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$BaTiO_3$-ceramics electrical model based on intergranular contacts

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Abstract

This paper presents the contribution to the development of methods for electronic parameters recognition in $BaTiO_3$-ceramics grains contacts. The model of intergranular impedance applied on two-grain contact is considered and it is established using the equivalent electrical scheme characterized by corresponding frequency characteristic. Globally, $BaTiO_3$-ceramics sample is consisted of a huge number of mutually contacted grains which form clusters. For each of them, it is possible to establish the equivalent electrical model and for defined set of input parameters using symbolic analysis to obtain the frequency diagram. The support for the idea of establishing the electrical model based on intergranular contacts is founded in the fact that results obtained for the equivalent impedance of the cluster (for more then three grains) by symbolic simulation are similar to results measured on real $BaTiO_3$-ceramics samples, which confirmed the validity of approach.

Keywords: $BaTiO_3$; Capacitors; Electrical properties; Impedance; Sintering

1. Introduction

Detailed investigation of $BaTiO_3$-ceramics intergranular contacts has shown that they determine the majority of electrical properties of the whole sample[1,2]. Intergranular contacts are formed during the sintering process. When particles of barium-titanate powder which should be sintered, form a contact, in that area interatomic forces start an action forming a 'neck' of particles. In further processing, 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. Finally, the contact zones are formed which shapes, dimensions and structures essentially influence electrical properties of the entire sample[3]. The simplified case of a two-sphere contact model is shown in Fig. 1a. Considering the previous research in this field[4,5], $BaTiO_3$-ceramics sample behaves as an impedance consisting of a capacitor C_1 in parallel with one RLC circuit (Fig. 1b). Since a ceramics sample consists of numerous sintered grains organized in clusters of different sizes, it is reasonable to suppose that each cluster of grains within the sample and even each intergranular contact within the cluster have similar electrical models. In this paper, the application of an intergranular impedance model on a five-grain cluster is considered. Obtained frequency diagrams are compared with results of frequency characteristics measured on real $BaTiO_3$-ceramics samples.

2. The intergranular impedance model

Let us consider the assumption that intergranular contact (Fig. 1a) can be presented by an impedance model of a $BaTiO_3$-ceramics sample (Fig. 1b). The model parameters are capacitances C_1 and C, inductance L and resistance R. In wide frequency range, the dominant model parameter is capacitance C_1. The relation between C_1 and geometrical parameters of two grains in contact can be established if the structure grain-contact-grain is seen as planar microcapacitor (Fig. 1a). The parameters of the model shown in Fig. 1a are: r_1, r_2-radii of the spherical grains, r_c-radius of the grains intersection, d-distance between centers of grains, x-grains' penetration thickness. Since the spherical shape of the grain is assumed, the contact surface is the circle of the area $S_c = \pi r_c^2$. It is obvious that r_c depends on d. If the capacitor plates are on distance x, where x is a function of d according to the relation $x = r_1 + r_2 - d$, the capacitance is given by

$$C = \varepsilon_0 \varepsilon_B \frac{\pi[4d^2 r_1^2 - (d^2 + r_1^2 - r_2^2)^2]}{4d^2(r_1 + r_2 - d)}. \quad (1)$$

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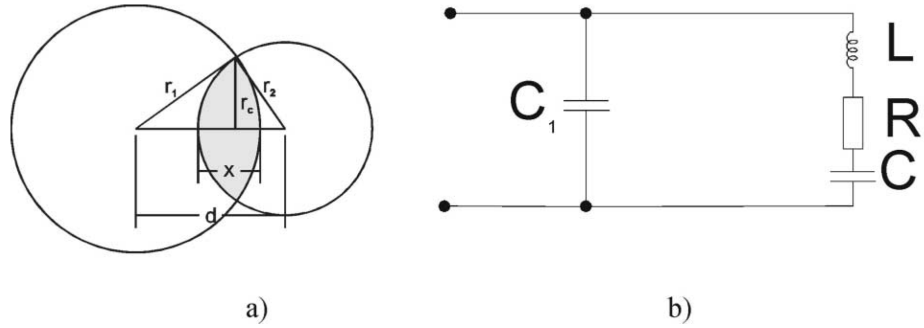

Fig. 1. (a) Two-sphere contact model presented in plane section; (b) the electrical model of $BaTiO_3$-ceramics sample.

