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Application of the Intergranular Impedance Model in Correlating Microstructure and Electrical Properties of Doped $BaTiO_3$

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Abstract:

Microstructure properties of barium-titanate based materials, expressed in grain boundary contacts, are of basic importance for electric properties of this material. In this study, the model of intergranular impedance applied on a two-grain contact is considered. Globally, a $BaTiO_3$-ceramics sample consists of a large number of mutually contacted grains, which form clusters. Such clusters can be presented as specific fractal formations. For each of them, it is possible to establish the equivalent electrical model and, for a defined set of input parameters, using symbolic analysis, obtain the frequency diagram. The influence of fractal structure is especially stressed. Realizing the totality of relations between cluster grain groups, their microelectrical schemes and corresponding frequency characteristics, on one hand, and the global equivalent electrical scheme and corresponding acquired frequency characteristics of $BaTiO_3$-ceramics samples, on the other hand, we set a goal of correlating experimental results with the summing effect of microelectric equivalent schemes. The model is successfully tested on doped barium- titanate ceramics.

Keywords: *Barium-titanate, Microstructure, Fractals, Clusters, Intergranular impedance, Optimization*

Introduction

Doped barium-titanate ceramic is attracting much interest for its application as resistors with a positive temperature coefficient of resistivity (PTCR), multilayer ceramic capacitors (MLCC), thermal sensors etc [1, 2]. In the process of $BaTiO_3$-ceramics consolidation, technological parameters like pressing pressure, initial sample's density, sintering temperature and time, as well as different dopants, essentially determine the final electrical properties of the ceramics. A slight change of a particular consolidation parameter, or the change of the dopant concentration can significantly change the microstructure, thus influencing electrical properties of the specimens. Since grain size and distribution considerably affect electrical properties of barium-titanate based materials, correlation of their microstructure and electrical properties has been investigated most extensively by numerous authors [3-5]. It has been shown that electrical properties of non-doped and doped $BaTiO_3$-ceramics are mainly controlled by the barrier structure, domain motion of domain boundaries and the effects of internal stress in the grains [6-7]. Using variable-frequency measurements,

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and irrespective of the nature of the material under study, it is possible to separate the effects of electroactive components such as grain boundary and grain [8]. As a result an impedance model can be used for probing the relaxational processes during charge transport within the electronic ceramics. The equivalent circuit can be envisaged as a series of grouped elements, i.e. several resistance and capacitance elements in parallel, each corresponding to a different process occurring at the electrode interface, at the grain boundaries or within the grains themselves [9].Therefore, microstructure properties of barium-titanate based materials, expressed in grain boundary contacts, are of basic importance for electric properties of this material. Usually, for electronic materials design, the microstructure of this type of ceramics can be considered to be as sketched in the cross section of Fig. l(a) and simplified by a brick wall model [10] (Fig. l(b)).

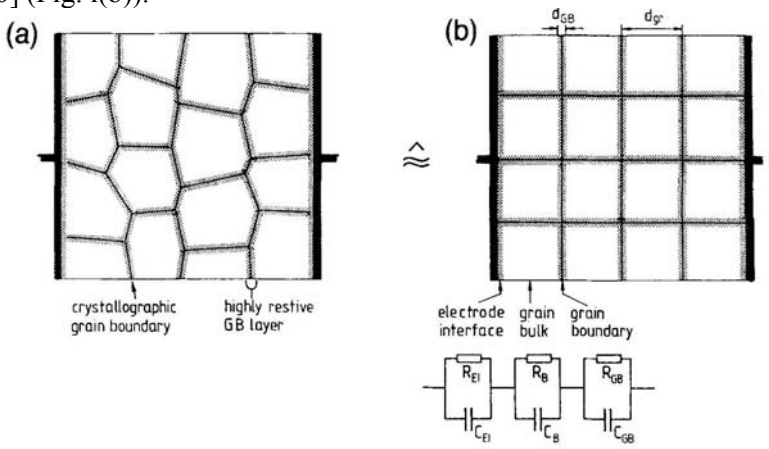

Fig. 1. Sketched cross section of a ceramic sample with electrodes applied (a), corresponding simplified brick wall model (b), and the equivalent electrical network

The model illustrates the polarization and the conduction contributions to the total impedance of the system, which can be represented by an electrical equivalent network consisting of three RC branches. The elements of the network may be attributed to the permittivities, conductivities, and geometrical extensions of the grain bulk (G), grain boundary regions (GB), and electrical interfaces (EI). It is well known that both the intergranular structure and electrical properties depend on the ceramics diffusion process. Therefore it is essential to have an equivalent circuit model that provides a realistic representation of the electrical properties. Having this in mind, the purpose of this article is to determine an intergranular impedance model based on intergranular capacity of $BaTiO_3$-ceramics doped with different rare earth additives.

