Nonlinear Scaling Corrections of the BaTiO3-Ceramics Microstructures

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Abstract.

A new approach, based on nonlinear scaling corrections fractal geometry and dimension for doped BaTiO$_3$-ceramics, is applied. The main conclusion was that intergranular capacities have various positive values then expected which is induced by contact surfaces sizes augmentation as a consequence of their new nonlinear fractal based nature, which includes the box size dependence of scaling. Also, introduced new model for intergaranular non-ideal capacitor, generalized Cole impedance element in conection with the parallel parasite capacity, resistivity and inductivity.

Keywords: *BaTiO3-ceramics, fractal, microstructure*

1. Introduction

Doped barium-titanate ceramic are one of the most important electronic materialss for the small size processing and designing, as a multilayer ceramic capacitors of high capacitance manufacture [1,2]. Theory of fractals [3–5] is a new approach for describing and modeling the grain's shape and relations between BaTiO3-ceramics structure and electrical, magnetic, mechanical, impednce and other properties. In this paper generalized concept of fractals and dimensions, also

Levenberg-Marquardt algorithm (LMA) of nonlinear least squares, based on the use of L_2 norm in the propagation of errors, was used for fitting of experimental data. Precisely, was used Levmar package in Octave or Matlab programming environment [6]. Without complications or this fitting calculation, maximally used 10 parameters. This restriction encourages the implementation of LAPACK libraries in C/C++. The main feature of this package is that with its use can determine the interval in which the values of each parameter.

This paper is organized as follows. In Section 3, based on the previous section, quadratic nonlinear scaling and appropriate fractals concepts is proposed in simplest way. Also, introduced two simple examples of quadratic fractals. In Section 4, based on [7-12], proposed a new generalized CPE and Cole impedance element. This element, in the special case, is used for the new model of grain-grain contact for doped BaTiO$_3$-ceramics. Finally, the conclusions are given in Section 5.

2. Quality of fits

Box - counting dimension is defined as follows. Shall be considered set S in a Euclidean space $\mathbb{R}^n$. Suppose that $N(\varepsilon)$ is the number of boxes of side length ε required to cover the set S.

Then the box-counting fractal dimension (lacunarity) is defined as

$$\dim_{Box}(S) := \lim_{\varepsilon \to 0} \frac{\log(N(\varepsilon))}{-\log(\varepsilon)}, \tag{1}$$

Where $N(\varepsilon)$ count the number of blocks diameter ε. This means, the box-counting dimension is the exponent d such that $N(1/n) \approx C\,n^d$ ($n = [\varepsilon]$, [.] is integer part of a number), which is what one would expect in the trivial case where S is a smooth space of integer dimension d [4]. Previously written can be interpreted and generalized on the next way (n is a number of details)

$$N(n)=N(\varepsilon) \approx C\,n^d\,(\,n = [\varepsilon^{-1}]\,, \varepsilon \to 0+\,). \tag{2}$$

The simplest of fractal dimension of the set S is the scaling dimension determined by the formula

$$d_{scf}(S) := \frac{\log N}{\log n}, \tag{3}$$

where N is the number of identical parts of the fractal object, being similar to the original one but n times smaller in linear size [5]. Box counting dimension not necessarily linked relationship between scale and details, a sa a scaling dimension, but may try to find a scaling rule.

First example: with the Cantor ternary set for each step $k=0,1,2,3,\ldots$, according to (2), have $\varepsilon = 1/3^k$, $n(\varepsilon) = n(k) = 3^k$ and $N(\varepsilon) = N(k) = 2^k$; with regard to (3), $N = 2$ and $n = 3$. Second example: in a similar way, for the Koch curve, $\varepsilon = 1/3^k$, $n(\varepsilon) = n(k) = 3^k$ and $N(\varepsilon) = N(k) = 4^k$; also, with regard to (3), $N = 4$ and $n = 3$.

Details of fitting procedures that follow are standard. The following equations for standard and new counting box method are

$$c(bs) = p(1) \cdot (bs)^{p(2)},\ c(bs) = p(1) \cdot (bs)^{p(2)+p(3)\cdot\log(bs)}, \tag{4}$$

Where $c(bs)$-count; bs-box size; $p(1), p(2), p(3)$ are parameters.

