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Influence of Complex Additives on Morphology, Phase Transitions, and Dielectric Properties of $0.36BiScO_3$-$0.64PbTiO_3$ Ceramics

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Ceramic solid solutions on the base of composition from morphotropic phase boundary $0.36BiScO_3$-$0.64PbTiO_3$ modified by the powdered $Bi_4Ti_3O_{12}$ and $Bi_{0.75}Sr_{0.25}O_{1.36}$ single crystals additives and by the low-melting LiF additive in amounts 5, 10, and 1 wt.%, respectively, have been prepared by the solid-state reactions method. The structure, microstructure, and dielectric properties of the ceramics have been studied. The influence of the additives on the morphology of ceramics, temperature of phase transitions, and effect of dielectric relaxation has been proved.

Keywords $BiScO_3$ - $PbTiO_3$ ceramics; morphology; ferroelectric properties

I. Introduction

Ceramic solid solutions from the morphotropic phase boundary (MPB) in the $BiSc0_3$ - $PbTiO_3$ (BSPT) system are being regarded among the most promising for the development of new piezoelectric materials for high-temperature applications. The composition $0.36BiScO_3$-$0.64PbTiO_3$ belongs to the MPB that separates the composition ranges with rhombohedral and tetragonal phases. These oxides are characterized by high Curie temperature (T_C) values above 700 K and large piezoelectric coefficients [1, 2]. Though the BSPT-based ceramics have been intensively studied last decade, the task of the optimization of their functional properties remains still an actual one [3–11]. In addition to high T_C values and large piezoelectric coefficients, of great importance is ability to reduce dielectric loss of ceramic materials and to regulate the microstructure properties.

Introduction of low-melting additives comprises one of effective approaches to improving the functional characteristics of piezoelectric ceramic materials [5–8, 10]. It has been experimentally proved that the addition of small amounts of bismuth and manganese oxides as donor additives favors to the electroresistivity of BSPT ceramics increasing, to high temperatures dielectric loss reducing, and provides an effective means of controlling the size of ferroelectric domains, domain switching and fatigue effects, and finally, improving the ferroelectric and piezoelectric performance of ceramics [5–7]. It was also shown

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that the addition of excess of bismuth oxide to BSPT ceramics compensated bismuth oxide losses during heat treatment at high temperatures and intensified the liquid-phase sintering process, improved polarizability of ceramics, and led to significant increasing of piezoelectric charge coefficient d_{33} [3, 4, 8]. It should be noted that amounts of such additives should be optimized separately for each composition, and a criterion for the optimization is final improvement in functional properties.

Earlier, we investigated the effect of cation substitutions and low-melting additives of bismuth, nickel, chromium, and manganese oxides and lithium fluoride on the phase composition, microstructure, ferroelectric and piezoelectric properties of $(1 - x)$(Bi,Nd)(Sc,B)O_3-xPbTiO$_3$ ($x = 0.60 - 0.66$, B - Lu, Yb, Er, Y) ceramics prepared by the solid-state reaction method [9, 10]. The T_C of the ceramics was found to increase with increasing lead titanate concentration, though dropping with the A- and B-site cations substitutions. The efficiency of the low-melting oxides additives in decreasing the solid solutions formation temperature, in improving the density of ceramics, in reducing the total electrical conductivity and dielectric loss at high temperatures by more than one order of magnitude, and in increasing piezoelectric coefficients d_{33} and k_t was proved.

In this work, the 0.36BiScO$_3$-0.64PbTiO$_3$ composition was modified by additives of powdered single crystals $Bi_4Ti_3O_{12}$ (BTO) and $Bi_{0.75}Sr_{0.25}O_{1.36}$ (BSO) obtained by the crystallization from molten fluxes. It was expected that highly anisotropic particles of BTO and BSO additives would stimulate the preparation of ceramics with uniaxial grain orientation. Similar approach known as reactive-templated grain growth process (RTGG) is widely used for fabrication of highly textured polycrystalline films and ceramics with controlled orientation of crystallites [12–15]. The presence of particles with anisotropic crystal structure favors to the formation of textured ceramics and is an effective approach for improving piezoelectric properties. So, the task of this work was the optimization of microstructure and dielectric properties of the 0.36BiScO$_3$-0.64PbTiO$_3$ ceramics modified by the powdered BTO and BSO single crystals. The additional low-melting LiF additive was intended to lower the sintering temperature of ceramics in order to maintain their stoichiometry and to control their grain size. Of particular interest was to check the effect of the combination of BTO or BSO with LiF on the ceramics properties.

