Phase formation, structure and dielectric properties of ceramics $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3-\text{BiFeO}_3^*$

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Influence of BiFeO_3 (BF) on phase formation, unit cell parameters, microstructure, dielectric and ferroelectric properties of solid solutions close to the morphotropic phase boundary in the $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ system additionally modified by the low-melting KCl additives has been studied. The formation of pure perovskite structure samples decrease in the unit cell parameters and increase in the T_C value stimulated by the BF addition have been revealed. It was proved that modification of compositions by small amounts of the BF and KCl additives leads to improvement of dielectric parameters.

Keywords: $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$, $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$; BiFeO_3 ; KCl; MPB; perovskite structure; microstructure; ferroelectric phase transitions.

1. Introduction

Piezoelectric materials are technologically important because of their application in various kinds of devices. They have also great potential for applications in new areas such as energy harvesting devices, magnetoelectric sensors, micro-motors and high power transformers. Due to their excellent piezoelectric and ferroelectric properties, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ and other lead-based materials have been dominating in various applications in the past few decades. However, increasing concern about environment stimulates the development of new ecologically friendly piezoelectric materials.^{1–9} In spite of the extensive research carried out, properties of new lead-free piezoelectric materials cannot compete with those of the lead-containing ones still.

Ceramic solid solutions with perovskite-type structure based on bismuth-sodium titanate $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and potassium-sodium niobate $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) are considered among the most promising and intensively studied materials.^{1–17} At room temperature BNT has rhombohedral $R3c$ symmetry. It gradually transforms to the tetragonal phase in a broad temperature range between ~ 500 and 700 K and then to a cubic phase at ~ 800 K. BNT has rather large remnant polarization $P_r \sim 38 \mu\text{C}/\text{cm}^2$ and high Curie temperature $T_C \sim 600$ K, however, high coercive field $E_C > 37$ kV/cm comprises its disadvantage.^{10–14} KNN has an

orthorhombic perovskite crystal structure at room temperature and exhibits two-phase transitions from ferroelectric orthorhombic to ferroelectric tetragonal phase at ~ 473 K and then from tetragonal to paraelectric cubic one at ~ 700 K.^{15–22} At room temperature piezoelectric coefficient $d_{33} = 80$ pC/N was received.^{14–17}

Rather promising results for improving piezoelectric properties were obtained for solid solutions in the BNT–KNN systems close to the morphotropic phase boundaries (MPB).^{19–26} In the BNT-rich system a rhombohedral to tetragonal MPB at ~ 6 – 7.5 mol% KNN and the rhombohedral to pseudocubic MPB at 3 – 5 mol% of KNN were reported.^{22,24} 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.⁸

Bismuth ferrite BiFeO_3 (BF) has a rhombohedral perovskite structure at room temperature and is characterized by very high $T_C \sim 1100$ K.¹² So, the purpose of this work was to synthesize ceramic samples based on the compositions from MPB in the system BNT–KNN modified by BF and to study the influence of BF and KCl additives on phase formation, unit cell parameters, microstructure, dielectric and ferroelectric properties of solid solutions. It was expected that

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introduction of BF could increase the T_C value, while the low-melting KCl additive could help to lower the sintering temperature of the ceramics and maintain their stoichiometry.

2. Experimental Procedure

Ceramic samples in the system $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3 - x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3] - y\text{BiFeO}_3$ ($= 0.06, 0.08, 0.10; y = 0.025, 0.05, 0.075, 0.10$) were prepared by the solid-state reaction method at $T_1 = 1073$ K (5 h) and $T_2 = 1413$ – 1473 K (2 h). Sodium carbonate Na_2CO_3 (“pure” grade), potassium carbonate K_2CO_3 (“analytical” grade) and oxides Bi_2O_3 (“pure” grade), TiO_2 , Nb_2O_5 , Fe_2O_3 (“extra pure” grade) were used as starting materials. 5 wt.% of KCl (“pure” grade) with melting temperature of ~ 1050 K were added after synthesis at T_1 . The phase content and crystal structure parameters were studied using the X-ray diffraction method (DRON-3M with $\text{Cu}_{K\alpha}$ -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). Spontaneous polarization was estimated using the Second Harmonic Generation method (SHG, Nd:YAG laser, $\lambda = 1.064 \mu\text{m}$). 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.

