismuth-sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) perovskite are considered among the most promising and intensively studied materials [1–8]. At room temperature (RT) BNT has rhombohedral structure with the $R3c$ symmetry which gradually transforms to the tetragonal phase in a broad temperature range between $\sim$ 500–700 K and than to a cubic phase at $\sim$ 800 K [9–19]. BNT has rather large remnant polarization $P_r \sim 38\ \mu C/cm^2$ and high Curie temperature $T_C \sim 600$ K, however, high coercive field $E_C > 37$ kV/cm comprises its disadvantage [19–21]. The $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) perovskite has an orthorhombic structure (sp. gr. $Pnnm$), which persists up to the decomposition temperature of the material [22].

The reported values of piezoelectric properties in these systems are not optimized yet, and improvements may be reached by further modification of compositions in order to control intrinsic structural instabilities and extrinsic domain wall contributions [7]. In this work ceramic samples based on the compositions from MPB in the system BNT – BT modified by

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BMT were studied in order to reveal the influence of composition on phase formation, unit cell parameters, microstructure, dielectric and ferroelectric properties of solid solutions. It was expected that introduction of BMT could increase the T_C value and improve dielectric properties.

Experimental

Ceramic samples in the system $(1\text{-}y)[(1\text{-}x)(Na_{0.5}Bi_{0.5})TiO_3 - xBaTiO_3] - y\ Bi(Mg_{0.5}Ti_{0.5})O_3$ with $x = 0.05, 0.1, 0.2$; $y = 0, 0.1, 0.2$ were prepared by the solid state reaction method at $T_1 = 973$ K (6 h), $T_2 = 1173$ K (6 h), $T_3 = 1373$ K (2 h). Sodium carbonate Na_2CO_3, Barium carbonate $BaCO_3$, magnesium carbonate $MgCO_3$ and oxides Bi_2O_3 (all "pure" grade), and TiO_2 ("extra pure" grade) were used as starting materials. The phase content and crystal structure parameters were studied using the X-ray diffraction method (DRON-3M with $Cu_{K\alpha}$-beam). The microstructure of ceramic samples was examined by the Scanning Electron Microscopy (SEM) method (JEOL YSM-7401F equipped with a JEOL JED-2300 energy dispersive X-ray spectrometer system). Existence of spontaneous polarization in the ceramics was proved using the Second Harmonic Generation method (SHG, Nd:YAG laser, $\lambda = 1.064\ \mu$m) in the reflection. Dielectric properties were studied using the dielectric spectroscopy method (Agilent 4284 A, 1 V) in the temperature range of 300 — 1000 K at frequencies 100 Hz — 1 MHz.

Results and discussion

According to the X-ray diffraction data, perovskite structure phase was formed at the calcination temperature $T_1 = 973$ K, though some amounts of impurity phases were registered as well. After sintering at temperatures of 1173 and 1373 K the amounts of the impurity phases were reduced, and single phase samples were obtained (Figure 1*a-c*). However, in samples with ($x = 0.1$, $y = 0.1, 0.2$) small amounts of impurity phases with pyrochlore structure were registered (Figure 1*b*). Figure 2 demonstrates the displacements of the diffraction peaks with $h^2+k^2+l^2 = 10$ to smaller angles which indicate to increase in the pseudocubic unit cell volume as a result of partial substitutions of A- and B- cations in the initial compositions by larger cations (Ba^{2+} and Mg^{2+}, respectively) with x and y increasing. Moreover, Figure 2*c* (*1*) clearly demonstrates broadening and splitting of the peak for composition with $x = 0.2$, $y = 0$. This corresponds to tetragonal symmetry of the lattice in accordance with phase diagram [13, 18, 19]. With increasing MBT content pseudocubic lattice is registered again. Microstructure of the samples was examined by the high-resolution SEM method. All samples consisted of dense packed isometric grains with the size of ~ 1—5 μm (Figure 3). At RT all the samples produce the SHG signals with intensities $I_{2\omega}$ substantially higher than $I_{2\omega}(SiO_2)$ obtained from α-SiO_2 powder standard, without doubt corresponding to non-centrosymmetric material. The relative intensity of the SHG signals $q = I_{2\omega}/I_{2\omega}(SiO_2)$ were in the range of $q = 10$–20 at RT and then vanished with temperature (Figure 4). Known from dielectric investigations ferroelectric phase transitions (see below) are marked on q(T) curves by more rapid changes of q value with temperature. Nevertheless, no distinct phase transitions of usual ferroelectric type are seen in the obtained ceramics. It is necessary to emphasize that q values at RT in these ceramics are at least two order smaller and in usual ferroelectric ceramics of BT or BNT. This fact corresponds to nature of MPB region where

