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Electrophysical Properties of Microalloyed Alumo-Silicate Ceramics as Active Dielectric

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Abstract: In this paper, electrophysical properties of porous alumo-silicate ceramics, modified by alloying with magnesium and microalloying with aluminum, were investigated. Complex multiphase system, as active microalloyed ceramics, has specific behavior under influence of external electrical field, which involves changes of dielectric losses and impedance, depending on frequency and temperature. Dielectric properties were measured in the frequency range 20 Hz – 1 MHz. Values for permittivity (ε_r) ranged between 140 – 430. Order of magnitude for electrical resistivity was about 10^6 Ωm, for impedance $10^4 - 10^8$ Ω, and loss tangent had values about and greater than 0.05. Current flow through active dielectric takes place through dielectric barrier and throughout conduction bands of thin aluminum and magnesium metal films. Permittivity has nonlinear distribution and complex functional dependences because of significant nonhomogeneity of active microalloyed ceramics. Lower values of electrical resistivity are the result of complex electron and ion transfer of charge through solid phase and pores, with decreased potential barriers height, due to the influence of additives, ingredients and defects.

Keywords: Alumo-silicate ceramics, Microalloying, Electrophysical properties, Active dielectric.

1 Introduction

Dielectric or electrical insulating materials are considered as the materials in which electrostatic fields can persist for a long time. These materials have very high resistance to electric current flow, due to a large band gap between valence and conduction band. New dielectric materials investigations are advanced, in the sense that, for passive dielectrics in high-voltage energy plants

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insulating properties are increased, and for active dielectrics insulating properties are decreased, towards semiconductive materials. Nowadays, numerous researchers' attention is devoted to nanostructure and composite materials, with multiphase, amorphous-crystal, microheterogeneous, metallized, very dispersive and porous nonhomogeneous dielectric materials. These advanced materials have complex dielectric and conductive properties, as a result of micromorphology and structure significant changes and incorporation of some additives and ingredients. Therefore, the presence of proper additives, defects and ingredients is crucially significant in dielectric materials. Proper defects and ingredients cause extrinsic discrete energy levels appearance in dielectric and change its passive into active condition [1 – 3]. Otherwise, the purest dielectric materials have $10^{12} – 10^{14}/cm^3$ proper defects and ingredients. Some earlier [3, 4], and recent papers about microalloying [5 – 7] report that extrinsic defects concentration in dielectric materials can be significantly increased by microalloying. Critical concentration of microalloying additives that certainly provides dielectric activity was found to be from 10^{18} to $10^{19}/cm^3$. Defects, ingredients and microalloying additives, as active centers for electrons capture, have dominant participation in active dielectric current conduction.

The subject of this paper is dielectric and electric characterization of alumo-silicate ceramics, modified with magnesium and microalloyed with aluminum, aimed at investigating physical and microstructure properties of multifunctional material. Micromorphology and structure of ceramics with such active additives are not significantly changed, but crystal grains surface microamorphisation occurs by forming amorphous magnesium and aluminum silicate thin layer on grain surface and by aluminum and magnesium thin layers deposition in intergranular volume and area. Alloying and microalloying additives surplus contributes to ceramics chemical activity and instability in contact with external medium. Appreciable changes of all structurally sensitive properties occur, especially electric and dielectric physical-chemical properties [8 – 10]. Porous ceramics microstructure results in developed surface, responsible for different energy levels of surface activity and surface states. Subthin monolayered and multilayered aluminum and magnesium films deposition on micro and mezzo alumo-silicate pores enable the occurrence of nonhomogeneous and cluster structures. Thin metal films and yet depositioned metal clusters, determine conductivity of active dielectric materials [12].

