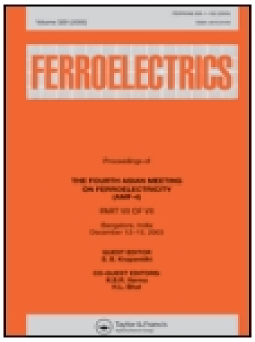

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Effects of KCl/LiF Additives on the Structure, Phase Transitions and Dielectric Properties of BSPT Ceramics

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The influence of the low-melting KCl/LiF additive with molar ratio 80:20 on the structure, dielectric and ferroelectric properties of solid solutions with compositions close to morphotropic phase boundary in the $(1-\mathrm{x})BiScO_3$ *-* $xPbTiO_3$ *system with* x=*0.635 (BSPT1) and* x=*0.645 (BSPT2) doped by 5, 10 and 15 w. % of KCl/LiF has been studied. Dense single phase ceramic samples have been prepared at 1313 – 1323 K (2 h) using as initial the BSPT1 and BSPT2 powders prepared from nitrate solutions. Addition of KCl/LiF led to displacement of BSPT1 and BSPT2 compositions from the initial mixture of rhombohedral and tetragonal phases to the region of the tetragonal one. This effect was accompanied by a small increase in the Curie temperature* T_C *value from 668 to 705* K *in case of BSPT1 and from 672 to 714* K *in case of BSPT2. Effects of additives on unit cell parameters of perovskite solid solutions, decrease in sintering temperatures, and improvement of the ceramic samples density were also found.*

Keywords Ceramic solid solutions $BiScO_3$-$PbTiO_3$; morphotropic phase boundary; additives KCl/LiF; ferroelectric phase transitions

Introduction

Development of new piezoelectric materials for high temperature applications is the actual task initiated by demands of various branches of industry, including control and operation of the auto, -air and cosmic transport, as well as the equipment for the medicine and atomic industry. Ceramic materials based on lead zirconate-titanate (PZT) are widely used in many branches of industry, however application of such materials is limited by their rather low working temperatures.

This problem stimulated intense investigations of perovskite-like $BiMe^{3+}O_3$ oxides [1 – 13]. Perovskite-like bismuth containing ceramics have real prospects for the development of materials with Curie temperatures $T_C > 700$ K for high temperature applications.

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In order to regulate their functional properties, the complex approach that includes modification of compositions, introduction of various over stoichiometric additives, and optimization of preparation conditions is used [4, 8, 10].

Ceramics of solid solutions from the morphotropic phase boundary (MPB) in the $(1-x)BiScO_3$ - $xPbTiO_3$ (BSPT) system may be considered as ones of the most studied because they revealed T_C values higher than 700 K and high piezoelectric coefficients [3, 4, 12]. For development of new effective piezoelectric materials the approach based on the investigation of compositions near the MPB is widely used. A decrease in the sintering temperature and electroconductivity of ceramics with the necessary composition stoichiometry and enhancement of piezoelectric properties comprise the most important tasks. In order to regulate functional characteristics, we used cation substitutions in A- and B- sublattices of the perovskite structure and special overstoichiometric additives [5 – 8]. Earlier, we studied an effect of overstoichiometric additives and cation substitutions on the phase composition, microstructure, phase transitions and properties of BSPT ceramics with x = 0.60 – 0.66 [5 – 12]. KCl additives with low melting temperature were shown to increase the density of ceramics and allow to better control of their microstructure and unit cell parameters. Besides, the improvement of functional properties of ceramics with $x = 0.64$ was proved [11].

In this work, characteristics of ceramic BSPT compositions from MPB with $x = 0.635$ (BSPT1) and $x = 0.645$ (BSPT2) modified by the complex KCl/LiF additive with molar ratio of 80:20 were studied. This additive has lower melting temperature ($\sim$985 K) as compared with melting temperature of KCl (1040 K), so a further decrease in sintering temperature of ceramics was expected. This diminishes Bi and/or Pb oxides loss during high temperature sintering and leads to conservation of the stoichiometry and optimization of functional properties of ceramics.

