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Complex Impedance Analyses of $Ba_{1-x}Li_{0.5x}Bi_{0.5x}TiO_3$ Solid Solution PTCR Ceramics

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Abstract. Conditions for the formation of $(1-x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ $(0 \leq x \leq 0.6)$ solid solutions with positive temperature coefficient of resistance (PTCR) effect were studied. Solid solutions were prepared by solid state reaction technique. Samples were sintered under reducing atmosphere N_2/H_2 in the temperature range 1200–1450 °C with subsequent oxidation in air. The phase composition was investigated by X-ray powder diffraction method. It was found that samples of $(1-x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ $(0 \leq x \leq 0.6)$ solid solutions at room temperature exhibit perovskite structure. Unit cell parameters of unstable at room temperature compound $Li_{0.5}Bi_{0.5}TiO_3$ were determined by extrapolation of concentration dependence of the unit cell parameters in the $(1-x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ system. It was shown that minimum value of resistivity ρ_{min} rises with increase in x value. Complex impedance method shows that ceramic grains of $(1-x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ materials consist of three areas with different electrical properties. Boundary and outerlayer region of grains make the main contribution to the PTCR effect in lithium-containing solid solutions. It was shown that magnitude of the potential barrier decreases with increasing x.

Introduction

Donor doped barium titanate exhibits positive temperature coefficient of resistance (PTCR) effect near the phase transition from ferroelectric to paraelectric state temperature (120°C) [1]. The introduction of bismuth Bi^{3+} and sodium Na^+ or potassium K^+ ions to barium sublattice leads to a shift of the Curie temperature to higher values and decrease in formation and sintering temperatures of solid solutions [2-4]. Properties of $(1-x)BaTiO_3-xM_{0.5}Bi_{0.5}TiO_3$ (M=Na, K) solid solutions are well studied in the literature, whereas there is no information about $(1-x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions and individual compound $Li_{0.5}Bi_{0.5}TiO_3$. Despite the lack of lithium bismuth titanate existence evidence this titanate is successfully used as a component of solid solutions to improve the piezoceramic properties in the system $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}]TiO_3$ [5]. Authors of [6] showed that addition of 2 mol % of lithium-bismuth titanate $Li_{0.5}Bi_{0.5}TiO_3$ to $(Na_{0.5}K_{0.5})NbO_3$ led to an increase in grain size of ceramics, density and decrease in porosity. This dependence is explained by the authors of [6] by increasing of liquid phase amount during sintering due to the lower melting temperature of Li_2CO_3 compared to potassium and sodium carbonates. It was found that increase in the bismuth lithium titanate content leads to a decrease in the Curie temperature in the system $(Na_{0.5}K_{0.5})NbO_3$. In contrast to these data, the authors of [7] showed that the introduction of lithium ions to the sodium-potassium sublattice leads to an increase in the Curie temperature in the system $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}]TiO_3$. It was shown that increasing lithium-bismuth titanate concentration leads to an increase in resistance and Curie temperature in Nb-doped PTCR solid solutions based on $Ba_{1-x}Bi_{0.5x}Li_{0.5x}Ti_{1-y}Nb_yO_3$ from 120ºC to 150ºC in the range of $0 \leq x \leq 0.03$ [8]. As was shown in [9], incorporation of Li^+ ions leads to a significant reduction in the sintering temperature and promotes densification of ceramics of the system $Bi_{0.5}Na_{0.5}TiO_3$–$Bi_{0.5}K_{0.5}TiO_3$–$Bi_{0.5}Li_{0.5}TiO_3$. According to [9] increase in lithium concentration leads to a decrease in ceramic grain size. From literature data one can assume that the introduction of lithium-bismuth titanate decreases sintering temperature and improves electrical properties of pure barium titanate due to the presence of liquid lithium- and bismuth-containing phase at the boundaries between grains.

The aim of this work is synthesis of solid solutions $(1\text{-}x)BaTiO_3$–$xLi_{0.5}Bi_{0.5}TiO_3$ and study of the effect of lithium-bismuth titanate on their crystal structure, microstructure and electrical properties.

