

Influence of the NaCl/LiF additives on structure, phase transitions and dielectric properties of BSPT ceramics

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Abstract. Influence of the NaCl/LiF additives (with ratio 60:40) on structure parameters, phase transitions and dielectric properties of solid solutions close to the Morphotropic Phase Boundary in the system $(1-x)\text{BiScO}_3 - x\text{PbTiO}_3$ ($x=0.635, 0.645$) has been studied. Using as initial the BSPT powders prepared from nitrate solutions, dense single phase ceramic samples doped by 5, 10 and 15 w. % of NaCl /LiF have been prepared at 1313 - 1323 K (2 h). Shift of the BSPT compositions phase content from initial mixtures of Rhombohedral and Tetragonal phases to the region of Tetragonal phase was stimulated by addition of the NaCl/LiF additives. This effect is accompanied by decrease of the unit cell volume, increase in the c/a ratio and increase in the Curie temperature value from 668 to 730 K for $x=0.635$ and from 672 to 724 K for $x=0.645$ in compositions doped by 10 w. % of the NaCl/LiF additive.

1. Introduction

Application of widely used ceramic materials based on the lead zirconate-titanate solid solutions is limited by temperatures determined by their depolarization temperature $\sim 0.5TC$ ($TC \sim 600$ K). This stimulated intensive study of bismuth containing oxides based on the perovskite structure $\text{BiMe}^{3+}\text{O}_3$ oxides with Curie temperatures $TC > 700$ K which have prospects for the development of materials for high temperature applications [1 - 4]. Regulation of functional properties is possible by substitutions of cations in the A- and B-sublattices, by modification of compositions using over stoichiometric additives, and by optimization of preparation conditions [4 -13]. Ceramics based on solid solutions from the Morphotropic Phase Boundary (MPB) in the system $(1-x) \text{BiScO}_3 - x\text{PbTiO}_3$ (BSPT) may be considered among the most studied as they revealed high TC values > 700 K and high piezoelectric coefficients. It is worth mentioning that investigation of compositions close to the MPB is widely used for the development of new effective piezoelectric materials. Usually, cation substitutions in the A and B-sublattices of perovskite structure are used to regulate functional characteristics. As for the BSPT- based compositions, in order to prevent Bi- and Pb-cation loss, the decrease of sintering temperature comprises one of the most important tasks.

Earlier, positive effect of over stoichiometric additives on the phase content, microstructure, and functional properties of the BSPT ceramics with $x = 0.60 - 0.66$ was proved [8, 11]. It was shown that addition of KCl with low melting temperature favored to increasing density of ceramics, allowed to regulate the unit cell parameters, microstructure and defined the improvement of functional properties of ceramics with $x = 0.64$ [11].

In this work, the BSPT ceramics with compositions from MPB with $x = 0.635$ (BSPT1) and $x=0.645$ (BSPT2) modified by complex additive NaCl/LiF (with molar ratio 60:40) have been studied.



This NaCl/LiF composition has low melting temperature ~ 950 K, so decrease of sintering temperature of ceramics may be expected. Moreover, this is important for the prevention of Bi and/or Pb oxides loss during the high temperature sintering, and favors to the stoichiometry preservation and functional properties optimization.

2. Experimental

Initial powders of the BSPT compositions with $x=0.635$ (BSPT1) and 0.645 (BSPT2) were prepared by the co-precipitation of nitrate solutions following the conventional procedure, and then calcined at 973 K (7 h) [9]. The NaCl /LiF additives, with molar ratios 60:40, were added in amounts 5, 10 and 15 w. % to the BSPT powders. The milled and pressed into tablets powders were sintered in air at 1323 K (2 h) and then slowly cooled to the room temperature.