II. Experimental

Ceramic samples 0.36BiScO$_3$-0.64PbTiO$_3$ were prepared using the solid-state reactions method. Initial composition was prepared from corresponding oxides, which stoichiometric mixtures were homogeneized and calcined at 973 K (7 h). The powdered BTO (compositions I and II) and BSO (compositions III and IV) single crystals were added to BSPT base composition in amounts of 5 w.% (compositions I and III) and 10 w.% (compositions II and IV). Homogenized mixtures were pressed into tablets and sintered at 1423 K, with additional intermediate annealing at 1223 and 1323 K without regrounding. The samples modified by the 1 w.% of LiF additives were sintered at 1473 K (1 h).

The phase content and crystal structure of the ceramics were studied by the X-ray diffraction method (DRON-3M, Cu-K_α radiation). The amount of admixture phase I_{adm} was estimated as $I_{adm} = (100 \text{ x } I_{adm})/(I_{adm} + I_{main})$, where I_{adm} and I_{main} – intensities of most intensive peaks of the corresponding phases.

Microstructure of samples was examined by the high-resolution scanning electron microscopy (SEM) method (JEOL JSM-7401F equipped with a JEOL JED-2300 energy dispersive X-ray spectrometer system). Dielectric properties of the ceramics were studied by

the dielectric spectroscopy method (Agilent 4284A, 1 V) in temperature range 300–1000 K and at frequencies 100 Hz-1 MHz.

III. Results and Discussion

According to the X-ray diffraction data, main perovskite structure phase is formed at temperatures of 973–1223 K. In samples I and III containing 5 w.% of BTO and SBO, respectively, small amounts ($I < 5\%$) of admixture phase Bi_2O_3 were observed. In samples III and IV amount of admixture phases increases up to $I \sim 10\%$. Besides, in samples III, approximately 5% of the BTO phase was observed. As the single-phase samples of undoped $0.36BiScO_3$-$0.64PbTiO_3$ were obtained only at higher temperatures ~1420 K, we concluded that the used additives intensified the phase formation process.

Dense single-phase ceramic samples were obtained at sintering temperatures T_s = 1423–1473 K (Fig. 1). After sintering at 1423 K, the X-ray diffraction patterns of all samples drastically changed. Intensity of the X-ray diffraction peaks with *hkl* (001) at 2θ ~23 grad increased, thus testifying the pronounce texture formation (Figs. 1a, 1b). Most pronounced texture was observed for samples II and IV containing ~10 w.% of BTO and BSO crystals. It should be noted that in samples I–III sintered at temperature 1473 K

