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Electrical Characteristics of Er Doped BaTiO₃ Ceramics

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Abstract:

In this study, the electrical resistivity (ρ) and PTC effect of Er doped BaTiO₃ ceramics are investigated. The concentrations of Er₂O₃ in the doped samples vary from 0.01 to 1.0 at% Er. The samples are prepared by the conventional solid state reaction, and sintered at 1320 ° and 1350 °C in air atmosphere for 4 hours.

The SEM analysis shows that all of measured samples are characterized by polygonal grains. The uniform and homogeneous microstructure with grain sizes from 20 to 45 μ m is the main characteristic of the low doped samples (0.01 and 0.1 at% Er). For the samples doped with the higher dopant concentration (0.5 and 1.0 at%) the average grains sizes have been ranged from 5 to 10 μ m.

The electrical resistivity is measured in the temperature range from 25 °C to 170 °C, at frequencies 1 kHz, 10 kHz and 100 kHz. The electrical resistivity values, measured at frequency of 1 kHz and room temperature, have been ranged from $1.62 \cdot 10^{-4}$ Ω cm to $4.24 \cdot 10^{-4}$ Ω cm, for samples sintered at 1320 °C and from $1.43 \cdot 10^{-4}$ Ω cm to $1.94 \cdot 10^{-4}$ Ω cm, for samples sintered at 1350 °C. A nearly flat and stable electrical resistivity-temperature response is characteristic for all samples at the temperature range from 25 °C to 120 °C. Above this temperature, the electrical resistivity increases rapidly. At 170 °C the value of electrical resistivity is ranged $9.84 \cdot 10^{-4}$ Ω cm - $1.62 \cdot 10^{-5}$ Ω cm, for $T_{sin}=1320$ °C, and $6.11 \cdot 10^{-4}$ Ω cm - $1.32 \cdot 10^{-5}$ Ω cm, for $T_{sin}=1350$ °C. The electrical resistivity decreases with concentration increment up to 0.5 at%, while above 0.5 at% it increases. Also, with increasing frequency, ρ decreases for a few orders of magnitude.

Keywords: BaTiO₃; microstructure; sintering; additive; electric properties; PTC effect.

1. Introduction

Modified BaTiO₃ ceramics is one of the most investigated dielectric materials due to its practical applications. The significance of this material is mainly based on its wide variety of applications such as multilayer ceramic capacitors (MLCCs), PTC thermistors, varistors, piezoelectric sensors, ultrasonic transducers, radio and communication filters and optoelectronic elements [1, 2].

The electrical properties of the modified BaTiO₃ ceramics depend on the ceramics composition, synthesis method of starting powders, sintering procedure and obtained microstructure. The BaTiO₃ powder is usually mixed with additives in order to adjust the

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sintering parameters and electrical properties to the requirements of electronic device [3-4]. It is known that the electric properties, especially PTC effect of polycrystalline BaTiO₃, depend to a great extent on the grain growth during sintering as well as the type and concentration of donors or acceptor dopants [5-7]. In addition, the electrical properties strongly depend on the site preference of dopant ions in BaTiO₃ sublattices.

Two types of dopants can be introduced into BaTiO₃ lattice. Ions with larger ionic radius and low valence like Er³⁺, Ho³⁺, and La³⁺, tend to enter the Ba²⁺ sites in perovskite lattice, while ions with smaller ionic radius and higher valence like Nb⁵⁺, can be incorporated into the Ti⁴⁺ sublattice [8-16].

At low concentrations of Er (below 0.5 at%), substitution of Ba²⁺ ions and formation of solid solutions occur. At higher concentrations of additives, over 0.5 at%, either Ba²⁺ or Ti⁴⁺ ions are substituted, causing very high electrical resistivity of the sample ($\rho=10^8 \Omega\text{m}$). The substitution of Er³⁺ on Ba²⁺ sites requires formation of negatively charged defects. For the samples sintered at air atmosphere, the principal doping mechanism is the ionic compensation mechanism (vacancy compensation mechanism) [17, 18].

The purpose of this paper is to analyze BaTiO₃ doped with various content of Er₂O₃, sintered at different sintering temperature. The influence of dopant on the microstructure and electrical properties (the electrical resistivity) in function of frequency and temperature has been investigated.

