Science of Sintering, **45** (2013) 223-232

doi: 10.2298/SOS1302223M

UDK 53.086;666.3.019

Electronic Ceramic Structure within the Voronoi Cells Model and Microstructure Fractals Contacts Surfaces New Frontier Applications

V. V. Mitić[1,2,*], V. Paunović[1], S. Janković[3], V. Pavlović[4], I. Antolović[1], D. Rančić[1]

[1]University of Nis, Faculty of Electronic Engineering, Aleksandra Medvedeva 14, Nis, Serbia

[2]Institute of Technical Sciences of SASA, Knez Mihailova 35, 11000 Belgrade, Serbia

[3]Mathematical Institute of SASA, Knez Mihailova 36, 11000 Belgrade, Serbia

[4]Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11000 Belgrade, Serbia

Abstract:

In this study, in order to establish grain shapes of sintered ceramics, new approach on correlation between microstructure and doped $BaTiO_3$ -ceramics properties based, on Voronoi model and mathematical statistics calculations on fractal geometry, has been developed. $BaTiO_3$-ceramics doped with Yb_2O_3 (from 0.1 to 1.0wt% of Yb) were prepared by using conventional solid state procedure and were sintered from 1320°C to 1380°C for four hours.

The microstructure of sintered specimens was investigated by Scanning electron microscope JEOL-SEM-5300. For better and deeper characterization and understanding of the ceramics material microstructure, the methods which include the fractal nature structure, and also Voronoi model and mathematical statistics calculations, are applied. In our research the Voronoi is one specific interface between fractal structure nature and different stochastically 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 based on correlation: synthesis-structures-properties.

Keywords: *$BaTiO_3$-ceramics, Voronoi model, Statistic method, Microstructure, Fractals.*

1. Introduction

Barium-titanate ceramics are one of the most important ferroelectric materials, used for obtaining different electro ceramic components. It has been shown that electrical properties of undoped and doped $BaTiO_3$-ceramics are mainly controlled by barrier structure, domain motion of domain boundaries and the effects of internal stress in the grains. Therefore, microstructure properties of barium-titanate based materials, expressed by grain boundary contacts, are of basic importance for electric properties of these material [1, 2].

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

Since both, intergranular structure and electrical properties depend on ceramics diffusion process, it is essential to have an equivalent circuit model that provides a more realistic representation of the electrical properties. Recently, it has been established modeling of random microstructures like aggregates of grains in polycrystals, patterns of intergranular cracks, and composites, theory of Iterated Function Systems (IFS) and the concept of Voronoi tessellation, also can be used [3, 4].

The Voronoi diagram, which can be also referred as thiessen or dirichlet tessellation, has many applications ranging from computer graphics to even archaeology and they are shown very useful structures by efficiently modeling object distance relationships and growth phenomena [5-7]. The main idea for such Voronoi approach has been based on the evident similarity of observed surface land morphology from the space distances watching with the looking grain surfaces structures on microstructure level.

The Voronoi diagram of a collection of geometric objects is a partition of space into cells, each of which consists of the points closer to one particular object than to any others, including models of crystal and cell growth. Considering its unique properties, the concept of Voronoi tessellation has recently been extensively used in materials science, especially for modeling random microstructures like aggregates of grains in polycrystals, patterns of intergranular cracks, and composites. Each grain is assumed to behave as a randomly oriented monocrystal, governed by the anisotropic elasticity and crystal plasticity models.

A Voronoi tessellation represents a cell structure, constructed from a Poisson point process by introducing planar cell walls perpendicular to lines connecting neighboring points. These results, in a set of convex polygons/polyhedra (Fig. 1.), embed the points and their domains of attraction, which partitioned the underlying space [8, 9].

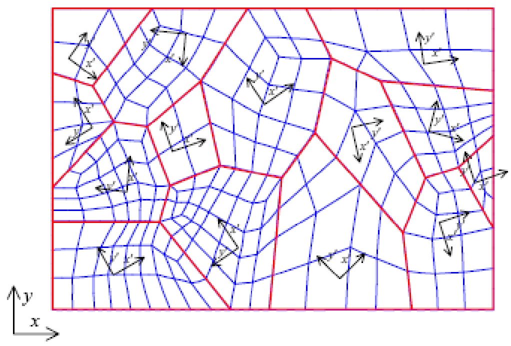


Fig. 1. Voronoi tessellation of 14-grain aggregate with grain boundaries, orientations of crystal lattices, finite element mesh and boundary conditions.

