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Lead-Free High-Temperature Barium Titanate-Based PTCR Ceramics and Its Electrical Properties

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Abstract. *The (1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ solid solutions have been synthesized by solid-state reaction technique. The parameters of the crystal structure of the ceramic samples were determined by means of Rietveld full-profile X-ray analysis. With increasing x, the values of ρ_{max} and ρ_{min} increase due to the growth of potential barrier at grain boundaries. It has been found that in (1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ system the grain boundary and the outer layer region make a contribution to the PTCR effect.*

Key words: PTCR, lead-free materials, perovskite, complex impedance analysis.

I. Introduction

It is known that ceramics based on donor-doped barium titanate exhibits the effect of positive temperature coefficient of resistance (PTCR) [1]. This effect is characterized by a sharp increase in electrical resistance at temperatures above the Curie temperature (for barium titanate 120 ºC). Materials exhibiting such an effect can be used in temperature sensors, self-regulating heaters and other appliances. In order to increase the Curie temperature above 120 ºC lead titanate is usually added to barium titanate [2]. Recently, the use of lead-containing materials in electrical and electronic equipment has been prohibited in order to protect the environment and human health [3]. Therefore, nowadays the development of lead-free PTCR-materials with high Curie temperature is very important.

It is known that the addition of {Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ to $BaTiO_3$ materials shifts T_C towards higher temperature. In the literature there are some reports about the possibility of obtaining PTCR properties at values of $0 \le x < 0.4$ [4]. These materials show the PTCR effect after sintering in air atmosphere at $x \le 0.06$ [5]. During sintering in a reducing atmosphere the concentration interval of PTCR effect extends to $x \le 0.4$ [6]. It was showed that the addition of small concentrations of manganese improves PTCR characteristics of materials. PTCR effect of barium titanate based materials depends on the structure of grain, which is electrically heterogeneous. The literature data on the contribution of different regions of the grain to PTCR effect for this system are limited [5, 6].

Therefore the purpose of this work was to study the electrophysical properties of (1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ solid solutions.

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II. Experimental Section

(1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ solid solutions were prepared by solid-state reaction technique. Extra-pure (purity 99.99%) {Na,K}$_2CO_3$, $BaCO_3$, Bi_2O_3 and TiO_2 (rutile) were used as initial reagents for preparation. The powders were mixed and ball-milled with ethyl alcohol in an agate mortar during 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 granulated with the addition of 10% polyvinyl alcohol, pressed into pellets (10 mm in diameter and 2 mm in thickness) by uniaxial pressing at 150 MPa. For dielectric measurements, pellets were sintered in air in the temperature range of 1200-1300 ºC with subsequent deposition of silver electrodes on the polished surfaces of the samples. To study the PTCR effect tablets were synthesized in a flow of gas mixture N_2/H_2 at 1300 ºC with subsequent deposition of aluminum electrodes on the polished surfaces of the samples. For investigations of PTCR properties, pellets were sintered in N_2/H_2 mixture at 1300 ºC. The heating and cooling rates for all samples were 300 °C/h.

The phases were characterized by X-ray powder diffractometry (XRPD) using DRON-4-07 (Cu Kα radiation; 40 kV, 20 mA). The structure parameters were refined by the Rietveld full-profile 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 6 s per data point. As external standards, we used SiO_2 (for 2Θ) and Al_2O_3 NIST SRM1976 (for intensity).

The temperature dependence of the electrical resistance of the samples was measured in the temperature range of 20°C to 400°C. Impedance data were obtained using a 1260 Impedance / Gain-phase Analyzer (Solartron Analytical) in the range 100 Hz to 1 MHz. The components of the equivalent circuit were identified using ZView software (Scribner Associates).

III. Results and Discution

The XRPD patterns of the powders fired at temperatures lower than 1000 °C contain reflections of several phases. The $BaTiO_3$-based phase was the dominant one within the entire temperature range.

The substitution of Na/K and Bi for Ba affects unit cell parameters of the samples studied in the (1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ system. The parameters *a* and *c* decrease with the substitution of Na/K and Bi ions for Ba ions.

