# Electrical Resistivity of Er/Yb doped $BaTiO_3$ ceramics

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***Abstract*-In this article, the specific electrical resistance ($\rho$) and PTCR (Positive Temperature Coefficient of Resistivity) effect Er/Yb doped $BaTiO_3$ ceramics were investigated. The content of additive $Er_2O_3$ and $Yb_2O_3$ in doped samples were ranged from 0.01 to 1.0 at% Er/Yb. The samples were prepared by a conventional solid state sintering procedure and sintered at 1320° and 1350°C for 4 hours. For low dopants concentration (0.01 at% Er/Yb), SEM analysis shows abnormal grain growth with the average size range between 20 μm - 40 μm for samples doped with $Er_2O_3$ and from 30 μm - 50 μm for samples doped with $Yb_2O_3$. The increase of dopants concentration in samples causes decrease of average grain size, and for samples doped with 1.0 at% Er/Yb, grain size range between 3 μm - 20 μm for Er doped samples and between 1 μm - 10 μm for samples doped with $Yb_2O_3$. The specific electrical resistance were measured in temperature range from 25°C to 170°C at different frequencies, from 100Hz to 1MHz. To a temperature of 120°C, resistance has a slight increase with increasing of temperature, but above this temperature the resistance rapidly increasing. The value of the specific electrical resistance decreases with increasing concentration of Er/Yb, to a concentration of 0.5 at% Er/Yb, and then resistance increases. Also, with increasing frequency, resistivity is lower for an order of magnitude.**

**Index Terms - $BaTiO_3$; microstructure; specific electrical resistance; PTCR effect.**

## I. Introduction

A modified $BaTiO_3$ ceramics with different additives/dopants belongs to the group of the most investigated ferroelectric material due to its attractive electrical, ferroelectric and piezoelectric properties.

It is used widely in electronic devices such as multilayer capacitors, thermistors, piezoelectric sensors, energy conversion systems, ultrasonic converters, radio filters, etc. [1 – 3]. The dielectric properties of polycrystalline $BaTiO_3$ strongly dependent on the microstructure development, which depends on the type, concentration and the distribution of dopants. In order to obtain $BaTiO_3$ ceramics with a high value of dielectric constant, it is necessary to establish high density, homogeneous and fine-grained microstructure, as well as uniform distribution of dopants and additives [4, 5].

Two types of dopants can be introduced into $BaTiO_3$ lattice. Ions with larger ionic radii of valence 3+ and higher replaces predominately $Ba^{2+}$ sites, and the ions with smaller ionic radii of valence 5+ and higher can be incorporated into the $Ti^{4+}$ sublattice. Considering the perovskite structure of $BaTiO_3$, the incorporation of trivalent rare-earth cations ($Ho^{3+}$, $Dy^{3+}$, $Er^{3+}$, $Yb^{3+}$) may modifies the microstructural and electrical properties of doped $BaTiO_3$. The PTCR effect of $BaTiO_3$ based ceramics depends on the additive concentration and sintering process. The ceramics were often modified by not only one dopant, and the relationship between the PTCR effect and donor content can be changed easily. For lower donor concentration (lower then 0.5 at%), the bimodal microstructure is obtained and abnormal grain growth occurred, which leads to semiconductive properties of ceramics at room temperature and PTCR effect [6 – 10]. In this paper, the specific electrical resistance and the PTCR effect in $BaTiO_3$ ceramics, doped with different dopant were studied. The samples were doped with $Er_2O_3$ and $Yb_2O_3$.

The microstructure of samples was observed by scanning electron microscope (SEM). The variation of specific electrical resistance with temperature was measured in the range from 100Hz to 1MHz.

## II. Experimental procedure

In this paper, $Er_2O_3$ and $Yb_2O_3$ doped $BaTiO_3$ ceramics, were studied. The content of additive ranged from 0.01 to 1.0 at% Er and Yb. The samples were prepared by a conventional solid state sintering procedure starting from reagent grade powder $BaTiO_3$ (Rhone Poulenc Ba/Ti=0.996±0.004) and $Er_2O_3$ (Fluka chemika) and $Yb_2O_3$ (Fluka chemika). Starting powders were ball milled in ethyl alcohol. After milling powders were drying for several hours, and pressed into pellets 2 mm thick and 7 mm in diameter under 120 MPa. The pellets were sintered in air at 1320°C and 1350°C for 4 hours.

