Science of Sintering, **43** (2011) 277-287

doi:

UDK 622.785:553.689

Sintering Process Influence on Microstructure and Intergranular Impedance of Rare-Earth Modified $BaTiO_3$-Ceramics

V. V. Mitic[1, 2*)], V. Paunovic[1], V. Pavlovic[2, 3], Lj. Zivkovic[1]

[1] University of Nis, Faculty of Electronic Engineering, Nis, Serbia

[2]Institute of Technical Science of SASA, Belgrade, Serbia

[3]Faculty of Agriculture, University of Belgrade, Belgrade, Serbia

Abstract:

Sintering process is a complex of different synergetic effects during the ceramics materials consolidation. The microstructural level properties control is very important as a stage in advanced materials prognosis. SEM analysis of Yb/$BaTiO_3$ doped ceramics showed that in samples doped with a low level of dopant and sintered at higher temperatures the grain size ranged from 10-60μm, while with the higher dopant concentration the grain size ranged between 2-15μm. The morphology of sintered $BaTiO_3$-ceramics grains points out the validity of developing new structure analytical methods based on different geometries of grains' model systems. The idea of electrical properties of $BaTiO_3$-ceramics being influenced by intergrain microcontacts can be successfully followed if we start with the two-sphere Coble's model and also the correction of the Coble's model.

In this paper, the grains contact models based on spherical, ellipsoidal and polyhedral geometries are presented making a new modeling tool for structure research of $BaTiO_3$-ceramics materials. Intergranular impedance analysis of grains clusters was also introduced. Obtained results enabled establishment of interrelation between structural and electrical parameters.

Keywords: *$BaTiO_3$, microstructure, Sintering, Intergranular impedance, Coble's model*

1. Introduction

Sintering process is widely used for synthesis and consolidation of advanced materials. Its kinetics depends on powder characteristics but also on particle and grain-size distribution, on formation of contact region, on volume fraction, on characteristic system state, etc. The explanation of these phenomena is largely based on empirically established laws that are only an approximation of real process. The sintering process is characterized by extreme complexity due to the simultaneous and successive action of elemental mechanisms. Generally speaking, following of their action and qualitative and quantitative description are very difficult [1-3].

Ceramic grains contacts are essential for understanding complex electrodynamics properties of sintered materials [4]. Microstructures of sintered $BaTiO_3$-ceramics, observed by SEM method, are characteristic example of complex shape geometry, which cannot easily be described or modeled. So, a possible approach for describing contact phenomena is

*) **Corresponding author**: vmitic.d2480@gmail.com

establishment of the grains contact models. Detailed research of $BaTiO_3$-ceramics intergranular contacts shows that they have the greatest influence on electrical properties of the entire sample [5, 6]. Intergranular contacts are formed during the sintering process. When particles of barium-titanate powder that are to be sintered, form a contact, in that area interatomic forces start forming a particle's neck. When a powder aggregate is sintered, necks between powder particles are formed, and the aggregate may increase in density. Transport mechanisms contribute to neck growth and to densification. A common driving force is the reduction in the surface area, and thus the reduction of surface free energy of the system. In further process, a neck begins to grow and this process is controlled by different diffusion mechanisms (lattice diffusion, grain boundary diffusion etc.) with the rates determined by total flux of atoms coming to the neck. The aim of this paper is to establish the model of three or more spherical grains in contact, as a base for calculating the values of possible contact areas in given geometry configuration. This can be used in two directions. First, the simulation of neck growth in time domain can be done by combining results for contact surfaces values with the kinetics of forming three or more contact areas. Second, the model of three or more grains in contact can be used for establishing an equivalent electrical model of such grains association. It was shown that $BaTiO_3$-ceramics sample can be modeled as impedance containing two capacitors, inductor and one resistor [7]. As a ceramics sample consists of numerous grains organized in clusters of different sizes, it could be supposed that each cluster and even each intergranular contact within the cluster, shows similar behavior. The dominant contribution to the equivalent impedance within a wide frequency range comes from a capacitance [7]. So, any intergranular contact can be observed as an intergranular microcondensor. On the base of these considerations, equivalent electrical models of three and four grains clusters are presented. All of these models and electrical contact surfaces processes are based on computer modelling and simulation methods application.