Experimental Procedures

Solid solutions $(1\text{-x})BaTiO_3\text{-x}Li_{0.5}Bi_{0.5}TiO_3$ ($0 \le x \le 0.6$) were prepared by solid state reaction technique. Li_2CO_3, $BaCO_3$, Bi_2O_3 and TiO_2 were used as the starting reagents. The powders were mixed for 4 hours in the presence of ethanol in a ball mill. Powders dried at 100–120 ºC were sieved through a nylon sieve. Samples were synthesized in the temperature range 1000–1100°C for 4 hours. The powders of solid solutions were pressed using a 5 % polyvinyl alcohol into tablets (10 mm in diameter and 2 mm in thickness) at a pressure of 150 MPa. Tablets were sintered in the gas mixture N_2/H_2 (99.5:0.5) at 1200–1450ºC with subsequent oxidation in air. The phases were characterized by X-ray powder diffractometry (XRPD) using DRON-4-07 diffractometer (Cu $K\alpha$-radiation; 40 kV, 20 mA). The lattice parameters were refined by the Rietveld fullprofile analysis. XRPD patterns were collected in the range $2\theta = 10–150°$ in step-scan mode with a step size of $\Delta 2\theta = 0.02°$ and a counting time of 6 s per data point. As external standards, we used SiO_2 (for 2θ) and Al_2O_3 NIST SRM1976 (for the intensity).

The temperature dependence of the electrical resistance of the samples was measured in the temperature range 20°C to 400°C. Impedance data were obtained using a 1260 Impedance / Gain-phase Analyzer (Solartron Analytical) in the range 10 Hz to 1 MHz. Microstructure of ceramic samples was analyzed using scanning electron microscopy (Jeol JSM 6510) and transmission electron microscopy (JEM-2100).

Results and Discussion

X-ray diffraction analysis showed that samples of $(1\text{-}x)BaTiO_3$–$xLi_{0.5}Bi_{0.5}TiO_3$ ($0 \le x \le 0.6$) solid solutions fired at temperatures above 1100°C are single phases (Fig. 1).

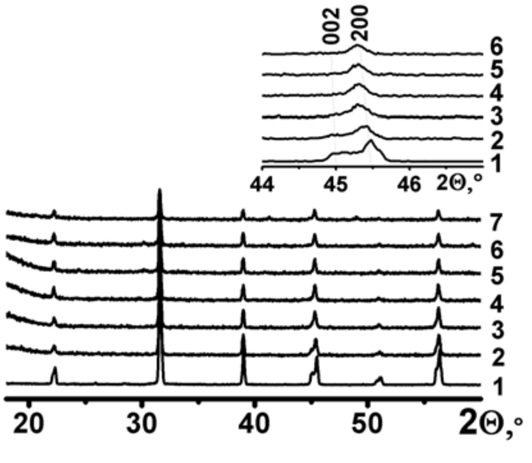

Fig. 1. XRPD patterns for $(1\text{-}x)BaTiO_3$–$xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions, $x = 0$ (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6), 0.6 (7). Insert: Change in 200 and 002 peak positions.

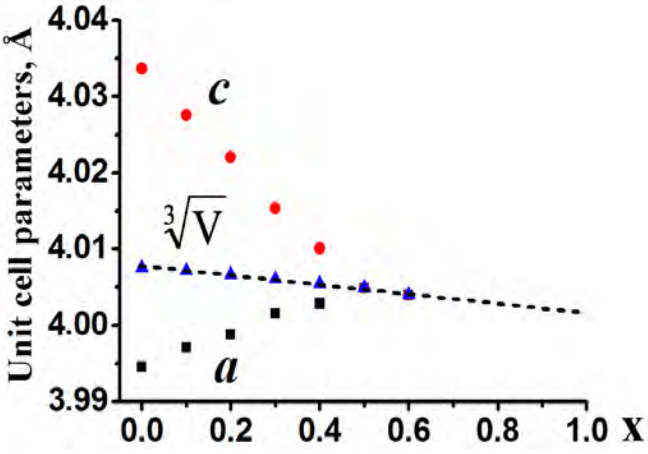

Fig. 2. The dependence of *a, c* and average unit cell parameter of $(1\text{-}x)BaTiO_3$–$xLi_{0.5}Bi_{0.5}TiO_3$ on x.

