Influence of KCl additives on ferroelectric peroperties of NBT-based ceramics

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Abstract - Influence of $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) and KCl additives on phase formation, crystal structure, microstructure, dielectric and ferroelectric properties of ceramics with compositions close to the Morphotropic Phase Boundary in the $(Na_{0.5}Bi_{0.5})TiO_3$ – $BaTiO_3$ (NBT-BT) system has been studied. The results obtained proved that modification of NBT-BT compositions by BMT and KCl additives promoted to improvement of dielectric properties.

Keywords - NBT, BT, BMT, MPB, perovskite structure, microstructure, ferroelectric phase transitions, dielectric properties.

I. INTRODUCTION

Increasing concern on the environment safety stimulated intensive studies of lead-free piezoelectric materials in order to develop new materials which could replace widely used Pb-based ones [1 - 6]. Perovskite structure oxides on the base of barium titanate $BaTiO_3$ (BT) and bismuth-sodium titanate $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) are being considered among the most promising ones [7 - 17]. Rhombohedral structure (sp. gr. R3c) of BNT compound transforms to a tetragonal phase in a temperature range of 500 - 700 K and then to a cubic one at ~ 800 K [7 – 9, 11, 12]. BNT is characterized by large remnant polarization P_r ~ 38 μC/cm^2 and high Curie temperature T_C ~ 600 K, however, it has high coercive field $E_C > 37$ kV/cm [16, 17]. Tetragonal $BaTiO_3$ has T_C ~ 390 K, and perovskite $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) has an orthorhombic structure (sp. gr. *Pnnm*) [18]. It was proved that compositions from Morphotropic Phase Boundary (MPB) in the BNT-BT system are promising for development of new lead free piezoelectic materials [10, 14 - 16].

In this work, influence of potassium chloride KCl additives with rather low melting temperature (1049 K) on phase formation, structure, microstructure, dielectric and ferroelectric properties of ceramics with compositions close to the Morphotropic Phase Boundaries in the $(Na_{1/2}Bi_{1/2})TiO_3$ - $BaTiO_3$ (NBT-BT) and $(Na_{1/2}Bi_{1/2})TiO_3$ - $BaTiO_3$ - $Bi(Mg_{1/2}Ti_{1/2})O_3$ (NBT-BT-BMT) systems has been studied. Improvement of sintering and dielectric properties was expected.

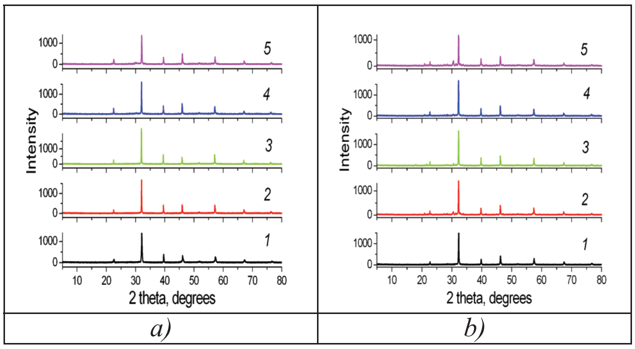
II. EXPERIMENTAL

Ceramic samples $(1-y)[(1-x)(Na_{0.5}Bi_{0.5})TiO_3 - xBaTiO_3] - yBi(Mg_{0.5}Ti_{0.5})O_3$ (NBT-BT-MBT) with x, y=0, 0.1, 0.2 and $(1-y)[0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y$KCl (NBT-BT-KCl) with y=0, 0.025, 0.05, 0.075, 0.10, 0.15 were prepared by the two-step solid state reaction method at temperatures T_1=973-1173 K (6 h), T_2=1373-1473 K (1-2 h). Carbonates $BaCO_3$, $MgCO_3$ and Na_2CO_3, oxides Bi_2O_3 and TiO_2 (“extra pure” grades) and cloride KCl (“pure” grade) were used as initial substances. KCl was added in amount of 2 w. % after synthesis to the compositions NBT-BT-BMT.