An extreme complexity of the sintering process influences the study of this process through different sintering models. Most of the sintering models have used two-sphere model as the simplest model for studying elemental mechanisms responsible for the progress of the sintering process. Such an idealization of the geometry of the sintering particles enables very detailed study of physical processes acting in the contact region. In this paper, Coble's two-sphere model [8] is used as initial one for developing a new two-ellipsoid model. Ellipsoidal geometry can approximate sintering particles in a better way than the spherical one. The relations connecting geometric parameters of the ellipsoidal model with consolidation parameters-sintering time and temperature are established. For better understanding of intergranular processes, Coble's model was generalized for other possible grains shapes (sphere-polyhedron, polyhedron-polyhedron). Then, the results of a new model are compared with those obtained from Coble's two-sphere model. All calculations are valid for initial stage of the sintering process.

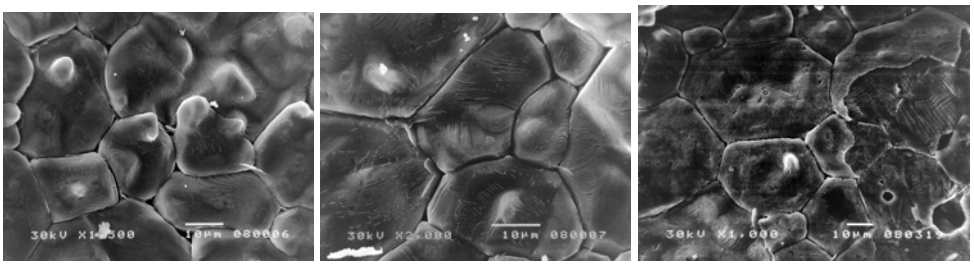
2. Experimental procedure

In this paper, Yb doped $BaTiO_3$-ceramics were used for microstructure characterization, modeling and intergranular impedance analysis. The samples were prepared from high purity (>99.98%) commercial $BaTiO_3$ powder (MURATA) with [Ba]/[Ti]=1,005 and reagent grade Yb_2O_3 powder (Fluka chemika), by conventional solid state sintering procedure. Yb_2O_3 dopant was used in the amounts from 0.01 to 1.0 wt%. Starting powders were ball-milled in ethyl alcohol for 24 hours. After drying at 200ºC for several hours, the powders were pressed into disk of 7mm in diameter and 3mm in thickness under 120 MPa. The compacts were sintered from 1320ºC to 1380ºC in air for two hours. The microstructures of sintered and chemically etched samples were observed by scanning electron microscope (JEOL-JSM 5300) equipped with energy dispersive spectrometer (EDS-QX 2000S).

Intergranular impedance measurements were done using Agilent 4284A precision LCR meter. The illustrations of the microstructure simulation, were generated by Mathematica 6.0 software. Obtained micrographs are the base for applying fractal and further modeling of grains structure.

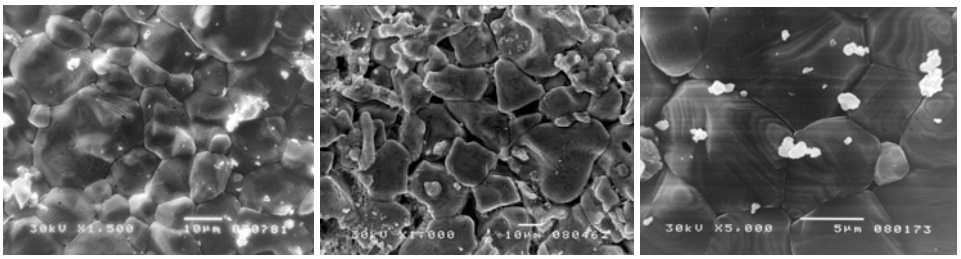
3. Microstructure characteristics

SEM microstructure investigations of Yb/$BaTiO_3$ ceramics samples showed that in samples doped with a low level of dopant (0.01 wt% Yb) the grain size ranged from 10-60μm, while with the higher dopant concentration (1.0 wt% Yb) the grain size ranged between 2-15μm (Fig. 1 and 2). Also, with the increase of sintering temperature from 1320°C to 1380°C, grains size increased.



a) b) c)

Fig. 1. SEM micrographs of 0.01 wt% Yb doped $BaTiO_3$ sintered at: a) 1320°C, b) 1350°C and c) 1380°C.



a) b) c)

Fig. 2. SEM micrographs of 1.0 wt% Yb doped $BaTiO_3$ sintered at: a) 1320°C, b) 1350°C and c) 1380°C.