2. Experimental procedure

In this paper, Er₂O₃ doped BaTiO₃ ceramics is used for microstructure and electrical characterization. The samples is prepared by conventional solid state sintering procedure starting from high purity commercial BaTiO₃ powder (MURATA) with [Ba]/[Ti]=1.005, and reagent grade Er₂O₃ powder (Fluka chemika). The content of Er₂O₃ is ranged from 0.01 to 1.0 at%. Starting powders are ball milled in ethyl alcohol for 24 hours. After milling the slurries were dried in an oven at 200 °C for several hours until constant weigh and PVA was added as a binder. The dried powders were then pressed under a uniaxial pressure of 120 MPa into disks of 7 mm in diameter and 3 mm of thickness. The compacts are sintered at 1320 °C and 1350 °C in the air atmosphere for 4 hours.

The microstructures of sintered samples are observed by scanning electron microscope (JEOL-JSM 5300) equipped with energy dispersive x-ray analysis spectrometer (EDS-QX 2000S system). X-ray diffraction (XRD) patterns are recorded with CuK α radiation in a PhilipsX'Pert diffractometer (Philips, the Netherlands). Prior to electrical measurements silver paste is applied on flat surfaces of specimens. Electrical resistivity are measured using Agilent 4284A precision LCR-meter in frequency range 100 Hz-1 MHz. The variation of electrical resistivity with temperature is measured in temperature interval from 20 °C to 180 °C.

3. Microstructure characteristics

The relative density of Er doped samples is ranged from 83 % to 93 % of theoretical density (TD). With increasing of sintering temperature, the density of the investigated samples increases. Also, with increasing of dopant content, the increment of porosity is evident and the density decreases. The highest value of density (93% TG) is measured for 0.01 at% doped samples, sintered at 1350 °C, while the lowest density value is measured for samples doped with 1.0 at% of additives and sintered at 1320 °C.

The Er₂O₃ doped BaTiO₃ samples are characterized by irregularly polygonal grains

microstructure (Fig. 1 and 2). For samples doped with lower additive content (0.01 at% Er), the abnormal growth of grains (grain size from 20 to 45 μm) for both sintering temperature, is characteristic (Fig. 1a and 2a).

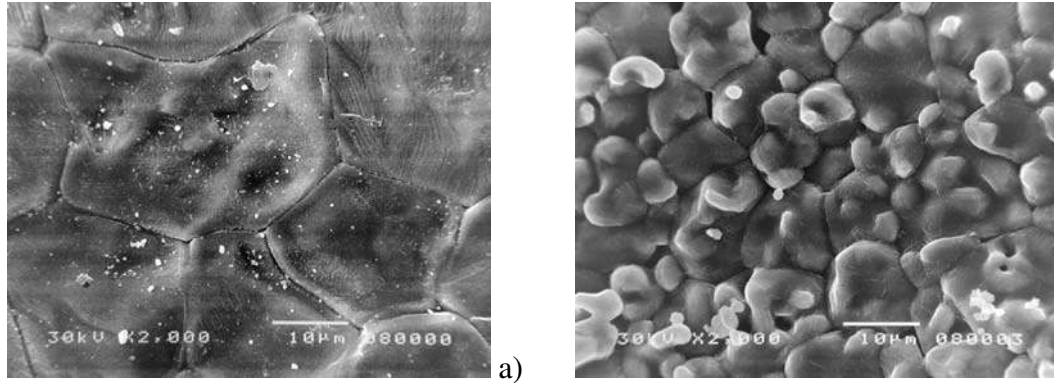


Fig. 1. SEM images of BaTiO₃ sintered at 1320 °C doped with a) 0.01 at% and b) 1.0 at% of Er₂O₃.