In this article we have developed methods for modeling grain geometry, grain boundary surface and doped $BaTiO_3$-ceramics grain contacts geometry. Most of these methods are based on $BaTiO_3$ microstructure analysis and on fractal correction, which expresses the grains surface irregularity through fractal dimension [10, 11]. Also, we showed some results for intergranular contact surfaces based on statistical methods and calculations.

2. Experimental procedure

The samples used in our investigations were prepared from high purity (>99.98%) commercial $BaTiO_3$-ceramics powder (MURATA) with [Ba]/[Ti]=1.005 and reagent grade Yb_2O_3 powders (Fluka chemika). Yb_2O_3, dopants were used in the amount to have 0.1, 0.5 and 1wt% Yb in $BaTiO_3$. Starting powders were ball-milled in ethyl alcohol for 24 hours using polypropylene bottle and zirconia balls. After drying at 200ºC 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 1320ºC to 1380ºC in air, for four hours. 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. Electrical characteristic were measured using Agilent 4284A precision LCR meter. The illustrations of the microstructure simulation, were generated by Mathematica 6.0 software**.**

3. Microstructure characteristics

For Yb doped $BaTiO_3$-ceramics, sintered at 1320ºC, 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 and for samples sintered at 1380 ºC and doped with 0.1 wt% of additive the density value is 93% of TD.

The SEM investigations of Yb/$BaTiO_3$ have shown homogeneous microstructure with irregularly polygonal shaped grains.

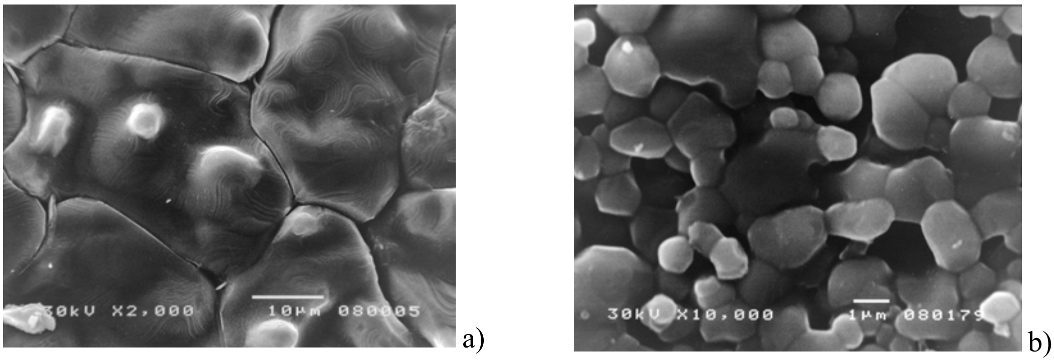


Fig. 2. SEM images of Yb doped $BaTiO_3$ sintered at 1320°C, doped with 0.1wt% and b) 1.0wt% of Yb.

For 0.1 wt% of Yb/$BaTiO_3$, sintered at 1320°C (Fig. 2.a), 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 2 μm to 10 μm (Fig. 2.b).