2 Experimental

2.1 Active dielectric synthesis

Microalloyed porous ceramics was obtained by chemical and thermal transformations of natural kaolinite and bentonite clay. Alloying was accomplished with water solution of Mg $(NO_3)_2 \cdot 6H_2O$ (8 wt.%) and microalloying with few ml of $Al(NO_3)_3 \cdot 9H_2O$ water solution. In order to achieve supplementary porosity during sintering, $(NH_4)_2CO_3$ was added to basic powders. The plastic clay mass was shaped into pellets, 10-15 mm in diameter and 3 – 4 mm of thickness. The pellets were dried at 180 – 200°C for 3 – 4 hours and thermally treated for 30 min. at 600°C, 700°C, 800°C, 900°C and 1100°C, in protective nitrogen atmosphere, and subsequently cooled down to room temperature. The as-sintered active dielectric samples were used for the characterization of the materials properties.

2.2 Material characterization

Given the basic physical properties and processes of dielectric materials, subjected active microalloyed ceramics, made from multiphase solid-solid system, belongs to a special type of active nonhomogeneous dielectric with multifunctional properties. Active microalloyed ceramics with modified microstructure is neither nonlinear dielectric nor a typical linear dielectric. It probably possesses some intermediate properties between linear and nonlinear dielectrics, hence electrophysical properties measurements, including changes of permittivity ε_r, electrical resistivity ρ, impedance Z and loss tangent $\mathrm{tg}\delta$, are interesting.

The microstructures and micromorphology of the sintered samples were observed by scanning electron microscope (SEM-JEOL-JSM 5300). Prior to examination, the specimens' surface was sputtered with gold. Electric and dielectric properties (capacitance, loss tangent, impedance, resistivity) measurements were performed by LCR-meter AGILENT 4284A, in frequency range 20 Hz – 1 MHz. The ratio input voltage/current, at resonant method, determines impedance, i.e. time depending resistance. Operating voltage was 1V and current ranged from 0.1 mA to 10 mA. Measurements included active microalloyed alumo-silicate ceramics samples with 8 wt.% additives.

3 Results Analysis

The morphology of the sintered samples is clearly revealed in SEM microphotographs (Figs. 1 and 2), which indicates high porosity, inhomogeneous microstructure and particles, with different shape and dimensions and exhibition of high degree of agglomeration. Non-uniform porous ceramics structure and well-developed surface was also observed. SEM microphotographs confirmed amorphous and metalized microstructure of active microalloyed alumo-silicate ceramics, as active dielectric material.

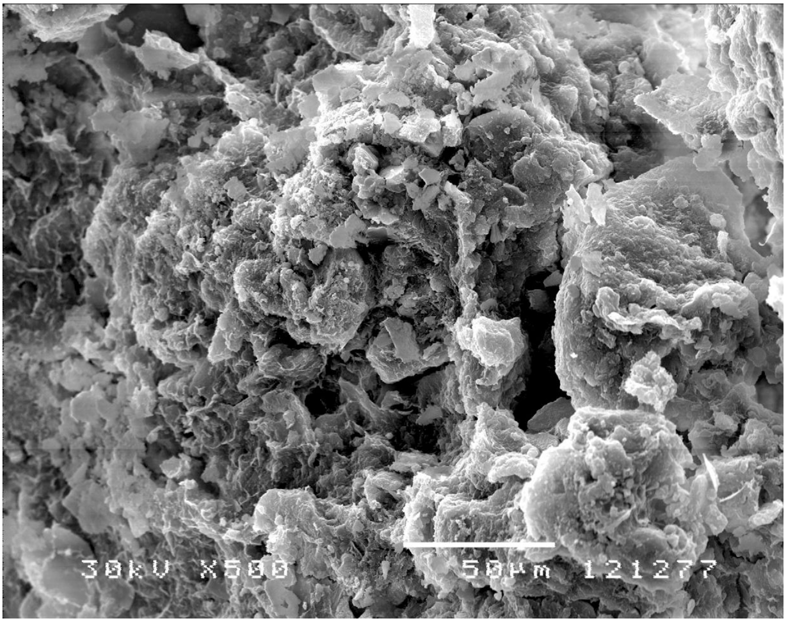

Fig. 1 – SEM *microphotograph of active microalloyed alumo-silicate ceramics, with* 8 wt. % *of additives, sintered at* 800°C.

