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Ceramics International 38 (2012) 1295–1301

CERAMICS INTERNATIONAL

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The contribution of fractal nature to $BaTiO_3$-ceramics microstructure analysis

V.V. Mitic [a,b,*], V. Paunovic [a], J. Purenovic [a], S. Jankovic [c], Lj. Kocic [a], I. Antolovic [a], D. Rancic [a]

[a] University of Nis, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, 18000 Nis, Serbia
[b] Institute of Technical Sciences, SASA, Knez Mihailova 35, 11000 Belgrade, Serbia
[c] Faculty of Mathematics, Studentski trg 16, 11000 Belgrade, Serbia

Received 19 May 2011; received in revised form 25 August 2011; accepted 1 September 2011
Available online 8 September 2011

Abstract

The structure of $BaTiO_3$ based materials can be controlled by using different technological parameters and different additives. In this paper, microstructure and dielectrical properties of Er_2O_3 doped $BaTiO_3$-ceramics, sintered from 1320 °C to 1380 °C have been investigated. Microstructural investigations were carried out using scanning electron microscope equipped with energy dispersive spectrometer. Grain size distribution was determined by quantitative metallography method.

The new correlation between microstructure and dielectric properties of doped $BaTiO_3$-ceramics, based on fractal geometry and contact surface probability, has been developed. Using the fractals and statistics of the grains contact surface, a reconstruction of microstructure configurations, as grains shapes or intergranular contacts, has been successfully done. Obtained results indicated that fractal analysis and statistics model for contact surfaces of different shapes were very important for the prognosis of $BaTiO_3$-ceramics microstructure and dielectric properties.

The morphology of ceramics grains pointed out the validity of developing new structure analytical methods, based on different grains' shape geometries. The grains contact model based on ellipsoidal geometry is presented as new modeling tool for structure research of $BaTiO_3$-ceramics materials. The directions of possible materials properties prognosis are determined according to the correlations synthesis–structure–property.The statistical approach to the investigation of $BaTiO_3$-ceramic grains concerning the relationship between the temperature and the area of the contact surface is also introduced.

Keywords: $BaTiO_3$-ceramics; Microstructure; Fractals; Grain contact surface

1. Introduction

$BaTiO_3$-based ceramics is one of the most investigated ferroelectric materials, with various applications. The broad application in advanced electronics nowadays demands a constant research of its structure, which leads to further prognosis and properties design of ceramics. Intergranular structure and dielectrical properties depend on consolidation parameters. Slight change of particular consolidation parameter, as pressing pressure, initial sample's density, sintering temperature and time, or the change of dopant concentration, can significantly change microstructure and final properties of electronic materials [1–4]. Since grain size distribution may considerably affect dielectrical properties of these materials, correlation between their microstructure and dielectrical properties has been investigated by numerous authors [5–8].

Lately, in the area of ceramic materials structural research a great importance of the application of fractal geometry methods and chaos of abstract or real points has been discovered. The fractal method enables applying methods of symmetrical and ordered view to disordered configurations in ceramic materials. Recently, it has been established that since the real intergrain contact surface is an irregular object, the theory of fractal sets can be introduced [9,10]. Fractal method traces a new approach for describing and modeling the grains shape, as well as relations among dielectrical properties and microstructure. It

* Corresponding author at: University of Niš, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, 18000 Niš, Serbia. Tel.: +381 63 400 250; fax: +381 18 588 399.
E-mail address: vmitic.d2480@gmail.com (V.V. Mitic).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.09.003

has been established that, modeling random microstructures, as grains aggregates in polycrystals, patterns of intergranular cracks theory of Iterated Function Systems (IFS) and the concept of Voronoi tessellation, can be used [11]. Voronoi tessellation represents cell structure constructed from a Poisson point process, by introducing planar cell walls perpendicular to lines connecting neighboring points. Considering all the above-mentioned, methods for modeling grain boundary surface and geometry of grain contacts of doped $BaTiO_3$-ceramics, are presented in this article. Most of these methods are based on microstructure analysis and fractal correction that expresses the irregularity of grains surface via fractal dimension [9–12]. Also, some results for intergranular contact surfaces, based on mathematical statistical methods and calculations, are shown.

In order to enable reconstruction of microstructure configuration (grains shapes and intergranular contacts), electroceramics microstructure fractal analysis and characterization have been performed.