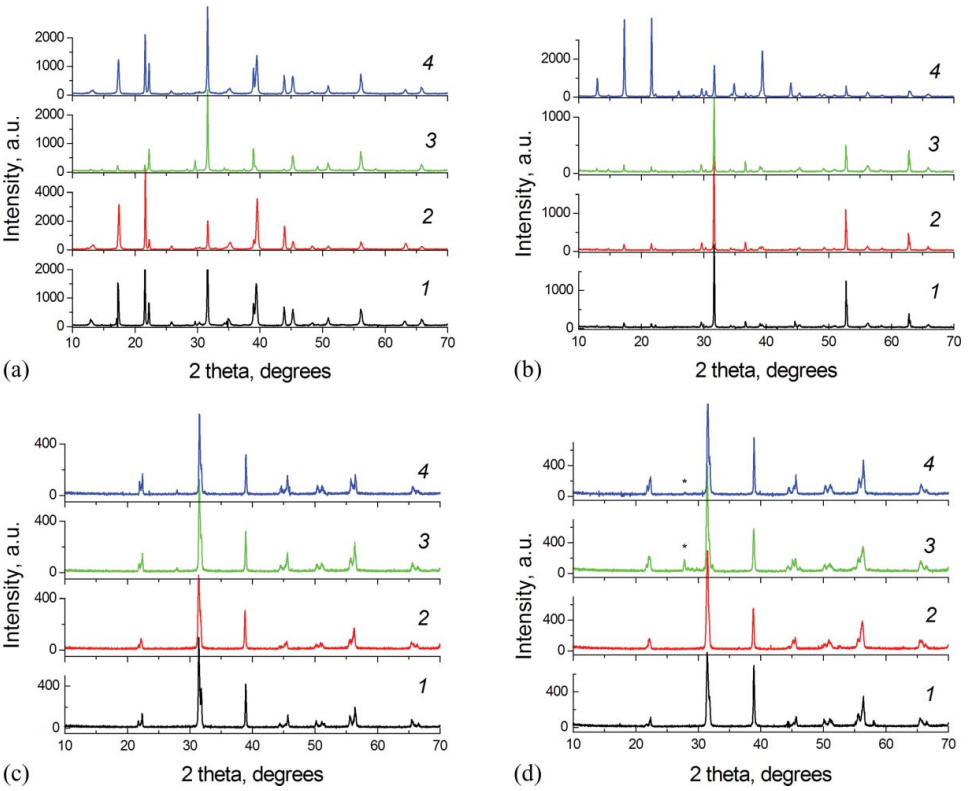

Figure 1. X-ray diffraction patterns of ceramic samples I–IV prepared at: (a) T_1 = 973 K; T_2 = 1223 K (1 h), T_3 = 1423 K (1 h); (b) T_1 = 973 K; T_2 = 1223 K (1 h), T_3 = 1473 K (1 h); compositions I–IV with 1 w.% LiF additive prepared at: (c) T_1 = 973 K; T_2 = 1223 K (1 h); (d) T_1 = 973 K; T_2 = 1473 K (1 h) (Figure available in color online).

the texture formation was not observed, probably because this temperature exceeded the temperature range of both the BTO and BSO phases existence. Beside the main perovskite phase, on the surface of all samples small amounts of the BTO or SBO phases were registered.

As it was expected, the addition of the low-melting fluoride LiF in amounts ∼1 w.% intensified the phase formation, and dense single-phase samples were obtained after sintering at 1473 K (Figs. 1c, 1d). The density of the ceramics was estimated using the results of shrinkage measurements. The shrinkage of initial, not doped, samples reached 12–14%, while increase in amounts of the BTO or BSO additives was followed by the increase in density of samples. The highest density was measured in samples doped by LiF, with the highest shrinkage values being reached in samples II and IV containing 10% of additives (∼21 and 16%, respectively).

The additives were found to influence the crystal structure of the solid solutions. The undoped $0.36BiScO_3$-$0.64PbTiO_3$ samples consisted of a mixture of tetragonal (major) and rhombohedral phases. The additives changed relative content of these phases, and the observed shift of the positions of the diffraction peaks pointed to slight changes in the lattice parameters of samples I–IV.

The microstructure of the doped ceramics was examined by the high-resolution SEM. As expected, orientation of grains is a specific feature of ceramics depending on sintering temperature and crystalline additives. In Fig. 2a surface of ceramics II containing 10 w.% of BTO sintered at 1473 K is shown. As it is clearly seen in Fig. 2a, thin well-faceted crystallites with submicron size (∼0.03–0.05) μm are arranged perpendicular to the surface in parallel to each other. On the contrary, ceramics IV containing 10 w.% of BSO crystallites, consist of rather large grains up to ∼ 10 μm in size (Figs. 2b, 2f). The samples modified with LiF have specific morphology, with oval-shaped grains, with several microns till 20 microns in size, with melted boundaries, indicative of liquid-phase sintering stimulated by the low-melted LiF additive (Figs. 2c, 2d, 2e, 2f). In ceramic samples I sintered at 1473 K effect of nanostructuring is revealed. Large grains consist of small nanometer size grains (20–50 nm), oriented along the special direction. The samples II doped with LiF and containing 10 w.% of BTO sintered at 1473 K are composed of practically equal grains with diameter 3–5 μm, dense packed that correlates with high values of shrinkage. Ceramics IV containing 10 w.% BSO besides large grains with 5 – 30 μm in diameter additionally contain regions with large number of submicron grains with grain size less than 1 μm (Fig. 2b).