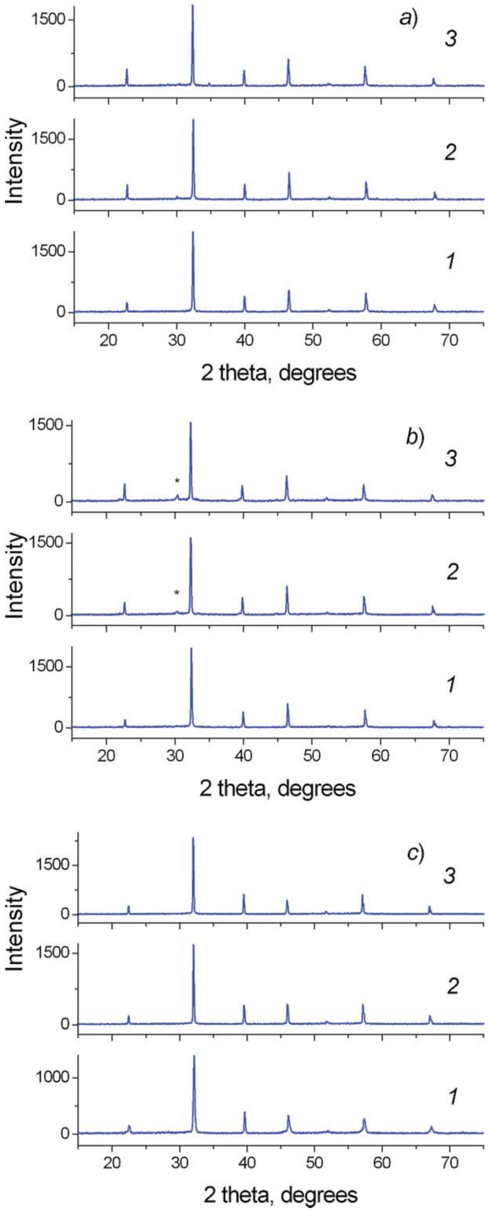

Figure 1. The X-ray diffraction patterns of the samples (1-y)[(1-x)($Na_{0.5}Bi_{0.5}$)TiO_3 – $x$$BaTiO_3$] – y Bi ($Mg_{0.5}Ti_{0.5}$)O_3: *a*) with $x = 0.05$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); *b*) with $x = 0.1$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); *c*) with $x = 0.2$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); sintered at $T_1 = 973$ K (6 h), $T_2 = 1173$ K (6 h), $T_3 = 1373$ K (2 h). * marks peaks from admixture phases.

different phases are believed to exist as nano-sized domains. Indeed, the ($Na_{0.5}Bi_{0.5}$) TiO_3 – $BaTiO_3$ compositions in the MPB region are now considered as composed of ferroelectric rhombohedral clusters embedded in a nonpolar tetragonal matrix existing in a wide temperature range up to $\sim$ 800 K [8, 10, 13]. Keeping in mind that the SHG response from structurally dispersed material depends as square of size of smallest structural inhomogeneities, low SHG activity of the ceramics, as well as the diffuse character of phase transitions