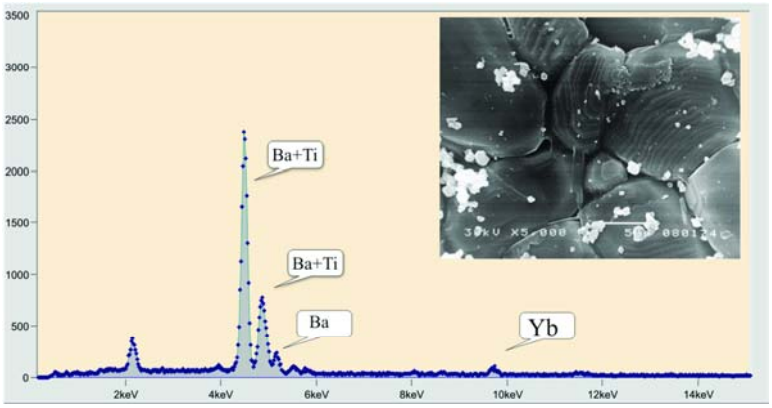


Fig. 3. SEM/EDS analysis of 1.0 wt% Yb/$BaTiO_3$, sintered at 1350°C.

EDS analysis for samples doped with a low concentration of Yb did not show Yb reached regions, that pointed out homogeneous additive distribution. With the increase of additive concentration (1.0 wt% Yb), agglomeration of Yb between grains appeared (Fig. 3).

4. Grains contact models

4.1. Sphere-sphere model

In order to explain two grains contact during sintering process and better understanding of electrical properties of $BaTiO_3$-ceramics, we start with the Coble's two-sphere model. In the process of the diffusion in initial-stage sintering, two grains, approximated by spheres penetrated each other slightly.

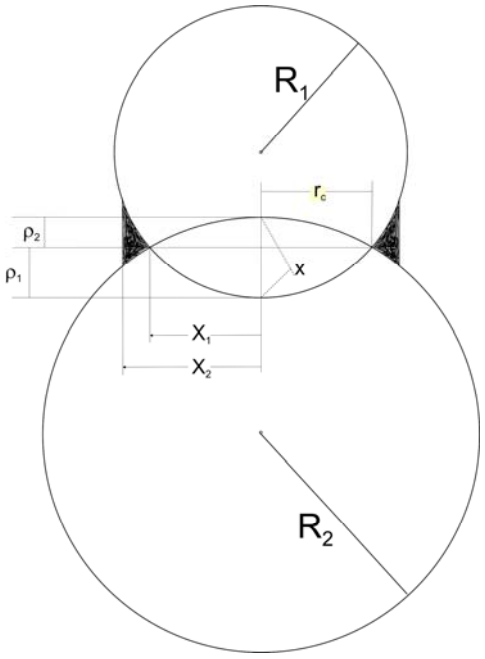


Fig. 4. The Coble's two sphere model.

The volume that fills intersection of spheres (the distance between centers is smaller than sum of two radii) transforms into a neck (a kind of collar that circumscribes the contact area). Starting model for simulation of densification during (initial) sintering process considered volume conservation principle. By volume conservation, according to the notation from the Fig. 4, we have relations

$$\rho_1 = \frac{X_2^{\,2}}{4 \cdot R_1} \qquad \rho_2 = \frac{X_2^{\,2}}{4 \cdot R_2} \qquad X_2 = \sqrt{2} \cdot X_1 \tag{1}$$

where ρ_1, ρ_2 - heights of spherical caps (forming the common volume of the spheres intersection), X_1- radius of a common circle, X_2 is the radius of the neck formed by diffusion in initial stage of sintering, R_1 and R_2 - radii of two spheres.

4.2. Ellipsoid-ellipsoid model

Grains of $BaTiO_3$-ceramics sample can be approximated by ellipsoids scattered throughout the material's volume. These ellipsoids can be seen as a model of grains in contact. Actually, due to sintering pressure and sintering process, one grain partly penetrates into another, forming a small contact area that can be pretty accurately approximated by intersection of ellipsoids E_1 and E_2. Our aim is to determine the value of this area as the function of grains' centers distance δ_E (Fig. 5).