The microstructure of the sintered samples were observed by scanning electron microscope JOEL-JSM 5300 equipped with EDS (QX 2000S) system. Before samples were observing, electrical contacts were prepared by silver paste. The variation of specific electrical resistance with temperature were measured in temperature interval from

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25°C to 170°C by using LCR meter Agilent 4248A at different frequencies, from 100Hz to 1MHz.

## III. Results and Discussion

### A. Microstructure characteristics

The relative density of Er doped samples was ranged from 83% to 93% of theoretical density (TD). For samples doped with Yb, the relative density was ranged from 87% to 90% TD. Density of all doped samples were increased with the increase of sintering temperature and decrease with the increase of dopant amount. So the highest values of density (93%) was measured for samples doped with 0.01 at% Er, sintered at 1350°C. The smallest density (83%) was measured for samples doped with 1.0 at% Er, sintered at 1320°C.

The samples of $BaTiO_3$ ceramics doped with $Er_2O_3$ characterized polygonal grains. The average grain size for samples doped with low content of $Er_2O_3$ (0.01 at% Er) ranged from 20 to 40μm (Fig. 1a. and Fig. 1b.) for both temperature sintering.

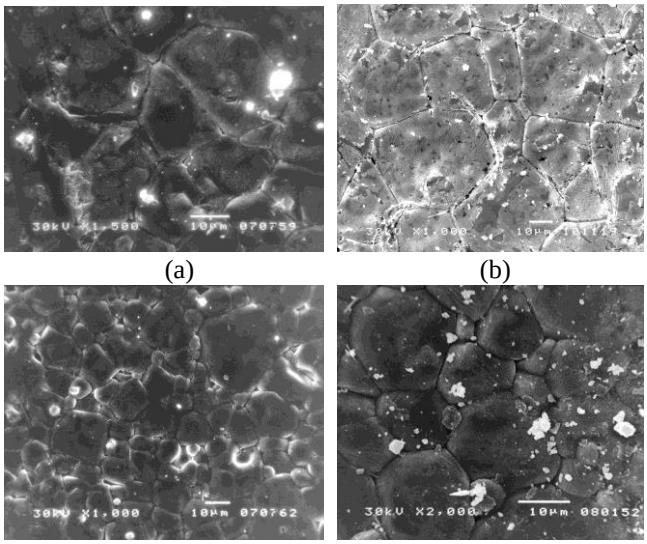


Fig. 1. SEM images of Er doped $BaTiO_3$ ceramics a) 0.01 at% Er, Tsin=1320°C and b) 0.01 at% Er, Tsin=1350°C and c) 1.0 at% Er, Tsin=1320°C and d) 1.0 at% Er, Tsin=1350°C.

By increasing dopant concentration the grain size decreases. As a result, for 1.0 at% Er of dopant the average grain size is from 5 μm to 10μm for samples sintered at 1320°C (Fig. 1c.). Average grain size for samples sintered at 1350°C is from 3 μm to 20 μm (Fig. 1d.).

For the samples of $BaTiO_3$ ceramics doped with low content of $Yb_2O_3$, for both sintering temperature, are characteristic spherical grains and abnormal grain growth. The average grain size for samples doped with 0.01 at% Yb sintered at 1320°C is from 5 μm to 20μm (Fig. 2(a)). For samples doped with 0.01 at% Yb sintered at 1350°C, the average grain size is from 30 μm to 50 μm (Fig. 2(b)). By increasing dopant concentration, there was a drastic reduction in grain size from a few μm for samples doped with 1.0 at% Yb sintered at 1320°C (Fig. 2(c)). The average grain size for samples doped with 1.0 at% Yb sintered at 1350°C is from 2 μm to 7 μm (Fig. 2(d)). Spiral concentric grain growth is typical for samples with lower concentrations of additives. Such grain growth is not observed in samples with a higher concentration of additives.