This formula enables investigation of the intergranular capacitance as a function of model geometrical parameters as well as consolidation parameters (d represents *the measure of consolidation* and it is dependent on sintering temperature and time).[6]

The basic idea for establishing the model of intergranular impedance came after the results considering intergranular capacitance mentioned above (formula (1). Actually, we supposed that between each two contacted grains there is an elementary intergranular impedance with the model presented in Fig. 1b. Indeed, finding the equivalent impedance of the sample based on connections between elementary intergranular impedances seems to be too complicated. However, it is known that grains tend to form clusters. Thus, we suggest a hierarchical approach. Firstly, we intend to determine the equivalent impedance of a cluster with the aim to approach to higher levels of abstraction in our subsequent research.

In order to generate the electrical model, it is necessary to define the relation for intergranular impedance. Using

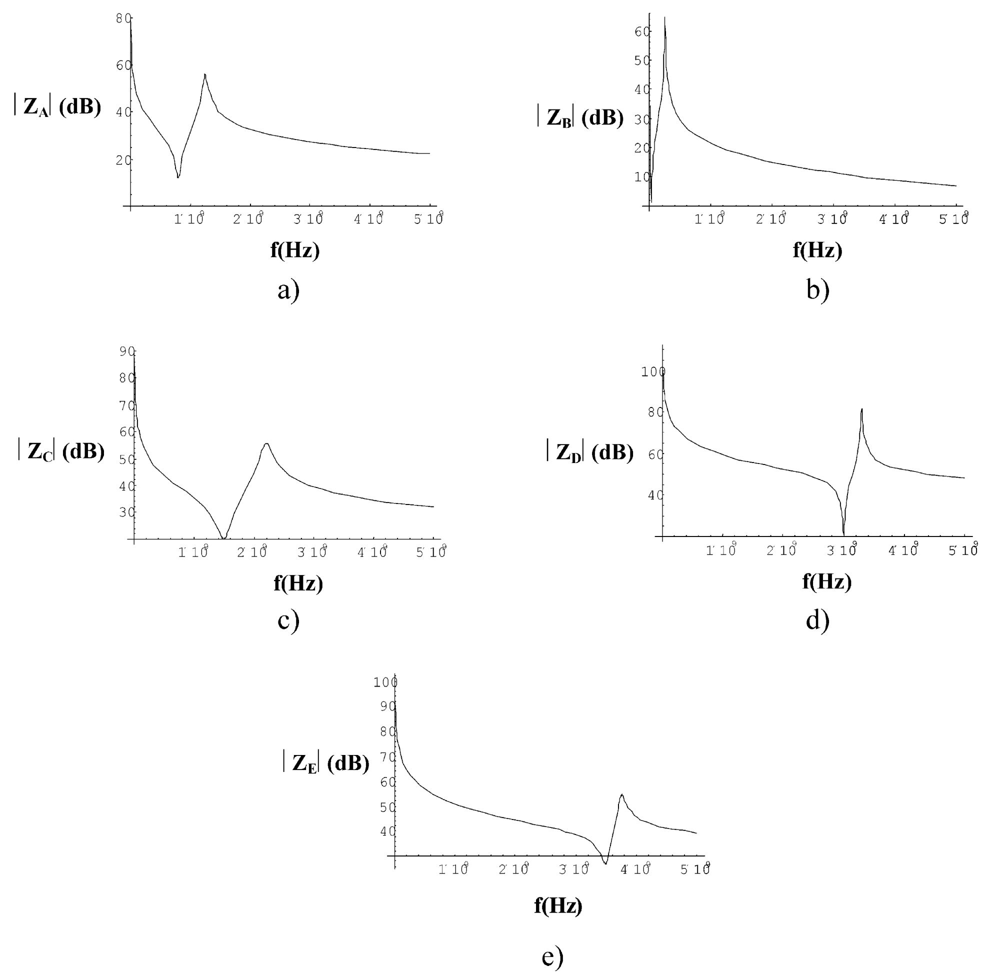

Fig. 2. The magnitudes of elementary impedances [Z (dB)] as a function of frequency $f(H_z)$ for five sets of model parameters: (a)–(e).

symbolic simulator Symsim[7] the expression for an elementary intergranular impedance can be written as

$$Z(s) = \frac{1 + CR\cdot s + CL\cdot s^2}{(C_1 + C)\cdot s + C_1 CR\cdot s^2 + C_1 CL\cdot s^3}, \qquad (2)$$

where $s = j\omega$, $\omega = 2\pi f$, f is frequency. Each set of defined values for model parameters results in corresponding frequency characteristics. In order to bring our model closer to real physics of intergranular processes as well as to apply the model on different grain structures, we defined five different sets of model parameters (C_1, C, L, R). Each set of model parameters is introduced in formula (2) and the corresponding frequency diagram is obtained (Fig. 2). The initial values of model parameters are resulted from the values of these parameters estimated on frequency characteristics of real $BaTiO_3$-ceramics samples.[8]