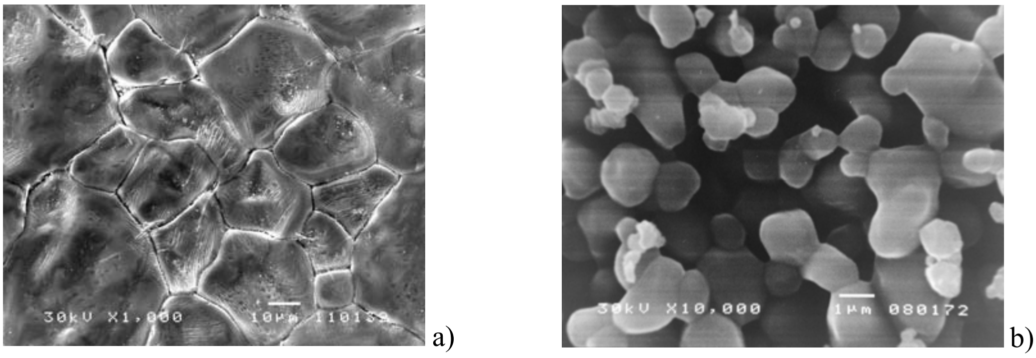
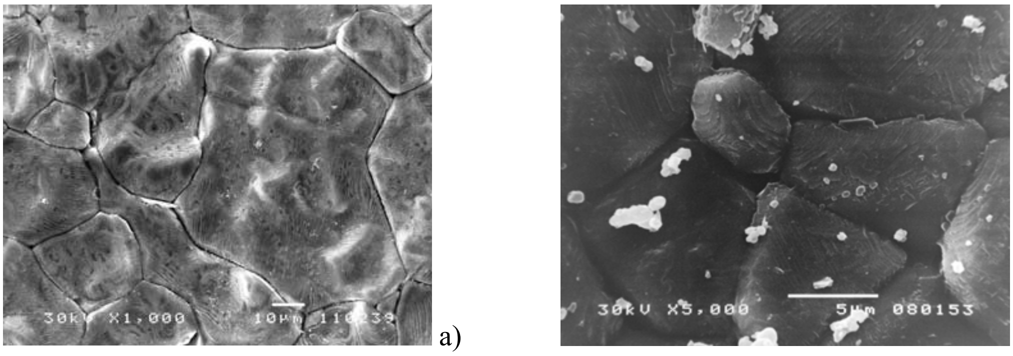


Fig. 3. SEM images of Yb doped $BaTiO_3$ sintered at 1350°C, doped with 0.1wt% and b) 1.0wt% of Yb.

The similar microstructure was observed in samples sintered at higher temperature 1350°C and 1380°C (Fig. 3. and Fig. 4.). Also, with sintering temperature increase, the grain size increase and for samples doped with 0.1wt% of additive and sintered at 1380°C, the grain size were 60µm.



a) b)

Fig. 4. SEM images of Yb doped $BaTiO_3$ sintered at 1380°C, doped with 0.1wt% and b) 1.0wt% of Yb.

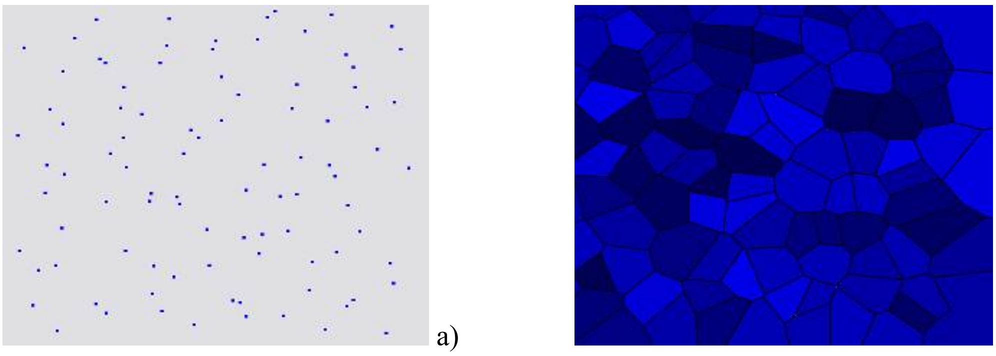
The EDS analysis [12] for all samples has shown that, for small concentrations of dopants the distribution is uniform, while the increase of dopant concentration led to the co-precipitation between grains.

4. Grains surface modeling

Considering shapes properties, method of Voronoi tessellation has 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 the microstructure surface, rather than the inner structure. The 3D modeling process can be divided in several steps as follows:

The first step consists of generating a set of n^2 points on a regular 2D grid (Fig. 5.a). The fact that the diameter of an individual grain ranges from 10 µm-100 µm directly influences the 2D grid incremental factor which can be set to 100 µm.

This is followed by a dislocation of each point by using a random function for both, x and y axes. In this way, a rather uniform distribution of initial points is achieved, while still providing a good base for various sizes Voronoi cells generation (Fig. 5.b).



a) b)

Fig. 5. a) Generating set of points which represent the distribution of micro-grains and b) forming set the Voronoi cells.