Experimental Procedure

The samples were prepared from high purity (>99.98) commercial $BaTiO_3$ powder (MURATA) with [Ba]/[Ti]=1,005 and reagent grade Er_2O_3 and Yb_2O_3 powders (Fluka chemika). Er_2O_3 and Yb_2O_3 dopants were used in the amounts to have 0.01, 0.1 and 0.5 wt% Er or Yb in $BaTiO_3$. Starting powders were ball milled in ethyl alcohol for 24 h using a polypropylene bottle and zirconia balls. After drying at 200^{o}C for several hours, the powders were pressed into disks 7 mm in diameter and 3 mm in thickness under 120 MPa. The compacts were sintered 4 h in air up to 1380^{o}C. The microstructures of as sintered or chemically etched samples were observed by a scanning electron microscope (JEOL-JSM 5300) equipped with an energy dispersive X-ray analysis spectrometer (EDS-QX 2000S system). Prior to electrical measurements silver paste was applied on flat surfaces of

specimens. Capacitance, dissipation factor and impedance measurements were done using an Agilent 4284A precision LCR meter in the frequency range of 20 to 10^6 Hz. The illustrations of the microstructure simulation were generated by Mathematica 6.0 software.

Results and Disscussion

The necessary step in designing $BaTiO_3$-ceramics is research of the correlation between the material's microstructure, consolidation parameters and final properties. Structure research based on the application of basic methods strongly provides better understanding of dielectric properties, especially for pure and doped $BaTiO_3$ ceramics. These properties are mainly influenced by the region near the grain boundary and in the grain contact. This is the reason for the great importance of modeling grain geometry, grain boundary surfaces and the geometry of grain contacts. In order to establish the model of intergranular impedance for doped barium titanate, it is important to notice that microstructure properties of $BaTiO_3$ based materials, expressed in their grain boundary contacts, are of basic importance for electric properties of these materials. The barrier character of the grain boundaries is especially pronounced for doped $BaTiO_3$ materials which are used as PTC resistors. Basically two types of dopants can be introduced into $BaTiO_3$: large ions of valence 3+ and higher, can be incorporated into Ba^{2+} positions, while the small ions of valence 5+ and higher, can be incorporated into the Ti^{4+} sublattice [11,12]. Usually, the extent of the solid solution of a dopant ion in a host structure depends on the site where the dopant ion is incorporated into the host structure, the compensation mechanism and the solid solubility limit [14]. For rare-earth-ion incorporation into the $BaTiO_3$ lattice, the $BaTiO_3$ defect chemistry mainly depends on the lattice site where the ion is incorporated [7].

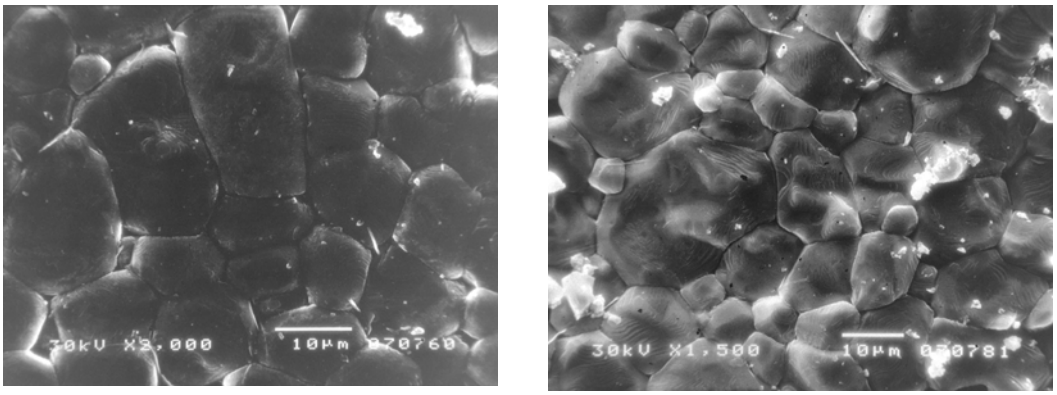

Fig.2. SEM micrograph of doped $BaTiO_3$ sintered at 1320°C a) 0.5Er-BT and b) 0.5Yb-BT.

