PROCESSING AND CHARACTERIZATION OF LEAD-FREE KNN- BASED PEROVSKITE CERAMICS MODIFIED BY ZNO

E.D. Politova[1], G.M. Kaleva[1], A.V. Mosunov[1], N.V. Sadovskaya[1], S.Yu. Stefanovich[1,2],
D.A. Kiselev[3,4], T.S. Ilina[3], A.M. Kislyuk[3], P.K. Panda[4]

[1]L.Ya.Karpov Institute of Physical Chemistry; Vorontsovo pole, 10, Moscow 105064 Russia

[2]Lomonosov Moscow State University, Leninskie gory 1, Moscow 119992 Russia

[3]National University of Science and Technology “MISiS”, Leninskiy pr. 4, Moscow 119049 Russia

[4]Fryazino branch of the Kotel’nikov Institute of Radioengineering and Electronics of Russian Academy of Sciences, Vvedensky Square 1, Fryazino, Moscow region, 141190 Russia

[5]National Aerospace Laboratories, Kodihalli, Bangalore-560017 India

Abstract

Influence of ZnO additive on structure, microstructure, dielectric, ferroelectric and local piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ *– based ceramics have been studied. Increase in dielectric parameters and effective* d_{33} *piezoelectric coefficients was observed.*

Keywords: $(Ka_{0.5}Na_{0.5})NbO_3$*, perovskite, ferroelectric, piezoelectric properties*

1. INTRODUCTION

Potassium-sodium niobate $(K,Na)NbO_3$ (KNN) based perovskite ceramics were intensively studied last ten years as the most promising for replacement of Pb-containing piezoelectrics [1 - 9]. Nevertheless, development of lead-free compositions with comparable to the lead zirconium-titanate (PZT) oxides properties is still a not solved task. It is known that preparation of stoichiometric compositions is difficult due to narrow sintering temperature interval of KNN-ceramics and alkaline oxides losses [10 - 13]. So, various additives are used to decrease the sintering temperature [14 - 17], and wide-gap semiconductor ZnO is among the used ones [18 - 21].

In this work, modification of KNN-based compositions with ZnO dopants is investigated. Its effect on structure, microstructure, dielectric, ferroelectric (FE) and local piezoelectric properties is analyzed for ceramic compositions close to the Morphotropic Phase Boundary (MPB) in the $(1\text{-}x)(K_{0.5}Na_{0.5})NbO_3$ – $x$$BaTiO_3$ (KNN-BT) system additionally doped by the Ni^{3+} acceptor dopants $[(K_{0.5}Na_{0.5})_{1-x}Ba_x][(Nb_{1-x}Ti_x)_{1-y}Ni_y]O_3$ (KNN-BT-Ni) (x=0.05, y=0.02).

2. MATERIALS AND METHODS

2.1. Materials

Ceramic samples in the KNN-BT-Ni system with x=0.05, y=0.02 were prepared by the solid state reaction method at calcinations temperature T_1=1073 K (6 h). Sodium carbonate Na_2CO_3, potassium carbonate K_2CO_3, barium carbonate $BaCO_3$, Nb_2O_5, Ni_2O_3 and TiO_2 oxides (“pure” grade) were used as starting materials. Carbonates were dried at 673 K before synthesis in order to remove absorbed water. After synthesis, ZnO additives in amounts 10, 20, 30, and 40 mol. % were added and the samples were sintered at T_2=1323 and 1403 K (2 h).

