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Granular metal-dielectric nanocomposites as an alternative to passive SMD

***Abstract**. AC electrical properties of granular metal-dielectric nanocomposites $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$ have been examined. The study was carried for frequencies from 50 Hz to 1 MHz and measurement temperatures of 81 K – 293 K. The samples above percolation threshold x_c considered to be resistive. Layers subdued to thermal treatment in air atmosphere behave as perfect capacitors, especially for low temperatures. Nanomaterials below x_c demonstrate inductive-like properties. Tested samples could provide an alternative to conventional SMD components.*

***Streszczenie.** Ziarniste nanokompozyty typu metal-dielektryk o strukturze $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$ zbadano pod kątem właściwości elektrycznych w przedziale temperatur pomiarowych 81 K – 293 K oraz częstotliwości pomiarowych 50 Hz – 1 MHz. Materiały powyżej progu perkolacji x_c wykazują rezystancyjny charakter, warstwy wygrzane w temperaturze 573 K – typowo pojemnościowy typ, natomiast nanokompozyty poniżej x_c poddane obróbce termicznej – właściwości indukcyjne. Badane nanostruktury stanowią alternatywę dla konwencjonalnych elementów SMD. (**Granulowany kompozyt metal-dielektryk jako alternatywa dla SMD**)*

Keywords: nanocomposites, metal-dielectric, SMD components, electrical properties.
Słowa kluczowe: nanokompozyty, metal-dielektryk, komponenty SMD, właściwości elektryczne.

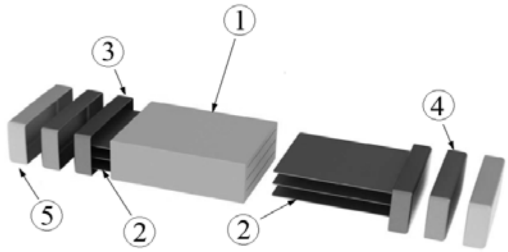
Introduction

Currently, we can observe a dynamic development of passive elements installed in electronic systems at various combinations and having different constructions. In the case of macroscopic systems, the most common elements from a given group are resistors, thermistors, capacitors, coils, inductors and anti-interference filters produced with use of surface mount (SMT) and through-hole (THT) technologies. With the reduction of component sizes to the micro or nano scale, SMT technology dominates. The greatest advantages of a SMT technology are: miniaturization of components, location of a large number of elements and their connections in a small working space, better resistance to mechanical impact (vibrations, shocks), low production costs, good resistance to electromagnetic disturbances [1, 2].

However, despite such a large number of advantages, SMT also has several key drawbacks that engineers from all over the world are trying to correct. Mass production of electronic components in the SMT technology is a complex technological process that required specialized equipment, very precise and expensive machines, qualified staff etc. The justification for this is: complex structure of surface mount devices (SMD), the selection of appropriate primary materials, the development of manufacturing technology and its precision. Figure 1.a shows an exemplary construction of an multilayer ceramic capacitor (MLCC) of SMD type manufactured by the KEMET Company (USA). It is composed of five elements made of four types of substances linked together. The main production stages of this component are following: obtaining and compacting the $BaTiO_3$ dielectric powder (1), forming a thin film, printing or sputtering a nickel layer (2) on it, stacking following films in a “sandwich” manner. The next steps are forming crude samples having appropriate dimensions and its thermal treatment in oven or furnaces at high temperatures. Then, on both sides of the heated samples, a paste made of a terminating material (3) is applied. Afterwards, another heating of the condenser in the furnace taking place. The penultimate stage is the galvanization of the capacitor on both sides by using a barrier layer (4) and electrodes (5). The final step in whole process is electrical properties examination of target products.

The second example of a complex passive element is SMD inductor manufactured by Viking Corporation (USA), shown in Figure 1.b. The coils structure includes 8 components, including substrate (a), internal electrode (b), barrier layer (c), external electrode (d), contacts (e), which in such low dimension scale requires high precision. Compared to the MLCC capacitor, in this case the coil also contain copper circuits (f), protective coating (lamination) (g) and marking (h). The most common methods for the production of coils are photolithography, 3D printing, plating or partially sputtering (internal electrode (f) implementation).

a)



b)

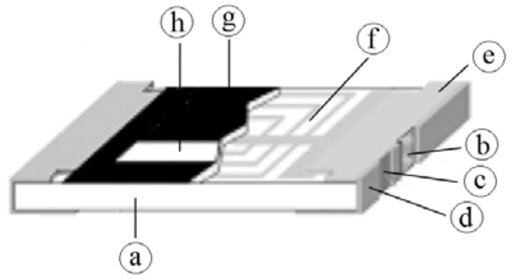


Fig.1. Exemplary constructions of conventional SMD elements: a) multilayered capacitor [3], b) SMD inductor [4]

Another problem with conventional SMD components is the limitation of their operating temperature, especially in the low temperature range. Analysis of the technical documentation of SMD passive elements available on the market [3, 4] shows, that the manufacturers declare the lowest operating temperature of T_p = -55 °C (for capacitors and coils) and T_p = -65 °C (for resistors). However, this prevents the use of such components in electronic devices (e.g. signal processing systems, automotive and space industry), temperature and pressure sensors, measurement probes used in extremely low temperatures conditions.

The main aim of this research is to present the results of electrical properties investigation of multifunctional thin-film materials, the production of which allows to eliminate the above-mentioned technological issues.