With increasing lithium-bismuth titanate concentration, double peak on X-ray diffractograms corresponding to 200 and 002 planes at $\Delta 2\theta = 44\text{-}46$ ° turns into a single peak, corresponding to 002 plane (Insert in Fig.1). This fact can be explained by a reduction in the tetragonal distortion and formation of cubic structure. At $x > 0.6$, in $(1\text{-}x)BaTiO_3\text{-}xLi_{0.5}Bi_{0.5}TiO_3$ system additional phases $Bi_4Ti_3O_{12}$ $Bi_2Ti_2O_7$ and $Li_4Ti_5O_{12}$ are formed. Thus, it can be concluded that the solid solution system $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ exists in limited concentration range $0 \le x \le 0.6$.

The crystal structure and the unit cell parameters of $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions were studied using fullprofile Rietveld analysis. It was shown that the structure of $(1\text{-}x)BaTiO_3\text{-}xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions for $0 \le x < 0.5$ is tetragonal, whereas at higher concentrations of lithium-bismuth titanate ($0.5 \le x \le 0.6$) it becomes cubic (Fig. 2). Change in the unit cell volume obeys the Vegard law. With increase in x the unit cell volume decreases due to lower values of lithium ionic radius compared with barium one.

Despite the fact that individual compound $Li_{0.5}Bi_{0.5}TiO_3$ is unstable at the room temperature it can be stabilized by formation of solid solutions $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ due to the partial cation substitution in barium sublattice. In order to determine the parameters of the unit cell, $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solution with $x = 1$ linear extrapolation of the concentration dependence of parameter V was used. Taking into account that the nature of the error in the determination of the straight line parameters is only instrumental and random it was found that the cubic lattice parameter for individual $Li_{0.5}Bi_{0.5}TiO_3$ is 4.0019(8) Å.

It was shown that the addition of lithium-bismuth titanate leads to a significant reduction in the sintering temperature of $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions. For instance, sintering temperature in $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions at $x = 0$ and 0.2 is 1450 ºC and 1260 ºC, respectively. Decrease in sintering temperature of Li-containing ceramics can be explained by the presence of a small amount of the liquid phase at the grain boundaries, evidences of existence of liquid phase may be observed in Fig. 3.