2.2. Methods

The samples were characterized by the X-ray Diffraction method (DRON-3M, Cu-K_α radiation with wavelength λ=1.5405 A, in the 2θ range of 5 – 80 degrees), Scanning Electron Microscopy (SEM) method (JEOL YSM-7401F with JEOL JED-2300 energy dispersive X-ray spectrometer system), the Second Harmonic Generation (SHG) method in the reflection (Nd:YAG laser, λ=1.064 μm), Dielectric Spectroscopy method on heating with 10 K/min. and cooling in the temperature interval of 300 – 1000 K, in the frequency range of 100 Hz – 1 MHz (Agilent 4284 A, 1 V). The domain structure and polarization switching behavior of KNN-BT-Ni ceramic samples was tested using Piezoresposne Force Microscopy (PFM) technique (AFM system MFP-3D, Asylum Research, USA). Before scanning and local switching, the inverse optical lever sensitivity (Δ, nm/V) and spring constant (k, N/m) were calibrated using the GetReal™ Automated Probe Calibration (Asylum Research, USA). Ti/Ir coated conductive AFM tips with an average radius of 28 nm and spring constant 38 N/m were used in the study. The same kind of cantilever was used for all measurements. Local hysteresis loops for polished samples were measured using switching spectroscopy PFM (SS-PFM) in the DART-PFM mode. The pulse square waves superimposed with triangular waveforms were applied to the tip at a frequency of 500 mHz with duration of each square pulse 25 ms. The AC drive voltage of 2 V and frequency of ~980 kHz were applied to the tip for the SS-PFM measurements and the sample were always grounded. Effective piezoelectric coefficient (d_{33} in pm/V) was calculated from PFM phase and PFM amplitude hysteresis loops using Igor Pro software version 6.37 (Asylum Research, USA). In this study, all measurements were repeated at least 5 times in the different locations of the same sample with strong PFM domains contrast.

3. RESULTS

Ceramic samples with perovskite structure were prepared (Fig. 1). Small amounts of admixture phase $K_2Nb_8O_{21}$ were observed in the X-ray diffraction patterns of the initial KNN-BT-Ni samples. ZnO admixture phase was also observed in the samples with larger ZnO concentration (30 and 40 mol. %) (Fig. 1, curves 3 and 4).]

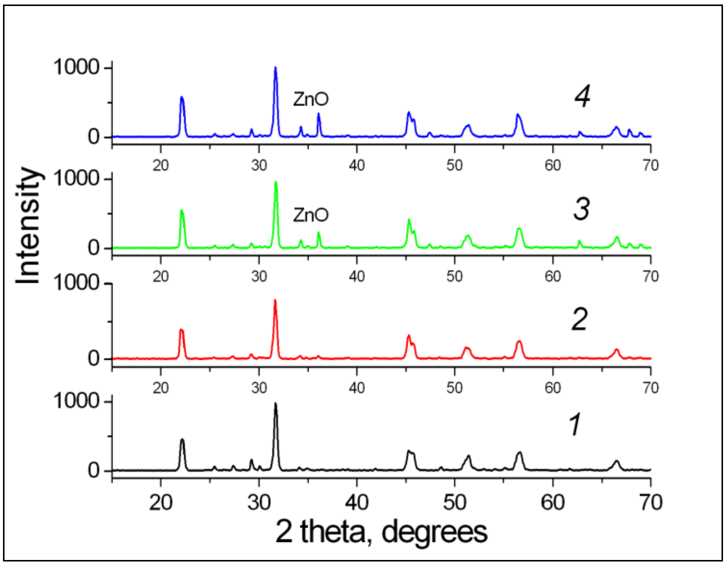
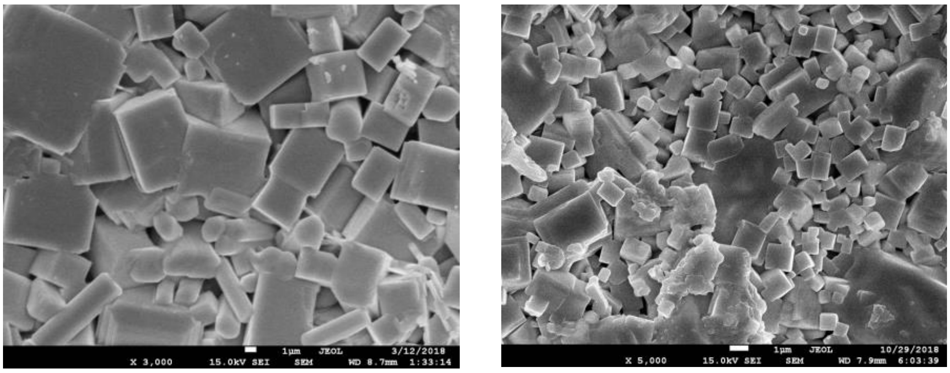


Fig. 1. The X-ray diffraction patterns of the KNN-BT-Ni samples with ZnO additives 10 mol.% (*1*), 20 mol. % (*2*), 30 mol. % (*3*), and 40 mol. % (*4*) prepared by the solid state reaction method at T_1=1073K (6 h), T_2=1403K (2 h).