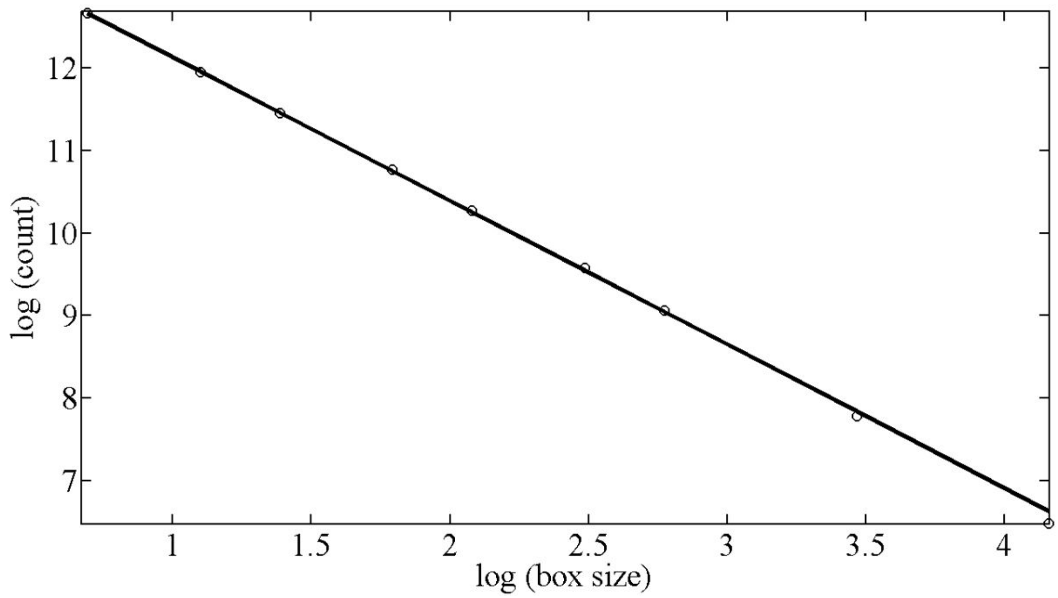

Fig. 1. Fitting function $count = p(1)\cdot(box\ \ size)^{p(2)}$, $p(1) = 1.0547\cdot10^{6}$, $p(2) = D_{sbcf}$=-1.74,

D_{sbcf} is a standard box-counting fractal dimension.

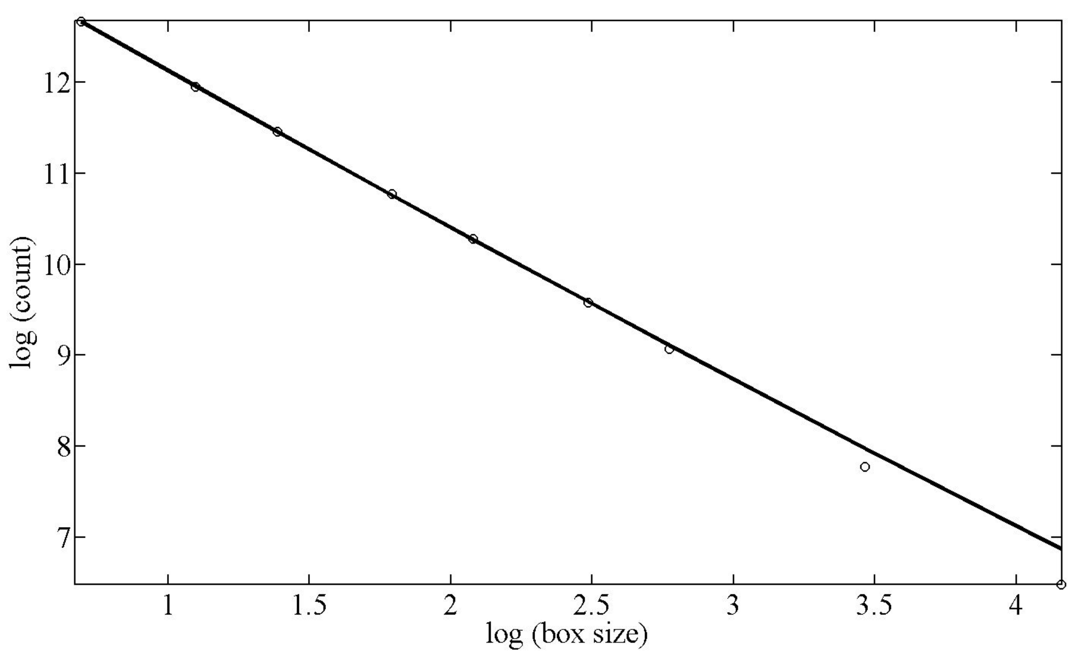

Fig.2. Fitting function $count = p(1)\cdot(box\ \ size)^{p(2)+\mathrm{p}(3)\cdot\log(\text{box size})}$, $p(1)=1.0878\cdot10^{6}$, $p(3)=\ 0.0268$. D_{ncbf} is a new box-counting fractal dimension, $p(3)$ is a quadratic, new, generalized fractal dimension.