3. Results and Discussion

According to the X-ray diffraction data, perovskite structure phase was formed at the calcination temperature $T_1 = 1073$ K, though some amounts of impurity phases were registered as well. After sintering at temperatures of 1413–1473 K the amounts of the impurity phases were reduced, and single-phase samples were obtained at optimal temperature of 1443–1473 K (Fig. 1(a)). However, in samples with larger BF content ($y = 0.08, 0.10$) small amounts of impurity phases FeTi_2O_5 and $\text{Na}_2\text{Ti}_{12}\text{O}_{25}$ were registered (Fig. 1(b)).

Figure 2 demonstrates the displacements of the diffraction peaks with $h^2 + k^2 + l^2 = 4$ to smaller angles with KNN and

Fig. 1. The X-ray diffraction patterns of the samples $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3 - x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3] - y\text{BiFeO}_3$: (a) With $x = 0.06$, $y = 0.025$ (1), 0.05 (2), 0.075 (3), 0.10 (4); (b) samples doped by 5 wt.% of KCl with $x = 0.08$ (1, 2), 0.10 (3, 4), $y = 0.05$ (1, 3), 0.075 (2, 4) sintered at 1443 K (a, 1–4), at 1463 K (b, 1, 3), at 1413 K (b, 2, 4). Note: * marks peaks from admixture phases.

Fig. 2. Parts of the X-ray diffraction patterns showing peaks with $h^2 + k^2 + l^2 = 4$ for the samples $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3 - x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3] - y\text{BiFeO}_3$ with $x = 0.06$ (a), (d), 0.08 (b), (e), 0.10 (c), (f); $y = 0.025$ (1, 5, 9), 0.05 (2, 6, 10), 0.075 (3, 7, 11), 0.10 (4, 8, 12) doped with 5 wt.% of KCl (d), (e), (f) sintered at 1443 K (2 h).

Fig. 2. (Continued)

KCl addition indicating to increase in the pseudocubic unit cell volume as a result of partial substitution of A-cations in the initial compositions by larger K^{1+} cations.

Microstructure of the samples was examined by the high-resolution SEM method. All samples consisted of dense packed cubic grains with the size of 2–8 μm (Fig. 3). Considerable decrease in grain sizes and improvement of density of ceramics was revealed for KCl-modified samples with $x = 0.08$ and $y = 0.10$ in comparison with unmodified samples. However, the formation of regions with larger grains of ~ 10 – $15 \mu\text{m}$ as well. Quantitative elemental analysis

revealed deficiency up to 30 at.% of K^{1+} -cations in some grains due to volatilization of alkali elements at high sintering temperatures $\sim 1473 \text{ K}$.

Ceramic samples obtained were studied by the SHG method. The relative intensity of the SHG signal $q = I_{2w}/I_{2w}(\text{SiO}_2)$ related to the spontaneous polarization P_s as $q \sim P_s^{0.5}$ was measured in the range of 0.1–1.2. Such small q values confirm that the samples may be characterized as anti- or ferroelectrics. It is worth noting that the initial KNN samples reveal good ferroelectric properties and are characterized by high values of the SHG signal up to $q \sim 7000$. So,

Fig. 3. Microstructure of the surface of the $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3]-y\text{BiFeO}_3$ samples with $x = 0.06$ (a), (b), 0.08 (c), (d), 0.10 (e), (f); with 5 wt.% of KCl (b), (d), (f). Bars — 10 μm .