The samples KNN-BT doped by the Ni^{3+} cations into B-site positions of perovskite lattice revealed tetragonal structure [16]. Slight decrease in the unit cell parameters was confirmed by changes in the A_1 (near 246-250 cm^{-1}) and A_2 (near 601-606 cm^{-1}) modes positions of Raman spectra as well [17]. ZnO additives do not influence on the unit cell parameters, so only small amount of Zn^{2+} cations may enter into B positions of perovskite lattice.

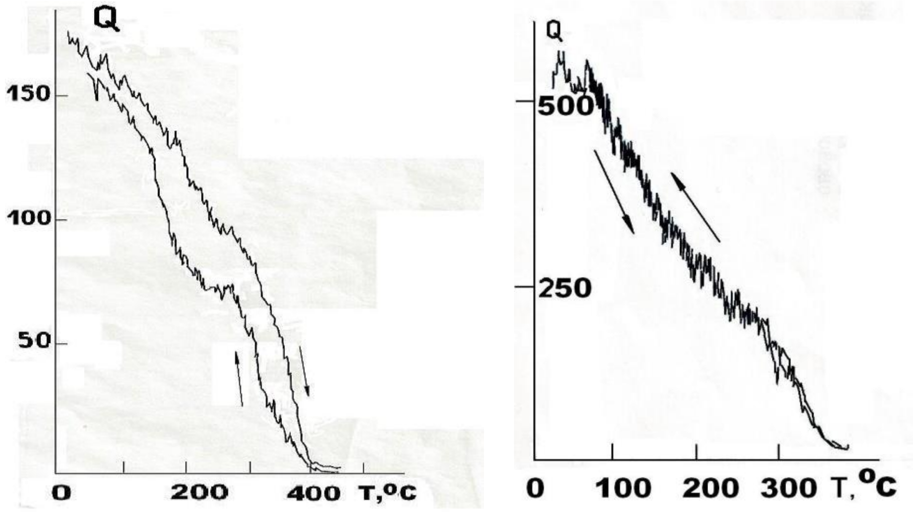
Microstructure of the samples is sensitive both to composition and sintering conditions. Enlargement of mean size of grains was observed in KNN-BT composition with Ni^{3+} cation additive (Fig. 2*a*) [16]. However, smaller grains were observed in the ZnO containing samples (Fig. 2*b*). The inhibited grain growth may be explained by the effect of impinging of the liquid phase produced in ZnO containing samples [21]. Such effect was also observed in KNN-based and other systems as well [14, 19].



a) *b)*

Fig. 2. Microstructure of the surface of the KNN-BT-Ni samples (*a*) and with 40 mol. % of ZnO additive (*b*). Bars – 1 μm.

Using the SHG method it was confirmed that the samples studied are ferroelectrics. Their ferroelectric phase transitions were revealed as appearance/disappearance of SHG signal in cooling/ heating circle. In ZnO-modified samples the highest intensity of the SHG signal $Q=I_{2\omega}/I_{2\omega}(SiO_2) = 500$ was registered in samples containing 20 mol.% ZnO (Fig. 3).

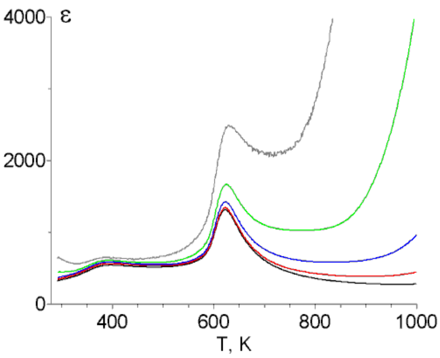


a) *b)*

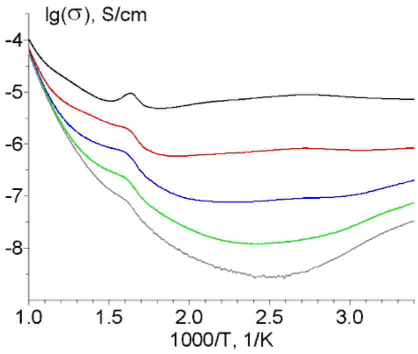
Fig. 3. Temperature dependences of the SHG signal, $Q=I_{2\omega}/I_{2\omega}(SiO_2)$ of the KNN-BT-Ni (*a*) and KNN-BT-Ni with 20 mol. % ZnO additive (*b*).