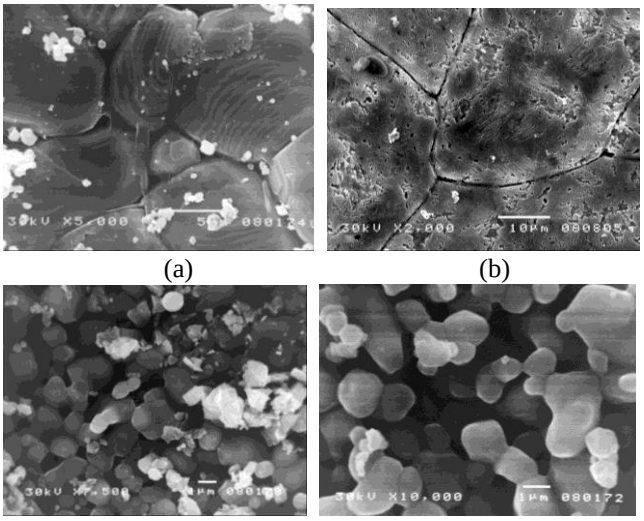
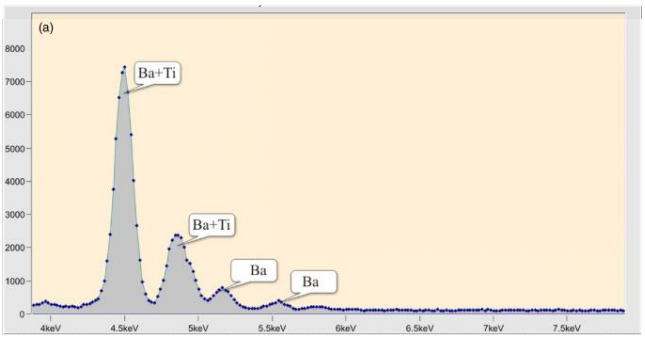


Fig. 2. SEM images of Yb doped $BaTiO_3$ ceramics a) 0.01 at% Yb, Tsin=1320°C and b) 0.01 at% Yb, Tsin=1350°C and c) 1.0 at% Yb, Tsin=1320°C and d) 1.0 at% Yb, Tsin=1350°C.

EDS analysis of samples doped with 0.01 at% $Er_2O_3$ and $Yb_2O_3$ did not reveal any Er- or Yb-rich regions, which indicated a uniform incorporation of dopants within the samples (Fig. 3(a)).

EDS analysis cannot detect the concentration of element less than 1.0 at% Er or Yb unless an inhomogeneous distribution or segregation of dopant is present. The increase of dopant concentration leads to the appearance of Er- or Yb-rich regions between grains (Fig. 3(b) and Fig. 3(c)). These areas, rich of additives, are also characteristic for fine-grained microstructure.



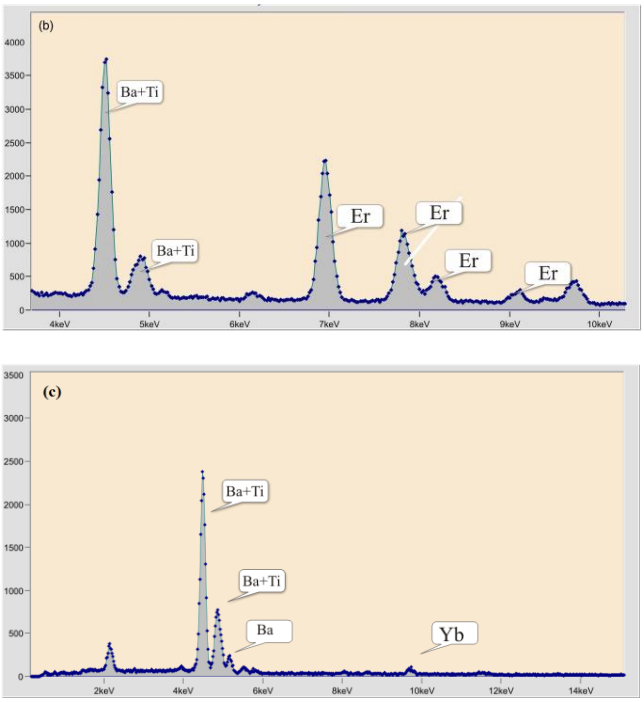



Fig. 3. EDS analysis of doped $BaTiO_3$ sintered at 1320°C: (a) 0.01 at% Er-$BaTiO_3$, where no Er is detected, (b) 1.0 at% Er-$BaTiO_3$, intergranularly located Er-rich regions and (c) 1.0 at% Yb- $BaTiO_3$ where is located Yb-rich regions.