The next step involves the application of a 2D Voronoi tessellation algorithm on the input set of points, thus producing the necessary Voronoi cell configuration (Fig. 6.). Finally, the produced 2D tessellation configuration is used, as a base for generating an elevated 3D microsurface model (Fig. 7.). Again, with the respect to the dimensions of a real microsurface grain, a random elevation factor d ranging from 0μm to 1μm, is used. Additionally, the elevation factor tends to decrease, near the Voronoi cell edges, thus emphasizing each individual grain.

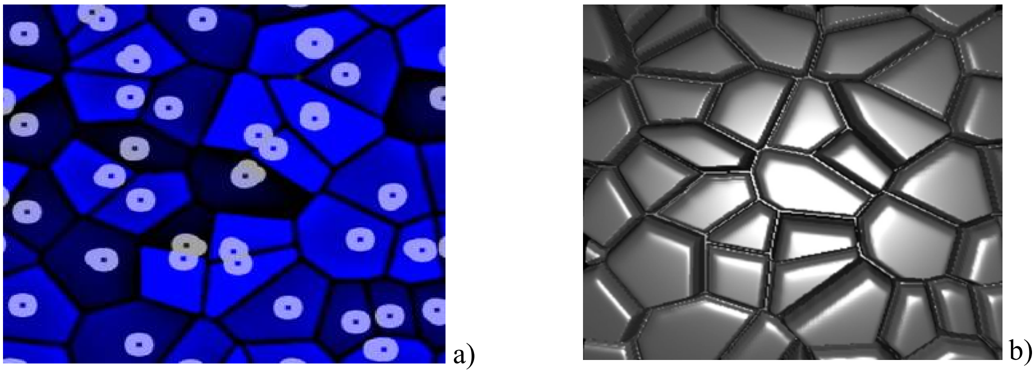


Fig. 6. Mapping Voronoi in 3D model.

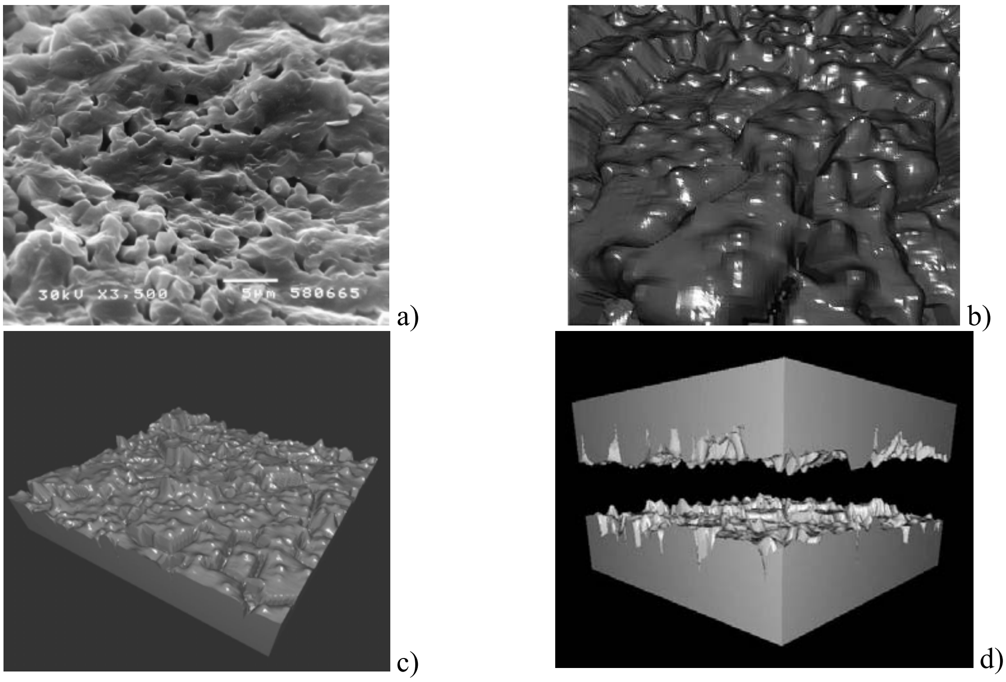


Fig. 7. a) SEM image of Yb doped $BaTiO_3$ ceramic, b) micro surface overview profile and c), d) 3D microsurface overiew.