2. Experimental procedure

The Er doped $BaTiO_3$ samples were prepared by conventional solid state reaction. Reagent grade $BaTiO_3$ powder (MURATA) with [Ba]/[Ti] =1.005 and Er_2O_3 powders (Fluka chemika) were used as starting materials. The content of additive oxides ranged from 0.1 to 1.0 wt% Er. Starting powders were ball-milled in ethyl alcohol for 24 h using polypropylene bottle and zirconia balls. After drying at 200 °C for several hours, the powders were pressed into disk of 7 mm in diameter and 3 mm in thickness under 120 MPa. The compacts were sintered from 1320 °C to 1380 °C in air for 4 h. The microstructures of sintered and chemically etched samples were observed by scanning electron microscope (JEOL-JSM 5300) equipped with energy dispersive X-ray analysis spectrometer (EDS-QX 2000S system). The grain size and porosity distribution of samples were obtained by LEICA Q500MC Image Processing and Analysis System. The linear intercept measurement method was used for estimation of grain size values, as well as the pores volume ratios. Prior to electrical measurements silver paste was applied on flat surfaces of specimens. Capacitance and impedance measurements were done using Agilent 4284A precision LCR meter. The illustrations of the microstructure simulation were generated by Mathematica 6.0 software. Statistical method was used for calculation of contact surfaces.

3. Results and discussion

For Er doped $BaTiO_3$-ceramics, sintered at 1320 °C, density varied from 80% of theoretical density (TD) for high doped samples (1.0 wt% of dopant), to 90% TD for samples doped with 0.1 wt% of dopant. Also, with the increase of sintering temperature, samples density increased.

The SEM investigations of Er/$BaTiO_3$ (Fig. 1) have shown homogeneous microstructure with irregularly polygonal shaped grains.

For 0.1 wt% of Er/$BaTiO_3$, grains size was large (up to 50 μm), but by increasing the dopant concentration the grain size decreased. For the samples doped with 1.0 wt% of dopant, the average grain size was from 4 μm to 10 μm. Difference between grains size for high and low doped $BaTiO_3$ samples has been confirmed from the cumulative grain size distribution curves, given in Fig. 2. Spiral concentric grain growth, which has been noticed for the samples sintered with 0.1 wt% of Er_2O_3, disappeared when the concentration increased up to 1.0 wt% of dopant.

EDS analysis [13] for all samples has shown that for small concentrations of dopants the distribution is uniform, while the increase of dopant concentration led to the coprecipitation between grains.

Ceramic grains contacts are essential for understanding complex electrodynamics properties of sintered materials. Microstructures of sintered $BaTiO_3$-ceramics obtained by SEM method are characteristic examples of complex shape geometry, which cannot easily be described or modeled. A possible approach for describing contact phenomena is establishing the grains contact models. Our new approach includes fractal geometry in describing complexity of the spatial distribution of electroceramic grains.

The grainy structure of $BaTiO_3$-ceramics is so fairly complicated that any method of classical geometry fails to describe it. The same refers to the distribution of intergrain contacts. Modeling method allows the presentation of grains in contact in the shape of sphere, ellipsoid and polyhedron. In spherical and ellipsoidal grain model systems there is a possibility for analytic expressions of grains shape and contact surface, presented as functions of distance between

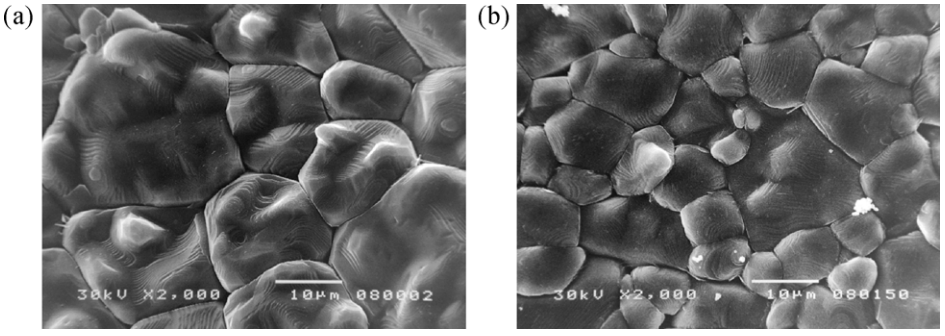

Fig. 1. SEM micrographs of Er doped $BaTiO_3$ sintered at 1320 °C (a) 0.1 wt% Er_2O_3 and (b) 1.0 wt% Er_2O_3.