In the dielectric permittivity versus temperature curves ferroelectric phase transitions were revealed as steps at T_{pt} ~ 400 K and as maxima at T_m ~ 600 K (Fig. 4). Slight decrease in temperatures of both phase transitions was observed in ceramic solid solutions with increasing ZnO content. At the room temperature, increase in dielectric permittivity and spontaneous polarization values was observed in modified compositions studied.

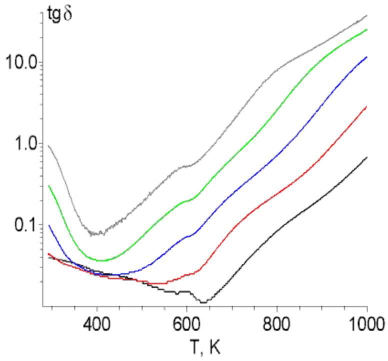
At high temperatures near 900 K additional peaks related to effect of dielectric relaxation were observed in the samples studied. Such peaks usually are explained by formation of oxygen vacancies in the lattice due to vacancies in the A-sublattice or by introduction of cations with lower valencies into the B-sublattice.



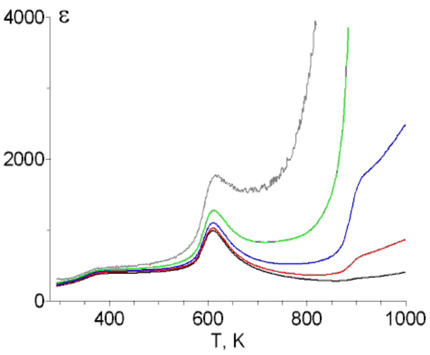
1a (10 % mol. ZnO)



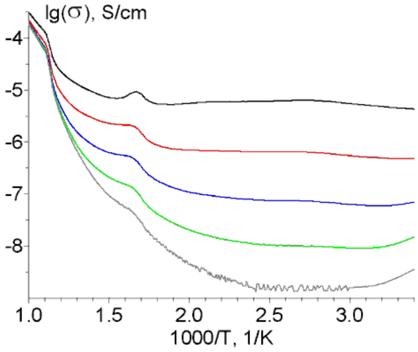
1b



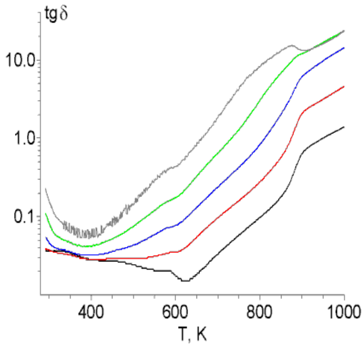
1c



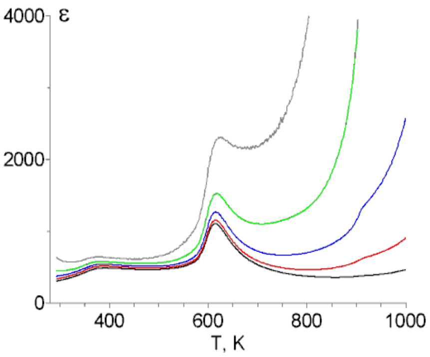
2a (20 % mol. ZnO)



