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Synthesis and Electrical Properties of $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ Solid Solutions

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Abstract—$(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions exhibiting positive temperature coefficient of resistance behavior have been prepared using $BaTiO_3$ presynthesized through oxalate coprecipitation. The peak in their dielectric permittivity has been shown to shift to higher temperatures (above 120°C) with increasing x. We have examined the effect of $K_{0.5}Bi_{0.5}TiO_3$ content on the microstructure of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions. The results demonstrate that, with increasing x, both the minimum and maximum resistivities of the materials in the temperature range of their positive temperature coefficient of resistance behavior increase. The materials prepared using barium titanate presynthesized by the oxalate route have higher Curie temperatures and temperatures where they exhibit positive temperature coefficient of resistance behavior and lower minimum resistivities than do the materials prepared by solid-state reactions.

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INTRODUCTION

$BaTiO_3$–$PbTiO_3$ solid solutions with a positive temperature coefficient of resistance (PTCR) are widely used in the fabrication of current limiters, self-regulating heaters, and other devices [1]. The PTCR effect manifests itself as a sharp increase in the resistivity of a material just above its Curie temperature ($t > 120$°C) [2, 3]. Lead-containing materials are, however, toxic and can accumulate in the human body, leading to a variety of diseases (including anemia, encephalopathy, and renal insufficiency) [4–8]. Because of this, there is increasing interest in the study of lead-free materials with a PTCR effect above 120°C [9–11].

As shown by Takeda et al. [12], $BaTiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ solid solutions sintered under a reducing atmosphere and then annealed in air exhibit a PTCR effect at temperatures above 140°C. Viviani et al. [13] and Vijaya Bhaskar Rao et al. [14] produced $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ ceramics by sintering in the temperature range 1280–1300°C. In this process, they observed considerable potassium and bismuth losses, which impaired the reproducibility of the properties of the resulting solid solutions and lowered their Curie temperature [15, 16].

The sintering temperature of undoped barium titanate is lower than that of potassium bismuth titanate [17, 18]. Therefore, to reduce the sintering temperature of $BaTiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ solid solutions, one should decrease the temperature of barium titanate formation. To reduce the formation temperature, use is commonly made of solution synthesis processes, such as sol–gel processing [19, 20], hydrothermal crystallization [21], and an oxalate route [22–25]. It is well known that oxalate coprecipitation (OC) allows one to obtain highly stoichiometric, finely dispersed $BaTiO_3$ powders, which can be sintered at lower temperatures in comparison with powders prepared by solid-state reactions (SRs).

The purpose of this work was to investigate the PTCR effect in $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared using $BaTiO_3$ presynthesized by an oxalate route.

EXPERIMENTAL

The starting chemicals used in the preparation of $BaTiO_3$ through OC were reagent-grade $TiCl_4$, $BaCl_2$, and $H_2C_2O_4$. Aqueous $BaCl_2$ and $TiCl_4$ solutions were mixed and then oxalic acid was added to the resultant solution with constant stirring. The solution was heated to boiling and left to stand for 2 h. The resultant white $BaTiO(C_2O_4)_2 \cdot 4H_2O$ precipitate was filtered off and thoroughly washed with distilled water. Next, the precipitate was dried at 150°C for 2 h. $BaTiO_3$ was prepared by calcining the $BaTiO(C_2O_4)_2$ at $t \geq 800$°C for 2 h.

In the second step of the synthesis process, extra-pure-grade K_2CO_3, Bi_2O_3, and TiO_2 were added to the $BaTiO_3$ in order to obtain solid solutions. The powders were mixed by ball milling with ethanol for 4 h. The resultant mixtures were fired for 4 h at temperatures from 800 to 870°C.