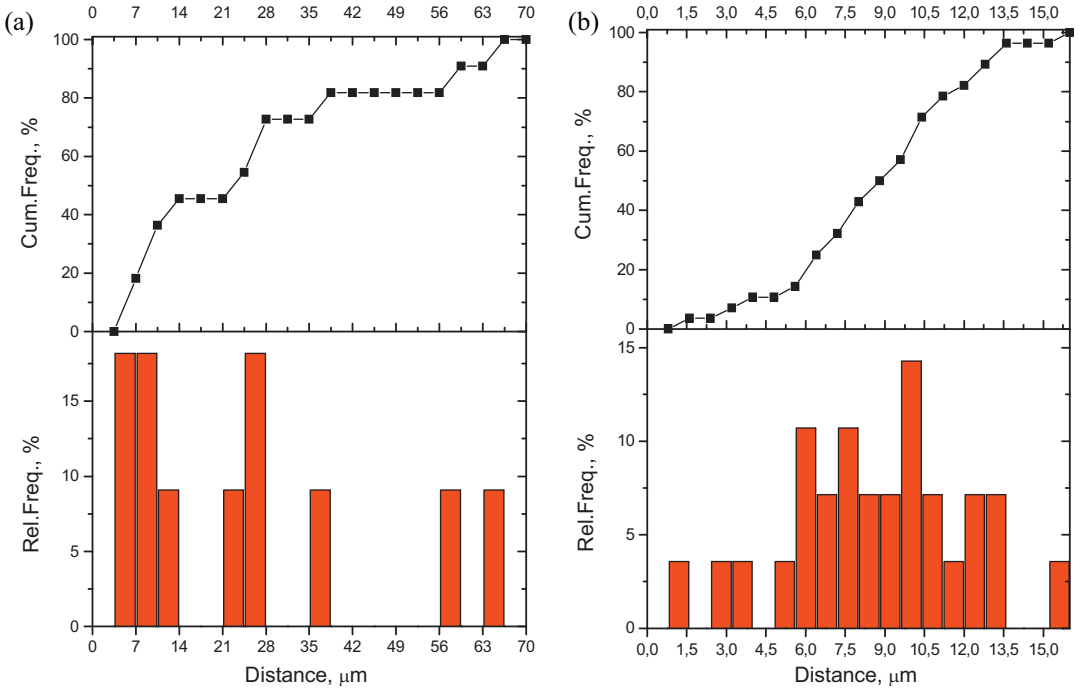

Fig. 2. Cumulative grain size distribution curves for $BaTiO_3$ doped with (a) 0.1 wt% Er_2O_3 and (b) 1.0 wt% Er_2O_3.

grains. On the other hand, the polyhedron–polyhedron model presents the real numerical procedure. In this paper, each grain is approximated by an ellipsoid. Also, it can be expected that the contact zone has ellipsoidal geometry as well. In fact, the contact surface between two grains must also inherit a trace of ellipsoidal geometry. But, this surface can be approximated by an ellipse having semi axes X/b, X/a. This means that the contact surface area between two grains after sintering process should be approximately

$$S = \frac{4\pi R^2 k}{ab} \cdot \left(\frac{\delta(\tau)}{\delta_E^0} - 1 \right), \tag{1}$$

where k is grains proportionality factor, $\delta(\tau)$ expresses the difference between grains centers distance at the beginning and at the end of sintering process during the elapsed sintering time τ, δ_E^0 is starting grains' distance, R represents penetration between grains.

Two grains in contact, approximated by ellipsoids, are shown in Fig. 3. In this way, a $BaTiO_3$-ceramics sample can be considered as a huge heap of randomly scattered ellipsoids throughout the sample's volume.

So, the function F that describes the position of grains in the ceramic sample contains some information that can be considered as a slightly controlled chaos. Using characteristic function of some set A

$$\chi_A(x) \leq \begin{cases} 1, & x \in A \\ 0, & \text{otherwise} \end{cases} \tag{2}$$

the function F will be given by:

$$F(\vec{r}) = \sum_{i \in I} \chi_{G_i}(\vec{r}), \tag{3}$$

where $\vec{r} = [x \ y \ z] \in \mathbf{R^3}$ is the space variable and $\{G_i : i \in I\}$ is the set of all contact zones in prescribed volume V. The function $F: \mathbf{R^3} \to \mathbf{R}$ is discontinuous at the surface points of these zones. If the definition of gradient of such function is extended by $+\infty$ at discontinuity points, it can be used in definition of the surface that is the union of all surfaces of intergrain contact areas in V.