It is also worth noting that the sintering process may be governed by different mechanisms. We assume that in the presence of the low-melting additives like Bi_2O_3, which occurs in the case of partial decomposition of BTO or BSO, and LiF, with melting points of 1098 and 1120 K, respectively, the main mechanism is liquid-phase sintering. However, the possibility of dissolving additives inside the parent solid solution should be taken into account. Mainly, bismuth or lead oxides losses during sintering are compensated by excess Bi_2O_3. In the case of incomplete compensation and/or partial Sr or Li cations substitution on the A site, the oxygen vacancies may occur in the perovskite anion sublattice. Certainly, the presence of additional titanium oxide effectively suppresses oxygen vacancy formation. Another important factor that should be taken into account is the variation in the relative content of the tetragonal and rhombohedral phases inside the morphotropic phase region that may give rise to mechanical stress, which would additionally influence the sintering process. Additionally, the presence of intergranular impurity phases leads to the formation of energy barriers, preventing further grain growth. These effects are illustrated by the difference in average grain size between the ceramics with compositions I–IV prepared at the same temperature (Fig. 2).

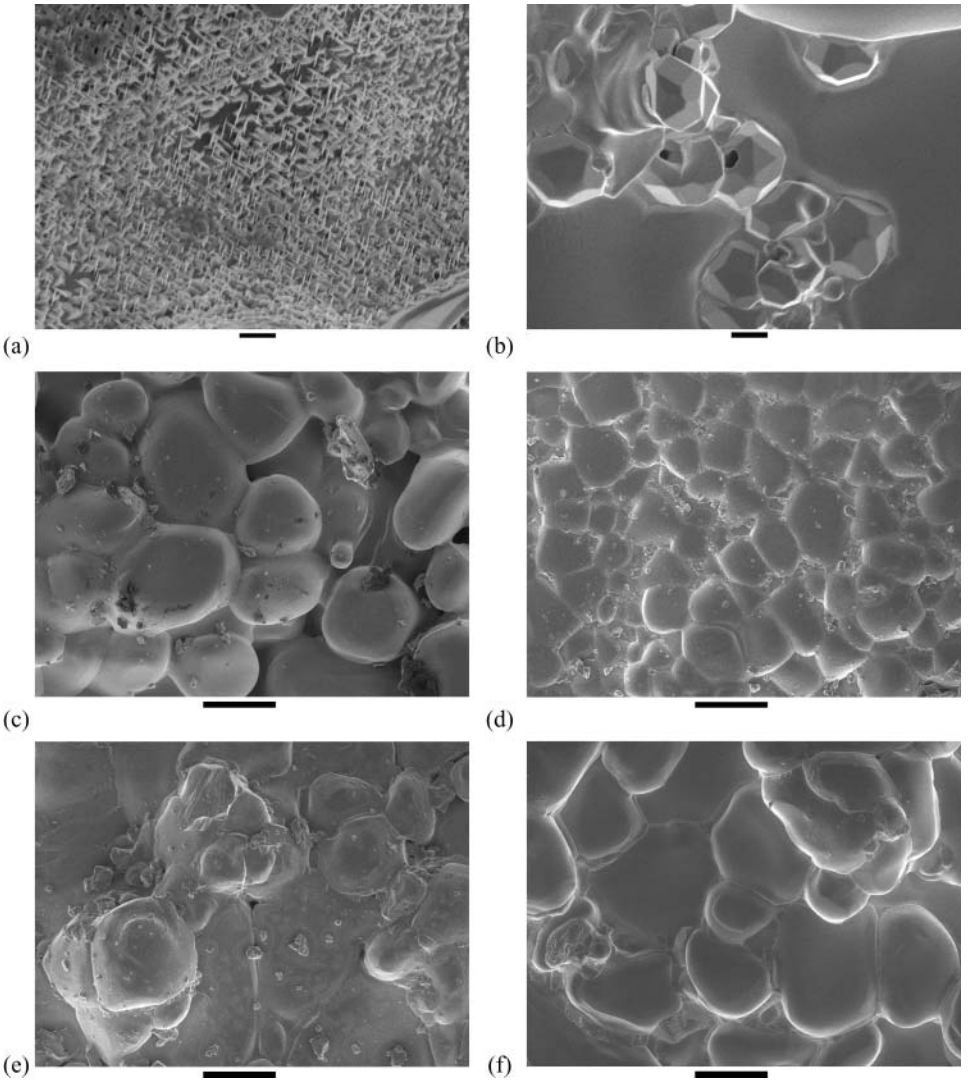

Figure 2. SEM images of surfaces of modified BSPT ceramics: (a) II (10 w.% BTO) prepared at $T_1 = 973$ K (7 h), $T_2 = 1323$ K (1 h), $T_3 = 1473$ K (1 h), $T_4 = 1073$ K (1 h); (b) IV (10 w.% BSO) + 1 w.% LiF; (c) I (5 w.% BTO) +1 w.% LiF; (d) II (10 w.% BTO) + 1 w.% LiF; (e) III (5 w.% BSO) + 1 w.% LiF; (f) IV (10 w.% BSO) + 1 w.% LiF prepared at $T_1 = 973$ K (7 h), $T_2 = 1473$ K (1 h). Black bars denote 1 μm (a, b) and 10 μm (c-f).

Dielectric measurements revealed the first order ferroelectric phase transitions, accompanied by sharp maxima in the temperature dependences of dielectric permittivity ε at 680, 674, 667, and 650 K, and minima in temperature dependences of dielectric losses, respectively, for samples I–IV (Fig. 3). Temperature positions of peaks in the $\varepsilon(t)$ curves for the samples I–IV slightly shifted to lower temperatures in accordance with the changes in lattice parameters reflecting the changes in T_C values caused by doping. The decrease in T_C values correlates with the shift of the composition to the rhombohedral phase region with lower T_C. Dielectric permittivity at room temperature increases starting from minimal value