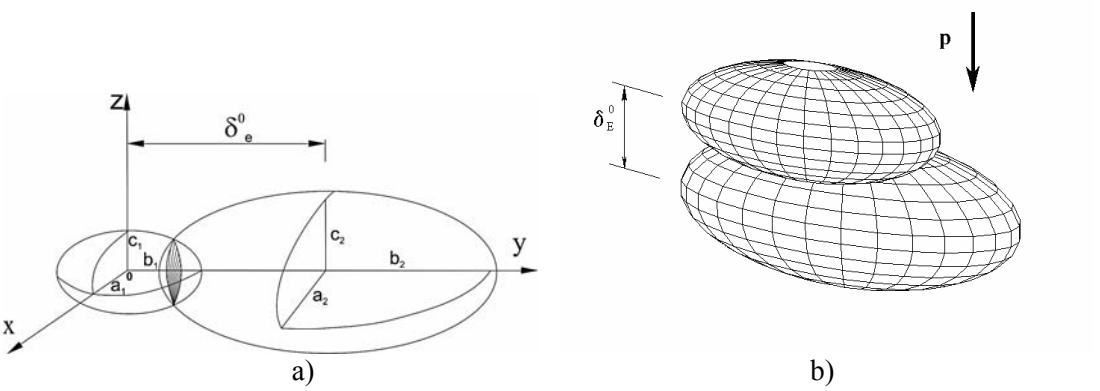


Fig. 5. a) Ellipsoidal grain approximation, b) neck growth of two ellipsoidal grains in sintering process.

We assumed that the ellipsoidal axes are pairwise parallel and lengths of the axes are propotional by the factor k. Consider two ellipsoids E_1 and E_2, having centers at $C_1 = (x_1, y_1, z_1)$ and $C_2 = (x_2, y_2, z_2)$ from R^3, being coaxial (having parallel axes) with semi-axes a_i, b_i, c_i (i=1, 2) provided that $a_i>b_i>c_i$, and $a_2/a_1=b_2/b_1=c_2/c_1=k$ (k>0). Suppose that E_1 and E_2 approximate two neighbor grains in sintered $BaTiO_3$-ceramics (Fig. 5b). Straightforward calculation gives that the distance between C_1 and C_2 in the beginning of sintering (sintering time $\tau=0$) is given by

$$\delta_E^o = \frac{1+k}{\sqrt{\frac{\cos^2\alpha}{a_1^2}+\frac{\cos^2\beta}{b_1^2}+\frac{\cos^2\gamma}{c_1^2}}} \tag{2}$$

where ($\cos\alpha$, $\cos\beta$, $\cos\gamma$) is the unit vector of C_1C_2-segment. It is clear that $(1+k)c_1 \le \delta_E{}^0 \le (1+k)a_1$. The difference between grain center distances at the beginning and at the end of sintering process during the ellapsed time τ is given by

$$\delta(\tau) = \delta_E{}^0 - \delta_E(\tau) = \left[1+\frac{X_2{}^2}{4\cdot R_1{}^2\cdot k}\right]\delta_E{}^0. \tag{3}$$

The value of $\delta(\tau)$ contains information about dynamics of the intergrain's neck formation. From this formula we can express the neck radius via the proportionality factor k as

$$X_2 = (4R_1^2 k\frac{\delta_E(\tau)}{\delta_E^o})^{1/2} \tag{4}$$

where R_1-the radius of spherical grain corresponds to ellipsoidal grain E_1.

4.3. Sphere-polyhedron model

Suppose that a ceramic grain has approximately spherical shape but the roughness of the surface approves replacing of a spherical model by a polyhedral one. For describing a constructive way of obtaining such a polyhedron we will consider a specific subdivision procedure illustrated in Fig. 6. Replace a sphere by a regular polyhedron inscribed in the sphere. Among five regular polyhedra, icosahedron is the best choice by two reasons. First, it is the best approximation of the sphere; second, all its faces are triangles, which simplifies subdivision procedure.

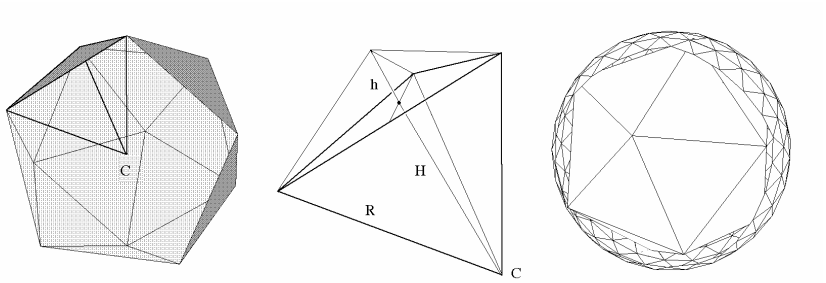


Fig. 6. Geometry of an icosahedron subdivision.

