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Effect of Reoxidation Temperature on Electrophysical Properties of High-T_C Barium Titanate-Based PTCR Ceramics

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Abstract. Ceramic samples of (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ system were prepared by sintering in reducing atmosphere of N_2/H_2 and were subsequently reoxidized in air. The influence of reoxidation temperature firing on the PTCR effect of (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ ceramics was investigated. The effect of $Na_{0.5}Bi_{0.5}TiO_3$ concentration on resistivity and microstructure of the reoxidized samples was investigated by means of complex impedance spectroscopy and scanning electron microscopy. It has been found that the grain size decreases with the increase in $Na_{0.5}Bi_{0.5}TiO_3$ content. The values of minimum ρ_{min} and maximum ρ_{max} resistivities of the samples were observed to increase with the increase in reoxidation temperature in the 600 – 1000°C temperature range. It was shown that with increasing in reoxidation temperature of (1-x)$BaTiO_3$-x$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions, potential barrier at grain boundaries increases.

Introduction

Ceramics with a positive temperature coefficient of resistance (PTCR) based on ferroelectric $BaTiO_3$ are important functional materials that are widely used in electronic devices, thermal sensors, self-regulating heaters, piezoelectric transducers, etc [D1D]. At room temperature, $BaTiO_3$ adopts a tetragonal perovskite structure and is a ferroelectric with high permittivity. It transforms to the cubic, paraelectric phase at the Curie temperature (T_C=120°C). In order to increase T_C of materials based on $BaTiO_3$, the small amount of $PbTiO_3$ is usually added. But lead-containing materials are characterized by high toxicity [D2D]; so it is important to synthesize lead-free materials with high T_C. One of the promising lead-free system is (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ [D3D]. The samples of (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ are electrically insulating, but the electrical resistance can be controlled effectively by sintering in reducing atmosphere with subsequent reoxidation in air. Heywang model have been suggested to explain the anomalous increase in the resistivity in PTCR-ceramics [D4D]. This model is based on the presence of depletion layers consisting of two-dimensional surface acceptor states on grain boundary, where absorbed oxygen atoms are present as impurities. These surface acceptor states seize conduction electrons to form potential barrier. The value of minimum resistance is heavily sensitive to the degree of reoxidation; therefore, the research of the influence of a reoxidation temperature on the PTCR effect is very important.

In this study, (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ ceramics sintered in N_2/H_2 and reoxidized in air were investigated. The changes of the PTCR effect and intergranular barrier height at the 600 – 1000°C temperature range were studied.

Experimental procedures

Lead-free materials (1-x)$BaTiO_3$-x$Na_{0.5}Bi_{0.5}TiO_3$ were synthesized by solid state reaction technique using extra-pure (purity 99.99%) Na_2CO_3, $BaCO_3$, Bi_2O_3 and TiO_2 as starting reagents. The powders were mixed and ball-milled with ethyl alcohol in an agate mortar for 4 h. After evaporating the residual water, the mixtures were dried at 100-120 ºC, passed through a capron sieve, and then calcined in air at 950-1000°C for 2-4 h. The resultant powders were ground with the addition of 5% polyvinyl alcohol, pressed into pellets (10 mm in diameter and 2 mm in thickness) by uniaxial pressing at 150 MPa. The pellets were sintered in the temperature range of 1150-1300 °C for 2h in a reducing atmosphere of N_2/H_2 (99.5:0.5). Subsequently, the samples were reoxidized in air for 30 minutes in the temperature range 600°C – 1000°C with subsequent deposition of aluminum electrodes on the polished surfaces of the samples. The phases were characterized by X-ray powder diffractometry (XRPD) using DRON-4-07 diffractometer (Cu Kα radiation; 40 kV, 20 mA). The structure parameters were refined by the Rietveld fullprofile analysis. XRPD patterns were collected in the range 2θ = 10-150° in step-scan mode with a step size of $\Delta 2\theta$ = 0.02° and a counting time of 10 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 at cooling using a 1260 Impedance / Gain-phase Analyzer (Solartron Analytical) in the range 10 Hz to 1 MHz. The microstructures of specimens were observed by field emission scanning electron microscopy REM 101 SEM (Sumy Electron Optics, Ukraine).

Results and discussion

The XRPD results showed that a single phase (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions are formed at temperatures higher than 1000°C. The parameters of the crystal structure of the ceramic samples were determined using Rietveld full-profile X-ray analysis (Fig. 1).