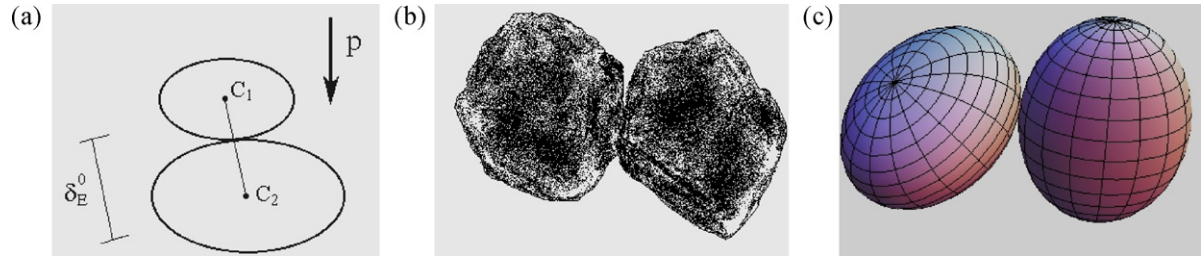

Fig. 3. (a) Ellipsoidal approximation, (b and c) two grains in contact according to ellipsoid–ellipsoid model.

This surface is given by

$$S = \{\vec{r} : |\nabla F(\vec{r})| > 1\}, \tag{4}$$

so, the volume of all contact zones in V is given by

$$A = \int_V F(\vec{r})dV. \tag{5}$$

In special case, when the grains are approximated by ellipsoids with parallel axes, formula (5) becomes a finite sum of all contact surfaces between grains. If two grains in contact are labeled by i and j, according to (1), contact surface S_{ij} will be given by

$$S_{ij} = \frac{4\pi a_i b_i}{a_j{}^2 b_j{}^2} \cdot R_{ij}^2 k_{ij} \cdot \left(\frac{\delta(\tau)}{\delta_E^0} - 1\right), \tag{6}$$

which reduces (5) to $A = \sum_{ij} S_{ij}$. This is an approximate value of the sum of all intergrains' contacts. This quantity is obviously connected with the global capacity of $BaTiO_3$-ceramic sample. Unfortunately, this connection is not known and some researches on this topic, that also use fractal geometry, are in progress.

Considering shapes properties, method of Voronoi tessellation has also been used for grains surface modeling. It is important to emphasize, that although polycrystal modeling generally represents a 3D problem, a 2D Voronoi tessellation approximation is used. This assumption is based on the fact that the sample properties mostly depend on microstructure surfaces.

Set of points is generated in order to represent the distribution of micro-grains. In this case, the distribution is semi-random and implemented in such manner that each point dislocates in relation to its position on the imaginary lattice. The main idea is to establish correlation between the different points-peaks and micro values between two contact surfaces, which practically represent the new level, more complex and realistic, micro intergranular capacitors-impedances network (Fig. 4).

Irregularity of the surface of ceramics grains can be expressed using the term called fractal dimension. Determination of grain contour fractal dimension includes several steps. First of all, coordinates of chosen points from the contour must be determined in relation to some rectangular coordinate system. Coordinates X and Y are linear dimensions. Then, the method of iterative functional systems (IFS) is applied, in the form of fractal interpolation, modified to parameter level. Method of fractal interpolation can be improved by taking contour points coordinates (sampling) in few different positions of the same contour. The contour of the grain obtained by fractal interpolation is given in Fig. 5. Resulting fractal dimension is estimated to range from 1.118 to 1.164.

Due to diffusional forces that appear in sintering process, it is supposed that an approximate form of contact surface is the shape of a minimal surface – the surface with minimal area size. But, the microstructure of the material makes this surface locally fractal (Fig. 6a). Considering that intergrain contact surface is a region, where processes occur at the electronic level in the electroceramic material, structural complex grain-contact-grain can be represented by an electrical equivalent network.

