

# Sintering Temperature Influence on Electrical Resistivity of Er doped BaTiO<sub>3</sub> ceramics

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**Abstract-** The electrical resistivity ( $\rho$ ) of Er doped BaTiO<sub>3</sub> ceramics in function of sintering temperature is investigated in this article. The concentrations of Er<sub>2</sub>O<sub>3</sub> in doped samples were ranged from 0.01 to 1.0 at% Er. The samples were prepared by a conventional solid state sintering procedure and sintered at 1320°C, 1350°C and 1380°C for 4 hours. For low dopants concentration (0.01 at% Er), SEM analysis shows abnormal grain growth with the average size range between 10  $\mu\text{m}$  - 50  $\mu\text{m}$ . The increase of dopants concentration and sintering temperature in samples causes decrease of average grain size, and for samples doped with 1.0 at% Er, grain size range between 2  $\mu\text{m}$  - 30  $\mu\text{m}$ . The electrical resistivity was measured in temperature range from 25°C to 170°C at different frequencies, from 100 Hz to 1 MHz. To temperature of 120°C, resistivity slightly increases with increasing of temperature, but above this temperature the resistivity increases rapidly. The value of the electrical resistivity decreases with increasing concentration of Er, to a concentration of 0.5 at% Er, and then resistivity increases. Also, with increasing sintering temperature the electrical resistivity decreases.

**Index Terms** - BaTiO<sub>3</sub> ceramics; microstructure; electrical resistivity.

## INTRODUCTION

Multilayer ceramic capacitors, thermistors, piezoelectric sensors and PTC resistors can be realized based on BaTiO<sub>3</sub> ceramics doped with suitable additives [1], [2]. A modified BaTiO<sub>3</sub> ceramics with different additives/dopants belongs to the group of the most investigated ferroelectric material due to its attractive electrical, ferroelectric and piezoelectric properties. The dielectric properties of polycrystalline BaTiO<sub>3</sub> strongly dependent on the microstructure development, which depends on the type, concentration and the distribution of dopants.

In order to obtain BaTiO<sub>3</sub> 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 [3]-[5]. Two types of dopants can be introduced into BaTiO<sub>3</sub> lattice. For the

rare-earth ion incorporation into the BaTiO<sub>3</sub> lattice, the BaTiO<sub>3</sub> defect chemistry mainly depends on the lattice site where the ion is incorporated [6]. It has been shown that the three-valent ions incorporated at the Ba<sup>2+</sup>-sites act as donors, which extra donor charge is compensated by ionized Ti vacancies ( $V_{\text{Ti}}^{\text{'''}}$ ), the three-valent ions incorporated at the Ti<sup>4+</sup>-sites act as acceptors which extra charge is compensated by ionized oxygen vacancies ( $V_{\text{O}}^{\text{'}}$ ), while the ions from the middle of the rare-earth series show amphoteric behavior and can occupy both cationic lattice sites in the BaTiO<sub>3</sub> structure [7]. As a result, the abnormal grain growth and the formation of deep and shallow traps at grain boundaries influenced by the presence of an acceptor-donor dopant can be observed. Depending on the size of the rare earth radius ions, which is in magnitude between the ionic radii Ba<sup>2+</sup> or Ti<sup>4+</sup> ions, rare earth cations such as Er<sup>3+</sup>, Yb<sup>3+</sup>, Ho<sup>3+</sup> and Dy<sup>3+</sup> can occupy Ba or Ti positions in the perovskite BaTiO<sub>3</sub> structure [8], [9]. The electric properties, especially electrical resistivity of polycrystalline BaTiO<sub>3</sub>, depend to a great extent on the grain growth during sintering as well as the type and concentration of dopants [10]-[12]. Also, the electrical resistivity of BaTiO<sub>3</sub> 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 electrical resistivity and donor content can be changed easily. For lower donor concentration (lower than 0.5 at %), the bimodal microstructure is obtained and abnormal grain growth occurred, which leads to semiconductive properties of ceramics at room temperature [13]. In this paper, the influence of sintering temperature on electrical resistivity of Er<sub>2</sub>O<sub>3</sub> doped BaTiO<sub>3</sub> ceramics, were studied.