Set of points is generated in order to represent the micro-grains distribution. 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 two contact surfaces points-peaks and micro values, which practically represent the new level, more complex and realistic, micro-intergranular capacitors-impendances network (Fig. 7.d). Especially, based on Fig. 7.d we are developing one frontier idea, that each of pick of one side surfaces with pick from another sample surface side or pick to valley, or valley to valley are possible network of different intergranular capacitance i.e. intergranular impedances. So, by Voronoi model we would like to open the new frontier, that each, of these pick or valley, could be also recognized as fractal surface, so we can establish more precision contact surface intergranular impedance network, what is giving the new approach idea, for deeper and higher electronic integrations level.

5. Statistical approach

To study the relationship between the temperature and the contact surface area for $BaTiO_3$-ceramic grains, we use the statistical approach. It can be applied to all kinds of grains and every ceramic structure, regardless of the actual shape of the ceramic grains and contact area between the grains. Also the statistical method was used to explain the fractal nature of the contact surfaces of each Voronoi cells pick or valley. The most important is the area of the contact surface on randomly chosen squares. 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 sample of the size n consists of randomly chosen squares of 0.1% Yb_2O_3 doped $BaTiO_3$-ceramic, with prescribed vertices. The areas of contact surfaces on these n squares are measured. The obtained values $X_1, X_2, ..., X_n$ are the measure of contact areas on each of the corresponding squares. Several statistical parameters obtained from the sample, in particular the sample mean $\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$, the sample variance

$$\overline{\sigma}^2 = \frac{1}{n}\sum_{i=1}^{n}(X_i - \overline{X})^2$$

and the unbased estimate of the variance

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

For chosen α=0.05, the confidence interval for the unknown mean μ is:

$$(\overline{X} - \frac{t_{n-1,\alpha/2}\overline{\sigma}_0}{n^{1/2}} < \mu < \overline{X} + \frac{t_{n-1,\alpha/2}\overline{\sigma}_0}{n^{1/2}}),$$

that is

$$P(\overline{X} - \frac{t_{n-1,\alpha/2}\overline{\sigma}_0}{n^{1/2}} < \mu < \overline{X} + \frac{t_{n-1,\alpha/2}\overline{\sigma}_0}{n^{1/2}}) = 1 - \alpha .$$

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

We study three samples, each of them of the size 30, of 0.1% Yb_2O_3 doped $BaTiO_3$-ceramic square-shaped surfaces. This sample size is sufficient for the statistical procedures that follow [13, 14]. The area of each surface is 14850 μm^2, the bar is 10 μm, and the enlargement is 1000. For each of the three samples, the relevant statistical parameters, and the corresponding histograms, are presented in Tab. I and Fig. 8.

Tab. I reveals that the averages of measured areas of contact surfaces are relatively close to each other: 99.98036, 99.98598 and 99.97651. We use t-Test to test the equality of these three averages. We first check the hypothesis $H_0(\mu_{1320} = \mu_{1350})$, then $H_0(\mu_{1320} = \mu_{1380})$, and finally the hypothesis $H_0(\mu_{1350} = \mu_{1380})$. The results of the three tests, with the significance level $\alpha = 0.05$, are presented in Tab. II.

Tab. I Descriptive statistics for contact surfaces.

0.1wt% Yb2O3	1320°C	1350°C	1380°C
Mean	99.98036	99.98598	99.97651
Standard Error	0.008099	0.00347	0.012147
Median	100	99.98949	99.98949
Mode	100	100	100
Standard Deviation	0.044361	0.019007	0.066529
Sample Variance	0.001968	0.000361	0.004426
Kurtosis	7.604821	5.323239	18.46444
Skewness	-2.84507	-2.02109	-4.21132
Range	0.16835	0.084175	0.3367
Minimum	99.83165	99.91582	99.6633
Maximum	100	100	100
Sum	2999.411	2999.579	2999.295
Count	30	30	30
Confidence Level(95.0%)	0.016565	0.007098	0.024842