Contact between two grains is observed as planar micro-capacitor (Fig. 6b). The surfaces of capacitor plates correspond to intersection surface (Sc) of two grains. Therefore, the formula for the capacitance of the planar capacitor, formed in the contact, is given by

$$C = \varepsilon_0 \varepsilon_B \frac{S_c}{x}, \tag{7}$$

where ε_0, ε_B are dielectric constants in vacuum and $BaTiO_3$-ceramic material, respectively; Sc – the area of the plates and x – distance between capacitor plates, i.e. the capacitor thickness.

In fractal case, according to fractal approach to the intergrain geometry, the formula (7) is modified by introducing correction factor α, $\alpha = (N\xi^2)^k$. Thus, the formula for the microcapacity of intergranular capacitor, seen as planar capacitor, is given in the following form:

$$C = \varepsilon_0 \varepsilon_B \alpha \cdot \frac{S}{x} = \varepsilon_0 \varepsilon_B (N\xi^2)^k \cdot \frac{S}{x}. \tag{8}$$

This approach uses an iterative algorithm that iterates N self-affine mappings with constant contractive (Lipschitz) factor $|\xi| < 1$ k-times. Typically, $\alpha = D - D_T$, where D is the fractal (Hausdorff) dimension of intergrain contact surface and D_T is topological dimension of the surface. $BaTiO_3$-ceramics contact surfaces are of low-irregularity, which is characterized by the small difference $D - D_T \approx 0.08744$.

Derived formula (8) indicates lower values of microcapacity, when fractal approach is applied. Thus, more accurate calculation of microcapacitance, generated in grains contact, can be carried out, leading to a more exact estimation of dielectric properties of the whole sample.

Microcapacitance values, generated in grains contacts, of $BaTiO_3$ doped with 0.1 wt% Er, for ellipsoidal approximation of grains ($\alpha = 1$) and with involved fractal correction

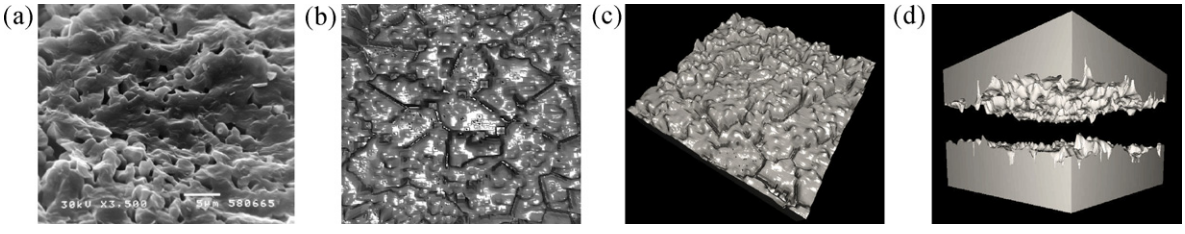

Fig. 4. (a) SEM image of $BaTiO_3$ ceramics and (b–d) corresponding 3D microsurface overview.

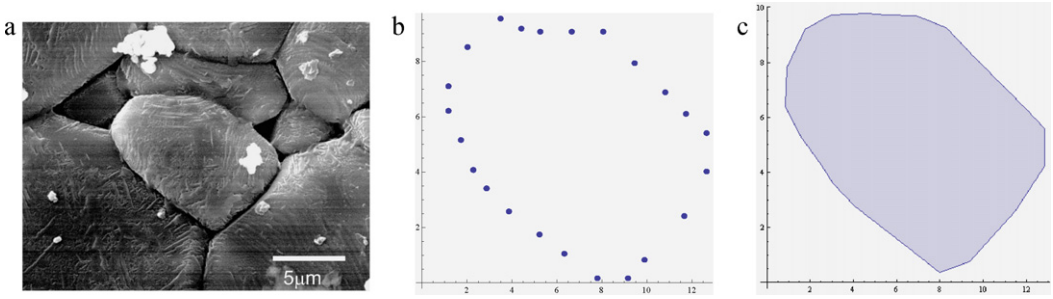

Fig. 5. (a) SEM microphotograph, (b) set of chosen points from the contour and (c) fractal interpolation method for segregate grain of 0.1 Er/$BaTiO_3$ ceramics.