Logarithm of equations (3) gives

$$\log(\mathrm{c})=\log\left(\mathrm{p}(1)\right)+\mathrm{p}(2)\cdot\log\left(bs\right),\ \log(\mathrm{c})=\log\left(\mathrm{p}(1)\right)+\mathrm{p}(2)\cdot\log\left(bs\right)+p(3)\cdot\log^{2}\left(bs\right). \qquad (5)$$

First equation in (5) is a linear, while second equation is a quadratic function from $\log\left(bs\right)$. This means that in second case it performed a non-linear version of the box – counting method.

Quality of fits determined by the equation for the expected sum of squares for *n* data points (bs_i, $c(bs_i)$), $i = 1,2,...,n$ is

$$Q=\frac{1}{n-m+1}\sum_{i=1}^{n}\left(c(\mathrm{bs}_{i})-\hat{\mathrm{c}}\left(bs_{i};\mathbf{p}\right)\right)^{2}, \qquad (6)$$

$\mathbf{p}=\left(p\left(1\right),p\left(2\right),...,p\left(m\right)\right)$ - Model parameters vector with *m* components and the curve-fit function $\hat{\mathrm{c}}\left(bs_{i};\mathbf{p}\right)$. For the first and second case of fitting function in (4), respectively, $Q_1=3.706\cdot10^{5}$ and $Q_2=\ 1.368\cdot10^{5}$. It is noticed that the difference between the quality of the two aforementioned fits significant. That is the main reason for a detailed discussion quadratic nonlinear corrections of fractality and scaling.

3. New scaling

Concept of (continuous) scale invariance is known: in a nutshell, it means reproducing itself on different time or space scales [4], [5], [10]. An observable $\mathrm{O}\left(x\right)$ which depends on a "control" parameter *x* is scale invariant under the arbitrary change $x \rightarrow \lambda x$, if there is a number $\mu(\lambda)$ such that

$$\mathrm{O}\left(x\right)=\mu\mathrm{O}\left(\lambda x\right) \qquad (7)$$

Its solution is a power law $\mathrm{O}\left(x\right)=Cx^{\alpha}$, with $\alpha=-\frac{\ln\mu}{\ln\lambda}$. The ratio $\frac{\mathrm{O}\left(\lambda x\right)}{\mathrm{O}\left(x\right)}=\lambda^{\alpha}$ not depend on *x*, i.e. the relative value of the observable at two different scales only depend on the ratio of the two scales. This is the fundamental property that associates self-similarity to scale invariance, power laws and criticality.

In physics, is a well-known construction of scaling function for a description of a disordered systems [12]. Keeping this in mind, in this paper presents correction to the scale invariance in the following way (*x>0*). For observable $\mathrm{O}(x)$ then exists two unique nonzero real numbers α, β which are subject to definition

$$\begin{aligned} &\mathrm{O}(x) := \mathrm{O}_1(x)\cdot \mathrm{O}_2(x), \\ &\frac{d\ln \mathrm{O}_1(x)}{d\ln x} := \alpha, \quad \mathrm{O}(1) := \mathrm{C}, \\ &\frac{d^2\ln \mathrm{O}_2(x)}{d\ln^2 x} := \beta, \quad \frac{d\ln \mathrm{O}_2(x)}{d\ln x}\Big|_{x=1} := 1. \end{aligned} \tag{8}$$

Previous definition mean that to be valid: $\mathrm{O}_1(x) = Cx^{\alpha}$ and $\mathrm{O}(x) = Cx^{\alpha}\cdot x^{\frac{\beta}{2}\ln x}$. The ratio $\dfrac{\mathrm{O}(\lambda x)}{\mathrm{O}(x)}$ for (8) complicated depend on *x*, but valid

$$e^{\frac{d\ln \mathrm{O}_2(\lambda x)}{d\ln(\lambda x)}} = \lambda^{\beta} e^{\frac{d\ln \mathrm{O}_2(x)}{d\ln(x)}}. \tag{9}$$