Phase content and crystal structure parameters of the samples were studied at the room temperature using the X-ray diffraction method (DRON-3M, CuK α -beam). Spontaneous polarization of ceramics was estimated using the Second Harmonic Generation method (SHG, Nd:YAG laser, $\lambda=1.064$ μ m). Phase transitions and 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, pure perovskite structure samples were prepared at sintering temperature 1323 K (Figure 1). Figure 2 shows parts of the diffraction patterns displaying peaks with $h^2+k^2+l^2=4$. Increase in the content of tetragonal phase was observed with increasing x value of initial samples. Displacement of the X-Ray diffraction peaks to higher 2θ values indicates the unit cell volume decreasing with increasing amount of the NaCl/LiF additive. This picture demonstrates transition to the tetragonal structure in the samples containing 5 w. % of the NaCl/LiF additive as well. So, addition of 5 w. % of the NaCl/LiF additive to the initial compositions with $x=0.635$ (BSPT1) and with $x=0.645$ (BSPT2) leads to the transformation of the R phase (BSPT1) or mixture of T and R phases (BSPT2) to the tetragonal phases. This means that the NaCl/LiF additive stimulates displacement of the compositions to the region with tetragonal structure.

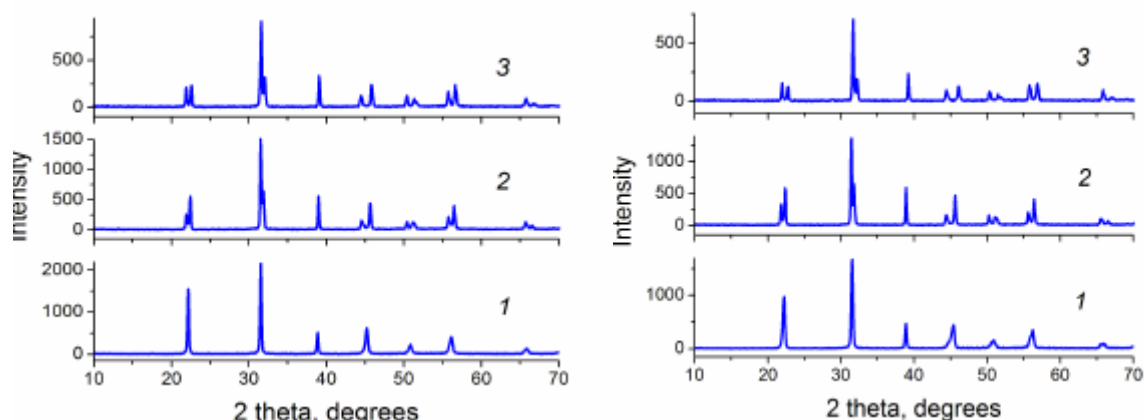


Figure 1. The X-Ray diffraction patterns of the samples $(1-x)\text{BiScO}_3 - x\text{PbTiO}_3$ with $x=0.635$ (a, curve 1), and with $x=0.645$ (b, curve 1) modified by the NaCl/LiF in amounts 5 w. % (curves 2), 10 w. % (curves 3), sintered at 1323 K (2 h)

The observed changes in the perovskite unit cell parameters (decrease of a , increase of c and increase of c/a ratio in compositions containing ≤ 10 w. % of additives) may be explained by the substitution of the Bi $^{3+}$ and/or Pb $^{2+}$ cations by the Li $^{+}$ and/or Na $^{+}$ cations in the A-positions of the perovskite lattice (Figure 3).