Experimental

Initial powders of BSPT1 and BSPT2 compositions were prepared by co-precipitation of corresponding nitrate solutions followed by the conventional procedure and calcination at 973 K (7 h) [9]. KCl/LiF additives with molar ratios of 80:20 were added in amounts of 5, 10 and 15 w. %. The pressed powders were sintered in air at 1323 K for 2 hours and slowly cooled to the room temperature.

The phase composition and crystal structure parameters were studied at the room temperature using the X-ray diffraction method (DRON-3M with $Cu_{K\alpha}$-beam). The microstructure of the samples was examined by the high-resolution scanning electron microscopy method (SEM) with a JEOL YSM-7401F instrument 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, λ=1.064 μm), dielectric properties and electroconductivity were studied with the use of 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 X-ray diffraction data, single phase samples with the perovskite structure were obtained at sintering temperature of 1323 K. Figure 1 demonstrate the diffraction peaks with $h^2+k^2+l^2= 4$. Small shift of the X-Ray diffraction peaks indicates unit cell parameters changes due to changes in the sample compositions. This picture clearly

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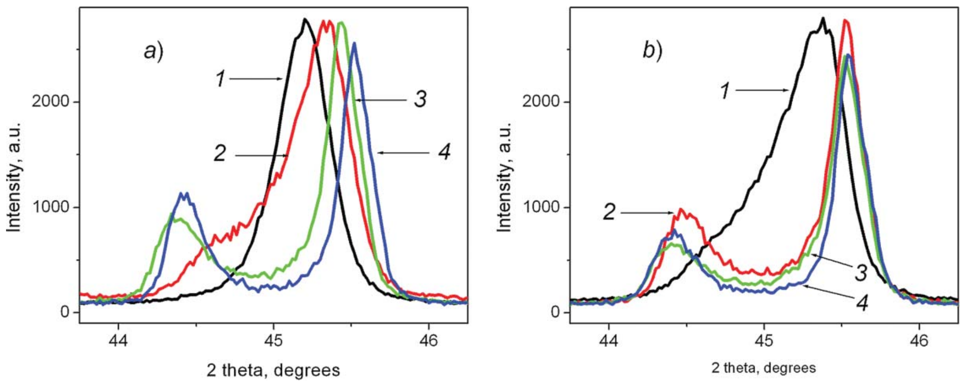

Figure 1. Parts of the X-ray diffraction patterns of the BSPT1 (*a*) and BSPT2 (*b*) ceramics: initial samples – curves *1*, samples modified by the KCl/LiF additives in amounts of 5 w. % - curves *2*, 10 w. % - curves *3*, and 15 w. % - curves *4*.

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demonstrates the dependence of the relative content of the tetragonal (T) and rhombohedral (R) phases in the compositions studied on the amount of the KCl/LiF additive. An increase in the additive content stimulates the T phase proportion increasing. So, addition of 5 w. % of KCl/LiF to initial compositions with $x = 0.635$ (BSPT1) and with $x = 0.645$ (BSPT2) leads to transformation of the R phase (BSPT1) or the mixture of T and R phases (BSPT2) to the mixture of T and R phases (BSPT1) and to the T phase (BSPT2), respectively. This means that the additives stimulate displacement of the MPB compositions studied to the region with T structure. The displacements of the 200 and 002 diffraction peaks stimulated by the KCl/LiF addition in amounts from 5 to 15 w. % clearly indicate a decrease in the *a*- parameter, an increase in the *c*- parameter of the perovskite lattice and increase in *c*/*a* ratio in the BSPT1 samples. This may be explained by substitution of Bi^{3+} and/or Pb^{2+} cations by Li^{+} and/or K^{+} cations in A-positions of the perovskite lattice.