Fig. 4. Temperature dependences of dielectric permittivity $\varepsilon(T)$ of the samples $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3]-y\text{BiFeO}_3$ with $x = 0.06$ (1, 2), 0.08 (3, 4), 0.10 (5, 6, 8), $y = 0.05$ (1, 3, 5), 0.10 (2, 4, 6), sintered at 1473 K (1, 3, 5), at 1443 K (2, 4, 6); samples doped by KCl with $x = 0.06$ (7), 0.10 (8), $y = 0.10$ (7, 8) sintered at 1443 K. Frequency of measurements $f = 1$ MHz.

the effect observed is consistent with the known characteristic of pure NBT samples composed of ferroelectric rhombohedral clusters embedded in a nonpolar tetragonal matrix.⁹

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 of $T_C \sim 530$ –600 (Figs. 4 and 5). Slight increase in the T_{pt} value was observed with increasing BF content: 5 K for compositions with $x = 0.06$, 2 K for compositions with $x = 0.08$ and 12 K for compositions with $x = 0.10$. Slight increase of ~ 20 K in the T_C value was also revealed with increasing BF content in the samples with $x = 0.06$ and $x = 0.10$. Addition of KCl leads to decrease in T_{pt} value from 422 to 402 K for the samples with $x = 0.06$, $y = 0.10$ and from 410 to 398 K for the samples with $x = 0.10$, $y = 0.10$. The phase transitions at 390–420 K reveal relaxor behavior similar to that observed in pure BNT samples and attributed to the presence of ferroelectric clusters in a nonpolar matrix.⁹ It should be noted that at temperatures higher than 700 K additional anomalies with strong frequency relaxation were revealed that may be stimulated by the presence of vacancies in oxygen sublattice resulting from the cation deficiency in the A-sublattice.²⁷

At the room temperature electroconductivity σ_{rt} of the samples decreases with y increasing. However, at high temperature ~ 950 K σ_{rt} value increases with BF content increasing. At 300 K the σ_{rt} value of the KCl-modified samples with $x = 0.06$ and $y = 0.10$ is higher ($\sigma_{rt} = 2.3 \cdot 10^{-8}$ S/cm at 1 kHz) than σ_{rt} value of initial samples ($\sigma_{rt} = 1.0 \cdot 10^{-8}$ S/cm), however, the σ_{rt} value of the KCl-modified samples with $x = 0.10$ and $y = 0.10$ is lower than σ_{rt} of initial samples ($\sigma_{rt} = 1.9 \cdot 10^{-8}$ S/cm and $2.4 \cdot 10^{-8}$ S/cm, correspondingly).

Fig. 5. Temperature dependences of dielectric permittivity $\varepsilon(T)$ of the samples $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3]-y\text{BiFeO}_3$ with $x = 0.06$, $y = 0.10$ (a, b) with 0 (a) and 5 wt.% KCl (b) sintered at 1443 K (a) and at 1453 K (b) measured at frequencies $f = 100$ Hz, 300 Hz, 1 kHz, 3 kHz, 10 kHz, 30 kHz, 100 kHz, 300 kHz and 1 MHz.

At the room temperature, the highest values of the dielectric permittivity $\varepsilon_{rt} \sim 750$ –1100 (at 1 kHz) were revealed in the samples with $y = 0.05$. And the ε_{rt} values of the KCl-modified samples with $x = 0.06$, 0.10, and $y = 0.10$ (~ 850 and 800) are higher than ε_{rt} in unmodified samples. These data allow us to expect an improvement of piezoelectric properties just in compositions modified by small amounts (~ 5 mol%) of the BF additives and in the KCl-modified samples taking into account the known correlation between piezoelectric coefficient d_{33} and the room-temperature dielectric permittivity ε_{rt} value observed that may serve as an indication on possible enhancement of piezoelectric properties.^{28,29}

4. Conclusions

The phase formation, structure, microstructure and dielectric properties of ceramic samples $(1-y)[(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3]-y\text{BiFeO}_3$ additionally modified by

the KCl additives have been studied. Single-phase solid solutions characterized by perovskite structure were prepared by the solid-state reaction method. The ceramics were shown to characterize the optimal microstructure with dense packed cubic grains. Dielectric measurements revealed two-phase transitions, accompanied by maxima in the temperature dependencies of relative dielectric permittivity at temperatures of ~ 390 – 420 K and ~ 530 – 600 K. It was proved that increase in the BF content led to slight increase in the Curie temperature value. Modification of compositions by small amounts of the BF and KCl additives leads to improvement of dielectric parameters favoring to the piezoelectric properties enhancement.

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