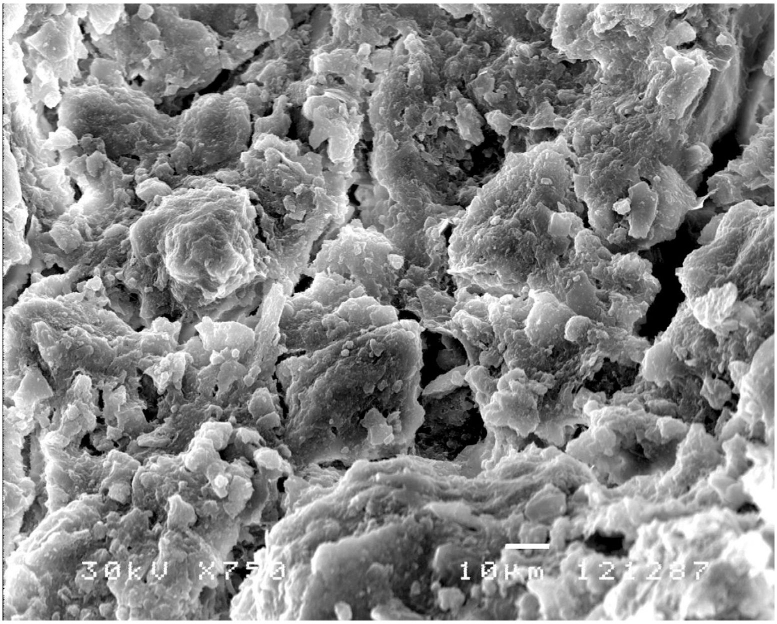

Fig. 2 – SEM *microphotograph of active microalloyed alumo-silicate ceramics,with* 8 wt. % *of additives, sintered at* 900°C.

Dielectric properties (permittivity, loss tangent, impedance, resistivity) of microalloyed alumo-silicate ceramics samples, with 8 wt.% of additives, at different sintering temperatures, were measured within 20 Hz – 1 MHz frequency range. As shown in diagram $\varepsilon_r(f)$ (Fig. 3), values for ε_r do not exceed 430, therefore they are within the interval 140 – 430. In the investigated frequency range, especially after curve inflection point on frequencies higher than 200 Hz, values of ε_r are approximately constant, about $\varepsilon_r = 140$. Meanwhile, in measuring range, obtained values for ε_r are considerably lower in relation to well-known results, accomplished for nonlinear active dielectrics [13, 14].

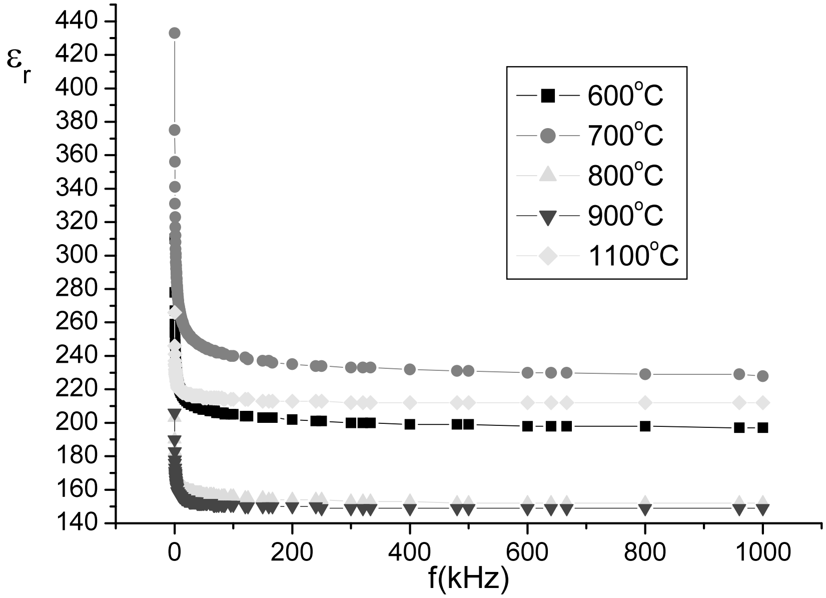

Fig. 3 – *Dependence of permittivity on frequency for active microalloyed alumo-silicate ceramics with* 8 wt. % *of additives.*

The diagram in Fig. 4 shows that resistivity of the investigated samples shows similar dependencies $\rho(f)$, hence resistivity tends towards zero on high frequencies, and when frequency tends towards zero, it is infinite. Electrical resistivity is order of magnitude 10^6 Ωm. From ε_r specifically, the changes in resistivity with frequency seem not to depend on sintering temperature.