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

## EXPERIMENTAL PROCEDURE

Modified BaTiO<sub>3</sub> ceramics doped with 0.01, 0.1, 0.5 and 1.0 at% of Er<sub>2</sub>O<sub>3</sub> was obtained by conventional solid-state sintering method starting from pure oxide powders BaTiO<sub>3</sub> (Rhone Poulenc Ba/Ti=0.996±0.004) and Er<sub>2</sub>O<sub>3</sub> (Fluka chemika). 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 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

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1320°C, 1350°C and 1380°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 electrical resistance with temperature were measured in temperature interval from 25°C to 170°C by using LCR meter Agilent 4248A at different frequencies, from 100Hz to 1MHz.

## RESULTS AND DISCUSSION

### Microstructure characteristics

The samples of BaTiO<sub>3</sub> ceramics doped with Er<sub>2</sub>O<sub>3</sub> are characterized by irregular polygonal grains. The average grain size for samples doped with low content of Er<sub>2</sub>O<sub>3</sub> (0.01 at% Er) ranged from 10 μm to 50 μm (Fig. 1.) for all temperature sintering.

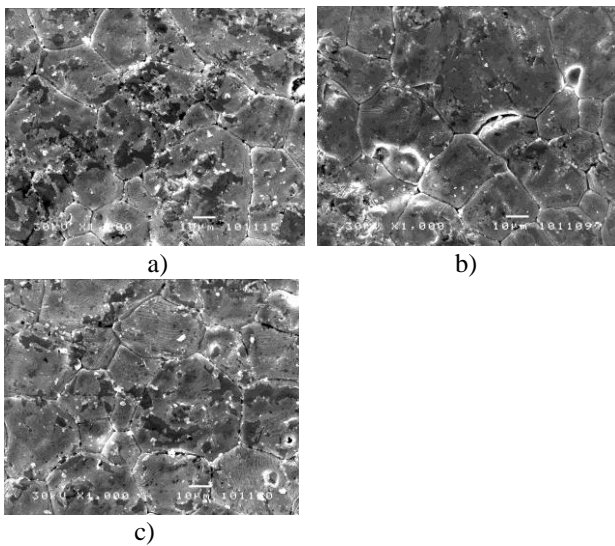


Fig. 1. SEM images of 0.01 at% Er doped BaTiO<sub>3</sub> ceramics sintered at a) Tsin=1320°C, b) Tsin=1350°C and c) Tsin=1380°C.

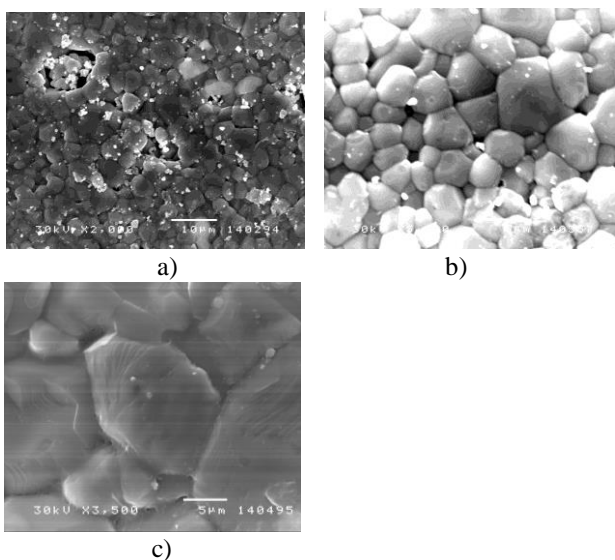


Fig. 2. SEM images of 1.0 at% Er doped BaTiO<sub>3</sub> ceramics sintered at a) Tsin=1320°C, b) Tsin=1350°C and c) Tsin=1380°C.

By increasing dopant concentration the grain size decreases. As a result, for 1.0 at% Er of dopant the average grain size is from 2 μm to 5 μm for samples sintered at 1320°C (Fig. 2a)). With increase sintering temperature the average grain size increase and for samples sintered at 1350°C is from 2 μm to 10 μm (Fig. 2b)), and for samples sintered at 1380°C, the average grain size is from 5 μm to 30 μm (Fig. 2c)).

Such a microstructure is in accordance with the change of density of the investigated samples, which ranged from 83% to 95% of the theoretical density (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 1380°C. The smallest density (83%) was measured for samples doped with 1.0 at% Er, sintered at 1320°C.

EDS analysis of samples doped with 0.01 at% Er<sub>2</sub>O<sub>3</sub> did not reveal any Er-rich regions, which indicated a uniform incorporation of dopants within the samples (Fig. 3a)).