Suppose that two grains, one approximated by an n-stage polyhedron (inscribed into a sphere having radius R_1) and another by a sphere (radius = R_2). Suppose that these two spheres penetrate each other for the same spacings ρ_1 and ρ_2 as in Fig. 4. Now, we need to evaluate the volume of the "cap" of n-stage polyhedron that contains into the R_2 - sphere. For this purpose we will use the cubic function that shows increasing the volume of the cap with the height ρ: $V_{cap} = \pi \rho^2(R - \rho/3)$. Finally, we got an approximate formula

$$\left(V_n\right)_{cap} = \frac{3 \cdot V_n}{R_1^{\,3}} \cdot \rho^2 \cdot \left(R_1 - \frac{\rho}{3}\right) \tag{5}$$

where $V_n = V_0\left[1 + k + k\beta \cdot \frac{1-\left(k\beta\right)^{n-1}}{1-k\beta}\right]$-polyhedron volume after n-steps, $\beta = \frac{\alpha}{1+k\alpha}$ and $\alpha = \frac{4 \cdot \pi \cdot \left(3-\sqrt{5}\right)-5}{5 \cdot k} - 1$.

During initial - stage sintering process, two grains penetrate each other and form a neck. Diameter of the neck is determined by the volume conservation law.

4.3. Polyhedron - polyhedron model

The importance of this model is in having a simple tool for manipulating and fast evaluating in the situation when we have a huge number of grains to process. Also, it can be used as a starting point for developing fractal model of intergrain configuration. Here, we start with two polyhedra, P_m and P_n obtained as an m - stage or n - stage output of the procedure described above (Fig. 7). So, we can use formula (5) with R_1 and R_2 as the corresponding radii of circumscribed spheres. Neck' radius value is dependent of parameters Vn, R_1, R_2, ρ, k, α and β. Using this procedure the geometry of two-polyhedral grains in contact can be successfully solved.

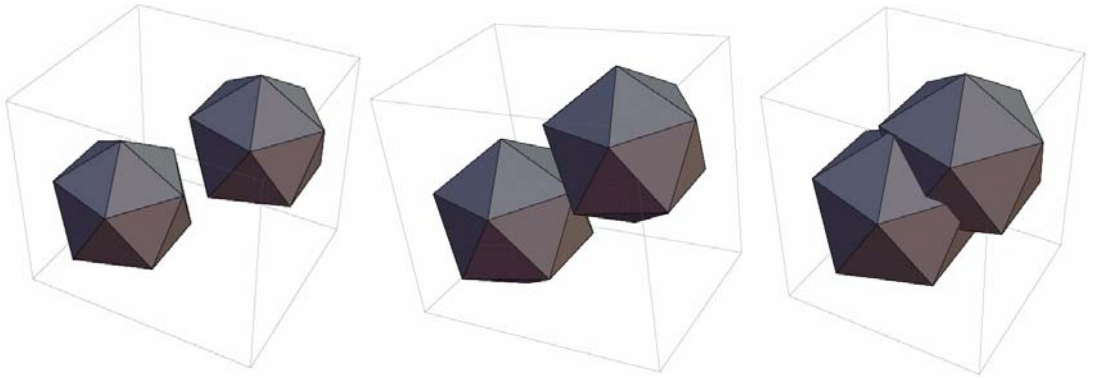


Fig. 7. Ceramic grains approximated by polyhedra in sintering process.

5. Results and discussion

5.1. Neck' growth

Neck' growth, in function of time and temperature, was analyzed for $BaTiO_3$-ceramics. The size of grain is extracted from microstructures obtained by SEM. For $BaTiO_3$ sintered in the temperature range from 1320°C to 1380°C, the average value of dielectric constant (ε_r) and dissipation factor ($\tan\delta$), at frequency of 1KHz, are 2500 and 0.0076, respectively. For the aggregate of spheres model, the radii of spherical grains where $r_1 = 15\ \mu$m and $r_2 = 40\ \mu$m. Diagrams for the neck growth at temperatures 1000°C and 1400°C (corresponding to our samples sintering temperature) and time interval 120 min are shown in Fig. 8.