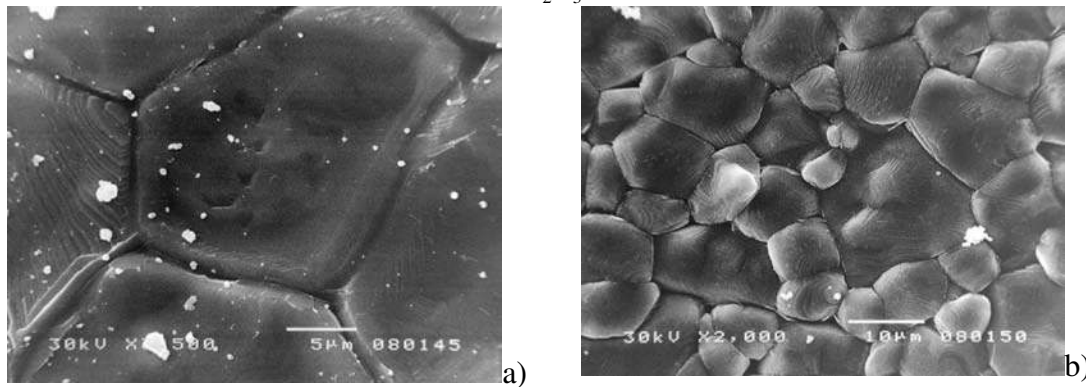


Fig. 2. SEM images of BaTiO₃ sintered at 1350 °C doped with a) 0.01 at% and b) 1.0 at% of Er₂O₃.

With an increase of the additive content the average grain size decreases. As a result, for 0.5 at% of dopant, the average grain size is from 10 μm to 15 μm , and for the samples doped with 1.0 at% of dopant grain size decreased to the value of 5-10 μm , for both sintering temperatures (Fig. 1b and 2b).

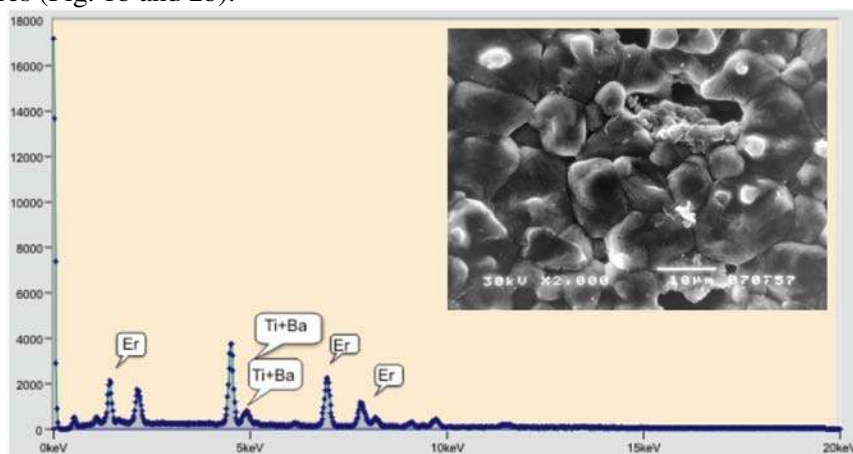


Fig. 3. SEM/EDS spectra of 1.0 at% Er doped BaTiO₃ sintered at 1350 °C.

EDS analysis of samples doped with 0.01 at% Er_2O_3 does not reveal any Er rich regions, thus indicated a uniform incorporation of dopants within the samples. It is worth noting that the concentrations less than 1.0 at% could not be detected by the EDS unless an inhomogeneous distribution or segregation of the additive was present. Increasing of dopant concentration leads to the appearance of Er rich regions between grains as shown in Fig. 3.

X-ray analysis of 0.01 at% Er doped BaTiO_3 samples shows only BaTiO_3 perovskite phase and uniform distribution of erbium. The increase of dopant content gives rise to the appearance of second phase $\text{Er}_2\text{Ti}_2\text{O}_7$ in 0.5 at% Er doped BaTiO_3 , (Fig. 4). By comparison of XRD peaks of undoped BaTiO_3 and Er doped BaTiO_3 , it is evident that XRD peaks of doped samples are shifted towards to lower values of 2θ thus indicating the increase of lattice parameters, i.e. the incorporation of Er on the Ti-sites rather than on Ba-sites in BaTiO_3 structure.