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

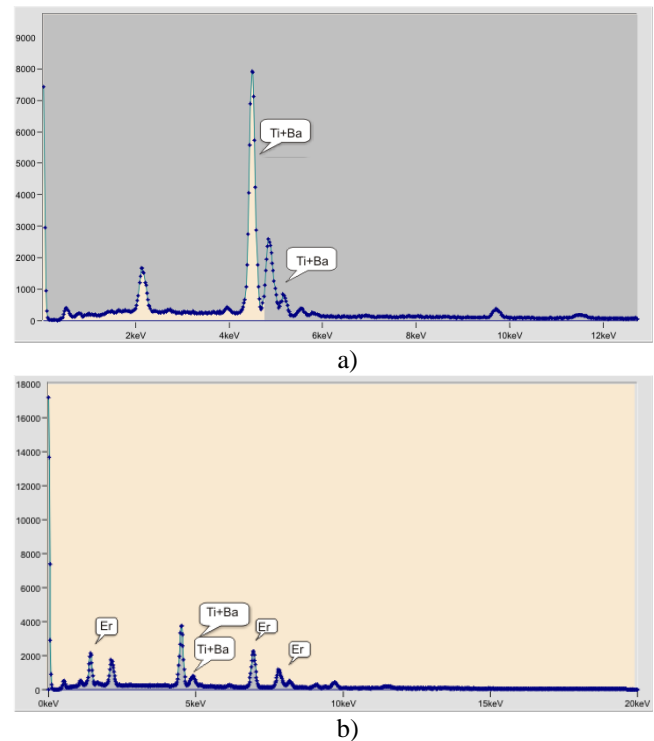


Fig. 3. EDS analysis of doped BaTiO<sub>3</sub> sintered at 1320°C: a) 0.01 at% Er-BaTiO<sub>3</sub>, where no Er is detected and b) Er-rich regions in 1.0 at% Er-BaTiO<sub>3</sub>.

### Electrical characteristics

The electrical resistivity of the samples doped with Er<sub>2</sub>O<sub>3</sub> measured at room temperature, sintered at 1320°C, 1350°C

and 1380°C at frequencies of 5 kHz and 500 kHz, as a function of dopant content is shown in Fig. 4. A similar relationship was observed at all other measured frequencies.

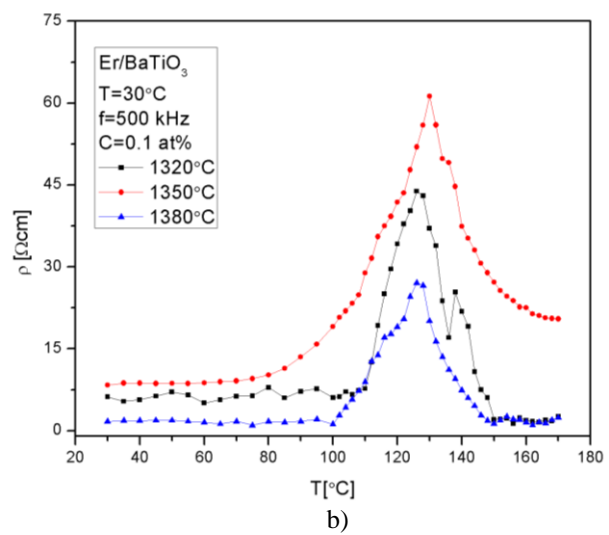
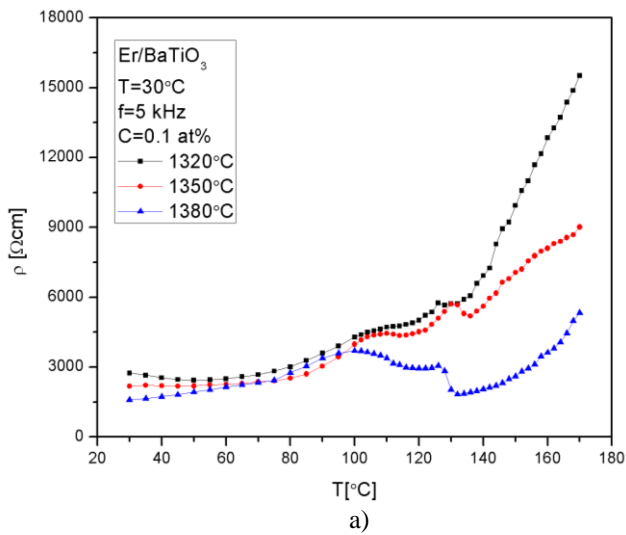
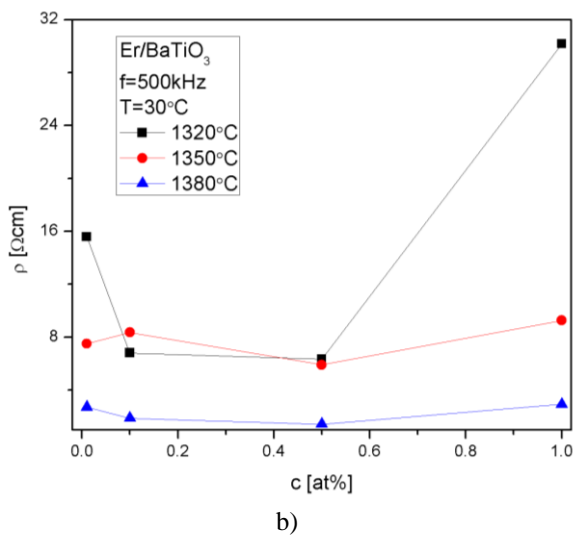
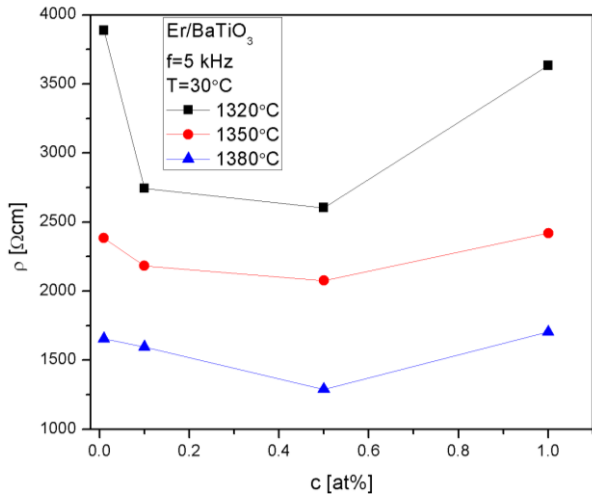
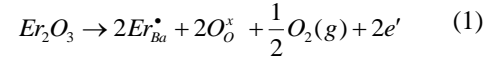