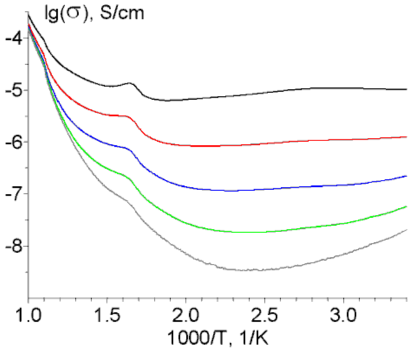
2b



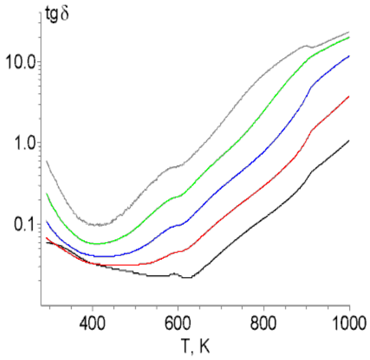
2c



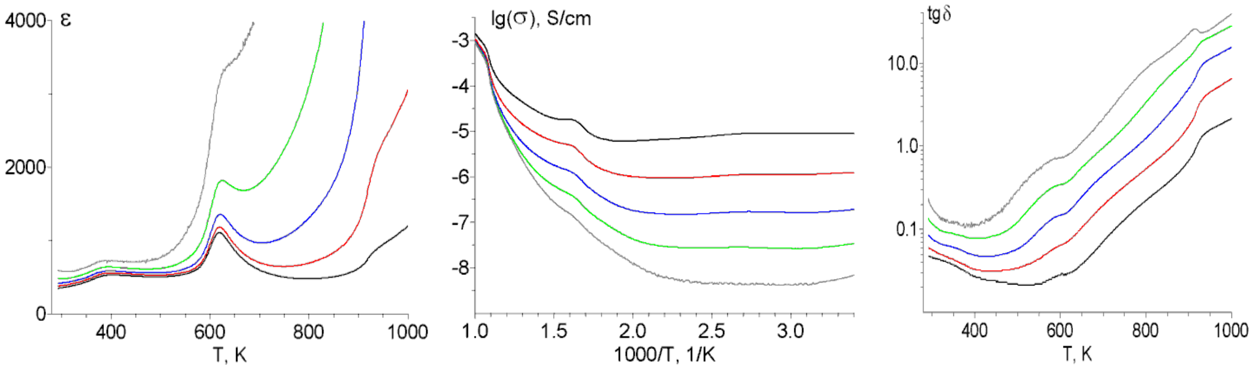
3a (30 % mol. ZnO)



3b



3c



4a (40 % mol. ZnO) *4b* *4c*

Fig. 4. Temperature dependences of dielectric permittivity $\varepsilon(T)(a)$, dielectric loss tan$\delta(T)(b)$ and electroconductivity lg Sigma (1/*T*) (*c*) of the KNN-BT-Ni samples doped with ZnO (10 – 40 mol. %) measured at frequencies *f*=1 kHz-1 MHz.

The as-grown domain structure was observed in ceramics prepared using the PFM method (Fig. 5). Simultaneous topography and out-of-plane PFM images confirmed that the imaged pattern were due to their piezoresponse [16]. In order to further study the domain switching behavior of KNN-BT-Ni-ZnO ceramics, electrical poling was performed by scanning in write mode with a conductive probe, which applying -30 V (15 × 15 µm^2) and +30 V (8 × 8 µm^2) DC bias on the tip. Fig. 5 (row “PFM image immediately after poling”) show the obvious PFM contrast, from which we can see both up and down polarized domains in the regions with polarization switching, contrast to “Initial PFM image” (top row). Most of domains in these squares switch to the same polarized state. Thus polarization directions in the squares patterns of most of domains apparently switch to the applied electric biases, which indicate that only minor amount of domains have not been switched after poling (non ferroelectric active grains). After 2 hours after the poling process, the PFM contrast of the written domains are stable (Fig. 5 (bottom row), and Z-scale on PFM images for each samples is the same).

The hysteresis behavior of the piezoresponse confirmed ferroelectric switching of the ceramic (Fig. 6). Effective d_{33} piezoelectric coefficient values increased from d_{33}=50 pm/V (10 mol. % ZnO) till d_{33}=200 pm/V in the ceramics with 30 mol. % of ZnO.