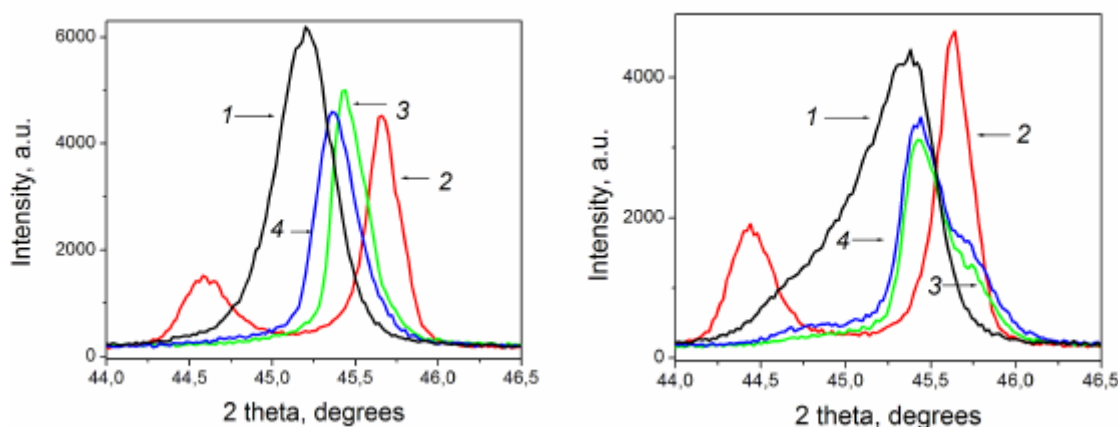


Figure 2. Parts of the X-Ray diffraction patterns of the samples BSPT1 (a, curve 1) and BSPT2 (b, curve 1) modified by the NaCl/LiF additives in amounts 5 w. % (curves 2), 10 w. % (curves 3) and 15w. % (curves 4)

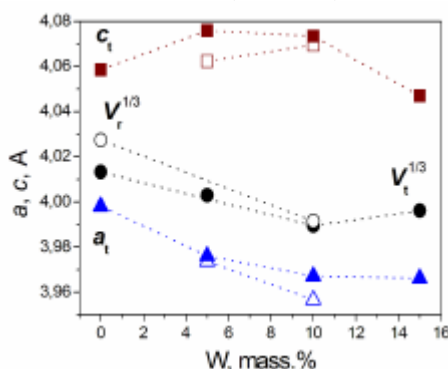


Figure 3. Concentration dependences of the perovskite unit cell parameters a , c and $V_{1/3}$ for modified samples BSPT1 (empty symbols) and BSPT2 (solid symbols)

Improvement of density of ceramics was stimulated by the NaCl/LiF additive introduction. The shrinkage of the samples increased from 15 to 17-19 %. This means that the additives intensified both processes of phase formation and sintering.

The relative intensity of the SHG signal $q = I_{2w}/I_{2w}(\text{SiO}_2)$ related to the spontaneous polarization P_s as $q \sim P_s^{0.5}$ increased from the 1200 (BSPT1) and 1500 (BSPT2) to the 1800 and 2200 values, respectively, with introduction of NaCl/LiF (5 w. %). This indicates to the enhancement of the P_s value with increasing amount of the additive.

Dielectric measurements revealed the 1st order sharp ferroelectric phase transitions marked by peaks in dielectric permittivity and corresponding minima in dielectric loss curves at temperatures $668 \div 730$ K (Figure 4). Small increase in the T_C value observed in modified ceramics correlates with the increase in relative content of the tetragonal phase and with changes in the c/a ratio proportional to the T_C value. The dielectric loss values of the doped samples are lower than dielectric loss values of the undoped samples at temperatures lower than 550 – 650 K, which are important for poling procedure.

However, the losses in the doped samples are higher than those of the undoped samples at temperatures higher than T_C . Evidently, such increase in dielectric loss at high temperatures is related to the effects of dielectric relaxation observed at high temperatures in the samples doped by the additives (Figure 5). It is necessary to mark that effects of dielectric relaxation may be related to the

presence of oxygen vacancies in the perovskite lattice [6 -8]. Increasing of the T_C value observed for the doped samples indicates to the presence of Li-cations in A- positions of the perovskite structure.