Fig. 4. Electrical resistivity as a function of  $\text{Er}_2\text{O}_3$  content measured at a)  $f=5$  kHz, and b)  $f=500$  kHz.

The electrical resistance measured at room temperature for samples doped with  $\text{Er}_2\text{O}_3$  (Fig. 4.) decreased with the increase dopant content in the low doping level (0.5 at%), reached the minimum at 0.5 at% dopant content and then increased rapidly with dopant content in high doping level. If the content of Erbium is below 0.5 at%, it replaces the Ba-sites in the  $\text{BaTiO}_3$  lattice. This is shown by the equation (1).



where  $\text{Er}_{\text{Ba}}^*$  is the Er ion on a Ba site,  $\text{O}_\text{O}^\times$  is an oxygen ion at O-site and  $e'$  is an electron in the conduction band.

The temperature dependence of electrical resistivity of 0.1 at% Er doped samples sintered at 1320°C, 1350°C and 1380°C is shown in Fig. 5.

Fig. 5. shows the values of resistivity for the samples doped with 0.1 at%  $\text{Er}_2\text{O}_3$  measured at frequencies of 5kHz and 500kHz (Fig. 5a) and Fig. 5b) and samples doped with 1.0 at%  $\text{Er}_2\text{O}_3$  at frequencies of 5kHz and 500kHz (Fig. 5c) and Fig. 5d). A similar relationship was observed for the other concentrations of measured samples. As can be seen from Fig. 5, electrical resistivity of measured samples depends largely on the type and concentration of the additive. Also, the obtained microstructure, which depend on the additive concentration and sintering temperature, have a direct influence on the electrical properties of doped samples. With increasing temperature, the electrical resistivity increases, so that the lowest value of  $\rho$  is measured at room temperature. The electrical resistivity, measured at room temperature and at frequency of 5 kHz for samples doped with 0.1 at% Er (Fig. 5a), is ranged from  $1.59 \cdot 10^4 \Omega\text{cm}$  for samples sintered at 1380°C, to  $2.74 \cdot 10^4 \Omega\text{cm}$  for samples sintered at 1320°C.