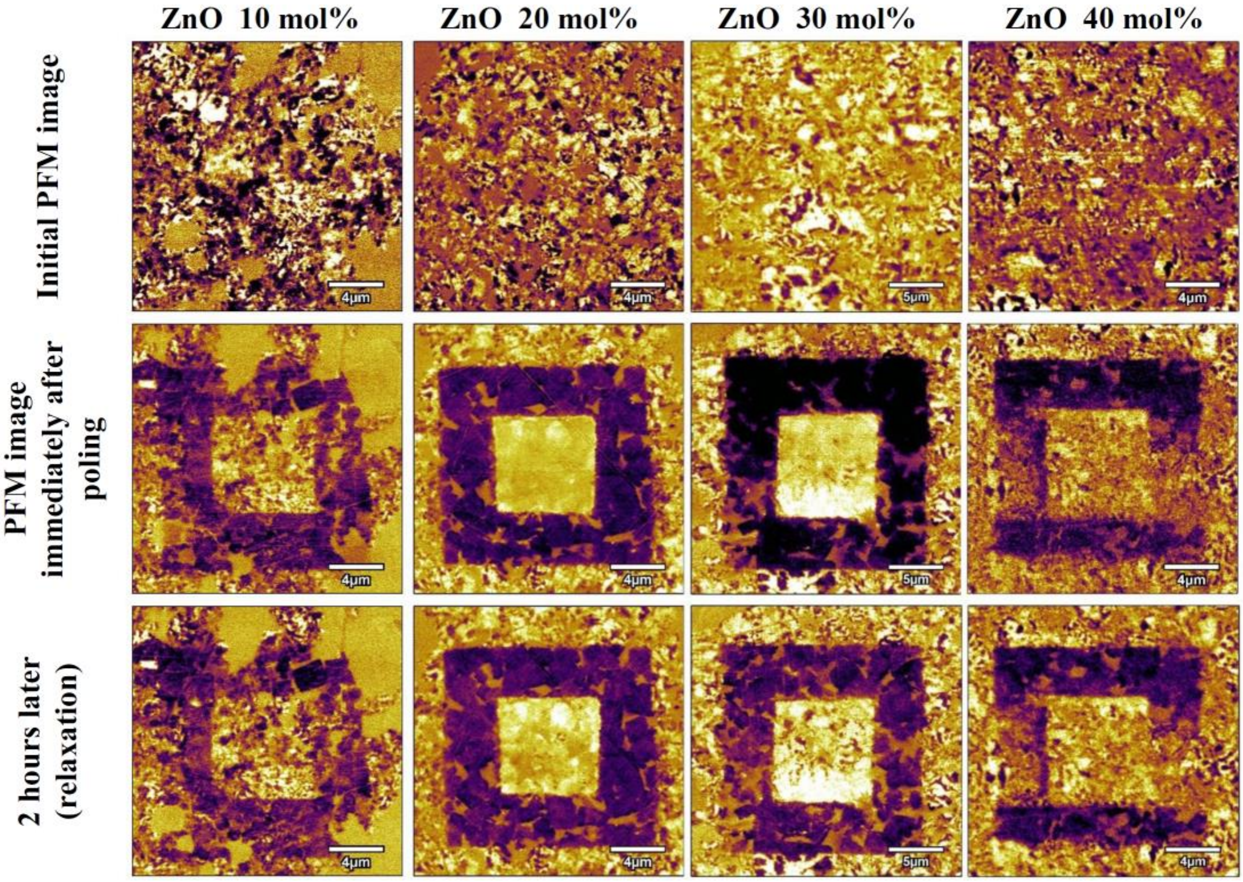


Fig. 5. Initial domain structure and time stability of the poled area in the KNN-BT-Ni ceramic with ZnO additives (10 – 40 mol. %).

4. DISCUSSION

It is clear that addition of the semi-conductive ZnO has an impact on the formation of ferroelectric domains as well as on their switching under electric field application. These influences can be seen through the difference between two temperature dependences of Q(T) curves in Fig. 3 *a*,*b*. Better coinciding of Q(T) curves in the heating/cooling circle in Fig. 3*b* evidence for easier mobility of electric domains upon change of temperature in the case of the KNN-BT-Ni composition containing ZnO additive. This observation is in agreement with polarization switching loops measurements fulfilled with the PFM method (Fig. 6).

The loops measured for KNN-BT and KNN-BT-Ni ceramic samples earlier were usually shifted towards either to positive or negative bias voltage [16, 17]. This indicated to the presence of internal bias fields stabilizing energetically favorable orientation of the polarization along their directions, and resulting in hindering the domain walls motion leading to an asymmetry of the switching process [22, 23]. This effect was observed in the acceptor doped materials and explained by the large energy difference between different positions of oxygen vacancies in the oxygen octahedra of the perovskite lattice [24]. However, the polarization switching loops are practically symmetric in the ZnO contaning samples (Fig. 6)..