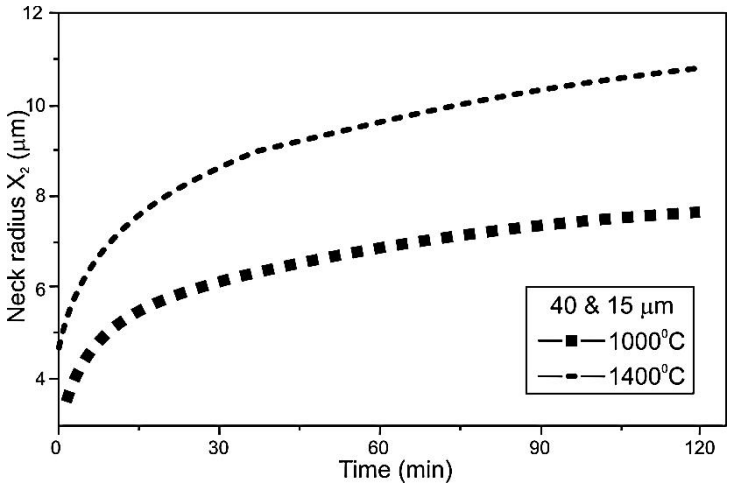


Fig. 8. Neck growth kinetics for two-sphere model in function of time and temperature.

With the increase of sintering time t, grains' center distance $\delta(\tau)$ decreases and the radius of the intersection X_2 grows. As it can be seen from Fig. 8, the dependence obtained is typical: the abrupt increase of neck at the initial sintering period (short time) and then a continual growth in further process. Neck growth is more explicit for temperature of 1400°C. It can be noticed that the curves have very similar slopes. For a longer simulation time the growth rate slowly approaches its limiting value.

5.2. Intergranular impedance model

It is well known that both intergranular structure and electrical properties of ceramics depend on processing parameters during sintering. Therefore, it is very important to correlate physical and technological characteristics in order to make proper prognosis of electrical properties. With that goal, an equivalent electrical model should be established. This model included the investigation based on Heywong model [9], intergrain contact surfaces aspect and specific application of mathematical methods.

The equivalent electrical model of a ceramic material can be introduced as impedance containing two capacitors, C and C*, an inductor L, and a resistor R (Fig. 9).

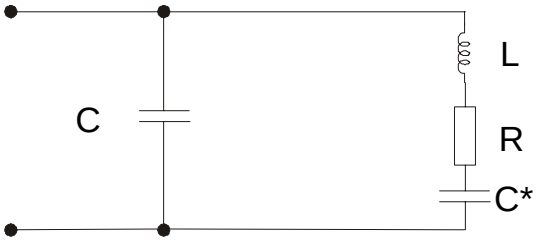


Fig. 9. Equivalent RLC circuit model.

From the microstructure it can be seen that ceramic sample consists of many clusters, where each is made of several contacted grains. Assuming that the equivalent electrical model stands for any sample disregarding the sizes of clusters in it, the same model can be accepted even for a single cluster and for every contact between two grains within the cluster.

The dominant electrical parameter of the impedance model in wide frequency range is capacitance C. The connection between C and geometrical parameters of two contacted grains can be established by an assumption that the contact area between two grains can be viewed as a planar condenser. Another dominant electrical parameter is conductance. It is common to view it as a parasitic parameter that is given in terms of capacitance with the $\tan\delta$ as a measure of losses, i.e. $1/R = G = \tan\delta(\omega C)$.

The intergranular impedance model contains two additional parameters: inductor L, and capacitor C*. Their nature as a part of the impedance model cannot be correlated with geometrical parameters of grains in an obvious way.

The aim of this paper is to determine qualitative and quantitative relations between the proposed electrical model of intergranular impedance and the consolidation parameters, such as time and temperature.

The first step towards that aim is to determine expression for intergranular impedance. For that purpose, the symbolic simulator Symsim [10, 11] can be used, i.e.

$$Z(s) = \frac{1 + C^*R \cdot \mathrm{s} + C^*L \cdot \mathrm{s}^2}{(C^* + C) \cdot \mathrm{s} + C^*CR \cdot \mathrm{s}^2 + C^*CL \cdot \mathrm{s}^3}. \quad (6)$$

where s =jω, ω=2πf, f is frequency.

This model can be inserted for the contact between any pair of grains. This will certainly result in very large circuitry. However, tools for large circuit analysis are possible to cope with this problem.

Of more practical interest and complexity is the intergranular impedance for the packed spherical grains, i.e. an aggregate of spheres, shown in Fig. 10. Then, the equivalent impedance is given by:

$$Z_e = \frac{Z_{12} \cdot (Z_{13} + Z_{23})}{Z_{12} + Z_{13} + Z_{23}} \quad (7),$$

where Z_{ij} is the intergranular impedance between grains numbered i and j $(i, j = 1,2,3; i \neq j)$.