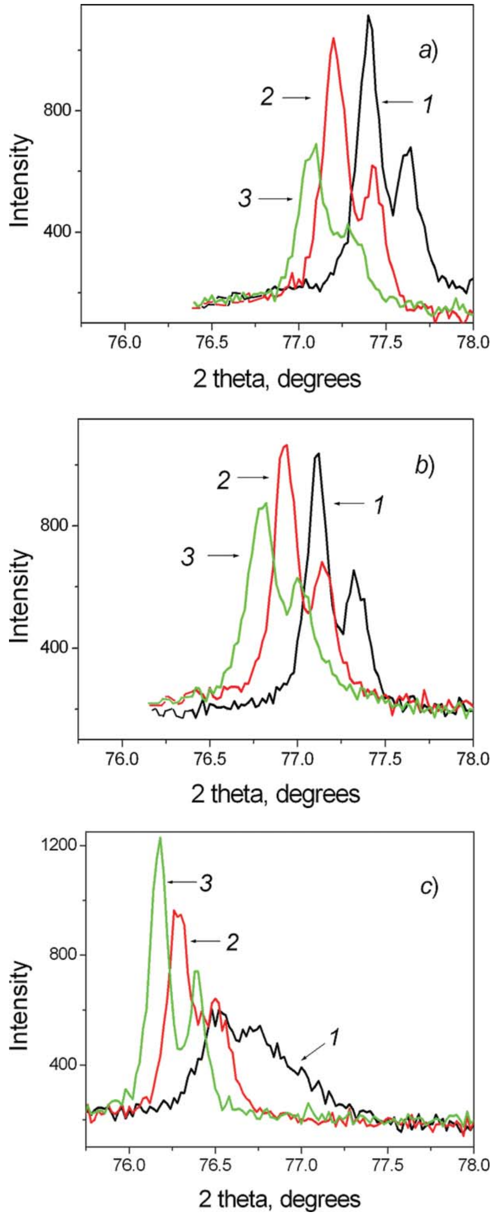

Figure 2. Parts of the X-ray diffraction patterns showing peaks with $h^2+k^2+l^2 = 10$ for the NBT – BT – BMT samples with: *a*) $x = 0.05$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); *b*) $x = 0.1$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); *c*) $x = 0.2$, $y = 0$ (*1*), $y = 0.1$ (*2*), $y = 0.2$ (*3*); sintered at $T_1 = 973$ K (6 h), $T_2 = 1173$ K (6 h), $T_3 = 1373$ K (2 h).

both result from a cluster-like medium-range structure of ceramics under examination. The clusters are known to be rather stable and exist in a wider temperature interval in comparison with ferroelectric-type ordering. Though in accordance with dielectric data, the upper temperature interval of ferroelectricity in the BNT – BT – BMT samples is restricted to 600 K, the SHG signal may be traced to much higher temperature of 1000 K.

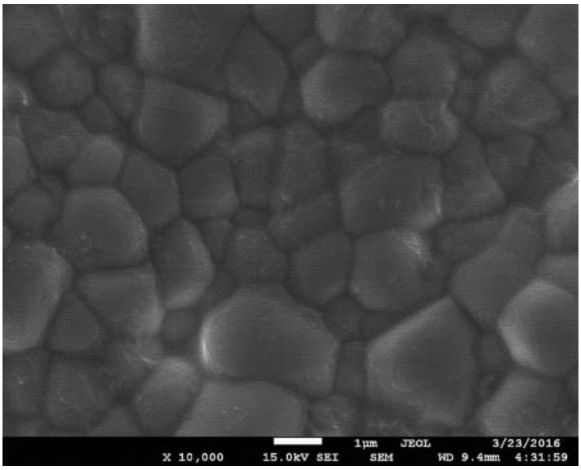

Figure 3. Microstructure of the surface of the (1-*y*)[(1-*x*)($Na_{0.5}Bi_{0.5}$)TiO_3 – *x*$BaTiO_3$] – *y* Bi($Mg_{0.5}Ti_{0.5}$)O_3: with $x = 0.05$, $y = 0$ (*a*) and with $x = 0.2$, $y = 0.2$ (*b*). Bars – 10 μm.

Origin of structural non-equivalency of relative perovskite-lile phases evidently stems from charge disorder in the A-sites being simultaneously randomly occupied by Bi^{3+}, Na^+, and Ba^{2+} cations. This results in the random electric fields, which may affect the local balance between the off-center shift of the B-site Ti^{4+} cation and the displacement of the A-site cations in opposite direction. These random electric fields destroy the long-range order and promote local dipole correlations [23]. As a result, dynamically fluctuating weak local dipole moments are assumed to be an origin of frequency dispersion of dielectric permittivity in relaxor BNT–BT compounds [8, 18].