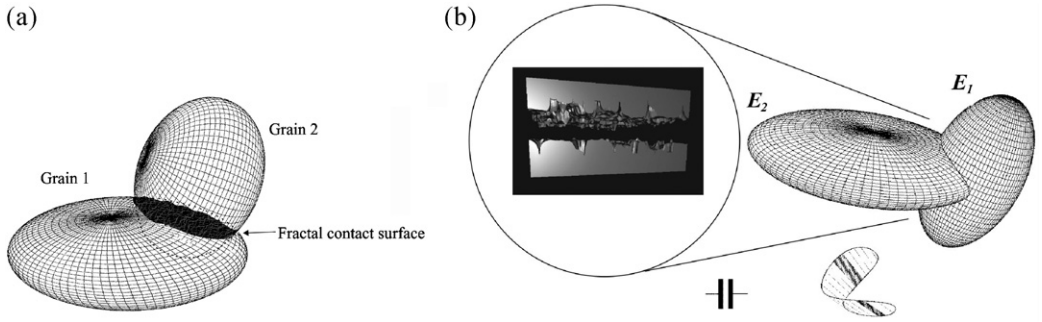

Fig. 6. (a) An intergrain contact surface has fractal form, (b) two grains in contact form a microcapacitor.

($\alpha = 0.08744$), have been performed in Fig. 7. It can be concluded that there is no significant difference between microcapacitance values, but that values obtained with fractal correction are in good agreement with experimental results [13].

In the sequel, a statistical approach to the investigation of $BaTiO_3$-ceramic grains, concerning the relationship between the temperature and the area of the contact surface, is presented. This method can be applied to all kinds of grains, to every ceramic structure, regardless of the actual shape of the ceramic grains and contact area between the grains. The most important is the area of the contact surface on the squares, chosen on investigated sample. It is assumed that the distribution of the contact area is the same on each square, with the unknown mean μ and the variance σ^2.

The following experiment is performed n times: sample consists of n randomly chosen squares, with prescribed vertices of $BaTiO_3$-ceramic. The areas of contact surfaces on these n squares are measured. As a result (Table 1.), obtained values are $X_1, X_2, \ldots, X_n$ – the measure of contact areas on each of the corresponding squares. Parameters obtained from the sample are the sample mean $\bar{X} = (1/n)\sum_{i=1}^{n} X_i$, the sample variance $\bar{\sigma}^2 = (1/n)\sum_{i=1}^{n} (X_i - \bar{X})^2$ and the unbiased estimate of the variance

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (X_i - \bar{X})^2. \tag{9}$$

For chosen $\alpha^* = 0.05$, the confidence interval for the unknown mean μ is the following one:

$$\left(\bar{X} - \frac{t_{n-1,\alpha^*/2}\bar{\sigma}_0}{n^{1/2}} < \mu < \bar{X} + \frac{t_{n-1,\alpha^*/2}\bar{\sigma}_0}{n^{1/2}}\right), \tag{10}$$

that is

$$P\left(\bar{X} - \frac{t_{n-1,\alpha^*/2}\bar{\sigma}_0}{n^{1/2}} < \mu < \bar{X} + \frac{t_{n-1,\alpha^*/2}\bar{\sigma}_0}{n^{1/2}}\right) = 1 - \alpha^*. \tag{11}$$

It is assumed that the relationship between the capacitance C and the contact area S is of the form $C = \theta S$, where θ is the unknown parameter that has to be estimated by taking the sample mean $\bar{X}$ instead of S in the formula $C = \theta S$.

The influence of different sintering temperature levels of (1320 °C, 1350 °C and 1380 °C) on the size of contact area for 0.1 wt% Er_2O_3 doped $BaTiO_3$ ceramic is investigated. Three samples, each of them of the size 30, of 0.1 wt% Er_2O_3 doped $BaTiO_3$ ceramic square-shaped surfaces are observed for the

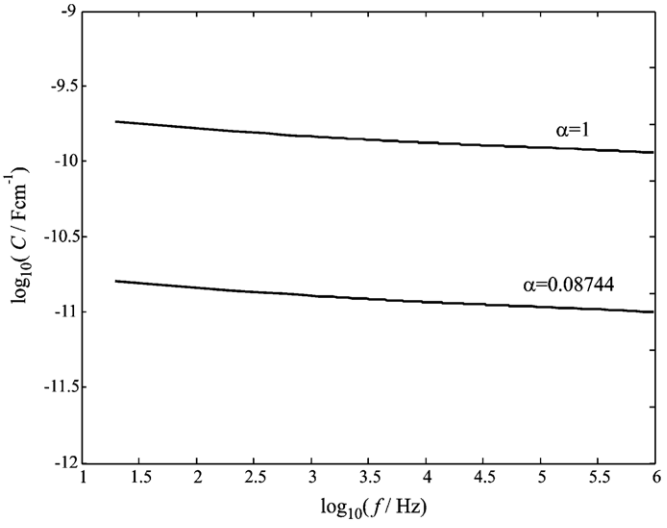

Fig. 7. Microcapacitance vs. frequency for $BaTiO_3$ doped with 0.1 wt% Er.