It has been shown that the three-valent ions incorporated at the Ba^{2+} -sites act as donors, where the extra donor charge is compensated by ionized Ti vacancies ($V_{Ti}^{''''}$), the three-valent ions incorporated at the Ti^{4+} -sites act as acceptors where the extra charge is compensated by ionized oxygen vacancies ($V_O^{\cdot\cdot}$), while the ions from the middle of the rare-earth series show amphoteric behavior and can occupy both cationic lattice sites in the $BaTiO_3$ structure [13]. It has been established that the Ba/Ti ratio also influences the incorporation of rare earth dopants into the barium titanate lattice [14]. Investigations of the influence of Er on $BaTiO_3$ defect chemistry pointed out that for Ba/Ti>1 Er^{3+} enters on the titanium site, and for Ba/Ti < 1, it enters on the barium site. Moreover, erbium incorporation on barium or titanium sites introduces a charge mismatch with the lattice (an aliovalent

dopant) that must be charge compensated to achieve overall neutrality [15]. As a result of rare-earth addition, 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.

Our investigations showed that the microstructure of the samples doped with Er_2O_3 or Yb_2O_3 exhibit similar microstructure characteristics with the existence of an intergranular capacity. The samples sintered with Er_2O_3 showed that the grains were irregularly polygonal shaped (Fig. 2a), although in Yb doped $BaTiO_3$ the grains are more spherical in shape (Fig.2.b).

For the lowest concentration, the size of the grains was large (up to 60 μm), but by increasing the dopant concentration the grain size decreased. As a result, for 0.1 wt% of dopant the average grain size was from 20 to 30 μm, and for the samples doped with 0.5 wt% of dopant grain size decreased to the value up to 10 μm as can be seen from the cumulative grain size distribution curves for doped $BaTiO_3$, given in Fig 3.

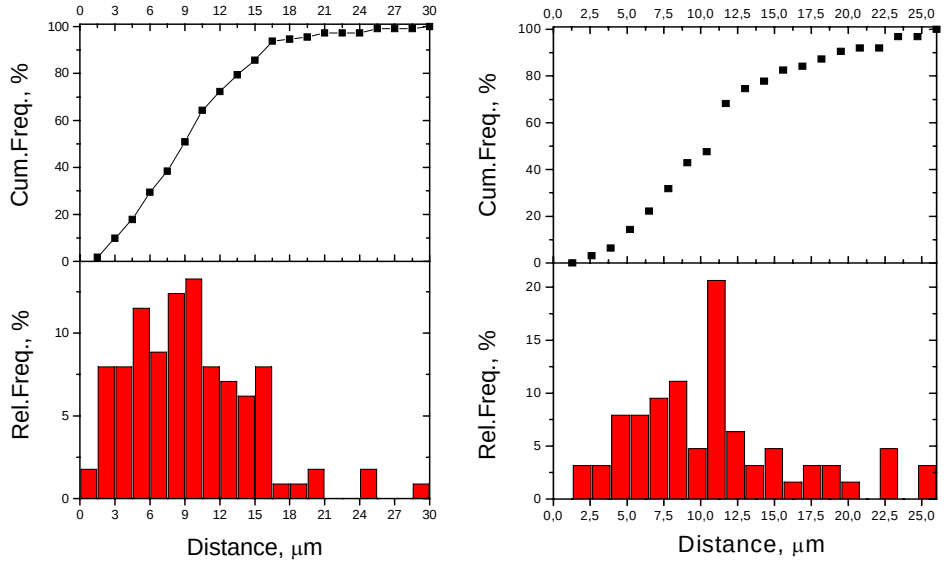

Fig. 3. Cumulative grain size distribution curves for doped $BaTiO_3$ with a) 0.5 wt% Er_2O_3, and b) 0.5 wt% Yb_2O_3.

Spiral concentric grain growth has been noticed for the samples sintered with a low concentration of Er_2O_3 or Yb_2O_3. For these samples the formation of a "glassy phase" indicated that sintering occurred in a liquid phase.