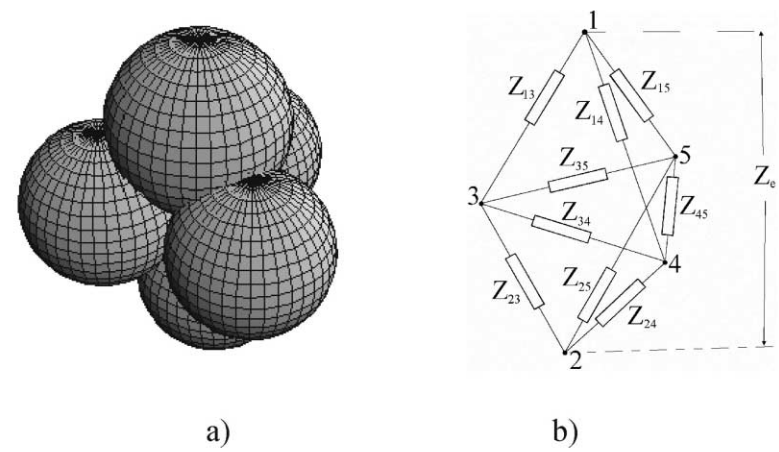

Fig. 3. (a) A cluster of five grains and (b) its equivalent electrical model.

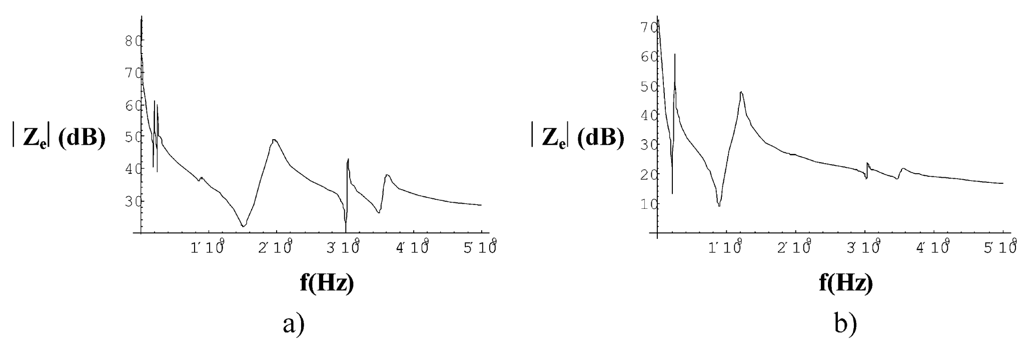

Fig. 4. The magnitudes of the equivalent impedances as a function of frequency: (a) $|Z_{12}|(dB) = f(H_z)$; (b) $|Z_{34}|(dB) = f(H_z)$.

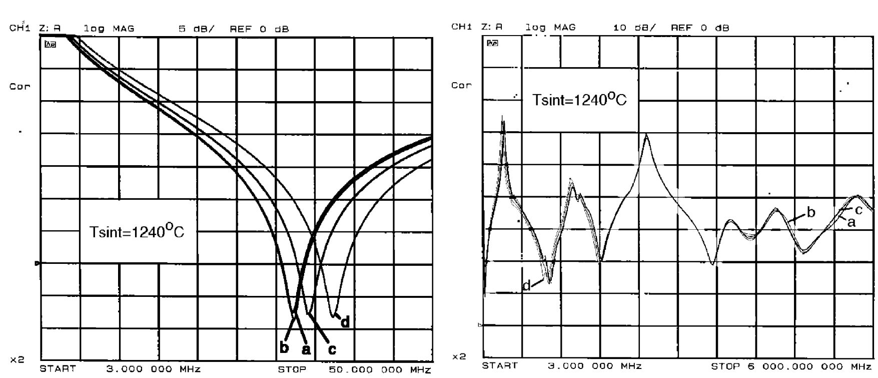

Fig. 5. Frequency characteristics of $BaTiO_3$-ceramics sintered on 1240 °C and pressed under the pressure: (a) 86 MPa; (b) 105 MPa; (c) 130 MPa; (d) 150 MPa.