## *B. Electrical characteristics*

The specific electrical resistance of the samples doped with $Er_2O_3$ and $Yb_2O_3$ measured at room temperature, at frequencies of 1 kHz and 10 kHz, as a function of dopant content is shown in Fig. 4 and Fig.5. A similar relationship was observed at other frequencies.

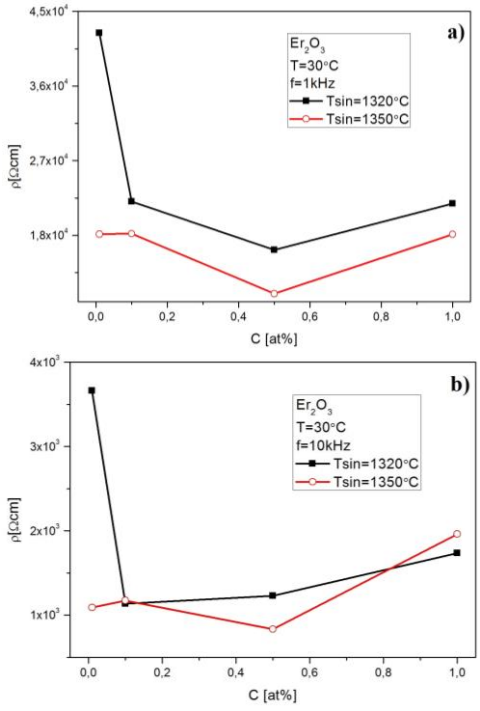



Fig. 4. Electrical resistivity as a function of $Er_2O_3$ content measured at a) *f*=1kHz, and b) *f*=10kHz.

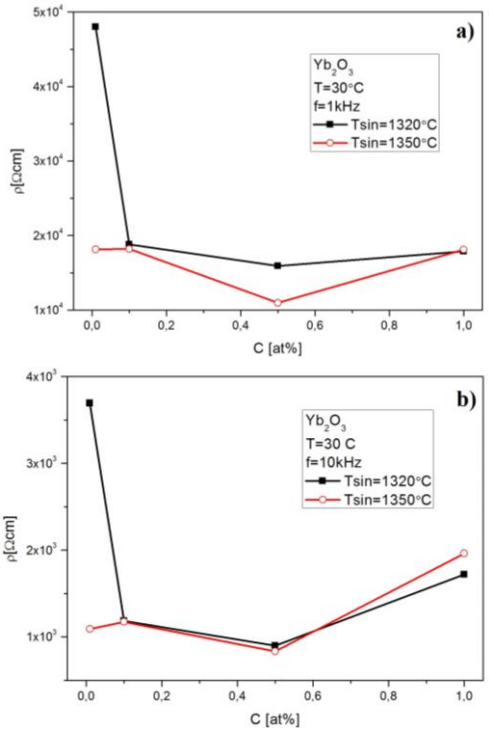



Fig. 5. Electrical resistivity as a function of $Yb_2O_3$ content measured at a) *f*=1kHz, and b) *f*=10kHz.

The room temperature resistance of measured samples doped with $Er_2O_3$ decreased with the dopant content in the low doping level, reached the minimum at certain dopant content (0.5 at%), then increased rapidly with dopant content in high doping level. Similar dependence have and room temperature resistance of the samples doped with $Yb_2O_3$. In the low doping level, dopant (where D is Er or Yb) replaces Ba-site as in equation (1) [11].

$$D_2O_3 \rightarrow 2D_{Ba}^{\bullet} + 2O_O^x + \frac{1}{2}O_2(g) + 2e' \qquad (1)$$

Equations (1) applies, because the conductivity of the materials decided by:

$$\sigma = ne\mu \qquad (2)$$

where $\sigma$ is electrical conductivity (reciprocal of resistivity), $n$ is free electron concentration and $\mu$ is electron mobility. The neutrality condition of samples doped with Er and Yb can be simplified as:

$$\left[Er_{Ba}^{\bullet}\right] = [e], \text{ and } \left[Yb_{Ba}^{\bullet}\right] = [e] \qquad (3)$$

Specific electrical resistance at room temperature is decreasing with increasing of dopant content. When dopant content increases up to a certain value, the dopant can be composed by cation vacancies:

$$D_2O_3 \rightarrow 2D_{Ba}^{\bullet} + 3O_O^x + V_{Ba}^{''} \quad (4)$$

or, dopant can occupy Ti-site act as acceptor

$$D_2O_3 + 2e' \rightarrow 2D_{Ti}^{''} + 3O_O^x + V_O^x \quad (5)$$

Free electron concentrations decrease, and the resistivity of samples increase for both dopant.