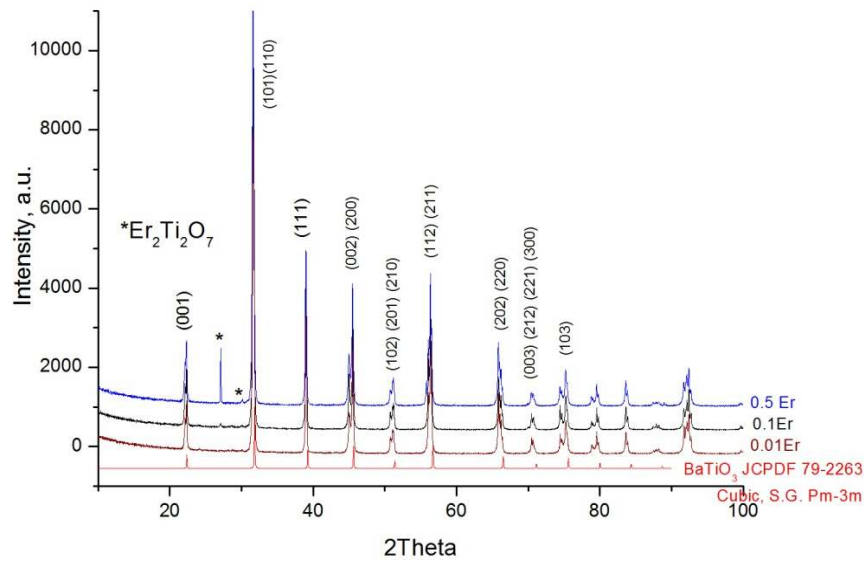


Fig. 4. X-ray analysis of Er doped BaTiO_3 .

4. Electrical characteristics

The observed microstructural characteristics, which depend on the type and concentration of additive, have a direct influence on the electrical properties.

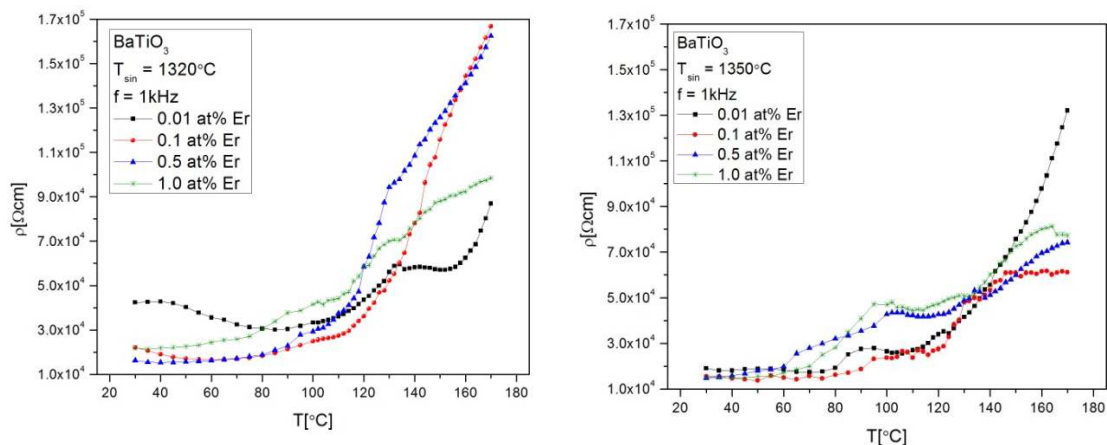


Fig. 5. The electrical resistivity – temperature dependence of Er doped BaTiO_3 ceramics, measured at frequency of 1 kHz.

Electrical resistivity of doped BaTiO₃ ceramics is measured as a function of frequency and temperature. The electrical resistivity – temperature dependences of Er doped BaTiO₃ ceramics, measured at frequency of 1 kHz, 10 kHz and 100 kHz, are shown in Fig. 5, 6 and 7, respectively. The lowest values of the electrical resistivity are measured at room temperature. The room temperature electrical resistivity, measured at frequency of 1 kHz, is ranged from $1.62 \cdot 10^4 \Omega\text{cm}$ to $4.24 \cdot 10^4 \Omega\text{cm}$ for the samples sintered at 1320 °C, and from $1.43 \cdot 10^4 \Omega\text{cm}$ to $1.94 \cdot 10^4 \Omega\text{cm}$ for samples sintered at 1350°C.

A relatively stable electrical resistivity response vs. temperature (from 25 °C to 120 °C) is noticed for all doped samples. Above this temperature, the electrical resistivity increases rapidly (Fig. 5). At the temperature of 170 °C and frequency of 1kHz, resistivity ranges from $9.84 \cdot 10^4 \Omega\text{cm}$ to $1.62 \cdot 10^5 \Omega\text{cm}$, for samples sintered at 1320 °C, and from $6.11 \cdot 10^4 \Omega\text{cm}$ to $1.32 \cdot 10^5 \Omega\text{cm}$ for T_{sin}=1350 °C.