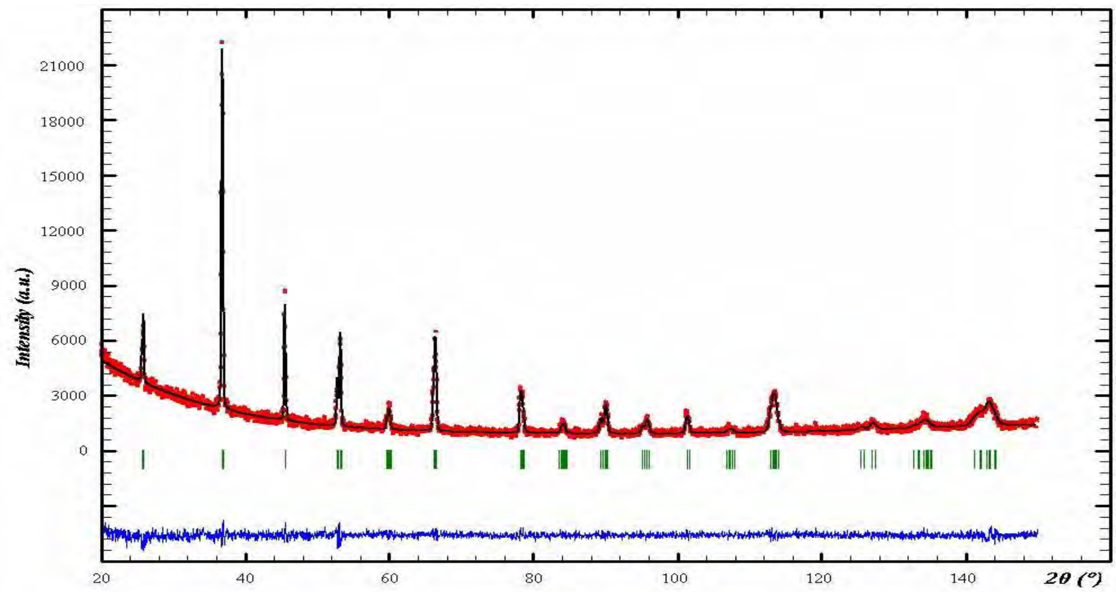

Fig. 1. Experimental (dots) and calculated (line) room-temperature powder X-ray diffraction patterns of (1-x)$BaTiO_3$-$x$$Na_{0.5}Bi_{0.5}TiO_3$ ceramics: x=0.1. Bars indicate the peak positions.

The a and c parameters (Fig. 2) and the unit cell volume decrease with increasing in x. Decrease in unit cell volume with increasing x is due to large difference between the value of the ionic radius of bismuth (1.17 Å), sodium (1.39 Å) and that of barium (1.42 Å).

Fig.3 shows SEM photographs of (1-x)$BaTiO_3$–x$Na_{0.5}Bi_{0.5}TiO_3$ samples. The grain size of ceramics in (1-x)$BaTiO_3$-$x$$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions decreases from 4.2 to 1 μm for x = 0.1 and 0.4 respectively. This may be due to the segregation of Na^+ ions near the grain boundaries and reduction of their mobility on densification. This retards the mass transport and, as a result, smaller grains are formed [5]. Pores in the porous ceramics cause easy oxygen adsorption at the grain boundaries so that they are also more favorable to form surface acceptor states, compared with ordinary dense ones [6].

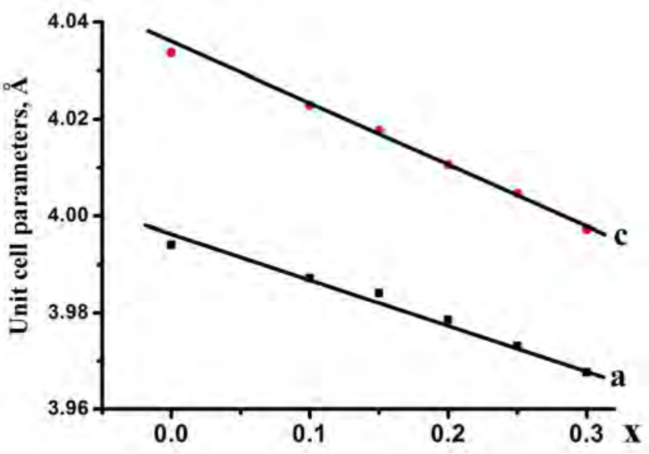

Fig.2. The dependence of the *a* and *c* parameters on x for $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ solid solutions.