EDS analysis has shown that for the small concentrations of Er and Yb, a uniform distribution can be noticed (Fig.4a), while the increase of dopant concentration led to coprecipitation between grains (Fig.4b).

As a result, the region between the grains can be represented by an electrical equivalent network consisting of three RC branches as noted in the introduction.

All this allowed us to consider the $BaTiO_3$-ceramics sample as a system with a large number of mutually contacted grains which form clusters. For each of them, it is possible to establish an equivalent electrical model and, for a defined set of input parameters, using symbolic analysis, obtain the frequency diagram. Realizing the totality of relations between clusters grains groups, their microelectrical schemes and corresponding frequency characteristics, on one hand, and a global equivalent electrical scheme and corresponding acquired frequency characteristics of $BaTiO_3$-ceramics samples, on the other hand, we set a goal of correlating experimental results with the summing effect of microelectric equivalent schemes.

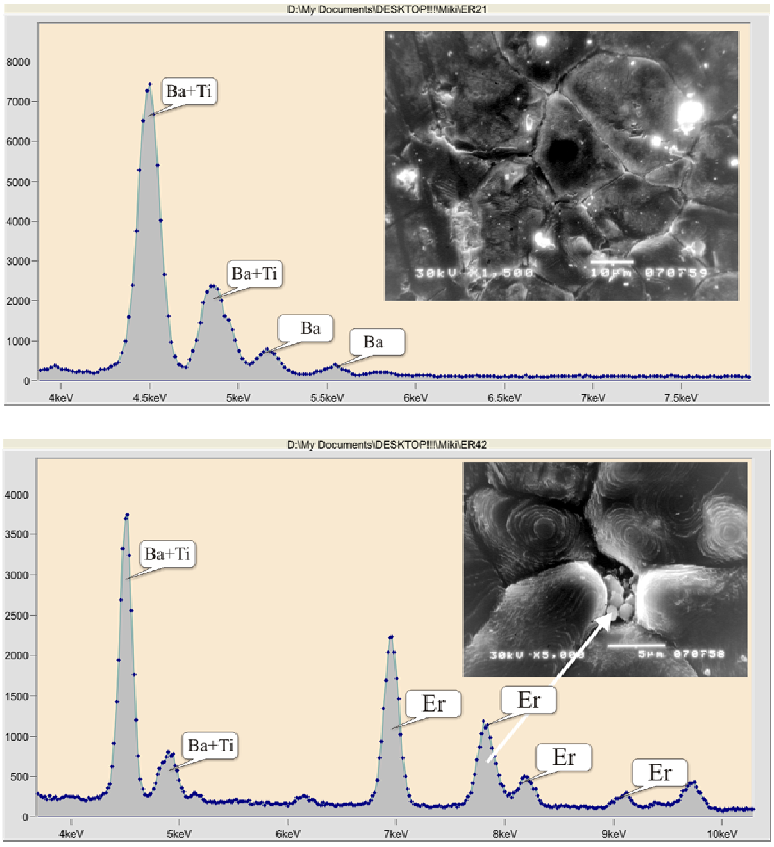

Fig.4. SEM/EDS spectra of doped $BaTiO_3$ sintered at 1320°C a) 0.1Er-BT and b) 0.5Er-BT

According to the microstructures we obtained for $BaTiO_3$ doped with Er_2O_3 and Yb_2O_3 it can be concluded that the global impedance of a barium-titanate ceramics sample, which contains both the resistor and capacity component, can be presented as a "sum" of many clusters of micro-resistors and micro-capacitors connected in tetrahedral lattice. Our microstructure analysis showed that at the beginning the microstructure can be simulated as cluster of spheres or ellipsoids which later deform as a result of the densification process and contacts formation. Therefore, for the general model of the stereological configuration of $BaTiO_3$ the density of the sample can be defined by mutual positions of neighboring grains (Fig. 5).

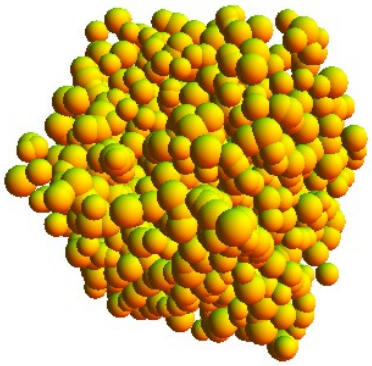

Fig 5. Simulation of the 1000 grains of $BaTiO_3$ obtained from the general model of the stereological configuration.