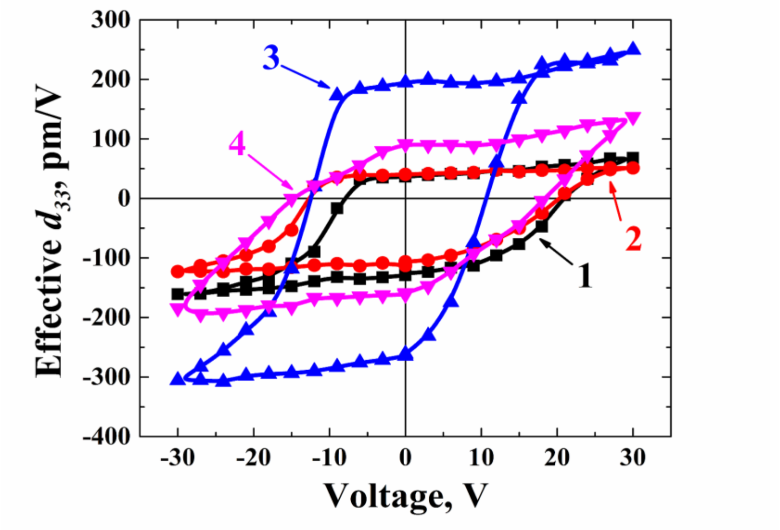


Fig. 6. Local PFM hysteresis loops for the samples containing ZnO additives: 10 mol.% (1), 20 mol.% (2), 30 mol. % (3), 40 mol. % (4).

It should be noted that in the samples doped by ZnO the values of effective d_{33} measured at +30 V are lower than those recorded at –30 V (Fig. 6). Such effect may be explained by the presence of non-180° domains in ceramics [25].

The PFM results correlate well with dielectric permittivity values measured at the room temperature. The results obtained confirmed prospects of new lead-free materials development by modification of the KNN-based compositions close to the MPB by the aliovalent cation substitutions and by the dopant decreasing sintering temperature.

5. CONCLUSIONS

Structure, microstructure, dielectric, ferroelectric and piezoelectric properties of ceramics $[(K_{0.5}Na_{0.5})_{1-x}Ba_x][(Nb_{1-x}Ti_x)_{1-y}Ni_y]O_3$ (KNN-BT-Ni) (x=0.05, y=0.02) doped by ZnO (10, 20, 30 and 40 mol. %) were studied. Slight changes in the unit cell volume and temperatures of phase transitions were observed. And high values of dielectric parameters and effective d_{33} piezoelectric coefficients measured confirmed prospects of the KNN-based ceramics for development of new efficient materials.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research (Projects 16-53-48009and 18-03-00372). PFM studies were performed at Center for Shared Use “Material Science and Metallurgy” at the National University of Science and Technology “MISiS” and were supported by the Ministry of Science and Higher Education of the Russian Federation (projects 11.9706.2017/7.8, 16.2811.2017/4.6).

REFERENCES

1. Zhang SJ, Xia R, and Shrout RT 2007, “Lead-Free Piezoelectric Ceramics: Alternatives for PZT?” *J. Electroceram*. vol. 19, pp. 251-257.
2. Takenaka T, Nagata H, and Hiruma Y 2008, “Current developments and prospective of lead-free piezoelectric ceramics”, *Jpn. J. Appl. Phys*. vol. 47, pp. 3787-3801.