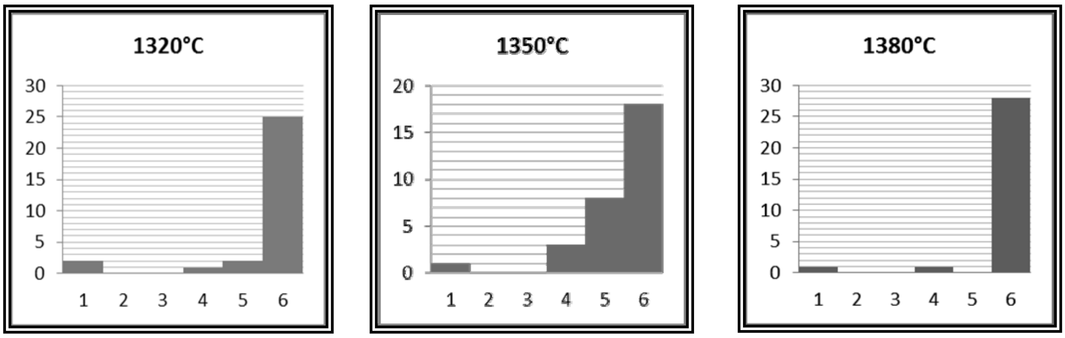


Fig. 8. Histograms corresponding to relevant statistical parameters for 0.1 Yb/$BaTiO_3$samples, sintered at: a) 1320ºC, b) 1350ºC and c) 1380ºC.

In the first test ($H_0(\mu_{1320} = \mu_{1350})$), the value of *t*-statistic -0.63764 is outside the two sided critical region (because -0.63764 > -2.022691). Therefore we cannot reject the hypothesis $H_0(\mu_{1320} = \mu_{1350})$, that averages from the corresponding two samples are equal, at the significance level $\alpha = 0.05$.

We have analogous situation in the next two tests. In the case when we test the hypothesis $H_0(\mu_{1320} = \mu_{1380})$ we obtain that, since 0.263841 < 2.007584, we cannot reject $H_0(\mu_{1320} = \mu_{1380})$ at the significance level $\alpha = 0.05$. Similarly, we cannot reject the hypothesis $H_0(\mu_{1350} = \mu_{1380})$ at $\alpha = 0.05$, because the value of t-statistic is again not in the critical region, since 0.749672 < 2.032244. This means that, at the significance level of $\alpha = 0.05$, we cannot reject the hypothesis that temperature levels of 1320°C, 1350°C and

1380°C have the same influence on the size of the contact area of 0.1 % Yb_2O_3 doped $BaTiO_3$-ceramic surfaces.

Tab. II t-Tests results.

t-Test: Two-Sample Assuming Unequal Variances.

	1320°C	1350°C
Mean	99.98036	99.98598
Variance	0.001968	0.000361
Observations	30	30
Hypothesized Mean Difference	0	
df	39	
t Stat	-0.63764	
P(T<=t) one-tail	0.263718	
t Critical one-tail	1.684875	
P(T<=t) two-tail	0.527436	
t Critical two-tail	2.022691	

t-Test: Two-Sample Assuming Unequal Variances.

	1320°C	1380°C
Mean	99.98036	99.97651
Variance	0.001968	0.004426
Observations	30	30
Hypothesized Mean Difference	0	
df	51	
t Stat	0.263841	
P(T<=t) one-tail	0.396483	
t Critical one-tail	1.675285	
P(T<=t) two-tail	0.792965	
t Critical two-tail	2.007584	

t-Test: Two-Sample Assuming Unequal Variances.

	1350°C	1380°C
Mean	99.98598	99.97651
Variance	0.000361	0.004426
Observations	30	30
Hypothesized Mean Difference	0	
df	34	
t Stat	0.749672	
P(T<=t) one-tail	0.229304	
t Critical one-tail	1.690924	
P(T<=t) two-tail	0.458609	

6. Conclusions

In this article a reconstruction of microstructure configurations, like grains shapes, contacts surfaces and intergranular contact, by using statistical mathematics and fractal modeling method have been successfully done. It has been shown that the control of shapes and numbers of contact surfaces on the level of the entire electroceramic sample, and over structural properties of these ceramics can be done. The Voronoi model represents a specific interface between fractal structure nature and different stochastically contact surfaces, practically provided possibility to control the ceramics microstructure fractal nature. The statistical method based on the contact surfaces fractal nature explanation of each Voronoi cells pick or valley. Statistical methods enable the establishing the real model for the synthesis-structures-properties prognosis correlation. Obtained results indicated that fractal analysis with Voronoi and statistical model for contact surfaces of different shapes leads to better understanding of fractal nature influence on final microstructure and dielectrical properties of $BaTiO_3$-ceramics in the new frontiers lights higher electronics circuit's integrations and miniaturization.