Dielectric measurements revealed two anomalies, accompanied by maxima in the temperature dependencies of relative dielectric permittivity at temperatures of $T_{\rm pt} \sim 390$ – 420 K and of $T_{\rm m} \sim 580$–610 K (Figures 5 and 6). Slight increase in the $T_{\rm m}$ value ~ 20 K was observed with increasing BMT content in compositions with $x = 0.05$–0.2. Phase transitions at 390 — 420 K reveal relaxor like frequency dependence similar to that observed in pure BNT samples and attributed to the presence of ferroelectric clusters in a nonpolar matrix [8]. Electric conductivity of the samples decreases with increasing MBT content.

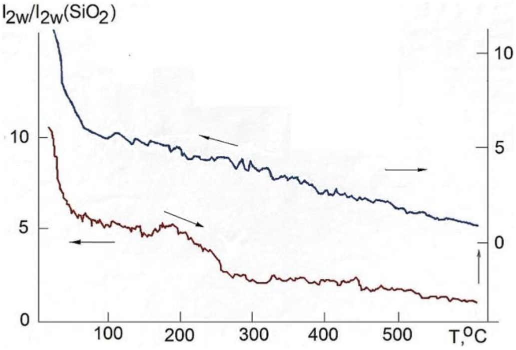

Figure 4. Temperature dependences of the intensity of the SHG signal from sample 0.95($Na_{0.5}Bi_{0.5}$)TiO_3 – 0.05$BaTiO_3$ on heating (1) and on cooling (2).

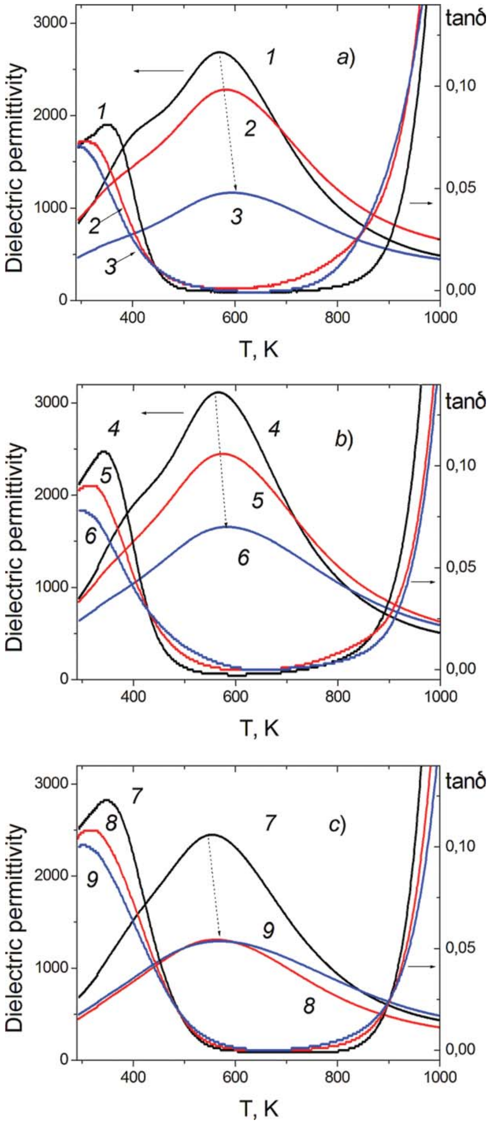

Figure 5. Temperature dependences of dielectric permittivity ε*(T)* and dielectric loss tanδ*(T)* (*a–c*) of the samples (1-*y*)[(1-*x*)($Na_{0.5}Bi_{0.5}$)TiO_3 – *x*$BaTiO_3$] – *y* Bi($Mg_{0.5}Ti_{0.5}$)O_3 with: *a*) $x = 0.05$, $y = 0$ (*1*), 0.1 (*2*), 0.2 (*3*); *b*) $x = 0.1$, $y = 0$ (*4*), 0.1 (*5*), 0.2 (*6*); *c*) $x = 0.2$, $y = 0$ (*7*), 0.1 (*8*), 0.2 (*9*); measured at frequency $f = 1$ MHz.