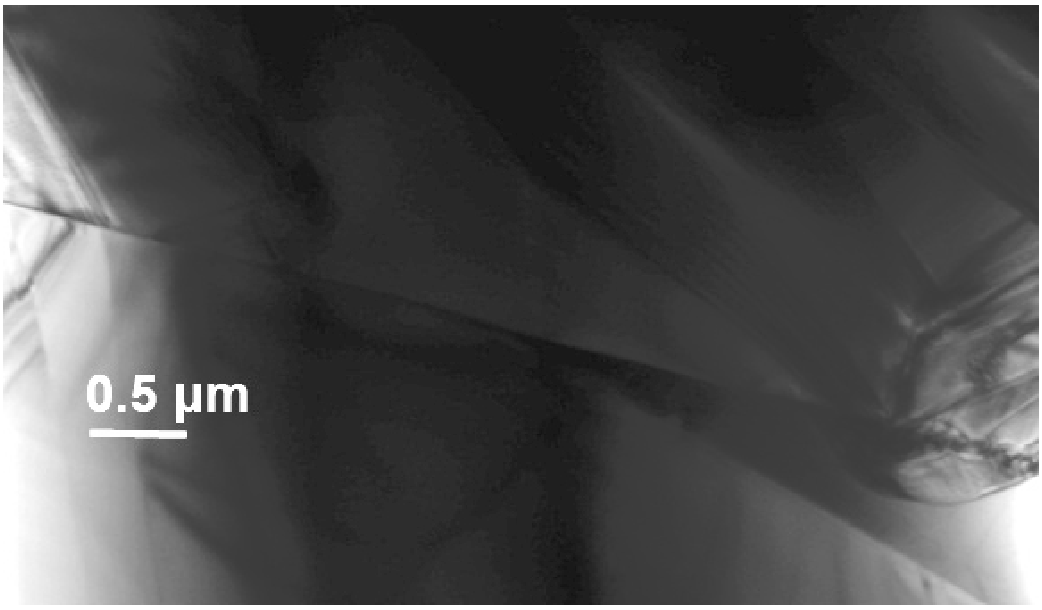

Fig. 3. TEM image of ceramic grain boundary in $(1\text{-}x)BaTiO_3\text{-}xLi_{0.5}Bi_{0.5}TiO_3$, $x = 0.2$.

With increase in x in the range of $0 \le x \le 0.6$ the grain size of $(1\text{-}x)BaTiO_3\text{-}xLi_{0.5}Bi_{0.5}TiO_3$ ceramic decreases (Fig. 4). Energy dispersive X-ray analysis showed that ceramic grain boundaries were enriched with bismuth compared to core. Therefore, the decrease in average grain size of ceramics with increase in x (Fig. 4) can be explained by bismuth segregation at grain boundaries during sintering of ceramics, which leads to a decrease in the rate of mass transfer during sintering and formation of smaller grains.

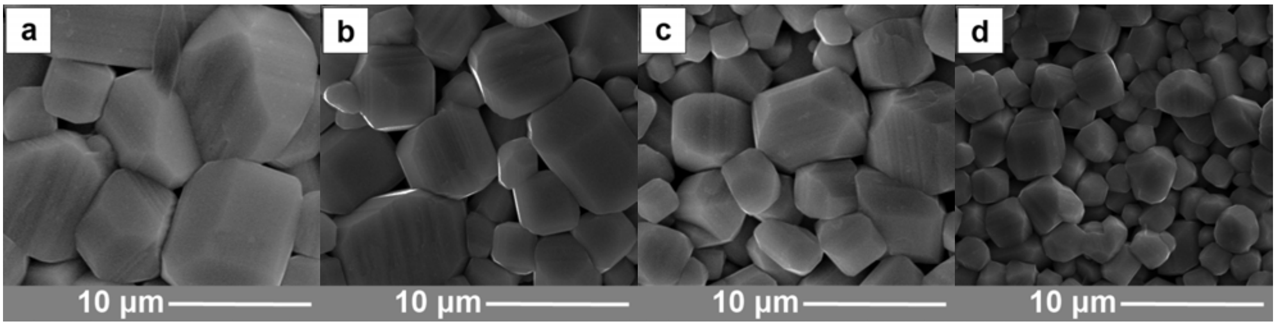

Fig. 4. SEM of (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ solid solutions, x = 0 (a), 0.10 (b) 0.15 (c) 0.20 (d).

It was shown that increase in lithium-bismuth titanate concentration in (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ system leads to a decrease in the maximum value of dielectric constant, whereas Curie temperature is constant for all x values (T_C=120 ºC). This confirms that the unstable cubic compound $Li_{0.5}Bi_{0.5}TiO_3$ is not ferroelectric.

The temperature dependence of the resistivity for (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ solid solutions is presented in Fig. 5. It is shown that lithium-containing solid solutions exhibit PTCR effect in the temperature range above 120 ºC. As can be seen the maximum resistance value ρ_{max} of pure barium titanate (Fig.5, curve 1) is much lower than that of lithium-containing materials (Fig.5, curves 2-4). With increase in lithium-bismuth titanate concentration, the temperature range of PTCR effect increases and the maximum resistance value decreases. In addition, with increasing x in solid solutions, minimal resistance ρ_{min} increases, which may be associated with decrease in average grain size (Fig.4).