Similar dependencies are also found for impedance of active microalloyed alumo-silicate ceramics, in function of frequency and sintering temperature. Impedance is order of magnitude $10^4 – 10^8$ Ω, which can be observed from the diagram in Fig. 5.

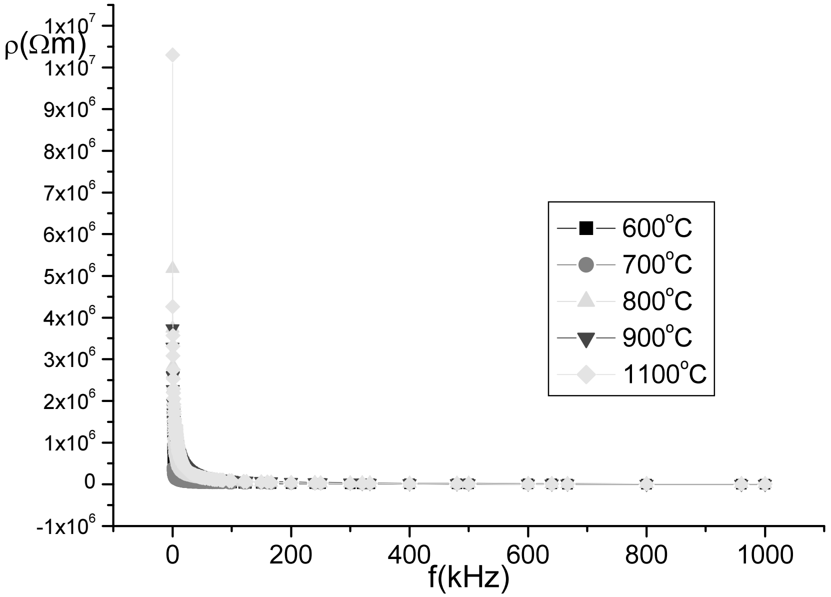

Fig. 4 – *Dependence of electric resistivity on frequency for active microalloyed alumo-silicate ceramics with* 8 wt.% *of additives.*

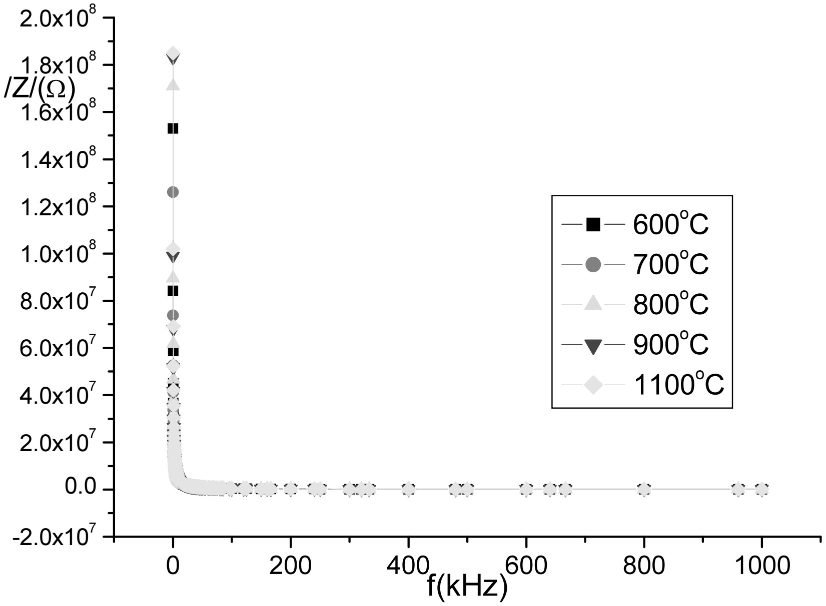

Fig. 5 – *Dependence of impedance on frequency for active microalloyed alumo-silicate ceramics with* 8 wt.% *of additives.*