Idea of definition (8) is a simple. The power law $\mathrm{O}(x) = Cx^{\alpha}$, for x>0, in a logarithmic scale represents the linear function $\ln \mathrm{O}(x) = \ln C + \alpha \ln x$ (i.e. formal Taylor series of the first degree at the point x=1). In this paper author present nonlinear, quadratic Taylor polynomial approximation. Cases $x \to 0+$ or $x \to \infty$ describes the behavior on the ends of the interval (i.e. asymptotics of functions) and it is one of the essential characteristics of the ways to determine the box-counting dimension of a set. Therefore, the proposed concept of Taylor series in logarithmic scale probably may understood as a next level of differential calculus and fractals, and also as a basics to new fractional derivatives and dimensions.

Scale dependent generalized dimension in this paper will be defined in the spirit of equation (2), and in the accordance with previous exposing (the establishment over Hausdorff dimension and, in general, more precise presentation of this problem, will be later).

The box-counting scale dependent generalized method for determination new dimensions α, β for nonempty compact subset *S* in a Euclidean space $\mathbb{R}^n$, for $N(\varepsilon)$ count the number of blocks (i.e. boxes) diameter ε and $n(\varepsilon) = [\varepsilon^{-1}]$ is a number of details; if $\varepsilon \to 0+$, *defined* in the following relation

$$N(n)=N(\varepsilon) \approx C\, n^{\alpha+\beta \ln\varepsilon}. \tag{10}$$

Relation (10), if $n = 1/\varepsilon$, can be written in the form $N(n) \approx C\, n^{\alpha-\beta \ln n}$.

One Illustrative Example

Nonlinear, scale depended fractal based on Cantor set

For each step $k \in \mathbb{N}_0$, the characteristic length of the interval (box size) is $\varepsilon = 1/3^k$. Then $n(\varepsilon) = 3^k$, $C = 1$, $\ln N = \frac{\ln 2}{\ln 3}\ln n + \frac{\ln s}{\ln^2 3}\ln^2 n$, and $\ln s = -\beta \ln^2 3$ ($\alpha = \frac{\ln 2}{\ln 3}$). Then

$$N(k) = 2^k \cdot s^{k^2} \tag{11}$$

Let s=2.

Step k=0. N=n=1;

Step k=1. Then n=3, N=4, $\varepsilon = 1/3$; as a Koch curve in step k=1.

Step k=2. Then n=9, N=64, $\varepsilon = 1/9$; for each interval length 1/9, over an empty middle third, constructed a regular pentadecagon.

Step k=3. Then n=27, N=4096, $\varepsilon = 1/27$; for each interval length 1/27, over an empty middle third, constructed a regular 255-sided polygon. Etc.

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In this example may be used and equation (3), but must be keep in mind that this relation depends on *n*.

4. Generalized CPE and new impedance model some $BaTiO_3$ ceramics

Fractional calculus used with description of electrical circuits through which flows alternating current [7], [10]. The similarity and fractals are, therefore, associated with the concept of CPE. Similar to Fricke CPE element [11], for variabile frequency $\omega > 0$, CPE my describe by the relations

$$Z'_{CPE} = Z'_{CPE\alpha} = R_1 \cdot (i \cdot \omega\tau_\alpha)^{-\alpha}, \quad \tau_\alpha > 0, \ \alpha \in [0,1]. \tag{13}$$

For $\alpha = 1$, $Z'_{CPE1} = R_1 \cdot (i\omega\tau_1)^{-1}$, i.e. electrical capacity is $C = C_1 = \tau_1 / R_1$. General case is a fractional electrical capacity $C_\alpha = \tau_\alpha^\alpha / R_1$. Also, if $\alpha = 0$, then $Z'_{CPE0} = R_1$. Bearing in mind that, the authors in the book [10] extended CPE in the concept of $\alpha = 0$ fractional reactance: Recap ($\alpha \in (0,1]$), Reind ($\alpha \in [-1,0)$), the most general CPE described by the relations

$$Z_{CPE} = Z_{CPE\alpha} = R_1 \cdot (i \cdot \omega\tau_\alpha)^{-\alpha}, \quad \tau_\alpha > 0, \ \alpha \in [-1,1]. \tag{14}$$

The previous equation is continuously scaling invariant by variable ω . In order to avoid in real cases singular behavior for $\omega \to 0+$ or $\omega \to \infty$, introduces a new realistic electric element. It consists of the parallel connection between CPE and resistance $R_0 - R_\infty$, that is at in series connection with R_∞. For $\alpha' = \alpha \in [0,1]$ this element called Cole impedance element.