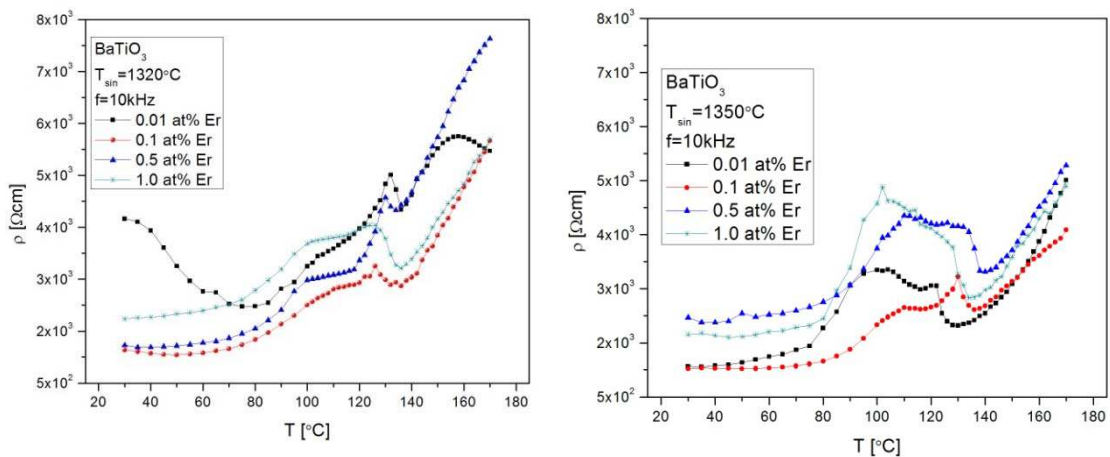


Fig. 6. The electrical resistivity of Er doped BaTiO₃ as a function of temperature, measured at frequency of 10 kHz.

With an increase frequency the electrical resistivity decreases (Fig. 6, 7). Electrical resistivity measured at frequencies of 10 kHz and 100 kHz is lower for two or three orders of magnitude in relation to the resistivity measured at 1 kHz. In the samples measured at these frequencies, a sharp increase in the electrical resistivity is observed, with maximum occurring between 100 °C and 130 °C, and after 130 °C the abrupt fall follows.

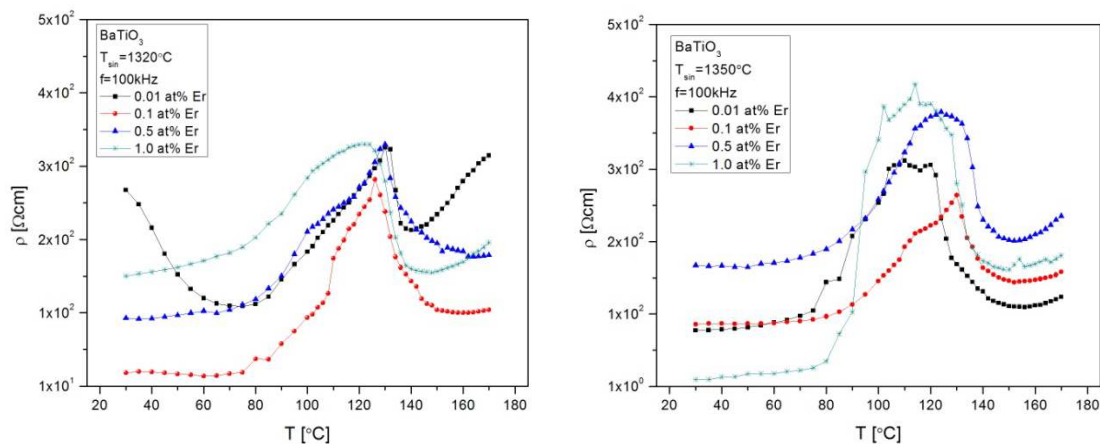


Fig. 7. The electrical resistivity of Er doped BaTiO₃ as a function of temperature, measured at frequency of 100 kHz.