Correspondingly, dielectric losses decrease, while relative dielectric permittivity at the room temperature remains at rather high level (700 — 1200 at $f = 1$ kHz) for the samples with $x = 0.05$, $y = 0$, 0.1 and 0.2; with $x = 0.1$, $y = 0.1$ and 0.2 and for $x = 0.2$ and $y = 0.2$. These samples have low dielectric losses (3.6 — 5%). As advantage of partial substitution with BMT we consider final combination of functional properties. So, high values of relative dielectric permittivity at room temperature in combination with low values of dielectric losses may serve as an indication to possible improvement of piezoelectric properties in compositions BNT-BT modified by the BMT additives taking into account the known

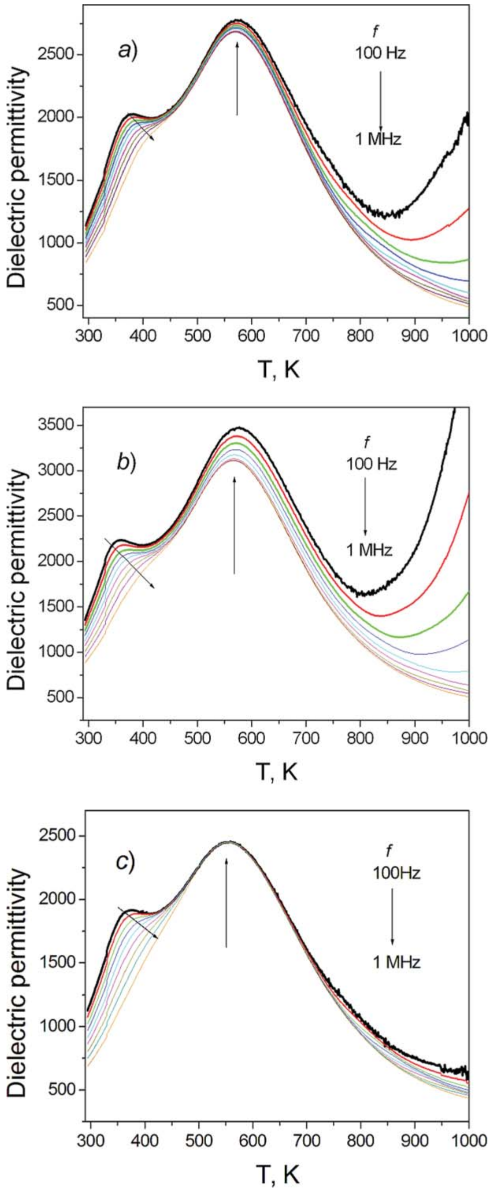

Figure 6. Temperature dependences of dielectric permittivity ε*(T)* of the samples (1-*y*)[(1-*x*)($Na_{0.5}Bi_{0.5}$)TiO_3 – *x*$BaTiO_3$] – *y* Bi($Mg_{0.5}Ti_{0.5}$)O_3 with $x = 0.05$ (*a*), 0.1 (*b*), 0.2 (*c*), $y = 0$ (*a-c*); measured at frequencies $f = 100$ Hz, 300 Hz, 1, 3, 10, 30, 100, 300 kHz and 1 MHz.

correlation between piezoelectric coefficient d_{33} and the room-temperature dielectric permittivity ε_{rt} value observed [24 – 26].

Conclusions

The phase formation, structure, microstructure and dielectric properties of ceramic samples (1-*y*)[(1-*x*)($Na_{0.5}Bi_{0.5}$)TiO_3 – *x*$BaTiO_3$] – *y* Bi($Mg_{0.5}Ti_{0.5}$)O_3 with $x = 0.05$, 0.1, 0.2; $y = 0, 0.1, 0.2$ have been studied. Single phase solid solutions characterized by perovskite structure were prepared by the solid state reaction method. The ceramics were shown to be characterized by the optimal microstructure with dense packed grains. Dielectric measurements revealed two phase transitions, accompanied by maxima in the temperature dependencies of relative dielectric permittivity at temperatures of $T_{pt} \sim 390–420$ K and $T_m \sim 580—610$ K. It was proved that increase in the BMT content led to slight increase in the T_m value. Finally, modification of compositions by small amounts of the BMT additive leads to improvement of dielectric parameters favoring to the piezoelectric properties enhancement.

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