The temperature dependence of specific electrical resistance of samples doped with Er and Yb, is shown in Fig. 6.

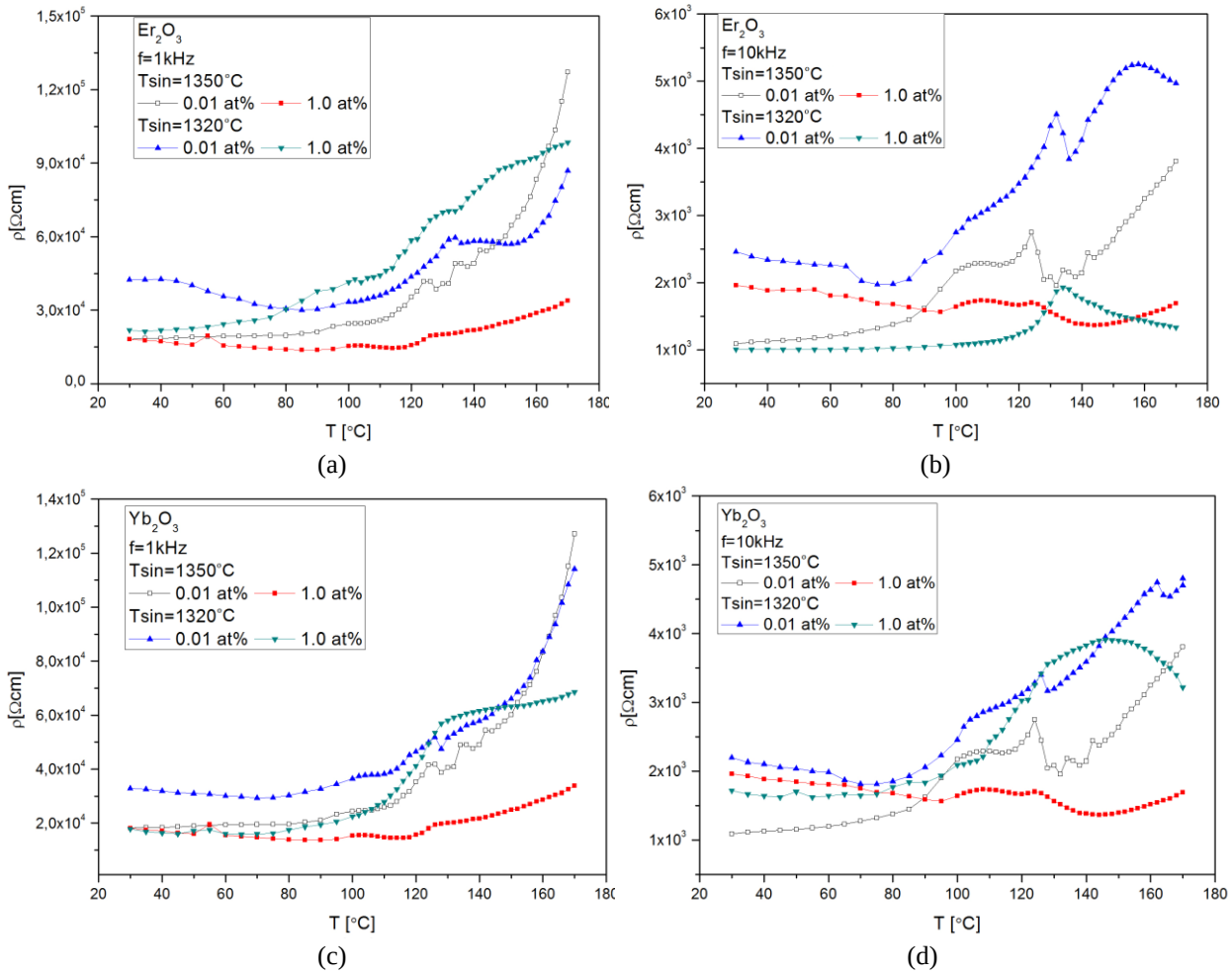



Fig. 6. Electrical resistivity as a function of temperature: (a) Er-doped samples at 1 kHz; (b) Er-doped samples at 10 kHz; (c) Yb-doped samples at 1 kHz; (d) Yb-doped samples at 10 kHz.