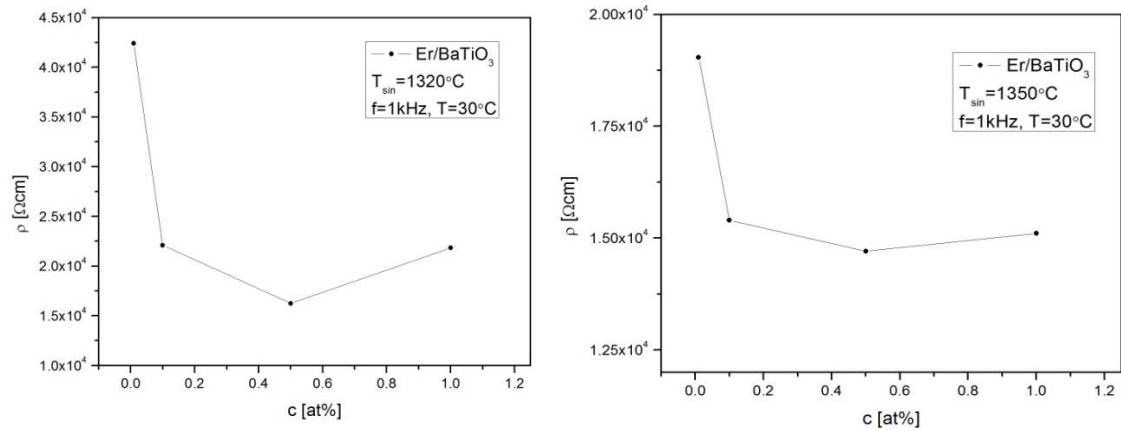
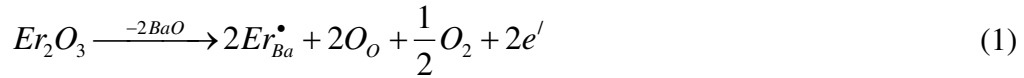


Fig. 8. The electrical resistivity of the Er doped BaTiO₃ as a function of additive content measured at room temperature and at a frequency of 1 kHz.

The electrical resistivity at room temperature decreases with increasing of donor content in the low doping level and reached the minimum at about 0.5 at% of donor concentration. Over 0.5 at%, ρ increased rapidly with increase of donor content (high doping level). The electrical resistivity of the Er doped samples as a function of additive content measured at room temperature and at a frequency of 1 kHz, is shown in Fig. 8. A similar relationship was observed at other frequencies.

At low doping level, Er occupies the Ba sites of BaTiO₃ perovskite lattice according to the equation:



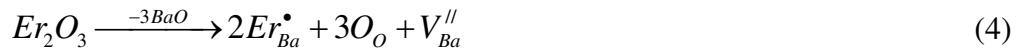
where Er_{Ba}^{\bullet} is the Er ion on a Ba site, O_O is an oxygen ion at O-site and e' is an electron in the conduction band. The equation (1) is in accordance with the expression of electrical resistivity:

$$\rho = \frac{1}{ne\mu} \quad (2)$$

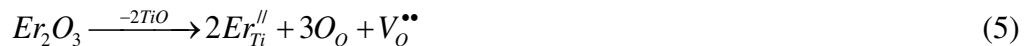
where n is free electron concentration and μ is electron mobility. The neutrality condition can be simplified as:

$$[Er_{Ba}^{\bullet}] = [e]. \quad (3)$$

The resistivity at room temperature decreases with increasing dopant concentration in the low doping level for the increasing conducting band electron. When the dopant content rises up to a certain value, Er can be compensated by negatively charged barium cation vacancies ($V_{Ba}^{//}$)



or, Er can occupy Ti site as acceptor and create oxygen vacancies ($V_O^{\bullet\bullet}$)

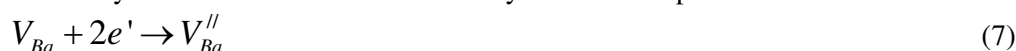


In this case free electron concentration decreases, resulting in the increase of the electric resistivity in the sample.

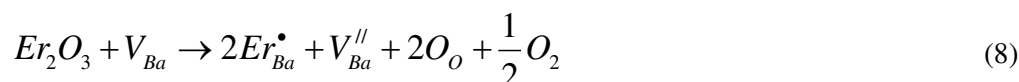
When the undoped BaTiO₃ is sintered in the air, the following defect reaction can occur:



In samples sintered in air, due to the high oxygen pressure at grain boundary, this reaction happens at the grain boundary rather than in the grain. The neutral barium vacancy may be ionized by the electron that is introduced by the donor dopant:



or



In doped BaTiO₃ ceramics, capturing of a free electron by neutral barium vacancy at the grain boundary or on the surface layers during the ferroelectric-paraelectric phase transition may be responsible for the considerable improvement of PTC effect. At low temperature, the PTC effect is determined by the concentration of neutral barium vacancies of the sample. With an increase of additive content, the concentration of neutral barium vacancies decreases.