To assess the effect of the synthesis procedure on the electrical properties of $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$, the solid solutions were also prepared by SRs using extra-pure-grade K_2CO_3, Bi_2O_3, TiO_2, and $BaCO_3$ as starting reagents. The powders were mixed by ball milling with

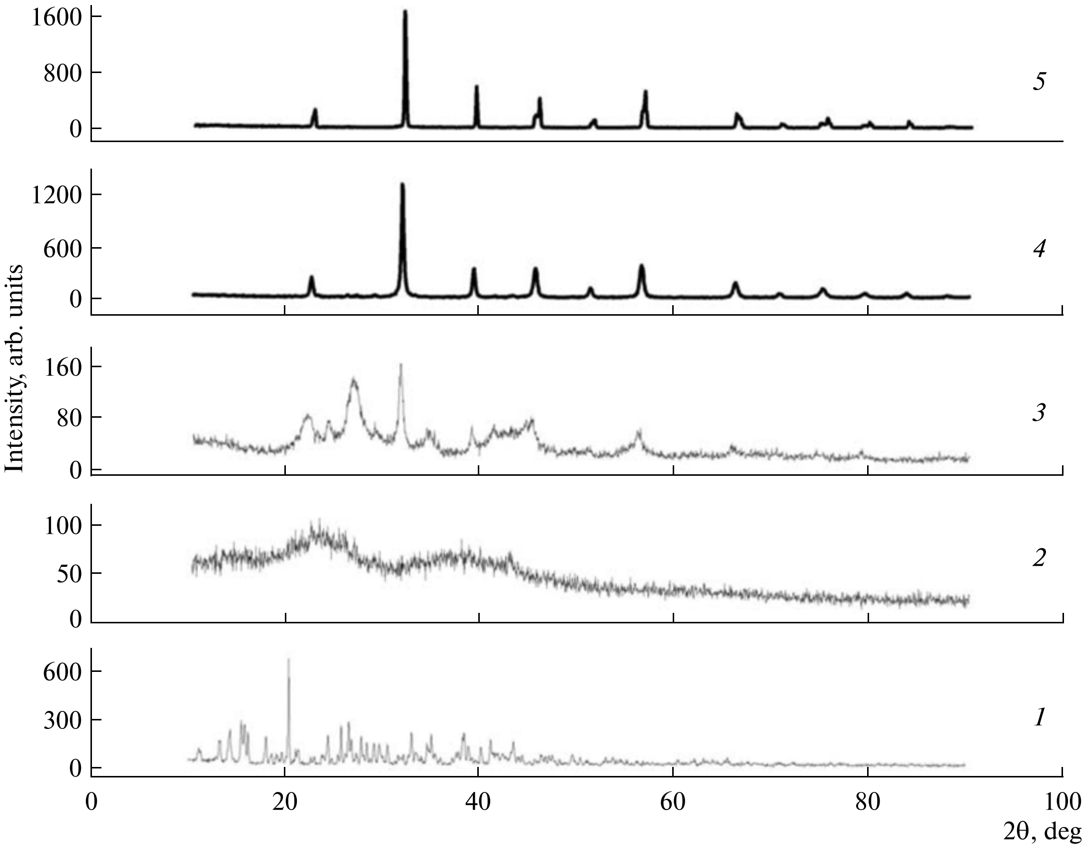

Fig. 1. XRD patterns of $BaTiO(C_2O_4)_2 \cdot 4H_2O$ (*1*) before and (*2*–*5*) after heat treatment for 2 h at (*2*) 250, (*3*) 550, (*4*) 800, and (*5*) 900°C.

ethanol for 4 h. The resultant mixtures were dried at 100–120°C, passed through a nylon-6 sieve, and then fired for 4 h at temperatures from 900 to 1100°C.

After firing, the powders prepared through both OC and SRs were pressed at 150 MPa in the presence of polyvinyl alcohol into pellets (10 mm in diameter and 2 mm in thickness), which were sintered in a flowing $N_2 + H_2$ (99.5 : 0.5) gas mixture in the temperature range 1100–1240°C and then oxidized in air at 700°C. The heating/cooling rate was 300°C/h in all of our preparations. Electrical contacts to the surface of the samples thus prepared were made by firing aluminum paste.