3. Panda PK 2009, “Review: Environmental friendly lead-free piezoelectric materials”, *J. Mater. Sci.* vol. 44, pp. 5049-5062.
4. Damjanovich D, Klein N, Li J and Porokhonskyy V 2010, “What can be expected from lead-free piezoelectric materials?”, *Funct. Mater. Lett*. vol. 3, pp. 5-13.
5. J. Suchanicz, I. Smeltere, A. Finder, K. Konieczny, B. Garbarz-Glos, R. Bujakiewicz-Koronska, M. Latas, M. Antonova, A. Sternberg, M. Sokolowski, 2011, “Dielectric and ferroelectric properties of lead-free NKN and NKN-based ceramics”, *Ferroelectrics,* vol. 424, pp. 53-58.
6. Coondoo I, Panwar N, Kholkin A 2013, “Lead-free piezoelectrics: Current status and perspectives”, *J. Adv. Dielectr*. vol. 3: 1330002 (22 pages).
7. Panda PK and Sahoo B 2015, “PZT to Lead-Free Piezo Ceramics”, *Ferroelectrics*. vol. 474, pp.128-143.
8. Hong CH, Kim HP, Choi BY, Han HS, Son JS, Ahn CW, Jo W 2016, “Lead-free piezoceramics. Where to move on?” *J. Materiomics.* vol. 2, pp. 1-24.
9. Rödel J and Li J 2018, “Lead-free piezoceramics: Status and perspectives”, *MRS Bulletin*, vol. 43, pp. 576 -580.
10. Fang J, Wang X, Zuo R, Tian Z, Zhong C, and Li L 2011, “Narrow sintering temperature window for (K,Na)NbO_3-based lead-free piezoceramics caused by compositional segregation”, *Phys. Status Solidi A,* vol. 208, pp. 791-794.
11. Cheng L, Wang K, Yao F, Zhu F and Li J 2013 “Composition Inhomogeneity due to Alkaline Volatilization in Li-Modified (K,Na)NbO_3 Lead-Free Piezoceramics”, *J. Am. Ceram. Soc.* vol. 96, pp. 2693-2695.
12. Tellier J, Malič B, Dkhil B, Jenko D, Cilensek J, Kosec M 2009, “Crystal structure and phase transitions of sodium potassium niobate perovskites”, *Solid State Sci*. vol. 11, pp. 320-324.
13. Malič B, Koruza J, Hreščak J, Bernard J, Wang K, Fisher JG, Benčan A 2015, “Sintering of lead-free piezoelectric sodium potassium niobate ceramics”, *Materials,* vol. 12, pp. 8117-8146.
14. Park HY, Ahn CW, Song HC, Lee JH, and Nahma S 2006, “Microstructure and piezoelectric properties of $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05BaTiO_3$ ceramics”, *App. Phys. Lett.* vol. 89, 062906-1-3.
15. Politova ED, Kaleva GM, Golubko NV, Mosunov AV, Akinfiev VS, Stefanovich SY, Fortalnova EA 2015, “Influence of NaCl/LiF Additives on Structure, Microstructure and Phase Transitions of $(K_{0.5}Na_{0.5})NbO_3$ Ceramics”, *Ferroelectrics,* vol. 489, pp. 147-155.
16. Politova ED, Golubko NV, Kaleva GM, Mosunov AV, Sadovskaya NV, Stefanovich SY, Kiselev DA, Kislyuk AM, Panda PK 2018, “Processing and characterization of lead-free ceramics on the base of sodium-potassium niobate”, *J. Adv. Diel.* vol. 8, 1850004.
17. Politova ED, Golubko NV, Kaleva GM, Mosunov AV, Sadovskaya NV, Stefanovich SY, Kiselev DA, Kislyuk AM, Chichkov MV, Panda PK 2019 “Structure, ferroelectric and piezoelectric properties of KNN-based perovskite ceramics”, *Ferroelectrics*, in press.
18. Look DC 2001, “Recent advances in ZnO materials and devices”, *Materials Science and Engineering B,* vol.80, pp. 383–387.
19. Park HY, Ahn CW, Cho KH, Nahm S. 2007, “Low-temperature sintering and piezoelectric properties of CuO-added $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05BaTiO_3$ ceramics”, *J. Amer. Ceram. Soc*. vol. 90, pp. 4066–4069.
20. Hayati R, Barzegar A 2010, “Microstructure and electrical properties of lead free potassium sodium niobate piezoceramics with nano ZnO additive”, *Materials Science and Engineering B*, vol. 172, pp. 121–126.

21. Kang In-Young, Seo In-Tae, Cha Yu-Joung, Choi Jae-Hong, Nahm Sahn, Sung Tae-Hyun, Paik Jong-Hoo 2012 “Low temperature sintering of ZnO and MnO_2-added $(Na_{0.5}K_{0.5})NbO_3$ ceramics”, *Journal of the European Ceramic Society*, vol. 32, pp. 2381–2387.
22. Jesse S, Baddorf AP, Kalinin SV 2006, “Switching spectroscopy piezoresponse force microscopy of ferroelectric materials”, *Appl. Phys. Lett.* vol. 88, 062908.
23. Trivedi H, Shvartsman VV, Lupascu DS, Medeiros MS, Pullar RC, Kholkin AL, Zelenovskiy P, Sosnovskikh A, Shur VY 2015, “Local manifestations of a static magnetoelectric effect in nanostructured $BaTiO_3$–$BaFe_{12}O_9$ composite multiferroics”, *Nanoscale*, vol. 7, pp. 4489-4496.
24. Rojac T and Damjanovic D 2017, “Domain walls and defects in ferroelectric materials”, *Jap. J. Appl. Phys*. vol. 56, 10PA01.
25. Dausch DE 1998, “Asymmetric 90^o domain switching in rainbow actuators”, *Ferroelectrics*, vol. 210, pp. 31–45.