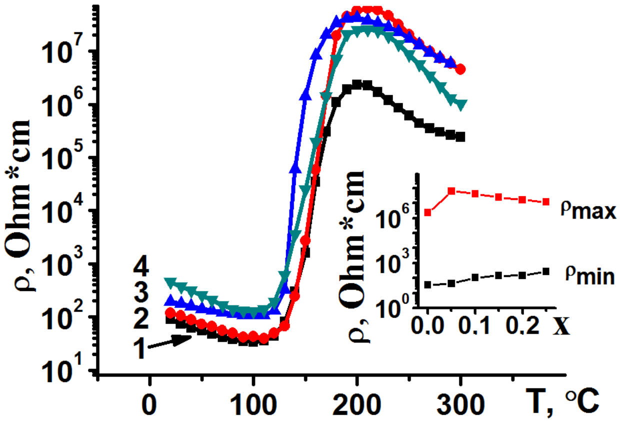

Fig. 5. Temperature dependence of resistivity for ceramic samples of (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$, x = 0 (1); 0.05 (2); 0.1 (3); 0.15 (4). Insert: Plots of the maximum ρ_{max} and minimum ρ_{min} values of resistivity in (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ as a function of x.

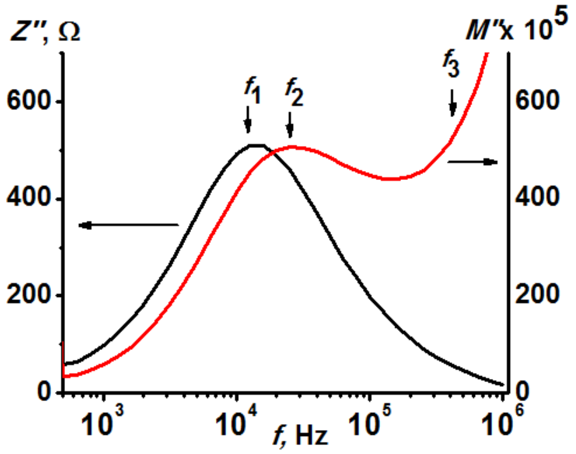

Fig. 6. Frequency dependence of Z'' and M'' for ceramic sample of $Ba_{0.9}Li_{0.05}Bi_{0.05}TiO_3$.

Complex impedance method was used to distinguish different areas of ceramic grain which differ in electrical properties. Frequency dependence of the imaginary parts of the impedance Z'' and the electric modulus M'' is presented in Fig. 6. As shown in [1], peaks in Fig. 6 indicate the presence of three electrically heterogeneous regions in ceramic grains: grain boundary, outerlayer region and core. Therefore, the data can be analyzed in terms of an equivalent circuit consisting of three RC elements connected in series, which represent bulk, outerlayer and grain-boundary components.

Fig. 7 shows complex impedance plots Z" = *f* (Z') for $Ba_{0.7}Li_{0.15}Bi_{0.15}TiO_3$ samples measured at different temperatures in an atmosphere of dry air. With increasing temperature above the Curie point resistance of material increases, this is associated with an increase in the potential barrier at grain boundaries at the transition from ferroelectric to paraelectric phase.

In order to determine electrical resistances of different areas in grains equivalent circuit of three series-connected RC-elements was used. The analysis confirmed that the ceramic grains in lithium-containing solid solutions consist of three different regions (Fig. 8) whereas in pure barium titanate only two areas were established [10]: the dielectric grain boundary and semiconducting core.

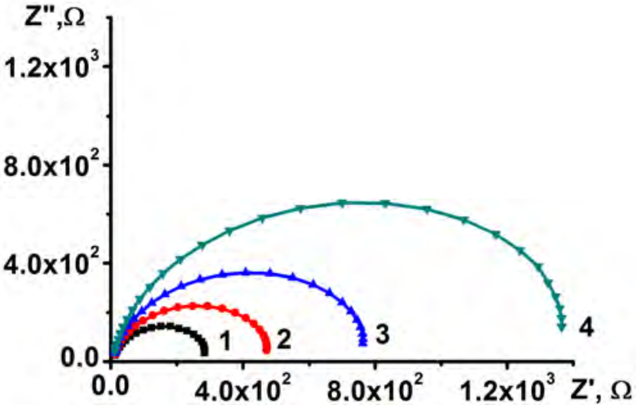

Fig. 7. Diagrams of complex impedance for $Ba_{0.7}Li_{0.15}Bi_{0.15}TiO_3$ solid solution at 150 (1), 160 (2), 170 (3) and 180 °C (4).