The developed model gives the distribution of grain contacts through the sample volume. As it can be seen from the typical spatial situation of a four grain cluster (Fig. 6), the positions of the neighboring grains can be: 1. in touching contact; 2. slightly immerging one into another and 3. not touching each other.

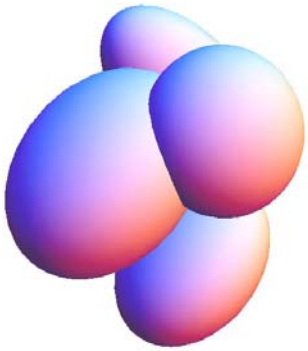

Fig. 6. Positions of neighboring grains for the four grains cluster.

This configuration logically leads to the tetrahedral scheme of mutual electrical influence of $BaTiO_3$ grains. The impedances are at each edge of the tetrahedron, as shown on Fig. 7. The vertices (in Fig. 7 displayed as small spheres) are stylized grains, while impedances contain resistance and capacity between two grains.

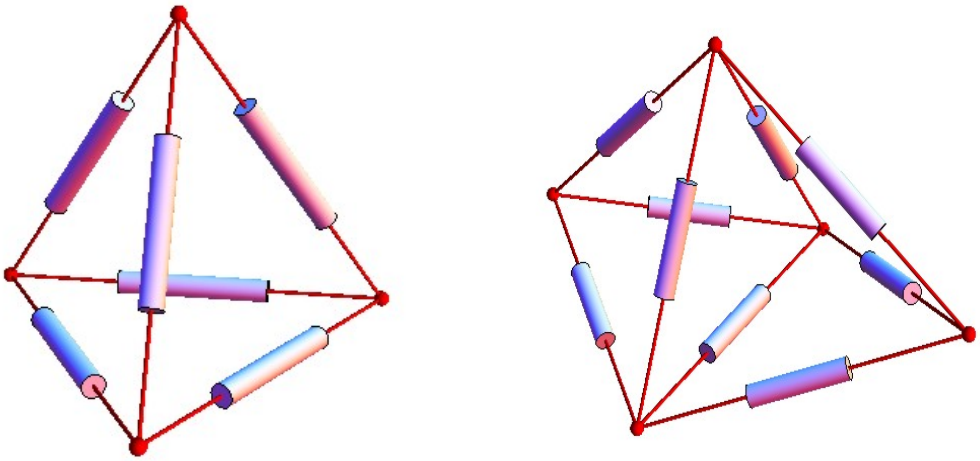

Fig. 7. Impedance model of tetrahedron.

Our new approach includes fractal geometry in describing the complexity of the spatial distribution of $BaTiO_3$ grains. The best fractal model is a sponge model, or and it is more correct to say, a kind of three –dimensional lacunary set (a set with voids). The structure of tetrahedral influence may be established in each spatial sense, which means that one has a tetrahedral lattice that fills the space.

This kind of fractals is sometimes identified with a deterministic construction like a *Cantor set* (in P), *Sierpinski triangle* or *Sierpinski square* (in P^2), with a *Sierpinski pyramid* or *Menger sponge* (in P^3), and so on. In our case of electric impedance property, the *Sierpinski pyramid* (Fig. 8) might be an adequate paradigm for the first instance inquiry. The starting pyramid $\mathbf{T}_0$ and the first two iterations, shown in Fig. 7, give the initial part of the orbit of the so called Hutchinson operator W, that is $\mathbf{T}_1 = W(\mathbf{T}_0)$, and $\mathbf{T}_2 = W(\mathbf{T}_1) = W^2(\mathbf{T}_0)$. The boundary case, $\mathbf{T} = W^{\infty}(\mathbf{T}_0)$ is an exact fractal set with a Hausdorff dimension $D_H = 2$.

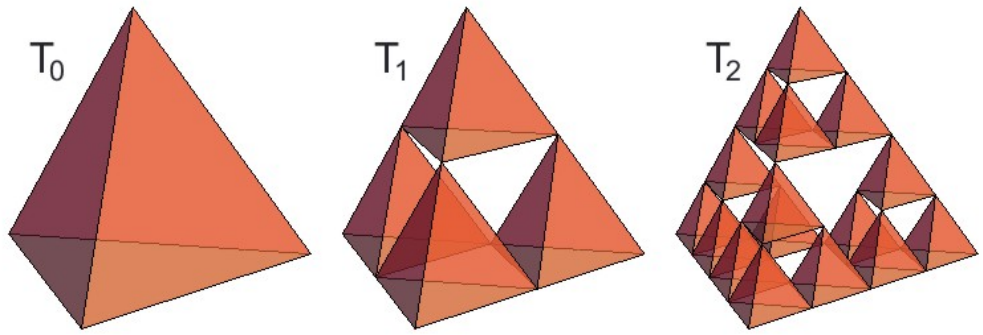

Fig. 8. Sierpinski pyramid.