The samples were characterized using the X-ray Diffraction (DRON-3M, $Cu_{K\alpha}$-beam), Scanning Electron Microscopy (SEM) (JEOL YSM-7401F with a JEOL JED-2300 energy dispersive X-ray spectrometer system), Second Harmonic Generation (SHG) (Nd:YAG laser, λ=1.064 μ), and Dielectric Spectroscopy (Agilent 4284 A, 1 V, in the temperature range of 300 – 1000 K, at frequencies 100 Hz – 1 MHz) methods.

III. RESULTS AND DISCUSSION

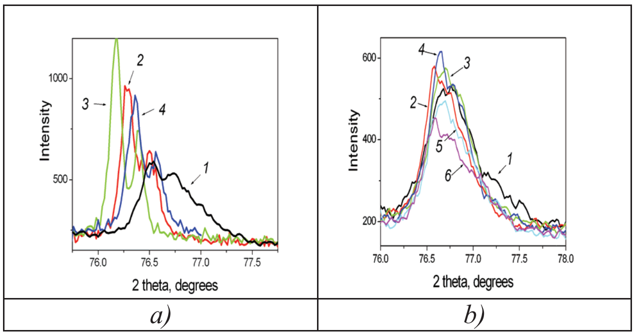
According to the X-Ray diffraction data, samples with perovskite structure are formed at T_1=973 - 1173 K. Dense single phase ceramic samples were prepared after sintering at temperatures of T_2=1373 - 1473 K (2 h) (Figs. 1*a*, *b*).



a) *b)*

Fig. 1. X-Ray diffraction patterns of the samples $(1-y)[(0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y\,Bi(Mg_{0.5}Ti_{0.5})O_3$ with y=0.0 (*1*), 0.1 (*2*), 0.2 (*1 - 3*), with 2 w. % KCl (*4, 5*) (*a*). X-Ray diffraction patterns of the samples $(1-y)[0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y$KCl with y=0 (*1*), 0.025 (*2*), 0.05 (*3*), 0.075 (*4*), 0.10 (*5*) (*b*).

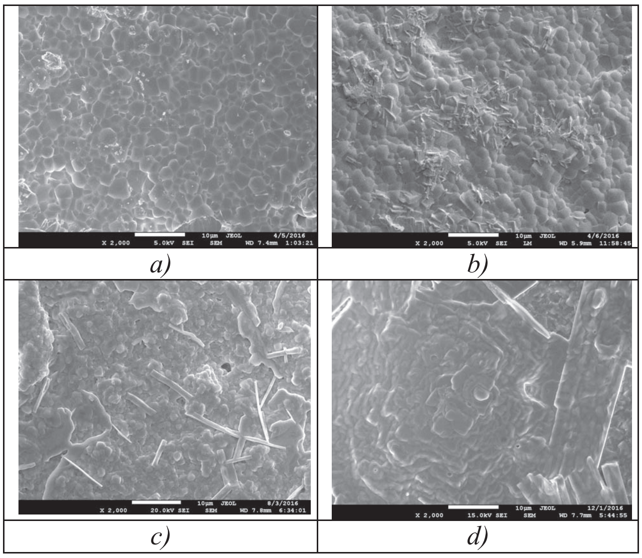
978-1-5090-4737-6/17/$31.00 @2017 IEEE



a) b)

Fig. 2. Parts of the X-Ray diffraction patterns of the samples $(1-y)[(1-x)(Na_{0.5}Bi_{0.5})TiO_3 - xBaTiO_3] - y\,Bi(Mg_{0.5}Ti_{0.5})O_3$ with x=0.2, y=0.0 (*1*), 0.1 (*2*), 0.2 (*3*), with 2 w. % KCl (*4*) (*a*). Parts of the X-Ray diffraction patterns of the samples $(1-y)[0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y$KCl with y=0 (*1*), 0.025 (*2*), 0.05 (*3*), 0.075 (*4*), 0.10 (*5*), 0.15 (*6*) (*b*).