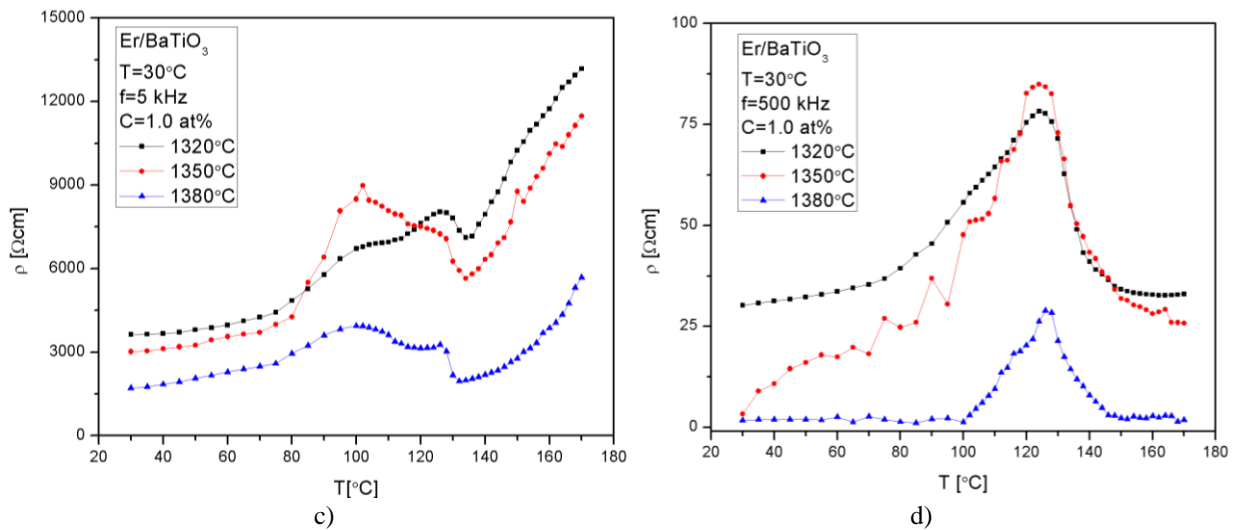


Fig. 5. Temperature dependence of resistivity: a) 0.1 at% Er-doped samples at 5 kHz; b) 0.1 at% Er-doped samples at 500 kHz; c) 1.0 at% Er-doped samples at 5 kHz; d) 1.0 at% Er-doped samples at 500 kHz.

As can be seen in Fig. 5a), in the temperature range from 25°C to 120°C, a relative stable electrical resistivity vs. temperature response was observed for all samples. Above this temperature there is a sudden increase in electrical resistivity. At 170°C resistivity for samples doped with 0.1 at% Er, was from  $5.33 \cdot 10^3 \Omega\text{cm}$  for samples sintered at 1380°C to  $1.55 \cdot 10^4 \Omega\text{cm}$  for samples sintered at 1320°C.

As can be seen from the results shown in Fig.5, for all the series of the investigated samples, with increasing sintering temperature, the electrical resistivity decrease. The lower value of the electrical resistivity was measured for samples sintered at 1380°C. For these samples is characteristic a larger grain size, homogeneity microstructure and higher density.

A similar relationship was observed for the other concentrations of measured samples. For samples doped with 1.0 at% Er (Fig. 5c)), measured at frequency of 5kHz, the lower value of  $\rho$  was measured for samples sintered at 1380°C,  $\rho = 1.70 \cdot 10^3 \Omega\text{cm}$ . The highest value of electrical resistivity was measured for samples sintered at 1320°C,  $\rho = 3.63 \cdot 10^3 \Omega\text{cm}$ .

With increasing frequency the electrical resistivity of the samples decreases. As it is shown in Fig. 5b) electrical resistivity measured at frequency of 500 kHz is reduced, and it is lower by two order of magnitude.

The 0.1 at%  $\text{Er}_2\text{O}_3$  doped samples at frequency of 500kHz (Fig. 5b)) have electrical resistivity at room temperature ranged from 1.68  $\Omega\text{cm}$  for the samples sintered at 1380°C to 6.21  $\Omega\text{cm}$  for samples sintered at 1320°C. Similar as like for samples measured at 5 kHz, in the temperature range from 25° to 120°C, a relative stable electrical resistivity vs. temperature response was observed for all samples. Above this temperature there is a sudden increase in electrical resistivity. At 170°C resistivity for samples doped with 0.1 at% Er and measured at frequency of 500kHz, was from 2.39  $\Omega\text{cm}$  for the samples sintered at 1380°C to 2.65  $\Omega\text{cm}$  for samples sintered at 1320°C.