Following this model of a Sierpinski pyramid, the induced model of impedances between clusters of ceramics grains is displayed in Fig 9. The task is to calculate the equivalent impedance for the pyramid $\mathbf{T}_k$ as a function of k.

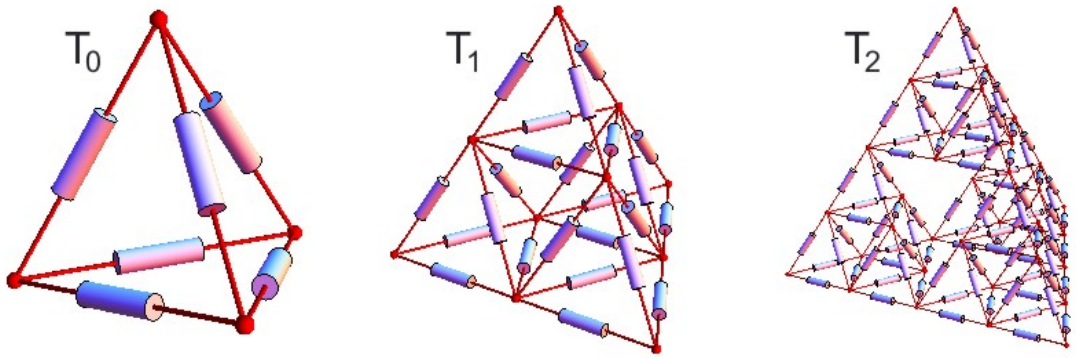

Fig. 9. Model of impedances between clusters of ceramics grains.

Some of the impedances in this lattice are missing following the lacunary fractal pattern. According to [16, 17], the fractal dimension of a typical ceramics sample is estimated to be about 2.087. So in this case, the fractal dimension of $BaTiO_3$ –ceramics is slightly below 3. The higher values of fractal dimensions can be obtained for a denser $BaTiO_3$ –ceramics. The dimension close to 3 means that not many impedances are lacking in the tetrahedral lattice. On the other hand, dimensions closer to 2.5 alert to a high presence of pores which means that many impedances are to be swept in the model of the tetrahedral impedance lattice. What is sure is that $BaTiO_3$ sintered ceramics can be considered as a lacunar fractal rather than a percolation fractal or succolar fractal [18].

In order to calculate equivalent impedance for a wide frequency range, the equivalent electrical circuit for a ceramic material can be introduced as a impedance containing two capacitances C and C_p, an inductance L and a resistance R.

The dominant electrical parameter of our model is the capacitance C. The connection between C and geometrical and/or structural properties can be established by an assumption that the contact region can be viewed as a planar micro-capacitance. Fig.10. shows a geometric model of two spheres in contact, where r_c is the radius of the spherical particles, and x is the neck radius.

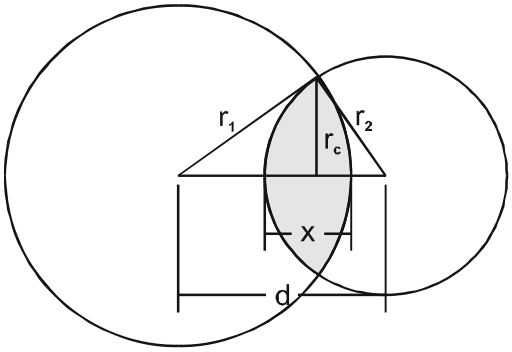

Fig .10 Two-sphere contact model presented in the plane section.