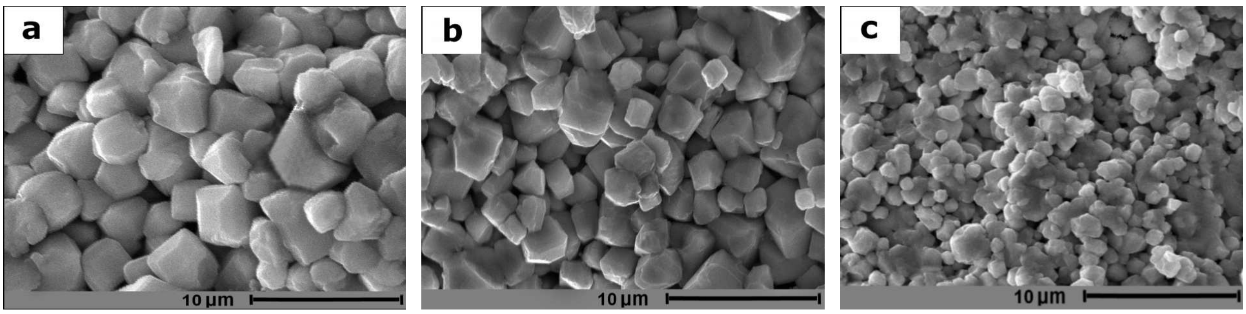

Fig. 1. Micrographs of $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ solid solutions: (a) $x = 0.10$; (b) $x = 0.20$; (c) $x = 0.30$.

Figure 4 illustrates the dependence of reoxidation temperature on the PTCR behavior of $Ba_{0.9}Na_{0.05}Bi_{0.05}TiO_3$ ceramics. Reduced samples were easily reoxidized in the air. The acceptor ions of oxygen appeared on grain boundary surface during reoxidizing process, which led to the PTCR effect. It can be noticed that the maximum ρ_{max} and minimum ρ_{min} values of resistivity increases monotonically with the reoxidation temperature. It is shown that the minimum value of ρ_{max} / ρ_{min} ratio were observed at the 600°C reoxidation temperature. It can be seen that an optimal ρ_{max}/ρ_{min} ratio was obtained at the reoxidation temperature 700 ºC. An improvement in the PTCR effect with an increase in reoxidation temperature was attributed to an increase in the density of the surface acceptor state.

The temperature dependence of resistivity for $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ solid solutions reoxidized at 700 ºC is shown in Fig.5. It was found that the resistivity increases with the increase in x. The values of ρ_{max} and ρ_{min} increase with increase in *x* (inset in Fig. 4). As is known, the total number of insulating grain boundaries increases with decrease in the grain size of PTCR ceramics. This causes an increase in the total resistance of the material [7]. Therefore, the increase in the value of ρ_{min} with increase in *x* (Fig. 4) for $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ solid solutions may be attributed to a decrease in ceramic's grain size (Fig. 3).

In order to investigate the role of oxygen at the grain boundaries, the change in potential barrier of $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ samples reoxidized at various temperatures was studied. The changes in potential barrier with increase in *x* were calculated for PTCR region using Heywang model [8,9]. The intergranular potential barrier height increases with increase in *x* (Fig. 6), and this accounts for the behavior of ρ_{max} (Fig.5).

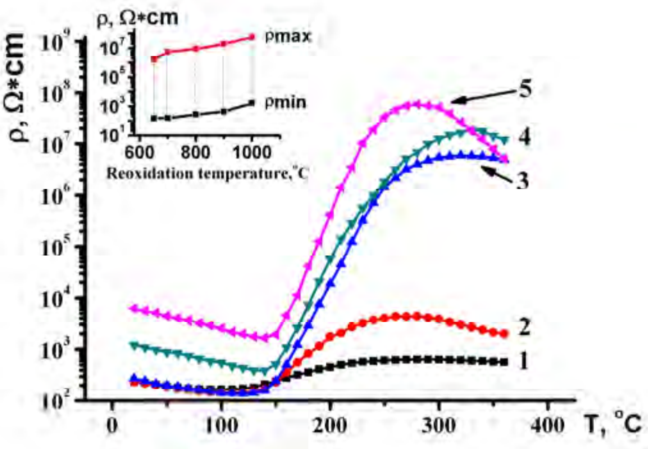

Fig. 4. Temperature dependence of resistivity for $Ba_{0.9}Na_{0.05}Bi_{0.05}TiO_3$ solid solutions reoxidized at 600 ºC (1); 650 ºC(2); 700 ºC(3); 900 ºC(4) and 1000 ºC(5). Inset: Plots of the maximum ρ_{max} and minimum ρ_{min} values of resistivity in $Ba_{0.9}Na_{0.05}Bi_{0.05}TiO_3$ solid solutions as a function of reoxidation temperature.