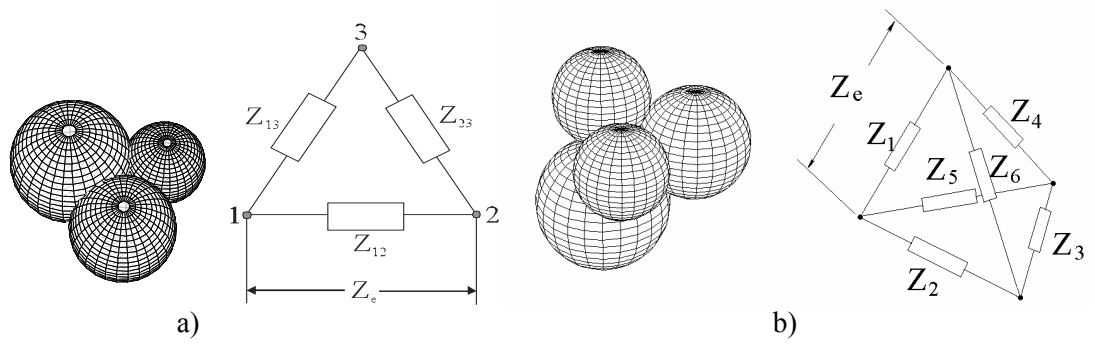


Fig. 10. An aggregate of spheres and equivalent impedance scheme: a) three grains and b) four grains cluster.

The four-grain cluster forms a pyramidal structure (Fig. 10b). Each impedance Z_1, ..., Z_6 has the form of (6) with different electrical parameters. The pyramidal structure of equivalent impedance can be transformed into a single triangle with impedances Z_a, Z_b and Z_c. Accordingly, Z_a will be a parallel connection of Z_1 and $Z_1'=Z_3+Z_4+Z_3Z_4/Z_5$. Similar expressions are valid for Z_b and Z_c, so the equivalent impedance parallel to Z_1 is then

$$Z_e = \frac{Z_a(Z_b + Z_c)}{Z_a + Z_b + Z_c}. \quad (8)$$

Fig. 11 shows that obtained plots for $|Z_e|$ are characterized by multiple 'leaves' that are typical for ceramic samples. It is obvious that the pyramidal configuration has three resonant frequencies since it is reduced to the triangle configuration.

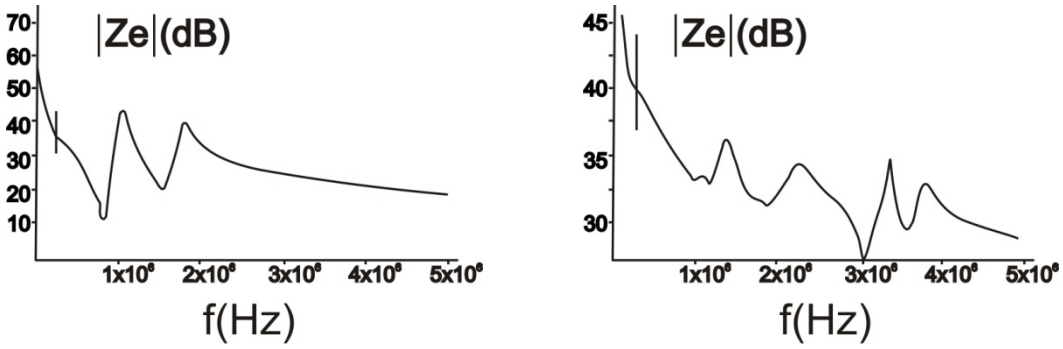


Fig. 11. The magnitude of the impedance for: a) a three-grains and b) four-grains cluster.

In the real sample of $BaTiO_3$-ceramics besides the three and four-contact clusters described, there are n-contact clusters ($n \geq 5$). In fact, a collection of n-contact clusters ($n \geq 2$) made the whole sample. But, behavior of n-contact clusters ($n \geq 5$) is similar to behavior of four-contact clusters as far as the electrical point of view is concerned. Only the number of resonant frequencies will be higher. So the frequency diagram of the whole sample will be similar to this shown in Fig. 11, but with the huge number of resonant peaks summing up to one bigger peak being referred to as the resonant frequency of the sample.