The potassium content of the ceramic samples was determined by flame photometry on a Pye Unicom SP9 spectrophotometer using an air–acetylene flame. Bismuth was determined by Trilon titration, with Xylenol Orange as an indicator.

The phase composition of the samples was determined by X-ray diffraction (XRD) on a DRON-4-07 powder diffractometer (CuK_α radiation, 40 kV, 20 mA). Structural parameters were evaluated by the Rietveld profile analysis method. Intensity data were collected in the angular range $2\theta = 10°–150°$ with a step size $\Delta 2\theta = 0.02°$ and a counting time of 10 s per data point. As external standards, we used SiO_2 (2θ calibration) and Al_2O_3 (NIST SRM 1976 intensity standard).

The electrical resistivity of our samples was measured as a function of temperature in the range 20 to 500°C. In impedance measurements, we used a Solartron Analytical 1260 impedance/gain-phase analyzer in the range 1 Hz to 1 MHz. The components of the equivalent electrical circuit were identified using ZView software (Scribner Associates).

RESULTS AND DISCUSSION

Heat treatments of barium titanyl oxalate tetrahydrate, $BaTiO(C_2O_4)_2 \cdot 4H_2O$, at various temperatures showed that single-phase crystalline barium titanate was formed at temperatures above 800°C (Fig. 1).

When K_2CO_3, Bi_2O_3, and TiO_2 were added to the $BaTiO_3$ prepared by the oxalate route, we obtained $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions.

Figure 2 shows the XRD pattern of the $Ba_{0.9}K_{0.05}Bi_{0.05}TiO_3$ solid solution.

According to XRD data, the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared through SRs and OC formed at different temperatures. For example, single-phase solid solutions with $x = 0.1$ were obtained at temperatures above 1000°C by SR and

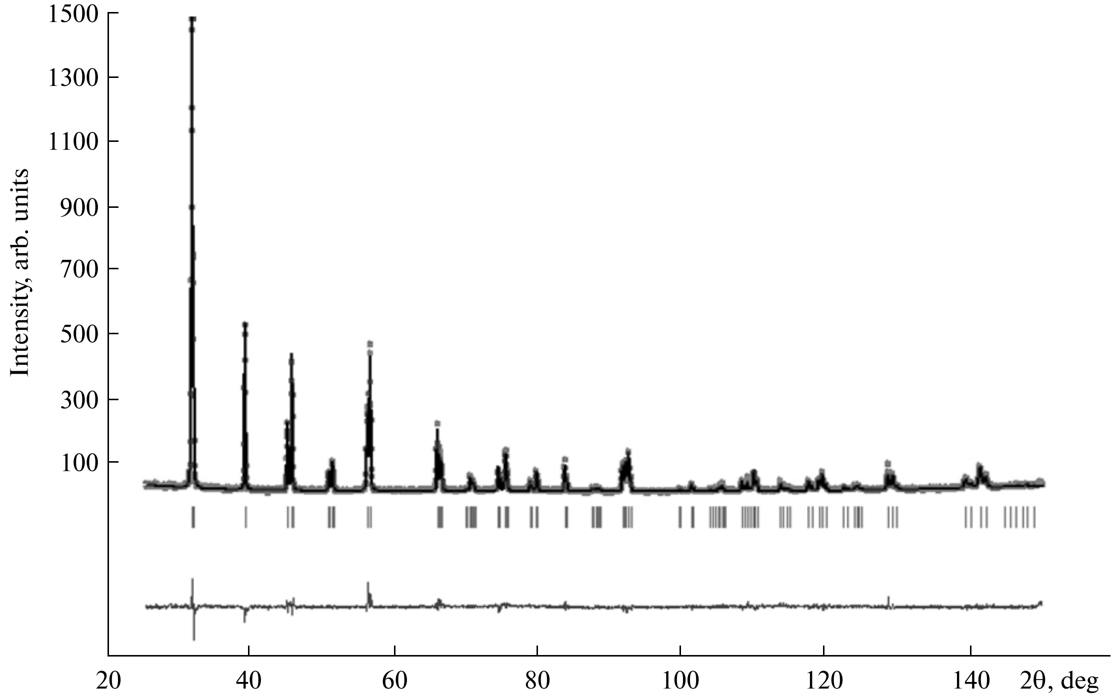

Fig. 2. Observed (open points) and calculated (solid line) XRD patterns of the $Ba_{0.9}K_{0.05}Bi_{0.05}TiO_3$ solid solution prepared through OC. Vertical tick marks show peak positions.