With increasing dopant content, for samples doped with 1.0 at% Er (Fig. 5d)) and measured at frequency of 500 kHz, increase and the value of electrical resistivity. Lowest value of  $\rho$  for samples measured at room temperature was ranged from 1.73  $\Omega\text{cm}$  for the samples sintered at 1380°C to  $2.65 \cdot 10^1 \Omega\text{cm}$  for samples sintered at 1320°C. In the similar way as in the samples measured at frequency of 500 kHz, the 0.1 at%  $\text{Er}_2\text{O}_3$  and 1.0 at%  $\text{Er}_2\text{O}_3$  doped samples measured at 500 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 1.0 at%  $\text{Er}_2\text{O}_3$  was from 1.88  $\Omega\text{cm}$  for samples sintered at 1380°C to  $3.30 \cdot 10^1 \Omega\text{cm}$  for samples sintered at 1380°C.

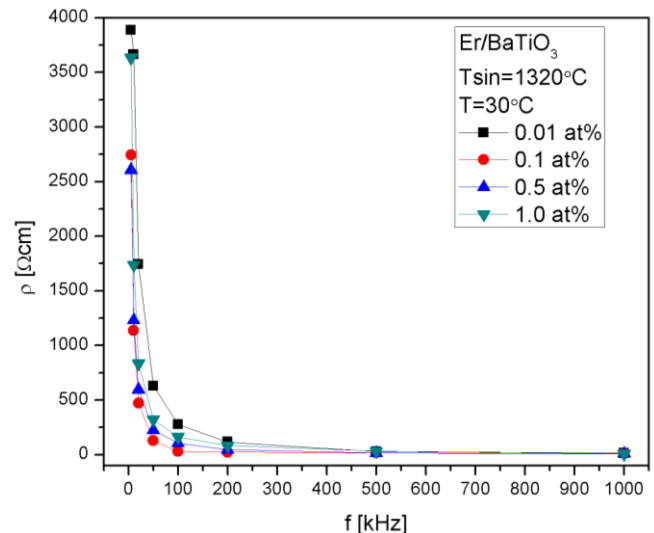
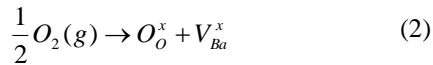


Fig. 6. Electrical resistivity as a function of frequency for Er doped  $\text{BaTiO}_3$  ceramic sintered at 1320°C .

As shown at Fig.6 the electrical resistivity of samples sintered at 1320°C decreasing with increases frequency, and for high frequencies it is lower by few order of magnitude. A

similar dependence of the resistivity with the frequency was obtained for the other two temperatures.

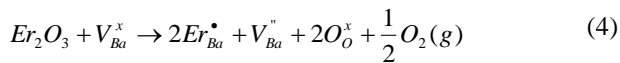
When the pure BaTiO<sub>3</sub> sintered in air, supporting the reaction defects:



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:



or,



At low temperature, the value of electrical resistivity is determined by the concentration of neutral barium vacancies of the sample. With an increase of additive content and sintering temperature, the concentration of neutral barium vacancies decreases. The relation between donor content and the value of electrical resistivity can be changed by adding other impurities, but only if it is modified by donor dopant, the value of electrical resistivity decreased with increase of donor content and sintering temperature.

#### IV. CONCLUSION

In this article the influence of donor (Er<sub>2</sub>O<sub>3</sub>) dopant content and sintering temperature on electrical resistivity of BaTiO<sub>3</sub> doped ceramics has been investigated. Microstructural studies have shown that for lower concentration of dopant (0.01 at% Er) characteristic abnormal grain growth with the average size range between 10-50 μm for samples sintered at all three temperatures. The increase of dopant concentration in samples, leads to decrease of average grain size and for samples doped with 1.0 at% Er, the average grain size range from 2-30 μm. The dependence of the electrical resistivity at room temperature in doped BaTiO<sub>3</sub> samples showed that the resistance of the samples depends on the donor concentration and sintering temperature. The value of the electrical resistivity decreases with increasing concentration of Er, to a concentration of 0.5 at% Er, and then increase. Also, at higher frequencies, the electrical resistivity is lower for an order of magnitude. The lowest values of electrical resistivity were measured at room temperature. With an increase of temperature the electrical resistivity increases. The value of electrical resistivity at room temperature range from

1.59·10<sup>3</sup> Ωcm to 3.6·10<sup>3</sup> Ωcm for samples doped with Er<sub>2</sub>O<sub>3</sub>. For all investigated samples, with an increase sintering temperature the electrical resistivity decreases. The lowest value of the electrical resistance was measured for samples sintered at 1380°C. Also with increasing frequency, the electrical resistivity decreases for a few orders of magnitude.

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