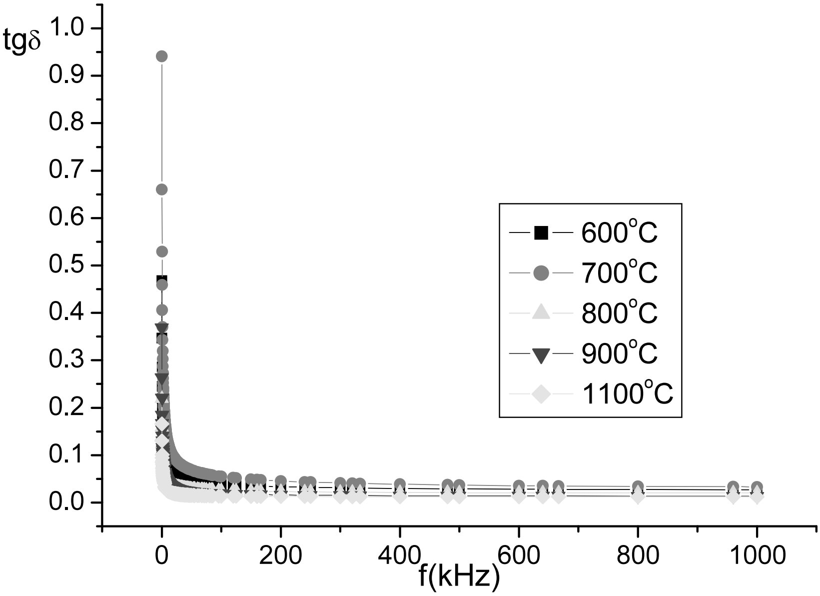

Fig. 6 – *Dependence of loss tangent on frequency for active microalloyed alumo-silicate ceramics with* 8 wt.% *of additives.*

Fig. 6 shows frequency dependence of loss tangent. Values of tgδ between 0.01 and 0.95 have been obtained. The distinctly differences associated with sintering temperature can be observed in the vicinity of the inflection points. Given these tgδ values, we can explicitly conclude that resonant method is not appropriate for investigation of active dielectric with such high dielectric losses. Resonant method is convenient for cases when tgδ is lower than 0.05 and high frequencies up to several hundreds of MHz [11]. For high loss tangent values (tgδ → 1), it is difficult to accomplish resonance and therefore attenuation occurs, which can be clearly seen in Fig. 6.

4 Discussion

Electrophysical and microstucture characterization results referring to active microalloyed alumo-silicate ceramics have shown that it belongs to intermediate species between linear and nonlinear nonhomogeneous active dielectrics. Nonuniform grains size and heterogeneous intergranular volume directly affect dielectric and electric properties of porous microalloyed alumo-silicate ceramics. That is explicitly confirmed by results for changes of permittivity, resistivity, impedance and loss tangent. Since active microalloyed ceramics has dominant amorphous microstructure and micromorphology, with perturbated crystal structure, in such complex structures microalloying additives and ingredients behave differently, forming some active centers and potential barriers. Therefore, electron states captured by potential barriers are named local states, and due to relation with microalloying elements and ingredients, they are also named extrinsic states. Developed active microalloyed ceramics specific surface is overlaid with numerous discrete surface energy levels of extrinsic, defect and other centers. Electron exchange and current flow through discrete energy bands occur between these active centers, of cluster type, on the surface. Therefore, conduction in active dielectric occurs by localized electrons skip from one discrete level to another [1 – 3, 12]. This fact is exactly the reason for significantly decreased conductivity in amorphous materials (metals, semiconductors and dielectrics).