Since the spherical shape and the circular neck profile are assumed, the contact surface is the circle of the area πx^2. Because of center-to center approach, the dielectric thickness 2h is a function of d (the distance between centers of particles) according to the relation $2h=2r_c-d$. Therefore, the capacitance can be written as:

$$C = \varepsilon_o \varepsilon_r \alpha \frac{\pi x^2}{2r_c - d} \qquad (d = 2\sqrt{r_c^{\,2} - x^2})$$

where ε_o and ε_r are the dielectric constants of vacuum and the ceramic material, respectively and α is a correction factor obtained by a constructive approach to the fractal structure. Taking into account that by the fractal theory α can be presented as:

$$\alpha = D - D_T$$

where $D \approx 2.08744$ is the fractal (Hausdorff) dimension of the intergrain contact surface and $D_T=2$ is the topological dimension of the surface, it can be concluded that for $BaTiO_3$ doped ceramics contact surfaces are of low-irregularity which is characterized by the small difference $D - D_T \approx 0.08744$.

Taking this into account, calculations of micro-capacitance generated in grains contacts of $BaTiO_3$ doped with Er_2O_3 and Yb_2O_3 have been performed (fig. 11).

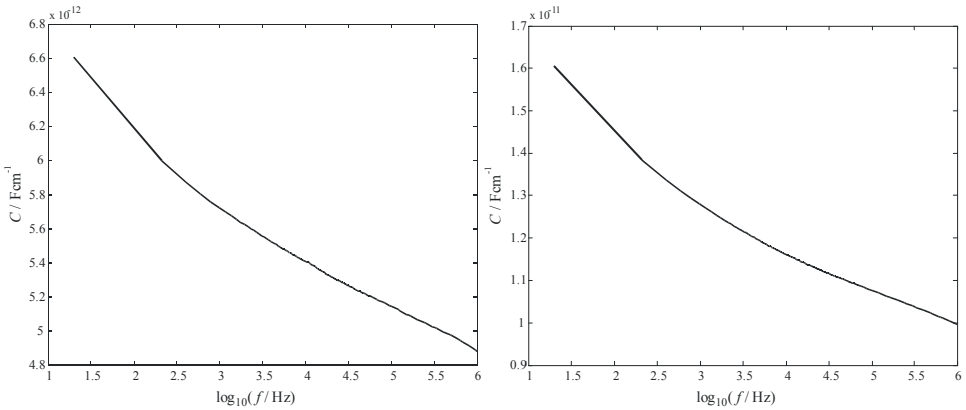

Fig. 11. Micro-capacitance vs. frequency for $BaTiO_3$ doped with a) 0.5 wt% Er_2O_3 b) 0.5 wt% Yb_2O_3.

In order to calculate equivalent impedance of the sample, conductance as another dominant electrical parameter should be taken into account. It is a parasitic parameter that is given in terms of capacitance with tanδ as a measure of losses, i.e., $1/R=G=\omega C \cdot \tan\delta$. The intergranular impedance model also contains two additional parameters; inductance L, and

capacitance C_p. Their nature cannot be correlated with geometrical parameters of grains in general way.

In order to determine an algebraic equation describing equivalent intergranular impedance in terms of circuit parameters the following equation can be used:

$$Z(s) = \frac{1 + CR \cdot \mathrm{s} + CL \cdot \mathrm{s}^2}{(Cp + C) \cdot \mathrm{s} + CpCR \cdot \mathrm{s}^2 + CpCL \cdot \mathrm{s}^3}$$

Based on the proposed equivalent circuit and the theory of impedance analysis for the model of three aggregate spheres the equivalent impedance can be defined by:

$$Z_e = \frac{Z_{12} \cdot (Z_{13} + Z_{23})}{Z_{12} + Z_{13} + Z_{23}}$$

where Z_{12}, Z_{13}, Z_{23} are the intergranular impedances between two adjacent particles. Then, this model can be inserted for any contact region inside the multi-particle model system during its microstructure development. Thus, electrical properties are determined in general by a series combination of such impedances.

Conclusion

Understanding the electrical properties of barium-titanate materials is important for modern devices applications and presents a challenge for simulation. In this study, the model of intergranular impedance is established using the equivalent electrical scheme characterized by a corresponding frequency characteristic. According to the microstructures we have obtained for $BaTiO_3$ doped with Er_2O_3 and Yb_2O_3 the global impedance of a barium-titanate ceramics sample contains both a resistor and capacity component. The resistor and capacity component was presented as a "sum" of many clusters of micro-resistors and micro-capacitors connected in the tetrahedral lattice. The positions of neighboring grains for the four grain cluster have been defined and according to them the tetrahedral scheme of mutual electrical influence of $BaTiO_3$ grains has been established. Fractal geometry has been used to describe the complexity of the spatial distribution of $BaTiO_3$ grains. The model of impedances between clusters of ceramics grains has been presented and calculations of micro-capacitance generated in grain contacts of $BaTiO_3$ doped with Er_2O_3 and Yb_2O_3 have been performed. By controlling shapes and numbers of contact surfaces on the level of the entire $BaTiO_3$–ceramic sample, control over structural properties of this ceramics can be done, with the aim of correlation between material electronic properties and corresponding microstructure.