Table 1
Various statistical parameters for contact surfaces.

0.1 wt% Er_2O_3	1320 °C	1350 °C	1380 °C
Mean	99.78711	99.90987	99.77168
Standard error	0.057974	0.034007	0.065058
Median	99.97899	99.95791	99.93687
Mode	100	100	100
Standard deviation	0.317538	0.186262	0.356337
Sample variance	0.10083	0.034693	0.126976
Kurtosis	0.082482	21.94624	3.350212
Skewness	−1.24962	−4.41491	−1.93657
Range	1.010101	1.010101	1.346801
Minimum	98.9899	98.9899	98.6532
Maximum	100	100	100
Sum	2993.613	2997.296	2993.15
Count	30	30	30
Confidence level (95,0%)	0.118571	0.069551	0.133058

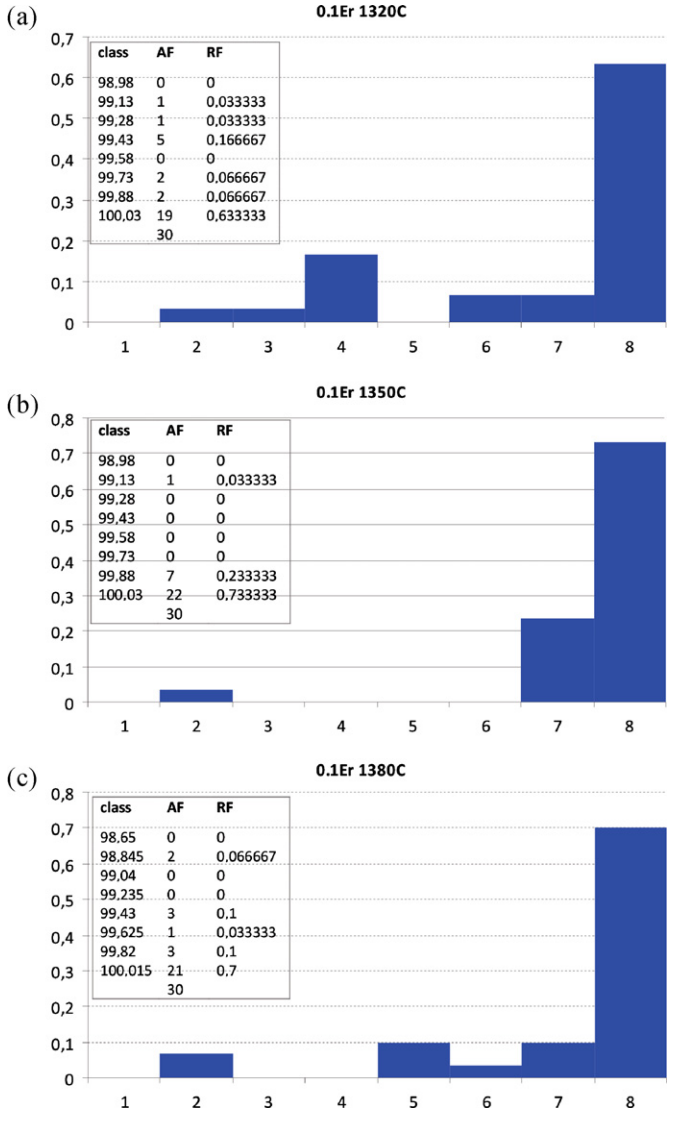

Fig. 8. Histograms corresponding to relevant statistical parameters for 0.1 Er/$BaTiO_3$ samples, sintered at: (a) 1320 °C, (b) 1350 °C and (c) 1380 °C.

Table 2
The results of *t*-tests.

