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DISTRIBUTION OF MANGANESE IONS AND ITS INFLUENCE ON THE PROPERTIES OF PTCR CERAMICS BASED ON BARIUM TITANATE

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Positive temperature coefficient of resistance (PTCR) occurs in ceramic materials based on doped barium titanate $(Ba,Y)TiO_3$ above the temperature of phase transition. Rise of potential barriers at grain boundaries is one of formation conditions of such effect. Therefore PTCR ceramics are purposefully synthesized under conditions when semiconducting grains and high-resistance grain boundaries are formed. This is achieved, in particular, when a small amount of yttrium ions is introduced in barium site and grain boundaries oxidize under sintering in air. In this case materials are characterized by small resistance change in PTCR temperature range and considerable varistor effect (decrease resistance under external electric voltages). This limits the application of such materials in devices operating under high electric voltages. Introduction of acceptor dopants (in particular manganese ions) in synthesized materials is known to improve the above electric characteristics due to change in resistance of grain boundaries [1]. Manganese dopants influence on PTCR effect because redox reactions in manganese oxide take place in the same temperature range in which partial transition $Ti^{4+} \leftrightarrow Ti^{3+}$ occurs in ceramics [2]. However distribution of manganese dopants in polycrystalline materials is studied insufficiently. These data would allow one to explain and to control purposefully the properties of PTCR ceramics.

Therefore the aim of this work was to study the distribution of manganese ions and its influence on properties of grains, outer grain layers and grain boundaries of PTCR ceramics.

Analysis of results of studying complex impedance (Z*) and complex electric modulus (M*) in wide frequency range at room temperature showed that regardless of yttrium content $(Ba,Y)TiO_3$ ceramics include electrically different regions: grain, outer grain layer and grain boundaries. However electric properties of grain and outer grain layer at room temperature are difficult to distinguish in high-conductivity samples because of small difference in resistance.

PTCR ceramics based on $(Ba,Y)TiO_3$ were synthesized by solid state reaction technique using extra-pure initial reagent. For uniform distribution of acceptor dopants in ceramics manganese has been precipitated from solutions. Electrophysical properties of materials were studied in a wide frequency and temperature range.

Analysis of temperature dependencies of resistance of grain, outer grain layer and grain boundaries of PTCR ceramic based on $(Ba,Y)TiO_3$ shows that the temperature dependence of resistance of grain and outer grain layer has similar value and character and does not have anomalies. Consequently, PTCR effect in $(Ba,Y)TiO_3$ ceramics without manganese dopants occurs due to change in electric properties of grain boundaries.

It has been found that increase of manganese content of $(Ba,Y)TiO_3$ ceramics increases the resistance of grain boundaries, but practically does not change the resistance of grain (Fig. 1). This occurs because manganese in the concentration range investigated does not incorporate in crystalline lattice of PTCR barium titanate and, therefore, does not compensate excess charge in titanium site. A difference in resistance value between grain and outer grain layer of PTCR ceramics becomes pronounced with temperature increase.

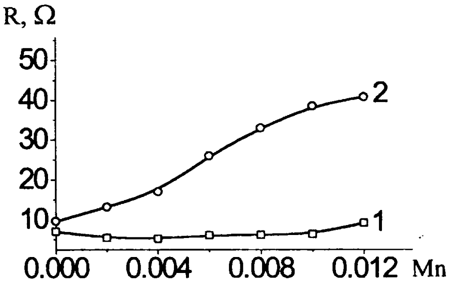

Fig. 1. Resistance of grain (1) and total resistance of outer grain layer and grain boundary (2) of PTCR ceramics as a function of manganese content (mol. %). $T_{meas.} = 20°C$.

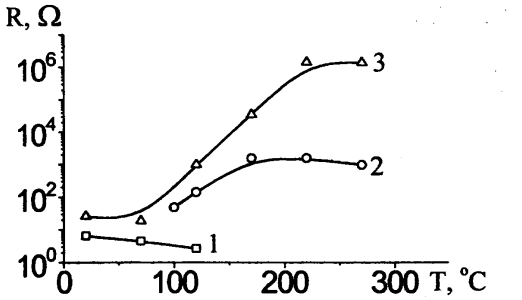

Fig. 2. Resistance of grain (1), outer grain layer (2) and grain boundary (3) of PTCR ceramics based on $(Ba,Y)TiO_3$ + 0.006 mol.% Mn as a function of temperature.

Analysis of temperature dependencies of resistance of grain, outer grain layer and grain boundaries of PTCR ceramic with manganese dopants shows that resistance of outer grain layer changes with temperature like resistance of grain (Fig. 2). Resistance of grain boundaries of PTCR barium titanate increases with manganese content.

The results obtained showed that increase of resistance change value of $(Ba,Y)TiO_3$ PTCR ceramics with manganese dopants occurs due to change of electrophysical properties of outer grain layers and grain boundaries.

Earlier it was shown that the amount of varistor effect in $(Ba,Y)TiO_3$ ceramics correlates with average grain size, *viz.* in fine-grained ceramics varistor effect is weaker [3]. Our research showed that introduction of manganese in ceramics $(Ba,Y)TiO_3$ is accompanied with considerable decrease (improvement) of varistor effect, but average grain size of ceramics practically does not change. Varistor effect depends on a number of factors, including oxidation degree of grain boundaries [4]. Therefore one can suppose that varistor effect in PTCR barium titanate decreases on manganese introduction due to the formation of high-resistance outer layer.

In order to clear out the origin of increase of resistance change value of PTCR ceramics with increasing manganese content, the potential barrier at grain boundaries has been calculated using equation from Heywang' model [5]. Results of calculation show that the potential barrier increases with manganese content of ceramics (Fig. 3). This leads to increase of resistance change value in PTCR range. Value obtained for potential barrier at grain boundaries of PTCR barium titanate agreed with literature data [6]. Therefore manganese dopants in PTCR barium titanate form high-resistance outer grain layer and increase the potential barrier at grain boundaries.

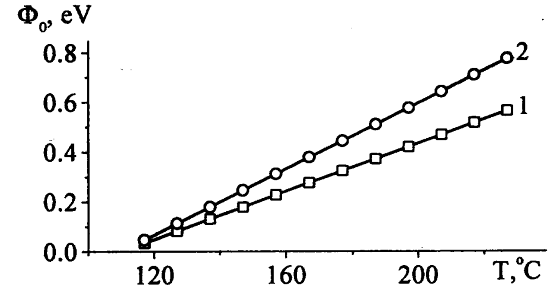

Fig. 3. Potential barrier (Φ_o) at grain boundaries of PTCR barium titanate ceramic $(Ba_{0.996}Y_{0.004})TiO_3$ + mol.% Mn at different manganese content: =0 (1); 0.012 (2).

Thus investigations of PTCR ceramics based on barium titanate in wide frequency and temperature ranges allow us to conclude that manganese content sligtly affects the resistance of grains. The manganese ions are mainly at grain boundaries and in outer grain layers, and act as acceptors. This essentially improves properties of PTCR materials, *viz.* resistance change value increases and varistor effect decreases.

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