Acknowledgements

The authors gratefully acknowledge the financial support of Serbian Ministry of Education, Science and Technological development for this work (projects 172057 and III44006).

7. References

1. D. Lu, X. Sun, M. Toda, Japanese Journal of Applied Physics 45, [11], (2006) 8782–8788.
2. N.Hirose, A.West, J.Am.Ceram.Soc, 79, [6], (1996) 1633-41.
3. V.V.Mitic, V.B.Pavlovic, Lj. Kocić,V.Paunovic, D.Mancic, Science of sintering, 41, 3, (2009), 247-256.
4. M. Grujicic, Y. Zhang, Materials Science and Engineering A251 (1998) 64–76.
5. H.Riesch-Oppermann, VorTess, Generation of 2-D Random Poisson-Voronoi Mosaics as Framework for theMicromechanical Modelling of Polycristalline Materials, Forschungszentrum Karlsruhe; 1999; Report FZKA 6325.
6. S.Weyer, A.Fröhlich, H.Riesch-Oppermann, L.Cizelj, M.Kovač, Engineering Fracture Mechanics, 69, 8, (2002) 945-958.
7. P. Vena, D. Gastaldi, Composites Part B: Engineering, 36, 2, 2005, 115–126
8. F. Aurenhammer, ACM Computing Surveys. 23, 3, (1991) 345-405.
9. Zhigang Fan, Yugong Wu, Xuanhe Zhao, Yuzhu Lu, Computational Materials Science, 29, (2004) 301–308.
10. V. Mitić, V. Paunović, D. Mančić, Lj. Kocić, Lj. Zivković ,V.B. Pavlović, Advances in Electroceramic Materials, Ceramic Transactions Vol. 204 2009, 137-144.
11. V.V. Mitić, V.Pavlović, Lj.Kocić, V. Paunović, Lj.Živković, Advances in Sciency and Technology, 67, 2010, 42-48.
12. V. V. Mitić, V. Paunović, V. Pavlović, Lj. Živković, Science of sintering, 43, 3 , 2011, 277-287.
13. D. C. Montgomery, G. C. Runger, Applied Statistics and Probability for Engineers, Wiley, 2002, p 241.

14. V. K. Rohatgi, An Introduction to Probability Theory and Mathematical Statistics, Wiley, 1976, p 452.

Садржај: *У овом раду, у циљу што боље контроле облика зрна синтероване керамике, развијен је нови приступ на корелацији између микроструктуре и карактеристика допиране $BaTiO_3$-керамике засновaн на Вороnoи моделу и математички статистичком методу.*

$BaTiO_3$-керамика допирана Yb_2O_3 (0.1 до 1.0wt% Yb) добијена је конвенционалном методом синтеровања у чврстој фази на температури синтеровања од 1320℃ до 1380℃ у трајању од 4h.

Микроструктура синтерованих узорака испитивана је скенинг електонским микроскопом JEOL SEM 5300.

Ради боље карактеризације и разумевања микроструктуре керамичких материјала у раду су примењене методе које се заснивају на фракталној природи структуре материјала, а такође и Вороnoи модел и математичко статистики метод прорачуна. Вороnoи модел је једна специфична веза између фракталне природе различитих контактних површина, зрна дефинисаних статистичким математичким методама. Такође, овај модел практично омогућава приступ и контролу фракталне микроструктурне природе материјала. Математички статистички модел даље омогућава успостављање правог модела за прогнозу корелације: синтеза-структура-својства материјала у светлу нових перспектива даље минијатуризације и виших нивоа интеграције функција у електронским керамичким материјалима.

Кључне речи: *$BaTiO_3$ керамика, Вороnoи модел, статистички модел, микроструктура, фрактали.*