In amorphous and partly metallized nonhomogeneous multiphase dielectrics, such as active microalloyed ceramics, there are two possible conduction mechanisms. The first one is established on Schottky overbarrier electron emission, which is possible when dielectric films are of 6 nm thickness, and the second one on Frenkel-Poule effect, which is possible for films thickness of 40 nm, but with extrinsic and local levels, present in dielectric films [12]. It is very important to point out that all surface discrete centers are subjected to fluctuation and relaxation processes. Therefore, the influence of applied electric voltage frequency is very important for active, and also for passive dielectrics. For conductance, with current frequent change, stands for $G \sim f^n$, where $n = 0.8$ for $f < 1$ MHz. Meanwhile, for $f > 1$ MHz, conductance is $G = f^m$, where $m = 0.3 – 0.5$. For frequencies $f = 4$ MHz, conductance almost does not depend on frequency [11, 12]. Since measurements in this work have been performed for frequency $f =$ 1MHz, it is obvious that electrical resistivity and capacity slightly depend on frequency, which is confirmed by obtained experimental results.

In addition, it is necessary to explain the presented results for complex permittivity, impedance and loss tangent, as they are very important structurally sensitive electrophysical properties. Slow or relaxing polarization type occurs in active microalloyed ceramics, which is polar dielectric. Since active microalloyed ceramics is multiphase nonhomogeneous active dielectric, the phenomenon of migrational polarization appears. This type of polarization occurs in nonhomogeneous dielectrics with water inclusions. Very porous and active microalloyed ceramics, unprotected from atmosphere, is always capable of adsorbing humidity by capilar condensation and thus forming water molecules thin films in interphase and intergranular area. The presence of humidity in form of water inclusions is the reason for observed changes of permittivity, electric resistivity and impedance. Hence, migrational polarization is characterized by viz., moistened dielectric, high voltage, intergranular phases, volume polarization, accumulation of electric charges on the different dielectric phases' boundaries and inclusions of surface water. Migrational polarization setting processes are slow and can take minutes or even hours [1].

Dielectric characterization has shown that, during microalloying process, very complex microstructure changes occur, which implies nonhomogeneous dielectric properties of microalloyed ceramics, as active dielectric. Active microalloyed ceramics is a very complex dielectric, where each phase, each contact between phases and phase's compound has its own dielectric properties. In such active dielectric, the total current (I) through the capacitor can be resolved into two components: active (I_a) and reactive (I_r) current. Hence, each phase in nonhomogeneous dielectric has proper tgδ, expressed as ratio I_a/I_r and influences on total change of tgδ. Therefore, macroscopic and microscopic (electron transfer) relaxation time exist in such dielectrics. Also, permittivity is complex one, with complex dielectric polarization. In periodic electric field, with high enough frequencies, active dielectric polarization does not manage to completely follow applied field changes during polarization. Hence, charge flow also changes periodically over time. Appreciable changes of examined parameters at lower frequencies, near hyperbolic curves inflection point were observed for all properties (Figs. 3 – 6).

5 Conclusion

In this paper, the results of electrophysical characterization confirmed that microalloyed alumo-silicate ceramics belongs to intermediate species between linear and nonlinear nonhomogeneous active dielectrics. This is also verified by results obtained for changes in ε_r, ρ, $|Z|$ and tgδ with frequency. These are directly related to microstructure, micromorphology, phenomena and processes in active dielectric. Microstructure characterization revealed porosity, agglomeration, amorphous and metalized microstructure of active microalloyed alumo-silicate ceramics. Microalloyed ceramics is featured by active cluster structures state. Current flow in active dielectric occurs by localized electrons skip from one discrete center to another, i.e., through surface discrete energy bands. Dielectric polarization has shown that complex microstructure changes, caused by microalloying, implied nonhomogeneous dielectric properties, migrational polarization phenomenon, dielectric dispersion appearance and macroscopic and microscopic relaxation time. In periodic electric field, with high enough frequencies, active dielectric polarization does not manage to completely follow applied field changes during polarization due to weakly pronounced dielectric properties and relatively long relaxation time.

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