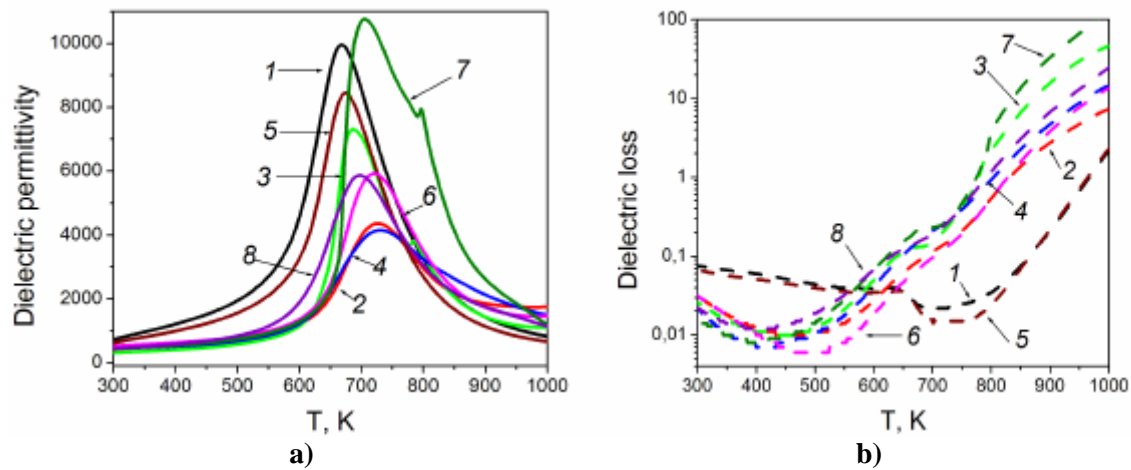
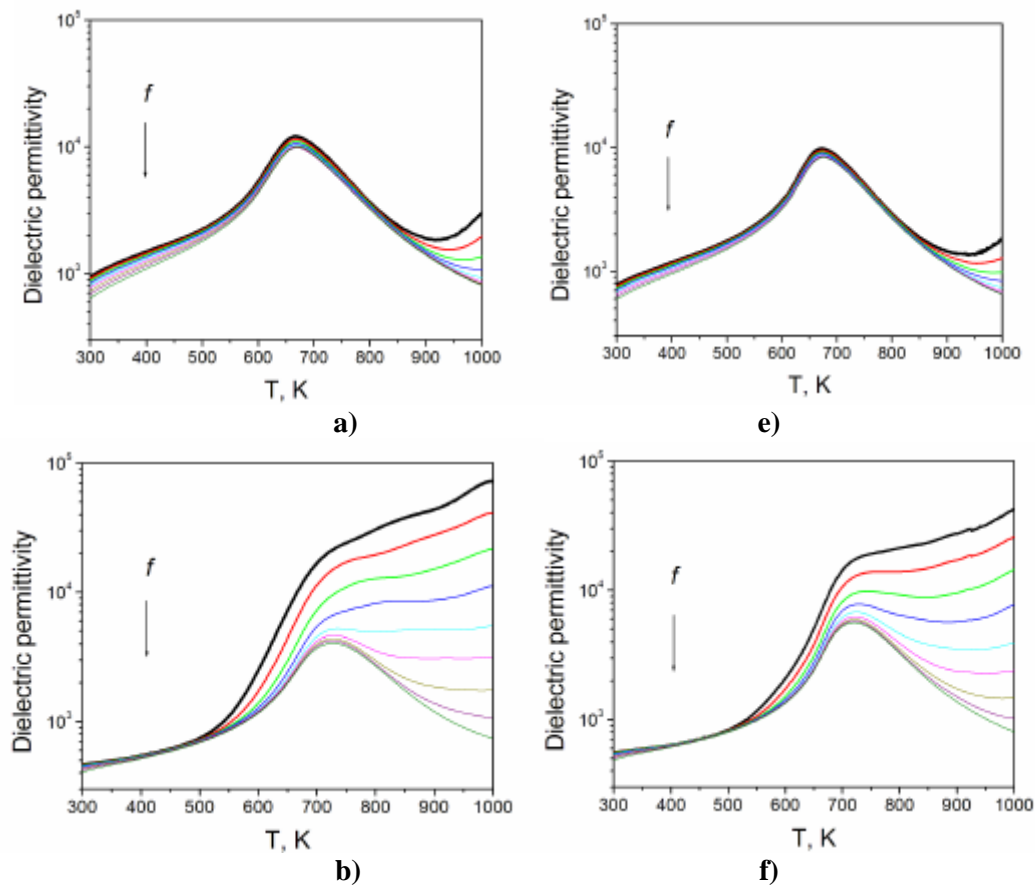


Figure 4. Temperature dependencies of dielectric permittivity (a) and dielectric loss (b) of ceramics BSPT1 and BSPT2 and ceramics modified by the NaCl/LiF additives (initial samples – curves 1, 5)