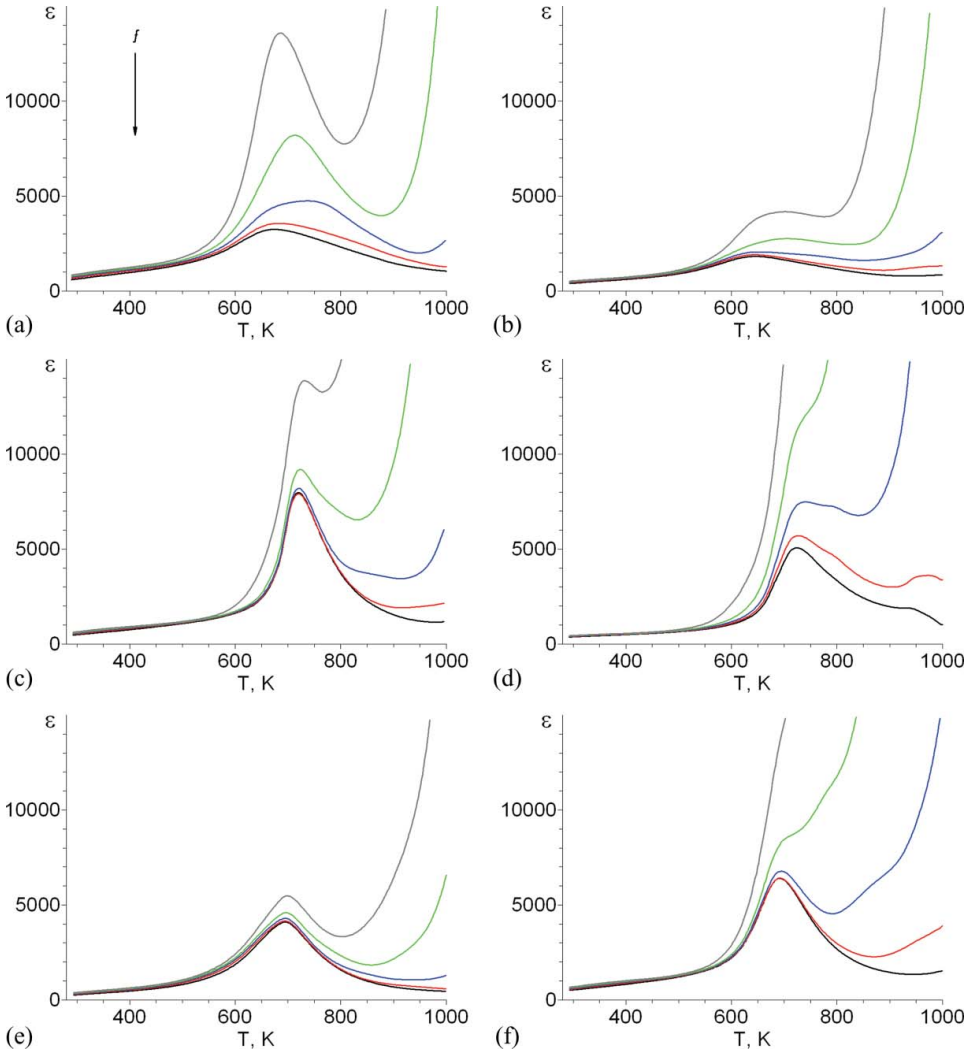

Figure 3. Dielectric permittivity versus temperature curves (cooling) of modified BSPT ceramics: (a) II (10 w.% BTO); (b) IV (10 w.% BSO) prepared at $T_1 = 973$ K (7 h), $T_2 = 1323$ K (1 h), $T_3 = 1473$ K (1 h), $T_4 = 1073$ K (1 h); (c) I (5 w.% BTO) + 1 w.% LiF; (d) II (5 w.% BSO) + 1 w.% LiF; (e) II (10 w.% BTO) + 1 w.% LiF; (f) IV (10 w.% BSO) + 1 w.% LiF prepared at $T_1 = 973$ K (7 h), $T_2 = 1473$ K (1 h). Measuring frequencies: 100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz.

$\sim$600 for samples I to maximal $\sim$1000 for samples III and IV. The dielectric permittivity at temperatures near the phase transition of samples I–IV behaves in the same manner. This tendency remains for samples I–IV additionally doped with LiF, though all ε values are a bit lower. The value of electroconductivity at room temperature varies from maximum value $\log\sigma \sim -6$ S/cm (samples I and II) to minimum value $\log\sigma \sim -6.5$ S/cm (samples III and IV). At $\sim$1000 K, the total conductivity value increases monotonous from $\log\sigma = -3.5$ S/cm for samples I to $\log\sigma = -3.1$ S/cm; -2.6 S/cm and -2.1 S/cm, respectively, for samples II–IV.