According to SEM data, the average size of initial particles synthesized varies from ~0.1 to ~1 μm, but the grain size of BSPT1 and BSPT2 ceramics do not exceed 2 – 3 μm. Figure 2 demonstrates that an increase in the KCl/LiF content up to 15 w. % leads to fabrication of homogeneous dense BSPT1-based ceramics with the average grain

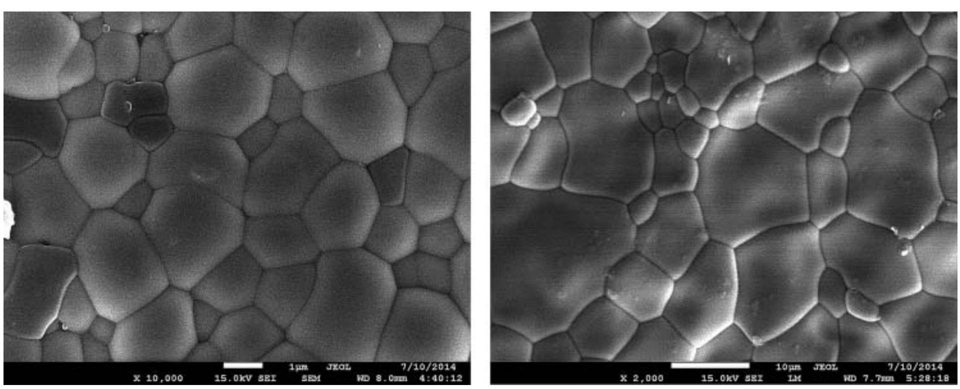

Figure 2. The microstructure of the BSPT1 ceramics modified by 5 w. % (left) and 15 w. % (right) of the KCl/LiF additives. Scale bars – 1 μm (left) and 10 μm (right).

size of ∼10 μm. The same tendency was also observed for samples of the BSPT2 composition. However, in the samples, containing 15 w. % of the additive, formation of larger grains was observed.

It is necessary to note that introduction of the KCl/LiF additive up to 15 w. % stimulates improvement of ceramics density, shrinkage of the samples increasing from 15 to 19 %. Obviously, the additives intensified processes both of phase formation and sintering as dense initial BSPT ceramics were obtained only at higher temperatures (1323 – 1423 K).

The relative intensity of the SHG signal $q = I_{2w}/I_{2w}(SiO_2)$ relating to spontaneous polarization P_s as $q \sim P_s^{0.5}$ increased from the 1200 and 1500 in initial BSPT1 samples to the 2300 and 2400 values, respectively with introduction of KCl/LiF in amount of 5 w. %. As average size of grains in these ceramics does not change, the observed increase in the *c/a* ration and *q* values indicates to the enhancement of spontaneous polarization.

Dielectric measurements revealed the 1st order sharp ferroelectric phase transitions marked by peaks in dielectric permittivity versus temperature $\varepsilon(T)$ curves and corresponding minima in dielectric loss tg$\delta(T)$ curves at high temperatures (Figure 3). A small increase in the T_C value from 668 to 705 K in case of BSPT1 and from 672 to 714 K in case of BSPT2 was observed for modified ceramics that correlated well with an increase in the relative content of the *T* phase and with changes in the *c/a* ratio which is proportional to the T_C value.

An enhancement of the dielectric permittivity, a significant decrease (down to 5 times) in electroconductivity values at room temperature, and corresponding decrease in dielectric loss tg$\delta(T)$ values (down to 2 times) were revealed in modified samples studied. Dielectric loss values of doped samples are slightly lower than those of undoped samples in the temperature interval of 300–700 K. However, an increase in total electroconductivity was observed at temperatures higher than T_C with increasing amount of additives. Evidently, this effect may be related to the dielectric relaxation effects observed at high temperatures in the samples with the highest amount of additives (Figure 4). It is necessary to note that effects of dielectric relaxation are typical of undoped BSPT samples [6 –8]. These effects were completely suppressed in the samples doped by 5 – 10 w. % of the KCl/LiF additives. An increase in the T_C observed indicates the presence of Li-cations in A-positions of the perovskite