	Variable 1	Variable 2
t-Test: two-sample assuming unequal variances (1320 °C, 1380 °C)		
Mean	99.77167901	99.78711336
Variance	0.12697587	0.1008302
Observations	30	30
Hypothesized mean difference	0	
df	57	
t stat	−0.17711940	
$P(T \leq t)$ two-tail	0.86004248	
t critical two-tail	2.00246544	
t-Test: two-sample assuming unequal variances (1350 °C, 1380 °C)		
Mean	99.77167901	99.90987205
Variance	0.12697587	0.034693353
Observations	30	30
Hypothesized mean difference	0	
df	44	
t stat	−1.88249194	
$P(T \leq t)$ two-tail	0.06639226	
t critical two-tail	2.01536754	
t-Test: two-sample assuming unequal variances (1320 °C, 1350 °C)		
Mean	99.78711336	99.90987205
Variance	0.1008302	0.034693353
Observations	30	30
Hypothesized mean difference	0	
df	47	
t stat	−1.82644042	
$P(T \leq t)$ two-tail	0.07413921	
t critical two-tail	2.0117404	

analysis. This sample size is sufficient for the statistical procedures that follow [14,15]. The area of each surface is 14,850 μm^2, the bar is 10 μm, and the enlargement is 1000. For each of the three samples, relevant statistical parameters, together with the corresponding histograms are presented in Table 1 and Fig. 8.

As could be seen from the statistical data above, the averages of the measured areas of contact surfaces are rather close to each other: 99.78711, 99.90987 and 99.77168, so it makes sense to test the equality of the three means. We use the *t*-test to check the equality of these three means. We first check the hypothesis $H_0(\mu_{1320} = \mu_{1380})$, then $H_0(\mu_{1350} = \mu_{1380})$, and finally the hypothesis $H_0(\mu_{1320} = \mu_{1350})$. The results of the three tests, with the level of significance 0.05, are presented in Table 2.

In the first test ($H_0(\mu_{1320} = \mu_{1350})$), we see that the *t*-value −0.17711940 is outside the two-sided critical region (because $-0.17711940 > -2.01536754$). Therefore, we cannot reject the hypothesis $H_0(\mu_{1320} = \mu_{1350})$ that the means from the corresponding two samples are equal, at the significance level of 0.05.

We have the similar situation in the next two tests. In the case when we test $H_0(\mu_{1350} = \mu_{1380})$, we obtain that, since $-1.88249194 > -2.01536754$, $H_0(\mu_{1350} = \mu_{1380})$ cannot be rejected. $H_0(\mu_{1320} = \mu_{1350})$ cannot be rejected either, since $-1.82644042 > -2.0117404$. This means that, with the significance level of 0.05, there is no reason to believe that the temperature levels of 1320 °C, 1350 °C and 1380 °C have different influences on the size of the contact area of 0.1 wt% Er_2O_3 doped $BaTiO_3$ ceramic surfaces.

4. Conclusions

The study of processes acting on contacts of two or more ceramics grains has great importance for establishing microstructure relations, which essentially influence ceramics dielectric properties. In that sense, starting with grains sizes extracted from SEM microphotographs, mathematical models of grains in contact are generated. The contact surfaces values directly define the value of microcapacitance generated at intergranular contact.

Fractal geometry has been used to describe complexity of the spatial distribution of electroceramics grains. It has been shown that the control of shapes and numbers of contact surfaces, at the level of the entire electroceramic sample and over structural properties of these ceramics, can be done. For better and deeper characterization and understanding of the ceramics material microstructure, the methods that include the fractal nature structure, and also Voronoi model and mathematical statistics calculations, are applied. Voronoi is one specific interface between fractal structure nature and different stochastical contact surfaces, defined by statistical mathematical methods. Also, the Voronoi model practically provided possibility to control the ceramics microstructure fractal nature. Mathematical statistic methods enabled establishing the real model for the prognosis of correlation: synthesis–structures–properties.

All of these analyses and different characterization methods are very important for the prognosis of final, especially dielectric and ferroelectric $BaTiO_3$-ceramics properties. So, it represents the beginning of the development of the original intergranular impedance model, based on intergranular capacity. One of the most important characteristics of such model is inclusion of different corrections in basic, already known electrophysics model of intergranular capacity. This model included fractal correction, contact surfaces aspect and specific application of mathematical statistics methods.

The presented research leads to better understanding of the influence of the fractal nature on final microstructure and dielectrical properties of $BaTiO_3$-ceramics.

Acknowledgements

This research is part of the project ‘‘Directed synthesis, structure and properties of multifunctional materials’’ (172057) and of the project III44006. The authors gratefully acknowledge the financial support of Serbian Ministry of Education and Science for this work.

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