Fig. 6. shows the values of resistivity for the samples measured at frequencies of 1kHz (Fig. 4(a) and Fig. 4(c)) and 10kHz (Fig. 4(b) and Fig. 4(d)). A similar relationship was observed for the other concentrations of measured samples. The lowest values of specific electrical resistance was measured at room temperature, and then the specific electrical resistance increases with increasing temperature.

The specific electrical resistance values at room temperature measured at 1kHz is ranged from $2.18 \cdot 10^4$ Ωcm to $4.24 \cdot 10^4$ Ωcm for samples doped with $Er_2O_3$ and sintered at 1320°C and from $1.81 \cdot 10^4$ Ωcm to $1.82 \cdot 10^4$ Ωcm for samples sintered at 1350°C. From room temperature to 120°C, a relative stable electrical resistance vs. temperature response was observed for all samples. Above this temperature is observed a sudden increase in electrical resistance. The specific electrical resistance at 170°C was from $8.69 \cdot 10^4$ Ωcm to $9.84 \cdot 10^4$ Ωcm for samples sintered at 1320°C and from $3.39 \cdot 10^4$ Ωcm to $1.27 \cdot 10^5$ Ωcm for samples sintered at 1350°C.

For samples doped with $Yb_2O_3$ are characteristic lower values of electrical resistance compared with values of samples doped with $Er_2O_3$. Lower values of electrical resistance as a result of the microstructural characteristics (fine-grained microstructure) and lower density of these samples. For 0.01 at% Yb samples, sintered at 1320°C specific electrical resistance at room temperature measured at 1 kHz is ranged from $1.79 \cdot 10^4$ Ωcm to $3.28 \cdot 10^4$ Ωcm. For samples sintered at 1350°C, the electrical resistivity is from $1.81 \cdot 10^4$ Ωcm to $1.82 \cdot 10^4$ Ωcm. As well as in samples doped with $Er_2O_3$, a relatively stable electrical resistance vs. temperature response was observed for temperature up

to 120°C, and a sudden rise in resistivity above this temperature. At 170°C the specific electrical resistance has value from $6.85 \cdot 10^4$ Ωcm to $1.14 \cdot 10^5$ Ωcm for $Yb_2O_3$ doped samples sintered at 1320°C and from $3.39 \cdot 10^4$ Ωcm to $1.27 \cdot 10^5$ Ωcm for samples sintered at 1350°C.

As it can be seen in Fig.4, for both series of samples, with an increase sintering temperature the specific electrical resistance decreases. The lower value of the electrical resistance was measured for samples sintered at 1350°C. For these samples is characteristic a larger grain size, homogeny microstructure and higher density.

With increasing frequency the electrical resistance of the samples decreases. As is shown in Fig. 4(b) and Fig. 4(d) specific electrical resistance measured at frequency of 10 kHz is reduced, and it is lower by an order of magnitude.

Specific electrical resistance at room temperature ranged from $1.01 \cdot 10^3$ Ωcm to $2.46 \cdot 10^3$ Ωcm for samples doped with $Er_2O_3$ and sintered at 1320°C and from $1.09 \cdot 10^3$ Ωcm to $1.96 \cdot 10^3$ Ωcm for samples sintered at 1350°C.

With an increase of temperature the electrical resistivity increase and at temperature of 170°C, $\rho$ was between $1.33 \cdot 10^3$ Ωcm to $4.97 \cdot 10^3$ Ωcm for Er/$BaTiO_3$ samples sintered at 1320°C and from $4.40 \cdot 10^3$ Ωcm to $4.51 \cdot 10^3$ Ωcm for samples sintered at 1350°C.