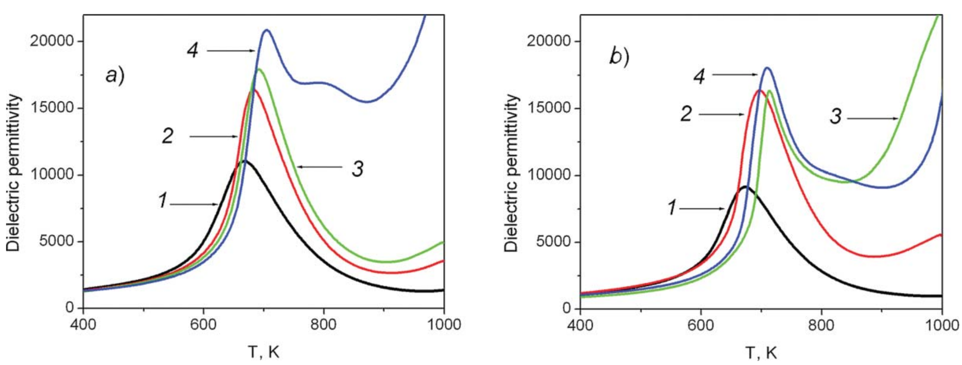

Figure 3. Temperature dependencies of dielectric permittivity of ceramics BSPT1 (*a*) and BSPT2 (*b*) modified by KCl/LiF additives (on cooling). Initial samples – curves *1*, samples with 5 w. % of KCl/LiF – curves *2*, with 10 w. % – curves *3*, with 15 w. % - curves *4*. Measuring frequency $f = 1$ κHz.

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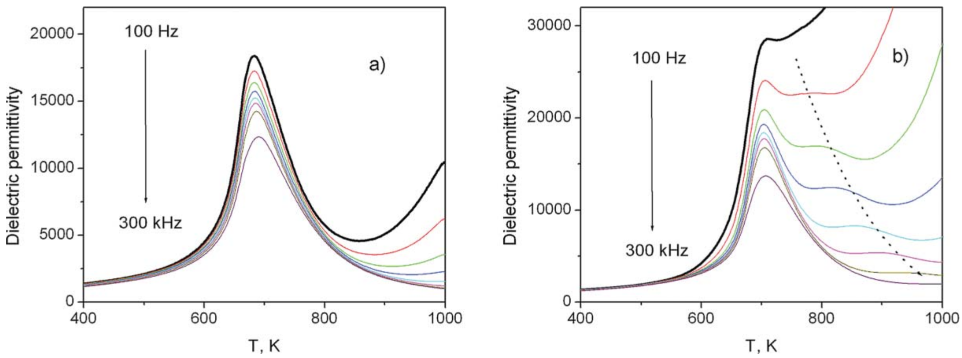

Figure 4. Temperature dependencies of dielectric permittivity of ceramics BSPT1 modified by 5 w. % KCl/LiF (*a*) and 15 w. % KCl/LiF (*b*) (on cooling). Measuring frequencies $f = 100$, 300 Hz, 1, 3, 10, 30, 100, 300 κHz.

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structure. Thus, BSPT samples doped by KCl/LiF additives are promising for the development of new compositions with improved piezoelectric properties.

Conclusions

The effects of KCl/LiF additives on the structure, microstructure, dielectric and ferroelectric properties of the MPB solid solutions in the $(1-x)BiScO_3$ - $xPbTiO_3$ system with $x = 0.635$ and $x = 0.645$ have been studied. The positive influence of KCl/LiF additives on phase formation, sintering process and ferroelectric properties was shown. A small increase in the T_C value observed correlates well with an increase in the relative proportion of the tetragonal phase and the *c/a* ratio in modified ceramics.