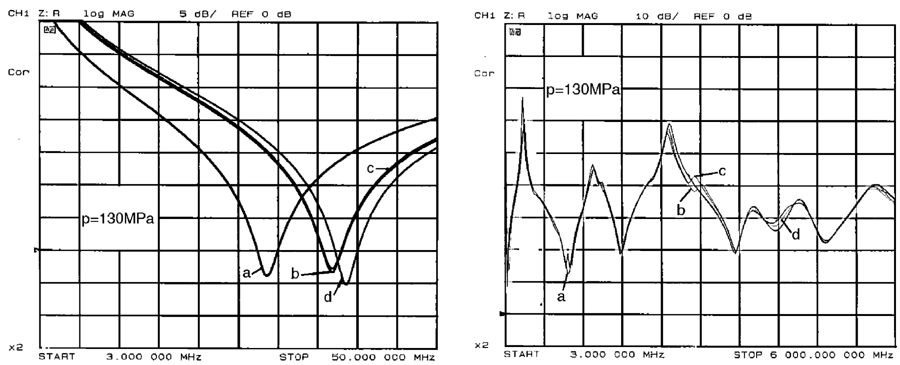

Fig. 6. Frequency characteristics of $BaTiO_3$-ceramics samples pressed under the pressure 130 MPa and sintered on temperatures: (a) 1190 °C; (b) 1240 °C; (c) 1290 °C; (d) 1370 °C.

3. The cluster intergranular impedance model

The relation (2) is valid only for one intergranular contact, and should be inserted for every contact between any pair of grains within the cluster. Let us consider an equivalent impedance of a cluster formed by five grains. This gives a hexahedron formed by two pyramids with a common triangular basis where the grains are placed as nodes (Fig. 3). Grains within a cluster make nine intergranular contacts. Thus, an equivalent impedance model consists of nine intergranular impedances connected as shown in Fig. 3b. The impedance parameters for the electrical model of five-grain cluster are chosen randomly from the set shown in Fig. 2 and they are as follows: $Z_{13}=Z_B$, $Z_{14}=Z_C$, $Z_{15}=Z_D$, $Z_{23}=Z_E$, $Z_{24}=Z_A$, $Z_{25}=Z_B$, $Z_{34}=Z_D$, $Z_{35}=Z_E$ and $Z_{45}=Z_A$. The resulted frequency diagrams are shown in Fig. 4. Fig. 4a presents the magnitude of the equivalent impedance ($|Z_e|$) when opposite peaks of pyramids were chosen for ports, while Fig. 4b shows $|Z_e|$ for the same cluster when the equivalent impedance is looked between two nodes from the basis.

4. Experimental results

Experimental study in this paper included the research of the influence of processing parameters on frequency characteristics of $BaTiO_3$-ceramics samples, pressed under the pressures 86, 105, 130 and 150 MPa and sintered in the temperatures 1190, 1240, 1290 and 1370 °C. Some of the results are presented in Figs. 5 and 6. The recording of frequency characteristics have been carried out using automatic spectrum analyzer in the frequency range 300 KHz–50 MHz, as well as in the range 3 MHz–6 GHz. Regarding the RLC behavior of frequency characteristics, it is possible to define the values of resistance, capacitance and inductance for each point on the frequency diagram. In Fig. 5 ($BaTiO_3$-ceramics samples sintered on 1240 °C) the minimum of frequency characteristics is shifted towards higher frequencies for the increase of pressure from 86 to 150 MPa. Similarly, when the pressing pressure is invariant the resonant frequency is moved towards higher frequencies for the increase of sintering temperature from 1190 to 1370 °C (Fig. 6). In both cases, the frequency range for the capacitor's application is expanded. In broad frequency region (Figs. 5 and 6, right) more resonant peaks are observed.

5. Conclusion

The problem of having a faithful electrical model for $BaTiO_3$-ceramics is a complex task. In this paper we intend to give a simplifing approach developing the model of intergranular impedance. For randomly chosen parameters for elementary intergranular impedances the results for magnitudes of the equivalent impedance of five-grain cluster in frequency domain are obtained. The resemblance of frequency diagrams obtained for five-grain cluster (Fig. 4) with frequency characteristics of samples obtained in broad frequency region (Figs. 5 and 6, right) is noticed. Actually, the number of contacts in a cluster, i.e. the number of intergranular impedances in the electrical model and the type of connection between them (serial, parallel or mixed) determine the position and heights of resonant peaks on diagrams. Regarding the fact that a smaller number of grains in contact are taken, the matching between theoretically obtained frequency diagrams with experimentally obtained frequency characteristics of $BaTiO_3$-ceramics samples cannot be expected. According to that, taking into consideration more interconnections between clusters within the sample from the electrical point of view would outcome in better matching of theoretical and experimental diagrams. The research results obtained in this paper present only a sublevel results in an overall hierarchically stated $BaTiO_3$-ceramics electrical model based on intergranular contacts. Further research towards establishing electrical model comprised of the summing effect of all microelectric equivalent schemes within the sample is in the progress.

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