near 850°C by the oxalate route, which might be due to a reduction in the temperature of the formation of the intermediate phase in the $BaTiO_3$ synthesis process.

Figure 3a shows the relative density as a function of sintering temperature for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ ceramic samples prepared by the two procedures. Figure 3b demonstrates that the powders prepared through OC can be sintered in the temperature range 1100–1200°C, whereas the powders prepared by SRs can be sintered in the range 1210–1290°C. The lower sintering temperature of the samples prepared through OC is attributable to the smaller particle size of $BaTiO_3$ prepared through the OC process [22–25]: the high reactivity of the powder leads to a reduction in sintering temperature.

Using flame photometry and Trilon titration, the bismuth loss during the sintering of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ materials with $x = 0.1$,

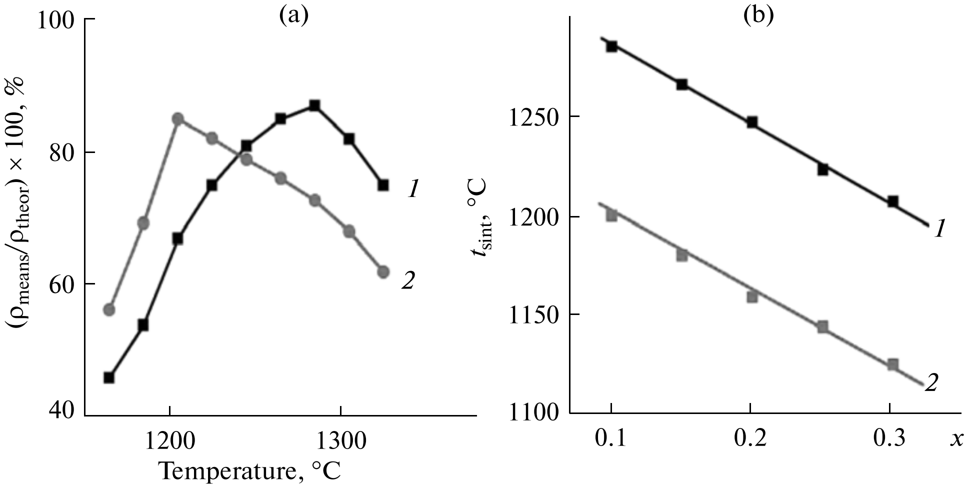

Fig. 3. (a) Relative density as a function of sintering temperature for the $Ba_{0.9}Na_{0.05}Bi_{0.05}TiO_3$ ceramic samples prepared (*1*) by SR and (*2*) through the OC process. (b) Sintering temperature as a function of *x* for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared (*1*) by SRs and (*2*) through the OC process.