Acknowledgements

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References

1. M.M.Vijatovic, J.D.Bobic, B.D.Stojanovic, Sci.Sintering 40 (2008) 155.

2. C.Pithan, D.Hennings, R. Waser, International Journal of Applied Ceramic Technology 2 (2005), 1.
3. V.V. Mitić, I. Mitrović, D. Mančić, , Sci. Sintering, 32 (2000) 141.
4. P.W.Rehrig, S.Park, S.Trolier-McKinstry, G.L.Messing, B.Jones, T.Shrout, J. Appl. Phys. 86 (1999) 1657.
5. S. Wang, G.O. Dayton, J. Am. Ceram. Soc. 82 (1999), 2677.
6. V.P.Pavlovic, M.V.Nikolic, V.B.Pavlovic, N. Labus, Lj. Zivkovic, B.D.Stojanovic, Ferroelectrics 319 (2005) 75.
7. D. Lu, X. Sun, M. Toda, Jap. J. Appl. Phys. 45 (2006) 8782.
8. N.Hirose, A.West, J. Am. Ceram. Soc, 79 (1996) 1633.
9. N. S. Hari, P. Padmini, T. R. N. Kutty J. Mat. Sci.: Materials in Electronics 815 (1997) 22.
10. M. Vollman, R. Waser, J.Am.Ceram.Soc. 77 (1994) 235.
11. V.V. Mitić, I. Mitrović, J. Eur. Ceram. Soc., 21 (2001), 2693.
12. H.M.Chan, M.P.Hamer, D.M.Smyth, J. Am. Ceram. Soc., 69 (1986) 507.
13. D.Makovec, Z.Samardzija M.Drofenik, J.Am.Ceram.Soc. 87 (2004) 1324.
14. M. T. Buscaglia, V. Buscaglia, P. Ghigna, M. Viviani, G. Spinolo, A. Testino, P. Nanni, Phys. Chem. Chem. Phys., 6 (2004) 3710.
15. J. D. Bak, J. C. Wright, J. Phys. Chem. B 109 (2005) 18391.
16. V.V.Mitić, Lj. M. Kocić, M. Miljković, I. Petković, , Mikrochim. Acta 15 (1998) 365.
17. V.Mitic Lj.Kocic, I.Mitrovic, M.M.Ristic Models of $BaTiO_3$ Ceramics Grains Contact Surfaces The 4th IUMRS International Conference in Asia OVTA Makuhari, Chiba, Japan 1997
18. B. Mandelbrot, The Fractal Geometry of Nature, W. H. Freeman and Co., New York, 1983.

Садржај: *Микроструктурна својства материјала на бази баријум-титаната, изражена контактима граница зрна од фундаменталне су важности за електрична својства ових материјала. У овом раду разматрана је примена модела импедансе између два зрна на контакт два зрна. Глобално посматрано, узорак $BaTiO_3$ –керамике састоји се од огромног броја зрна у међусобном контакту који формирају кластере. Такви кластери могу бити представљени као специфичне фракталне формације. За сваку од ових формација могуће је успоставити еквивалентни електрични модел за дефинисани сет улазних параметара користећи метод симболичке анализе и добити одговарајућу фреквентну карактеристику. Посебно је наглашен утицај фракталне структуре. Реализујући комплетну релацију између кластера зрна, њихових микроелектричних шема и одговарајућих фреквентних карактеристика с једне стране, и глобалних еквивалентних електричних шема и одговарајућих фреквентних карактеристика узорака $BaTiO_3$-керамике, с друге стране, успостављамо сет циљаних коинцидентних експерименталних резултата са сумарним ефектима израчунаваних микроелектричних еквивалентних шема. Модел је успешно тестиран на узорцима баријум-титанатне керамике.*

Кључне речи: *баријум-титанат, микроструктура, фрактали, кластери,..... оптимизација*