Fig. 1 shows permittivity as a function of temperature for the sintered ceramics of (1-x)$BaTiO_3$-x$Na_{0.5}Bi_{0.5}TiO_3$ solid solutions at 100 kHz. As x increases the temperature of maximum ε (T), which corresponds to phase transition temperature in (1-x)$BaTiO_3$-x{Na,K}$_{0.5}$$Bi_{0.5}TiO_3$ solid solutions, increases (inset in Fig. 1). The permittivity of studied compositions above the Curie point obeys the Curie-Weiss law.

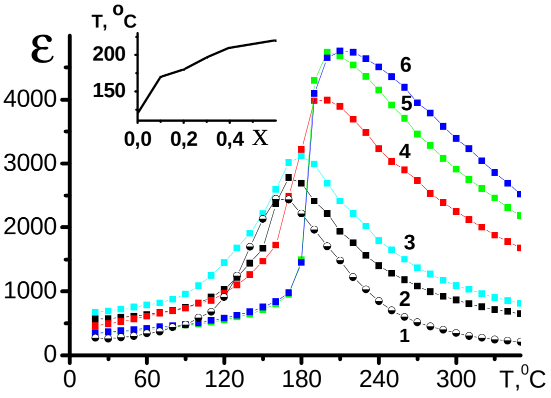

Fig. 1. Temperature dependence of permittivity of the (1-x)$BaTiO_3$-x$Na_{0.5}Bi_{0.5}TiO_3$ ceramics, x = 0.08 (1); 0.1 (2); 0.2 (3); 0.3 (4); 0.4 (5); 0.6 (6). *f* = 100 kHz. Inset: Variation of Curie temperature (1-x)$BaTiO_3$-x$Na_{0.5}Bi_{0.5}TiO_3$ ceramics as a function of x.

Fig. 2 shows the temperature dependence of resistivity in (1-x)$BaTiO_3$-x$K_{0.5}Bi_{0.5}TiO_3$ solid solutions, for samples with x = 0.1, 0.2 and 0.3. The PTCR effect is observed at temperatures above the phase transition temperature. The ρ_{max}/ρ_{min} ratio decreases with increase in x$\{Na,K\}_{0.5}Bi_{0.5}TiO_3$ concentration. The values of ρ_{max} and ρ_{min} increase with increase in *x*.

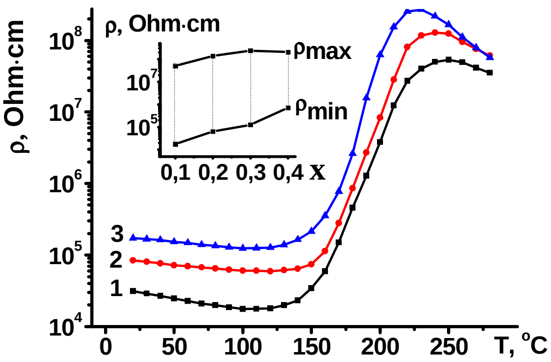

Fig. 2. Temperature dependence of resistivity of (1-x)$BaTiO_3$-x$K_{0.5}Bi_{0.5}TiO_3$ solid solutions, x = 0.1 (1) 0.2 (2), 0.3 (3). Inset: Plots of the maximum ρmax and ρ_{min} values of resistivity in (1-x)$BaTiO_3$-x$K_{0.5}Bi_{0.5}TiO_3$ solid solutions as a function of x.

Using complex impedance spectroscopy it has been found that the ceramic's grain consists of core with semiconducting properties and surface layer with dielectric properties. Between these two areas there is a transition region, in which the resistivity is higher than in the semiconducting inner region, but lower than in the grain boundary dielectric layer. These areas of ceramics are electrically non-uniform. The results of the analysis showed that the resistance of grain bulk varies little in the investigated temperature range. At the same time the temperature dependencies of the resistance of the grain boundary and the outer layer pass through a maximum. This indicates that both the grain boundary and the outer layer region make a contribution to the PTCR effect in studied materials.

IV. Conclusions

It has been found that in (1-x)$BaTiO_3$-x$\{Na,K\}_{0.5}Bi_{0.5}TiO_3$ system the grain boundary and the outer layer region make a contribution to the PTCR effect. With increasing x, the values of ρ_{max} and ρ_{min} were observed to increase due to the growth of potential barrier at grain boundaries. The resistance and PTCR jump in sodium-containing system are similar to those in lead-containing system, and these materials can be used in practice as current limiters and temperature controllers.

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