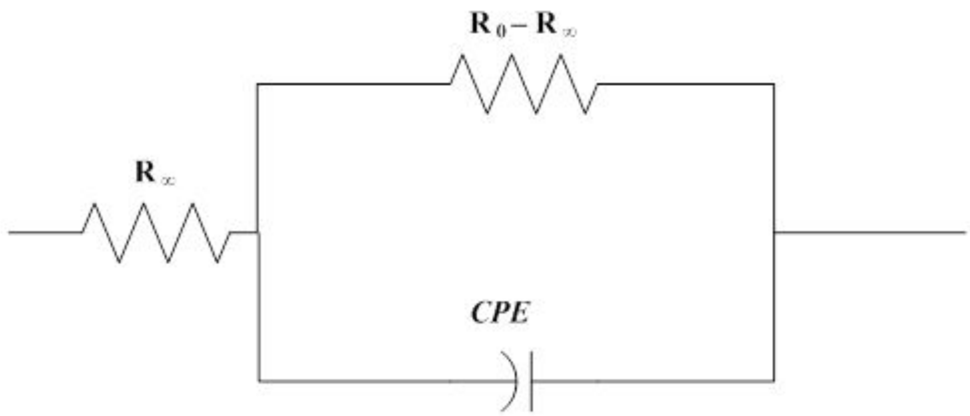

Fig.3. Real CPE element.

Generalization on (14) within fractals-impedance analogie is

$$Z_{GCPE} = Z_{CPE\alpha\beta} = R_1 \cdot \left(i \cdot \omega\tau_\alpha\right)^{-\alpha-\beta\ln\left(\omega\tau_{\alpha\beta}\right)}, \quad \tau_{\alpha\beta} > 0,\ \alpha \in [-1,1],\quad \beta \in \mathbb{R}. \qquad (15)$$

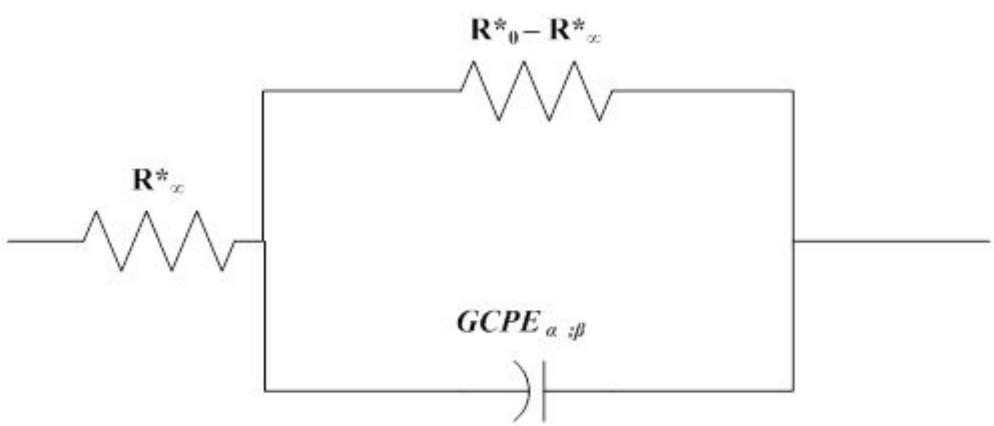

Fig.4. Real GCPE element.

In the special case, in accordance with [7],

$$\underline{Z}_{\alpha;\beta}(\omega) = R_\infty^* + \frac{R_0^* - R_\infty^*}{1 + (i \cdot \omega \cdot \tau_{\alpha\beta})^{\alpha + \beta \cdot \log(i \cdot \omega \cdot \tau_{\alpha\beta})}} \tag{16}$$

This element is a natural candidate to replace meat of capacity for equivalent micro-impedance of G1-G2 contact for $BaTiO_3$ ceramics in Fig.7. in [1].

5. Conclusions

Fractal – impedance analogy used herein, there are probably deeper ground, which is not sufficiently explored. New, generalized fractal and scaling method significantly better describes the form of grains.

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