Funding

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References

1. R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Paul, W. Hackenberger, and S. E. Park, New High Temperature Morphotropic Phase Boundary Piezoelectrics Based on $Bi(Me)O_3$–$PbTiO_3$ Ceramics. *Jpn J Appl Phys.* **40**, 5999–6002 (2001).
2. R. E. Eitel, C. A. Randall, T. R. Shrout, and S. E. Park, Preparation and characterization of high temperature perovskite ferroelectrics in the solid solutions $(1-x)BiScO_3$-$xPbTiO_3$. *Jpn J Appl Phys.* **41**, 2099–2104 (2002).
3. S. J. Zhang, C. A. Randall, and T. R. Shrout, Dielectric and Piezoelectric Properties of $BiScO_3$-$PbTiO_3$ Crystals with Morphotropic Phase Boundary Compositions. *Jpn J Appl Phys.* **43**, 6199–6203 (2004).
4. A. Sehirlioglu, A. Sayir, and F. Dynys, Doping of BiScO3–PbTiO3 Ceramics for Enhanced Properties. *J. Am. Ceram. Soc.* **93**, 1718–1724 (2010).
5. E. D. Politova, B. V. Egorova, G. M. Kaleva, A. V. Mosunov, SYu. Stefanovich, A. G. Segalla, and J. Zeng, Phase Transitions and the Dielectric and Piezoelectric Properties of Ceramic Solid Solutions Based on $BiScO_3$–$PbTiO_3$. *Bull Russ Acad Sci.* **75**, 1166–1169 (2011).

6. E. D. Politova, B. V. Egorova, G. M. Kaleva, A. V. Mosunov, SYu. Stefanovich, A. G. Segalla, and J. Zeng, Phase Transitions, Piezo- and Ferroelectric Properties of $BiScO_3$-$PbTiO_3$ Solid Solutions. *Ferroelectrics.* **419**, 83–89 (2011).
7. E. D. Politova, G. M. Kaleva, A. V. Mosunov, A. G. Segalla, and J. Zeng, Phase transitions, dielectric and piezoelectric properties of $BiScO_3$-$PbTiO_3$ ceramic solid solutions. *Key Engineering Materials.* **512–515**, 1363–1366 (2012).
8. G. M. Kaleva, E. D. Politova, A. V. Mosunov, N. V. Sadovskaya, A. G. Segalla, and J. Zeng, Effect of low-melting additives on the structure, phase transitions, and dielectric properties of $0.36BiScO_3$-$0.64PbTiO_3$ ceramics. *Inorganic Materials.* **48**, 953–959 (2012).
9. E. D. Politova, G. M. Kaleva, A. V. Mosunov, A. H. Segalla, A. E. Dosovitskiy, and A. L. Mikhlin, Processing, phase transitions, and dielectric properties of BSPT ceramics. *Journal of Advanced Dielectrics.*; **3**, 1350024 (5 pages). (2013).
10. E. D. Politova, G. M. Kaleva, A. V. Mosunov, N. V. Sadovskaya, A. H. Segalla, and A. A. Bush, Influence of Complex Additives on Morphology, Phase Transitions, and Dielectric Properties of $0.36BiScO_3 - 0.64PbTiO_3$ Ceramics. *Ferroelectrics*; **440**, 105–112 (2013).
11. E. Politova, V. Akinfiev, G. Kaleva, A. Mosunov, S. Stefanovich, and A. Segalla, Effects of KCl Additives on Structure, Phase Transitions and Dielectric Properties of $0.36BiScO_3 - 0.64PbTiO_3$ Ceramics. *Ferroelectrics*; **464**, 1–7 (2014).
12. A. H. Segalla, S. S. Nersesov, G. M. Kaleva, and E. D. Politova, To the enhancement of functional properties of high temperature ferro-piezoelectric ceramics of the base of solid solutions $BiScO_3 - PbTiO_3$. *Inorganic materials.*:**50**, 655–660. (2014).
13. J. Chen, J. Cheng, and S. h. Dong, Review on high temperature piezoelectric ceramics and actuators based on $BiScO_3$–$PbTiO_3$ solid solutions. *J. Adv. Dielectrics.*; **4**, 1430002 (14 pages). (2014).

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