Figure 2a shows displacements of the diffraction peaks with $h^2+k^2+l^2=10$ to smaller angles indicating to increase in the unit cell volume in the system NBT-BT-BMT as a result of partial substitutions in the A- and B- sites by larger Ba^{2+} and Mg^{2+} cations, accordingly. Pseudocubic lattice is formed with the MBT content increasing. Slight increase in the unit cell volume is observed in the NBT-BT samples modified by KCl as well (Figure 2b). This indicates to substitution of A-sites in perovskite lattice by larger K^{1+} cations.



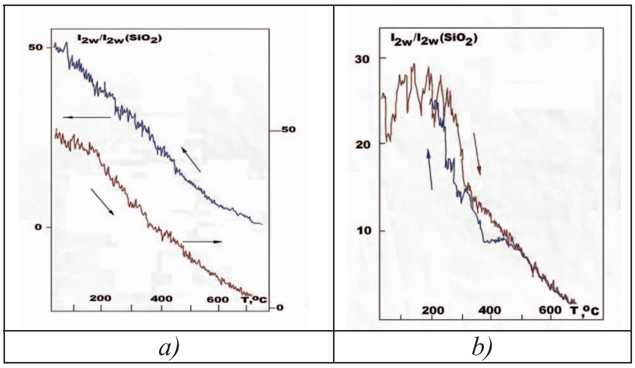
a) b)

c) d)

Fig. 3. Microstructure of the samples $(1-y)[(1-x)(Na_{0.5}Bi_{0.5})TiO_3 - xBaTiO_3] - yBi(Mg_{0.5}Ti_{0.5})O_3$ with x=0.2, y=0.2 (*a*), with 2 w. % KCl (*b*), of the samples $(1-y)[0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y$KCl with y=0 (*c*), 0.05 (*d*).

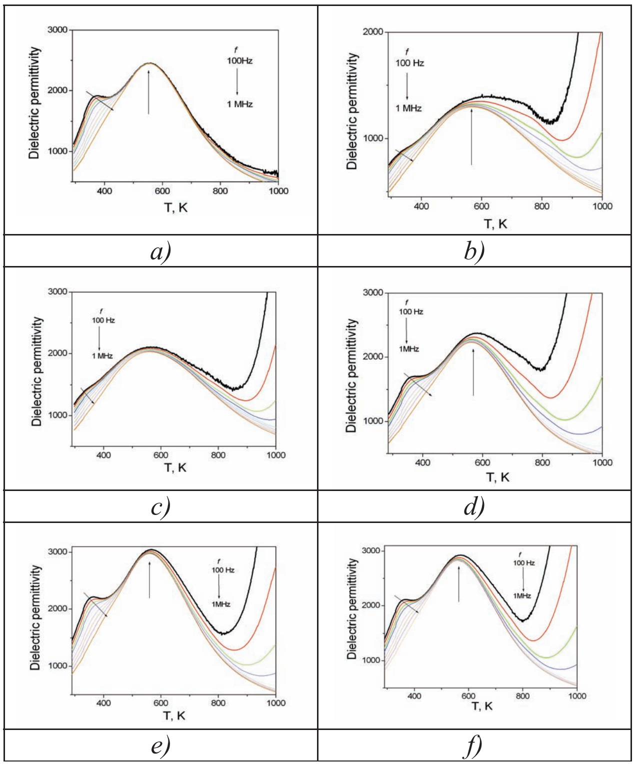
According to SEM data the NBT-BT-MBT(KCl) and NBT-BT-KCl samples are characterized by dense packed isometric grains with average size less than 5 µm (Fig. 3).