It should be noted that the dielectric relaxation effects, typical of undoped $0.36BiScO_3$ -$0.64PbTiO_3$ [11] were completely suppressed in the samples I, II, and IV but still were observed in the samples III. The observed high temperature relaxation anomalies in $\varepsilon(t)$ are most likely due to oxygen vacancies, which may appear due to the lead oxide loss during the high-temperature synthesis. The formation of dipoles relaxing in the *ac* electric field often accompanies the oxygen ion transport in the perovskite anion deficient ceramics [16–18].

IV. Conclusions

The structure, microstructure, and dielectric properties of the $0.36BiScO_3$-$0.64PbTiO_3$ ceramics modified by the powdered $Bi_4Ti_3O_{12}$ and $Bi_{0.75}Sr_{0.25}O_{1.36}$ single crystals and by the LiF additive were studied. The formation of textured layer on surfaces of ceramics was revealed. Dense, single-phase ceramic samples with submicron microstructure were obtained by LiF doping. The first order ferroelectric phase transitions were revealed at temperatures 650–680 K. The obtained results allowed us to conclude that the optimization of additives and heat treatment conditions of the BSPT-based perovskite ceramics ensured the fabrication of dense single-phase ceramics with a controlled grain size and suppressed the dielectric relaxation effect.

Acknowledgments

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