The samples doped with $Yb_2O_3$ measured at frequency of 10kHz has $\rho$ at room temperature ranged from $1.71 \cdot 10^3$ Ωcm to $2.20 \cdot 10^3$ Ωcm for samples sintered at 1320°C, and from $1.09 \cdot 10^3$ Ωcm to $1.96 \cdot 10^3$ Ωcm for samples sintered at 1350°C.

In the similar way as in the samples measured at frequency of 1 kHz, the$Yb_2O_3$ and $Er_2O_3$ doped samples measured at 10 kHz, have a slight increase in resistance with temperature to 120°C. Above this temperature the resistance suddenly increases.

Value of specific electrical resistance at 170°C for samples doped with $Yb_2O_3$ was from $3.21 \cdot 10^3$ Ωcm to $4.70 \cdot 10^3$ Ωcm for samples sintered at 1320°C and from $1.69 \cdot 10^3$ Ωcm to $3.80 \cdot 10^3$ Ωcm for samples sintered at 1350°C.

When the pure $BaTiO_3$ sintered in air, supporting the reaction defects:

$$\frac{1}{2}O_2(g) \rightarrow O_O^x + V_{Ba}^x \tag{6}$$

Because of the high pressure air at the grain boundaries when the samples were sintered in air, the reaction is going on at the grain boundaries rather than in the grains of the grid. Neutral barium vacancies can be ionized electron, which is incorporated by donor dopants:

$$V_{Ba}^x + 2e' \rightarrow V_{Ba}^{''} \tag{7}$$

or,

$$D_2O_3 + V_{Ba}^x \rightarrow 2D_{Ba}^{\bullet} + V_{Ba}^{''} + 2O_O^x + \frac{1}{2}O_2(g) \tag{8}$$

In $Er_2O_3$ and $Yb_2O_3$ doped $BaTiO_3$ ceramics, the concentration of barium cation vacancies at the grain boundaries or on the surface layers may be responsible for the considerable improvement of the PTCR effect.

From equations (7) and (8), with the rising of the donor content, the concentration of neutral barium vacancy, which the excess donor is decreasing. As can be seen from equation (8), the high pressure oxygen cannot protect the neutral barium vacancies of ionization. At the same time it can promote the production of neutral barium vacancy as (6).

## IV. Conclusion

In this article the influence of donor ($Er_2O_3$ and $Yb_2O_3$) dopant content on specific electrical resistance and PTCR effect of $BaTiO_3$ doped ceramics sintered at 1320°C and 1350°C has been investigated. Microstructural studies have shown that for lower concentration of dopant (0.01 at% Er/Yb) characteristic abnormal grain growth with the average size range between 20-40 μm for samples doped with $Er_2O_3$ for both sintering temperature and from 30-50 μm for samples doped with $Yb_2O_3$. The increase of dopant concentration in samples, leads to decrease of average grain size and for samples doped with 1.0 at% Er/Yb, the average grain size range from 3-20μm for samples doped with $Er_2O_3$ and from 1-3 μm for samples doped with $Yb_2O_3$. The dependence of the specific electrical resistance at room temperature in doped $BaTiO_3$ samples showed that the resistance of the samples depends on the donor concentration. The value of the specific electrical resistance decreases with increasing concentration of Er/Yb, to a concentration of 0.5 at% Er/Yb, and then increase. Also, at higher frequencies, the electrical resistance is lower for an order of magnitude. The lowest values of specific electrical resistance were measured at room temperature. With an increase of temperature the specific electrical resistance increases. The value of specific electrical resistance at room temperature range from $1.81 \cdot 10^4$ Ωcm to $4.24 \cdot 10^4$ Ωcm for samples doped with $Er_2O_3$ and from $1.79 \cdot 10^4$ Ωcm to $3.28 \cdot 10^4$ Ωcm for 0.01 at% Yb doped samples. For both series of samples, with an increase sintering temperature the specific electrical resistance decreases. The lower value of the electrical resistance was measured for samples sintered at 1350°C. Also with increasing frequency, the specific electrical resistance decreases for a few orders of magnitude.

## Acknowledgment

The authors gratefully acknowledge the financial support of Serbian Ministry of Education, Science and Technological Development. This research is a part of the Projects OI-172057, TR-32026 and TR-33035.

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