At the room temperature (RT) for all the samples the SHG signals were measured with intensities $q=I_{2\omega}/I_{2w}(SiO_2)$ higher than that typical for the α-SiO_2 powder standard. This corresponds to non-centrosymmetric materials. The SHG relative intensity smoothly vanishes with temperature and no distinct ferroelectric phase transitions may be seen for ceramics studied (Fig. 4). It should be noted that q values at RT are ~ two order smaller than those of the ferroelectric BT ceramics. This corresponds to nature of the MPB regions considered as composed of ferroelectric rhombohedral clusters embedded in a nonpolar tetragonal matrix which exists in a wide temperature range [5, 8, 11]. So, charge disorder in the A-sites randomly occupied by Bi^{3+}, Na^{+}, Ba^{2+} and K^{+} cations results in the random electric fields which destroy the long-range order and promote local dipole correlations leading to frequency dispersion of dielectric permittivity in relaxor BNT–BT compounds [5, 19].



a) b)

Fig. 4. Temperature dependences of the Second Harmonic Generation signal $I_{2w}/I_{2w}(SiO_2)$ measured on reflection of the samples $0.8(Na_{1/2}Bi_{1/2})TiO_3 - 0.2BaTiO_3$ (*a*) and $(1-y)[0.8(Na_{0.5}Bi_{0.5})TiO_3 - 0.2BaTiO_3] - y$KCl with y=0.05 (*b*).



a) b)

c) d)

e) f)

Fig. 5. Temperature dependences of dielectric permittivity of ceramic samples NBT-BT with x=0.2 (*a*), NBT-BT-BMT with x=0.2, y=0.2 (*b*), ceramics NBT-BT-BMT with x=0.2, y=0.2 and 2 w. % KCl (*c*), ceramics NBT-BT-KCl with x=0.2, y=0.025 (*d*), 0.05 (*e*), 0.075 (*f*) measured at f=100 Hz - 1 MHz.

Phase transitions are marked by steps near 350-400 K and by peaks at ~ 550 K in dielectric permittivity versus temperature curves (Fig. 5). Slight increase in the T_C value ~ 20 K was observed with increasing BMT content. Ferroelectric phase transitions near 350-400 K revealed typical relaxor-type behavior attributed to the presence of ferroelectric clusters in a nonpolar matrix [5]. Additionally, effects of dielectric relaxation related to the presence of oxygen vacancies were revealed at high temperatures in the compositions studied characterized by the presence of B-site cations with mixed valency and by deficiency in the A-sites of the perovskite lattice.

Electric conductivity of the samples at the RT decreases with increasing MBT content, while relative dielectric permittivity at the RT ε_{rt} remains at high level (> 700 at f=1 kHz) for the samples with for x=0.2 and y=0.2. These samples have rather low dielectric losses ~ 5 %.

At the room temperature, increase in the dielectric permittivity ε_{rt} value was observed in modified compositions BNT-BT with KCl content of 2.5-7.5 mol. % (ε_{rt} =1100 - 1400). Increase in the dielectric permittivity ε_{rt} was revealed for compositions NBT-BT-BMT doped by the KCl additives as well.

The changes in the electric conductivity observed showed that KCl additives stimulated increase in total conductivity at the room temperature. At the high temperatures of ~1000 K total conductivity decreased in the KCl doped samples pointing to decrease in number of vacancies in the A-sites and in the oxygen sublattice.

So, high values of relative dielectric permittivity at the RT may indicate to improvement of piezoelectric properties in modified NBT-BT-BMT and NBT-BT compositions taking into account the known correlation between piezoelectric coefficient d_{33} and the RT dielectric permittivity ε_{rt} value observed earlier [20]. The results obtained confirmed prospects of new lead-free piezoelectric materials development by modification of the NBT-based compositions close to MPB.

IV. CONCLUSIONS

Phase formation, structure, microstructure, dielectric and ferroelectric properties of ceramic samples NBT-BT-BMT and NBT-BT-KCl have been studied. Single phase perovskite solid solutions were prepared by the solid state reaction method. Dielectric measurements revealed phase transitions at temperatures near ~350 - 400 K and ~ 550 K. It was proved that modification of compositions by small amounts of the BMT and KCl additives favor to improvement of dielectric and ferroelectric properties.

ACKNOWLEDGEMENT

The work was supported by the Russian Fund for Basic Research (Project 15-03-03269).

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