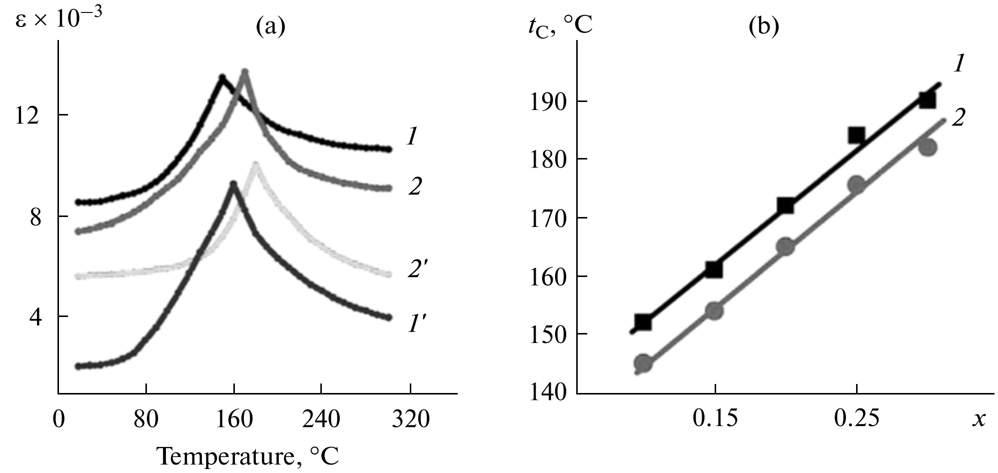

Fig. 4. (a) Temperature dependences of 100-kHz dielectric permittivity for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions with x = (*1*, *1*') 0.1 and (*2*, *2*') 0.2 prepared (*1*, *2*) by SRs and (*1*', *2*') through the OC process. (b) Curie temperature as a function of x for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared (*1*) through the OC process and (*2*) by SRs.

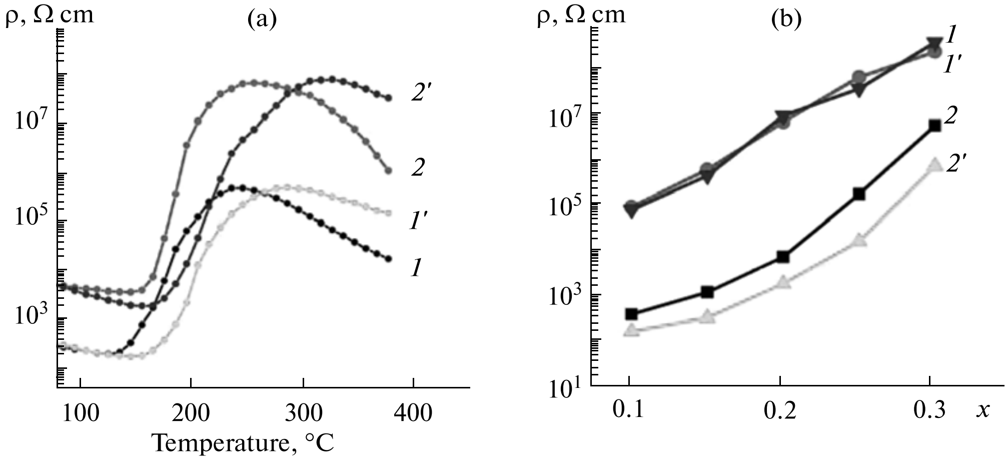

Fig. 5. (a) Temperature dependences of resistivity for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions with x = (*1*, *1*') 0.1 and (*2*, *2*') 0.2 prepared (*1*, *2*) by SRs and (*1*', *2*') through the OC process. (b) (*1*, *1*') Maximum and (*2*, *2*') minimum resistivities as functions of x for the solid solutions prepared (*1, 2*) by SRs and (*1*', *2*') through the OC process.

0.2, and 0.3 prepared through the OC process was shown to be insignificant, 0.1, 0.4, and 0.6 wt %, respectively, whereas the potassium loss was 7.6, 11.4, and 19 wt %, respectively. At the same time, the materials prepared by SRs lost 2, 2.6, and 3.5 wt % bismuth and 16, 22, and 28 wt % potassium, respectively. The smaller loss of the volatile components during sintering of the powders prepared through the OC process is attributable to the fact that their sintering temperatures were lower (Fig. 3).

To determine the phase transition temperatures of the solid solutions, we measured their relative dielectric permittivity (ε) in wide ranges of temperatures and frequencies. The phase transition temperature corresponds to a maximum in permittivity in the ε(*T*) curve (Fig. 4a). As seen, the phase transition temperature of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions increases with increasing x. The reason for this is that the Curie temperature of $K_{0.5}Bi_{0.5}TiO_3$ exceeds that of $BaTiO_3$ [12]. The data in Fig. 4b demonstrate that the Curie temperatures of the materials prepared through the OC process exceed those of the materials prepared by SRs, which can be accounted for by the smaller potassium and bismuth losses during sintering.