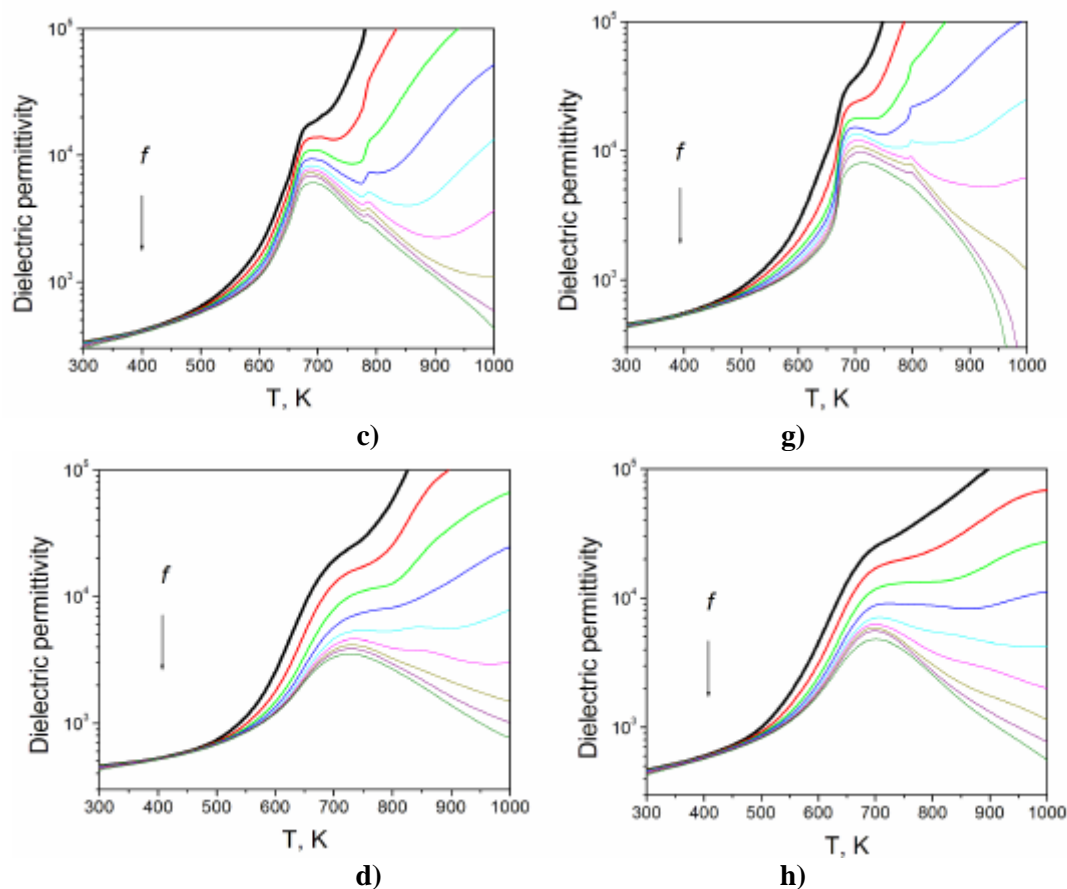


Figure 5. Temperature dependencies of dielectric permittivity (*a-h*) of the BSPT1 (*a-d*) and BSPT2 (*e-h*) ceramics modified by the NaCl/LiF additives (initial samples – *a, e*; samples containing 5 w. % – *b, f*; 10 w. % – *c, g*; 15 w. % – *d, h*). Measuring frequencies $f = 100, 300$ Hz; 1, 3, 10, 30, 100, 300 kHz, 1 MHz (cooling)

Thus, the BSPT samples doped by NaCl/LiF additives may be promising for the development of new compositions with improved piezoelectric properties.

4. Conclusions

The effects additives NaCl/LiF on the structure parameters, dielectric and ferroelectric properties of compositions from the morphotropic phase boundary in the system $(1-x)\text{BiScO}_3 - x\text{PbTiO}_3$ with $x=0.635$ and $x=0.645$ have been studied. Positive influence of NaCl/LiF additives on phase formation, sintering process and ferroelectric properties was proved. Small increase in the TC value observed in modified ceramics correlates well with the increase in relative content of tetragonal phase and the c/a ratio.

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