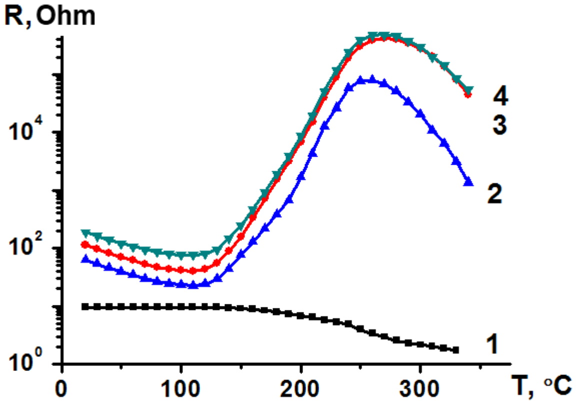

Fig. 8. Temperature dependence of resistance of core (1) outerlayer (2), grain boundary (3) and overall resistance (4) for $Ba_{0.7}Li_{0.15}Bi_{0.15}TiO_3$ ceramic sample.

It was shown that the grain boundary and outerlayer regions in lithium-containing samples of (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ make the main contribution to the PTCR effect in solid solutions. Thus it can be concluded that increase in the maximum resistance ρ_{max} in lithium-containing materials, compared with samples of pure barium titanate, is due to the presence of an additional dielectric outerlayer region in lithium-containing samples.

Using methodology described in [11] the value of potential barrier height (φ_0) at grain boundaries for solid solutions (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$ was calculated. With increasing x, the value of the potential barrier height decreases (Fig. 9).

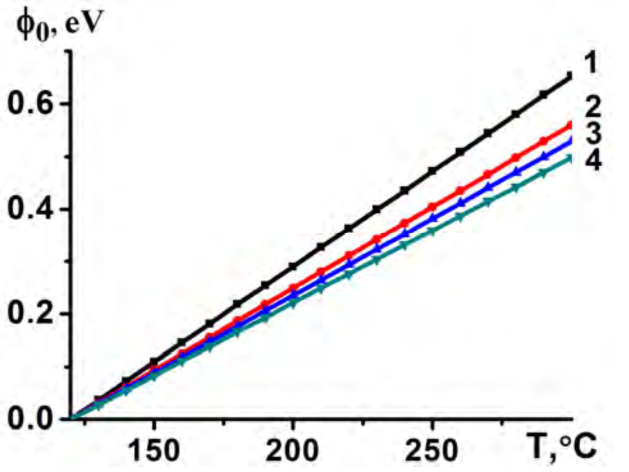

Fig. 9. Temperature dependence of potential barrier height for ceramics (1-x)$BaTiO_3$-$x$$Li_{0.5}Bi_{0.5}TiO_3$, x = 0.06 (1) 0.1 (2) 0.2 (3) 0.3 (4).

Increase in potential barrier height may cause reduction in the maximum resistance value of lithium-containing materials (Fig. 5). Reduction in the potential barrier may be associated with an increase in bismuth-rich liquid phase at the grain boundaries.

Conclusion

Using X-ray diffraction analysis it was shown that solid solutions $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ $(0 \leq x \leq 0.6)$ are formed at temperatures above 1100°C. It was found that the structure of the solid solutions in $(1\text{-}x)BaTiO_3\text{-}xLi_{0.5}Bi_{0.5}TiO_3$ system for $0 \leq x \leq 0.4$ is tetragonal, whereas at higher concentrations of lithium-bismuth titanate $(0.4 \leq x \leq 0.6)$ it becomes cubic. It was found that unstable at room temperature compound $Li_{0.5}Bi_{0.5}TiO_3$ is not ferroelectric. It was shown that lithium-containing solid solutions exhibit PTCR effect in the temperature range above 120˚C. It was established that grain boundary and outerlayer regions make the main contribution to the PTCR effect of $(1\text{-}x)BaTiO_3–xLi_{0.5}Bi_{0.5}TiO_3$ solid solutions.

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