Figure 5a shows the temperature dependences of resistivity for the solid solutions prepared by the two procedures. All of our samples possess semiconducting properties and exhibit PTCR behavior. The PTCR effect is observed at higher temperatures in the materials prepared through the OC process (Fig. 5a, curves *1*', *2*'). The resistivity of the materials is seen to increase with increasing $K_{0.5}Bi_{0.5}TiO_3$ content. Figure 5b shows the maximum and minimum resistivities of the solid solutions as functions of x. The increase in maximum resistivity with x is attributable to an increase in grain-boundary potential barrier height [26]. It is

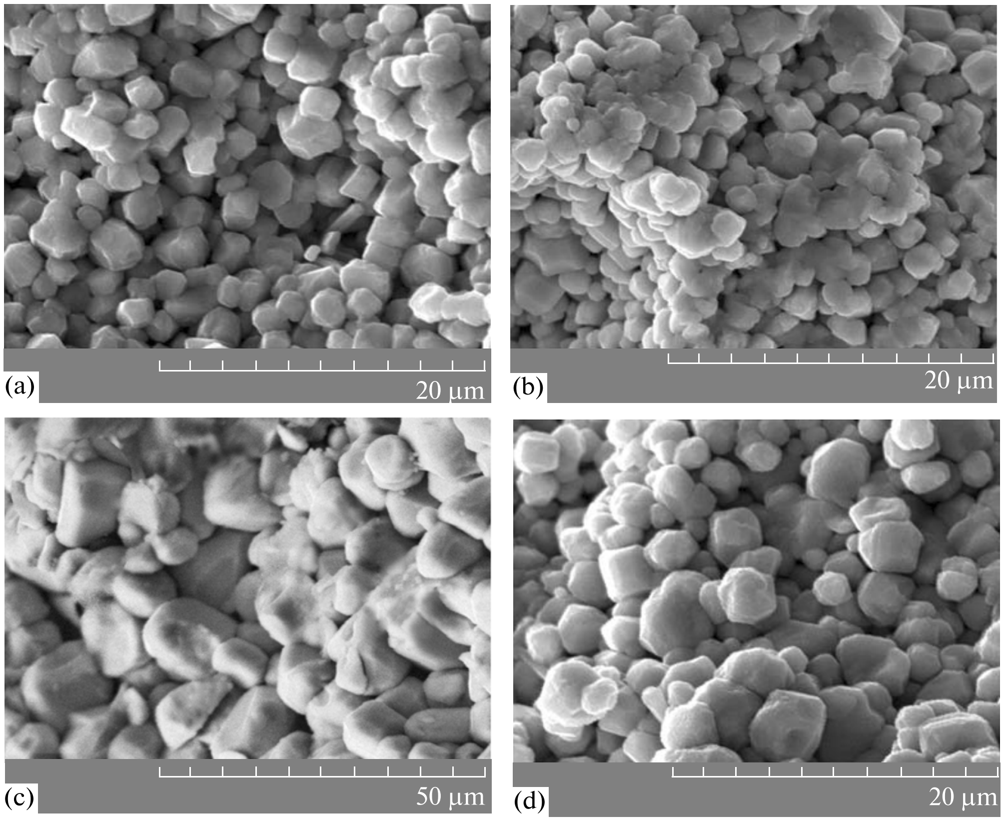

Fig. 6. Electron micrographs of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions with x = (a, c) 0.1 and (b, d) 0.2 prepared (a, b) by SRs and (c, d) through the OC process.

seen in Fig. 5b that the maximum resistivities of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared by SRs and the OC process differ little, whereas the minimum resistivity of the materials prepared through OC is lower (Fig. 5b).