6. Conclusions

The study of processes acting on contacts of two or more ceramics grains has great importance for establishing microstructure relations that essentially influence ceramics dielectric properties. Up to now, studying of sintering process has been basically realized through two-sphere models. In this paper, the developed model is a step further because it offers a possibility for transition from spherical to ellipsoidal ceramic grain geometry. Starting from the Coble's two-sphere model the equation of ceramic grains' neck radius as a function of both geometrical and kinetics parameters is derived. Observing of $BaTiO_3$-ceramics morphology by SEM method confirmed the fact that $BaTiO_3$ grains can be approximated by ellipsoids of different sizes and orientations. So, the neck radius equation is applied on $BaTiO_3$ grains. Obtained curves represent a good correlation between structural/geometrical and kinetics/physical parameters making possible control under structural properties of $BaTiO_3$-ceramics. The given structural model can be an effective tool not only in $BaTiO_3$-ceramics materials prognosis, but in ceramic study and prognosis in general.

The contact surfaces values directly define the value of microcapacitance generated at intergranular contact. Starting with the equivalent electrical model of $BaTiO_3$-ceramics sample, electrical models of three and four grains clusters are discussed. The diagrams showing magnitudes of impedances as a function of frequency are given. The simplified model of intergranular impedance is introduced. The contact between two grains is defined as a parallel connection of microcapacitance and microconductance. The equivalent intergranular impedance $|Z_e|$ is characterized by multiple "leaves" that are typical for ceramic samples. The presented research leads to better understanding of the influence of the microstructure on final electrical properties of $BaTiO_3$-ceramics.

Acknowledgements

This research is a part of the project „Directed synthesis, structure and properties of multifunctional materials" (172057) and projects F-7 and F/198 supported by Serbian Academy of Sciences and Arts. The authors gratefully acknowledge the financial support of Serbian Ministry of Education and Science for this work.

References

1. D. Zhang, G. Weng, S. Gong, D. Zhou, Materials Science and Engineering B, 99 [1-3] (2003) 88-92.
2. Y. Hotta, K. Tsunekawa, C. Duran, K. Sato, T. Nagaoka, K. Watari, Materials Science and Engineering: A, 475 [1-2] 2008 57-61.
3. F. Kongoli, I. McBow, R. Budd, S. Llubani and Akira Yazawa, J. Min. Metall. Sect. B-Metall., 46 [2] B (2010) 123-130.
4. Y.K. Cho, S.L.Kang, D.Y. Yoon, J. Am. Ceram. Soc., 87 (2004) 119-124.
5. V. V. Mitic, V. B. Pavlovic, Lj. Kocic, V. Paunovic, D. Mancic, Science of Sintering, 41 [3] (2009) 247-256.
6. V. Mitić, V. Paunović, D. Mančić, Lj. Kocić, Lj. Zivković, V.B. Pavlović, Ceramic Transactions, 204 (2009) 137-144.
7. D.Mancic, V.Paunović, M.Vijatović, B. Stojanović, Lj. Živković, Science of Sintering, 40 [3] (2008) 283-294.
8. R.L. Coble, J. Am. Ceram. Soc. 56 (1973) 461-466.
9. W. Heywang, H. Thomann, Electronic Ceramics, London and New York, 1991.

10. P. Petković and V. Živković, "18th International Spring Seminar on Semiconductor and Hybrid Technologies", Vol. 12, No. 1, Sozopol, Bulgaria, 1996, p. 275-284.
11. P. Petković, R. Stevanović and V. Litovski, "2nd Serbian Conf. on Microelectronics and Optoelectronics", MIOPEL'93, Niš, 1993, p. 437-442.

Садржај: *Процес синтеровања представља скуп различитих параметара у току процеса консолидације керамичких материјала. Контрола микроструктурних особина је веома важна, као једна од фаза прогнозе савремених материјала. SEM анализа Yb/$BaTiO_3$ допиране керамике је показала да је за узорке допиране мањом количином допанта и синтероване на вишим температурама, карактеристична величина зрна од 10 до 60μm, док се за узорке са већом концентрацијом допанта кретала у опсегу 2-15μm. Морфологија зрна синтероване $BaTiO_3$-керамике указује на важност развоја нових аналитичких метода које се заснивају на различитим моделима контакта између зрна. Идеја да микроконтакти између зрна утичу на електричне особине $BaTiO_3$-керамике се заснива на Коблеовом моделу две сфере и коригованом Коблеовом моделу.*

У овом раду је представљен нови начин испитивања структуре $BaTiO_3$-керамике заснован на сферном, елипсоидном и полиедарском моделу контакта између зрна. Такође је уведена интергрануларна импедансна анализа за кластере зрна. Добијени резултати су омогућили успостављање корелације између структуре и електричних параметара.

Кључне речи: *$BaTiO_3$, микроструктура, синтеровање, интергрануларна импеданса, Коблеов модел*