High oxygen pressure can prevent the neutral barium vacancy from ionizing, as shown in equation (8). At the same time, high oxygen pressure can promote the production of neutral barium vacancy as in equation (6). The relation between donor content and the PTC effect may be changed by other impurities, but in the case of only being modified by donor dopant the PTC effect decreased with increase of donor content. The formation of the secondary phase may also affect the PTC properties for the possible difference in electrical characteristics between the BaTiO₃ and the secondary phase. If the formation of the secondary phase results from the Er₂O₃ additive, the real amount of the donor for the reactions as shown in Eqs. (1), (4) and (8) decreases and affect the quality of the electrical properties of BaTiO₃.

5. Conclusions

In this article the investigations of the influence of Er₂O₃ on BaTiO₃ ceramics microstructure and electrical resistivity have been presented. An abnormal grains growth and the average grain size ranged from 20 to 45 μm for both sintering temperature is characteristic for lower concentration of Er. With an increase of additive content the grain size decreases and for samples doped with 0.5 at% of additive the grain sizes are ranged from 10 to 15 μm, while for samples doped with 1.0 at% additive these are ranged from 2 to 5 μm. The electrical resistivity values at room temperature, measured at frequency of 1 kHz are ranged from 1.62·10⁴ Ωcm to 4.24·10⁴ Ωcm, for samples sintered at 1320 °C and from 1.4310⁴ Ωcm to 1.94·10⁴ Ωcm, for samples sintered at 1350 °C. Starting from room temperature to 120 °C a small variation in electrical resistivity and nearly flat and stable response is characteristic for all samples. Above this temperature, the electrical resistivity increases rapidly. With increasing additives concentration the electrical resistivity decreases to concentration of 0.5 at% and above 0.5 at% resistivity increases. Also with increasing frequency, electrical resistivity decreases for a few orders of magnitude.

Among others, the new doors are opening to further investigations of temperature correlation with number of particles and fractal temperature correction.

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Садржај: У овом раду испитивана су специфична електрична отпорност и РТС ефекат Er допирани ВаTiO₃ керамике. Концентрација Er₂O₃ у допираним узорцима кретала се у опсегу од 0.01 до 1.0 at% Er. Узорци су добијени конвенционалном методом синтеровања у чврстој фази и синтеровани на 1320 °C и 1350 °C у трајању од 4h. SEM анализа показала је да све узорке карактеришу полигонална зрна. Узорке са нижом концентрацијом адитива (0.01 и 0.1 at%) карактерише хомогена микроструктура са величином зрна од 20-45 μm. Код узорака допираних већом концентрацијом адитива (0.5 и 1.0 at%) карактеристичне су мање димензије зрна од 5 до 10 μm. Специфична електрична отпорност мерена је у температурном интервалу од 25 °C до 170 °C на фреквенцијама 1 kHz, 10 kHz и 100 kHz. Вредност специфичне електричне отпорности на собној температури мерена на фреквенцији од 1kHz

кретала се од $1.62 \cdot 10^{-4} \Omega \text{cm}$ до $4.24 \cdot 10^{-4} \Omega \text{cm}$ за узорке синтероване на 1320°C и од $1.43 \cdot 10^{-4} \Omega \text{cm}$ до $1.94 \cdot 10^{-4} \Omega \text{cm}$ за узорке синтероване на 1350°C . У интервалу од собне температуре до 120°C раст специфичне електричне отпорности је мањи, а изнад ове температуре долази до наглог пораста отпорности. На температури од 170°C вредност ρ кретала се од $9.84 \cdot 10^{-4} \Omega \text{cm}$ до $1.62 \cdot 10^{-5} \Omega \text{cm}$ за $T_{\text{sin}}=1320^\circ \text{C}$ и од $6.11 \cdot 10^{-4} \Omega \text{cm}$ до $1.32 \cdot 10^{-5} \Omega \text{cm}$ за $T_{\text{sin}}=1350^\circ \text{C}$. Са порастом концентрације адитива специфична електрична отпорност опада до концентрације од 0.5 at\% а затим почиње да расте. Такође са повећањем фреквенције вредност ρ опада и до неколико редова величине.

Кључне речи: BaTiO_3 ; микроструктура; синтеровање; адитиви; електричне карактеристике; РТС ефекат.

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