Microstructural analysis results for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions demonstrate that the $K_{0.5}Bi_{0.5}TiO_3$ content and synthesis procedure have a significant effect on the grain size of the ceramic samples. With increasing x, the grain size of the ceramic materials prepared through both SRs and OC decreases (Fig. 6). The reduction in grain size leads to an increase in the total number of dielectric grain boundaries. Since the grain-boundary resistance exceeds the grain bulk resistance, the total resistance of the material increases with decreasing grain size, leading to an increase in minimum resistivity (Fig. 5b) [27].

In addition, it is seen in Fig. 6 that the ceramic materials prepared through the OC process consist of larger grains. The grain size of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ ceramic samples with $x = 0.1$ and 0.2 prepared by SRs is 3.5 and 2 μm, respectively (Figs. 6a, 6b), whereas the grain size of the materials prepared through the OC process is 10 and 3.6 μm (Figs. 6c, 6d). The larger grain size in the case of the OC process seems to be due to the higher reactivity of the barium titanate powder prepared through OC [22–25]. In this process, the mass transport rate during sintering is higher, which contributes to grain growth. This seems to be responsible for the lower total resistivity of the materials prepared through the OC process.

It is well known that the grain structure in PTCR ceramics can be divided into several regions differing in electrical properties. In particular, the grain bulk has semiconducting properties, whereas grain boundaries have dielectric properties. There is also an intermediate region between the grain bulk and grain boundaries. Morrison et al. [28, 29] and Sinclair and West [30] developed a procedure for assessing the electrical properties of each region of grains using $Z'' = f(Z')$ complex impedance data. Figure 7 presents complex impedance data for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ materials in the form of plots of Z'' against Z' at different temperatures. In the range 170–200°C, the total resistance of the materials (Z') increases with temperature. The reason for this is that, above the Curie temperature, the grain-boundary potential barrier height increases.

Analysis of the data for the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions demonstrates that the grains in the ceramics studied comprise three, electrically inhomogeneous regions. The data in Fig. 8 illustrate the contributions of the different grain regions to the PTCR effect in the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions prepared by the two procedures.