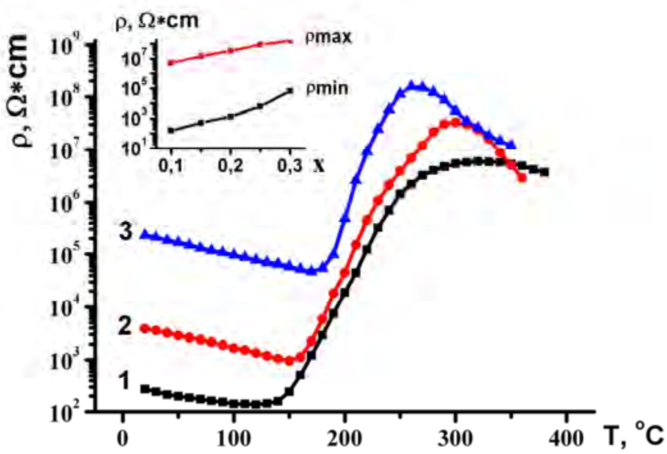

Fig. 5. Temperature dependence of resistivity of (1-x)$BaTiO_3$-$x$$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions, x = 0.1 (1) 0.2 (2), 0.3 (3). Inset: Plots of the maximum ρ_{max} and minimum ρ_{min} values of resistivity in (1-x)$BaTiO_3$-$x$$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions as a function of x.

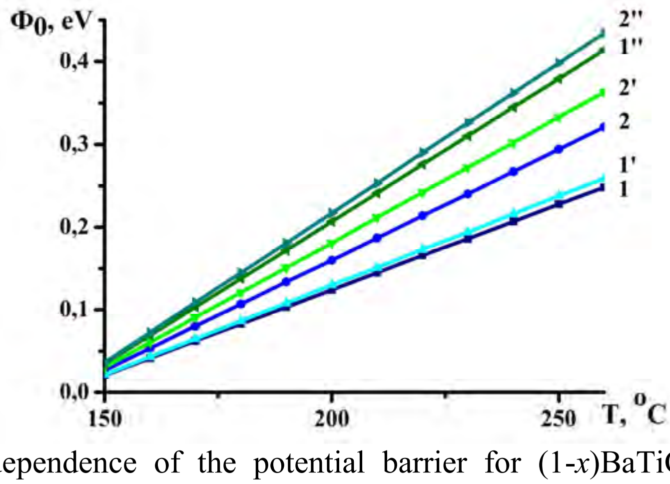

Fig. 6. Temperature dependence of the potential barrier for (1-x)$BaTiO_3$-$x$$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions, x = 0.1 (1) 0.2 (2) reoxidized at 600 ºC; 700 ºC(1',2') and 900 ºC(1'',2'').

During the reoxidation process, oxygen diffused from the grain boundary toward the center of the grains. It can be seen from Fig.4 that with increase in reoxidation temperature the potential barrier at grain boundaries increases. These can be explained by increment in the amount of adsorbed oxygen in the grain boundaries and oxidated dielectric layer thin with growth in reoxidation temperature.

Conclusion

Semiconducting solid solutions of $(1\text{-}x)BaTiO_3\text{-}xNa_{0.5}Bi_{0.5}TiO_3$ were prepared by the conventional solid state reaction technique. Sintering of samples was carried out in reducing atmosphere of N_2/H_2 in the temperature range 1200-1300 °C with subsequent oxidation at temperature interval 600-1000 °C. Curie temperature was enhanced on increasing of $Na_{0.5}Bi_{0.5}TiO_3$ content. Through a growth of reoxidation temperature in the interval of 600-1000 °C, the PTCR effect was improved impressively. The grain size decreased with the increase in x. With increasing x the ρ_{max}/ρ_{min} ratio decreases. It was shown that the value of the potential barriers at the grain boundaries increases with reoxidation temperature increasing. It has been shown that an optimal ρ_{max}/ρ_{min} ratio was obtained at the reoxidation temperature 700 ºC.

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