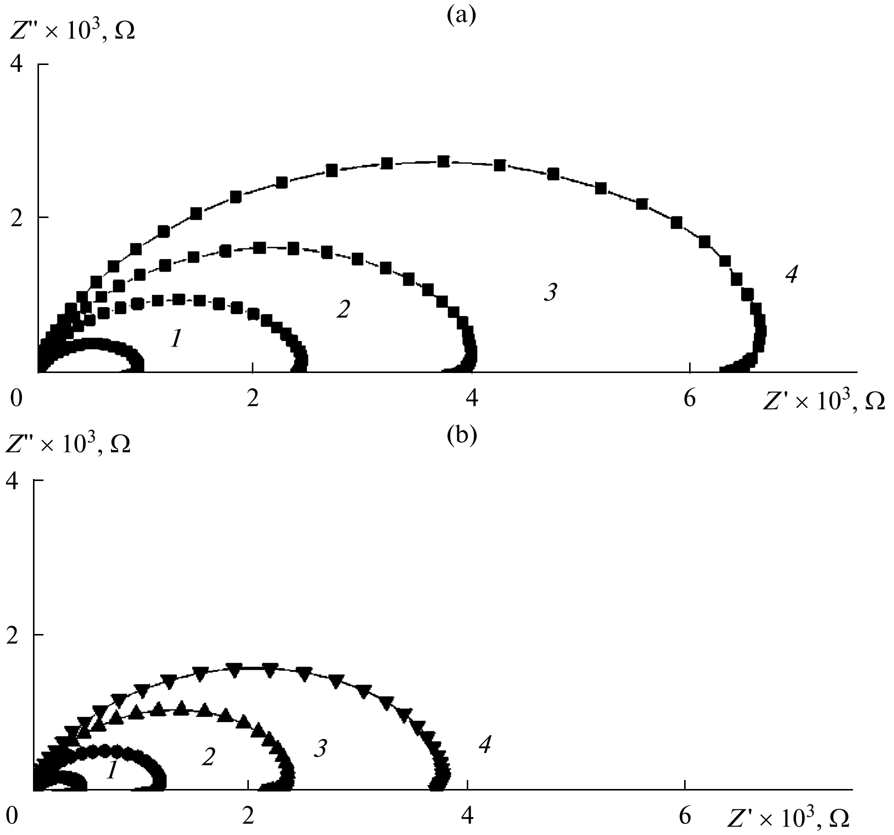

Fig. 7. Complex impedance spectra at (*1*) 170, (*2*) 180, (*3*) 190, and (*4*) 200°C for the $Ba_{0.9}K_{0.05}Bi_{0.05}TiO_3$ solid solution prepared (a) by SR and (b) through the OC process.

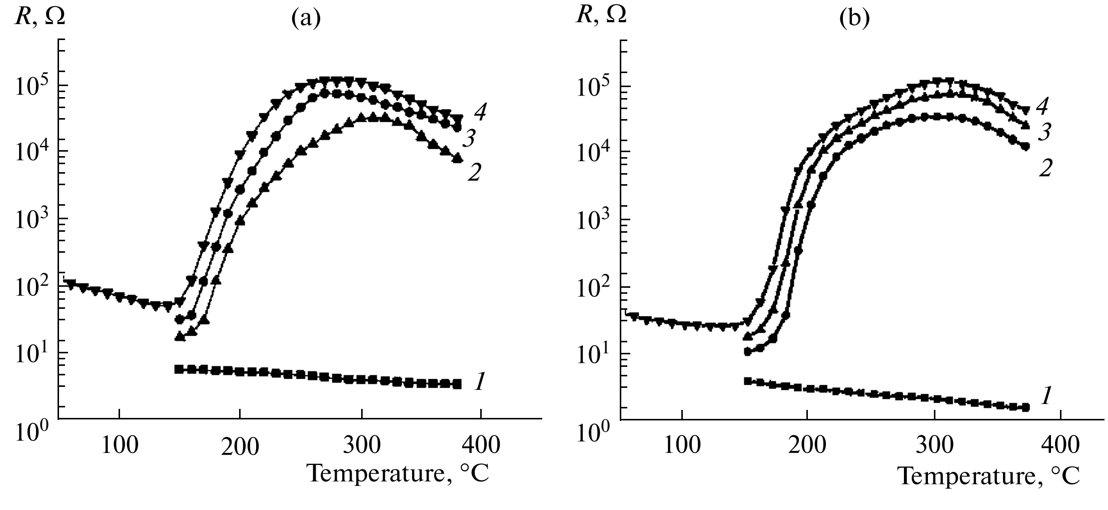

Fig. 8. (*1*) Grain-bulk, (*2*) surface-layer, (*3*) grain-boundary, and (*4*) total resistances as functions of temperature for the $Ba_{0.9}K_{0.05}Bi_{0.05}TiO_3$ solid solution prepared (a) by SR and (b) through the OC process.

In the grain structure of the $(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ ceramic samples, one can distinguish the resistance of the semiconducting grain bulk, which decreases with increasing temperature (Fig. 8, curve *1*). In addition, we determined the properties of the surface layer and dielectric grain boundaries (Fig. 8, curves *2*, *3*). As seen in Fig. 8, the grain boundaries and surface layers in the samples prepared by the two procedures differ little in properties. At the same time, the grain bulk resistance of the materials prepared through the OC process is lower.

CONCLUSIONS

$(BaTiO_3)_{1-x}(K_{0.5}Bi_{0.5}TiO_3)_x$ solid solutions have been prepared by solid-state reactions (SRs) and through oxalate coprecipitation (OC process) using presynthesized barium titanate.

The present results demonstrate that, with increasing x, both the minimum and maximum resistivities of the solid solutions increase. The OC process allows one to increase the Curie temperature of the materials and the temperatures where they exhibit PTCR behavior. The materials prepared through the OC process have a lower grain bulk resistance and minimum resistivity, which is attributable to the decrease in the total number of dielectric grain boundaries because of the increase in the grain size of the ceramics.

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