Synthesis and methodology

The objects of present research are granular metal-dielectric nanocomposites with $(FeCoZr)_x(PbZrTiO_3)_{100-x}$ structure. The nanomaterials have been produced by using ion-beam sputtering method. The technological process is presented on Figure 2. Vacuum chamber (1) contained three ion sources, two of which (5) were used for targets (4) sputtering and one (6) for cleaning the glass-ceramic substrates (3) on which the nanocomposite was deposited. The sputtering targets (4) consisted of $Fe_{45}Co_{45}Zr_{10}$ ferromagnetic alloy plate and attached to its surface $PbZrTiO_3$ dielectric stripes. Glass-ceramic substrates were mounted on the platform (2), which rotated with speed of up to 2 rpm. Argon and oxygen beams (7) falling on the targets, knocked out atoms or clusters of metallic alloy and dielectric components (8). Stamped components were deposited on glass-ceramic substrates. In such a way forming a nanocomposite layer $(FeCoZr)_x$ $(PbZrTiO_3)_{(100-x)}$ (where x - metallic phase content, at.%) was completed. Compensators (9) were used to space charge elimination appearing on the substrates surfaces during the technological process.

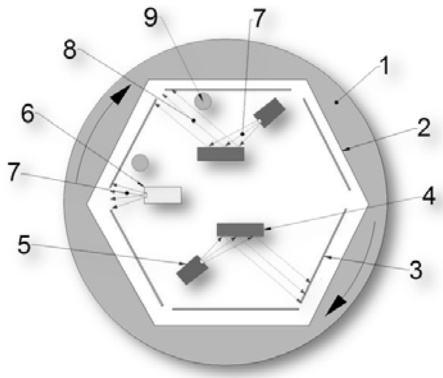
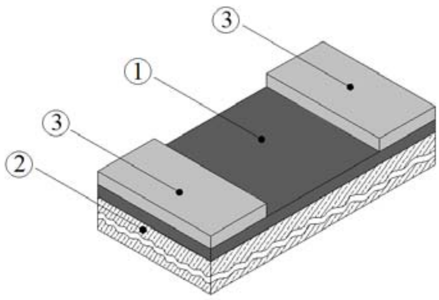


Fig.2. Station for the production of granular metal-dielectric nanocomposites [5]



Rys.3. View of $(FeCoZr)_x(PbZrTiO_3)_{100-x}$ nanocomposite sample

In this way, two series of $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$ nanomaterials were obtained: first one produced in an atmosphere with low oxygen content (*x* ranging from 39.9 at.% to 88.4 at.%), and the second series produced in an atmosphere with high oxygen content (*x* ranging from 29.0 at.% to 90 at.%). Typical view of obtained sample is shown in Figure 3, where (1) – nanocomposite layer, (2) – glass-ceramic substrate, (3) – silver paste used in order to improve the electrical contact with the measuring probes. The produced samples are 10 mm long, 2 mm wide and approx. 1 µm thick.

Nanocomposites $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$ are called “granular” because of their structure. It contains nanoparticles and/or clusters of $Fe_{45}Co_{45}Zr_{10}$ alloy (dark spots in Fig. 4) randomly distributed in the $PbZrTiO_3$ dielectric matrix (gray background in Fig. 4). The schematic structure of the examined layers is presented in Figure 4.

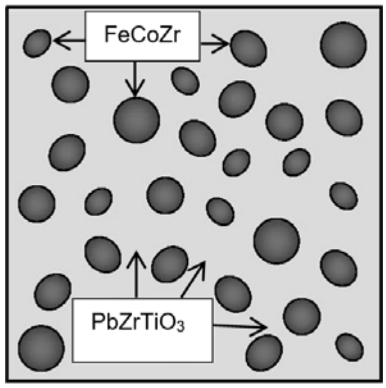


Fig.4. Schematic structure of $(FeCoZr)_x(PbZrTiO_3)_{100-x}$ layers

The AC electrical properties of the manufactured nanomaterials were tested by using the station described in [6]. The stand allows for the determination of electrical parameters such as: phase shift angle φ, dielectric loss factor tgδ, resistance R_p and capacitance C_p measured in a parallel equivalent system for frequencies ranging from 50 Hz to 5 MHz. The cryostat, which is the basic element of the station, allows for conducting of electrical measurements in the temperature T_p range of 10 K – 473 K. After measuring the electrical parameters the samples are heat treated in a tubular furnace at temperatures T_w ranging from 398 K to 873 K with step of 25 K. After each annealing the measurement cycle is repeated. In this way, it is possible to determine the effect of annealing on the electrical properties of the tested layers.

Selected measurement results and analysis

The electrical properties of granular metal-dielectric nanocomposites mainly depend on the concentration of metal nanoparticles *x* and the distribution of these particles in the dielectric matrix. The author's previous research [7] describes the existence of a critical value of metallic content x_c, so-called the percolation threshold, at which the material changes its character from dielectric ($d\sigma/dT_p > 0$) to metallic ($d\sigma/dT_p < 0$), where σ – layers conductivity. This parameter for the first sample series is 53.0 ± 2.0 at.%, while in case of second series – all samples behave as materials below the percolation threshold x_c.

Figure 5 shows selected frequency dependencies of the phase shift angle *φ* (Fig. 5.a) and the resistance R_p (Fig. 5.b) of the layer $(FeCoZr)_{88.4}(PbZrTiO3)_{11.6}$ from the first series above the percolation threshold. The results were obtained for the frequency range 50 Hz – 1 MHz and the measuring temperatures ranging from 81 K to 293 K. Zero values of phase shift for all temperatures T_p and frequencies $f < 10^5$ Hz can be observed in Figure 5.a. Such situation indicates that the material has a typically resistive nature. Negative values of phase angle φ corresponding to the influence of the non-zero imaginary component of the nanocomposite’s impedance could be observed for the frequencies $f \geq 10^5$ Hz. From Figure 5.b it can be seen that the resistance R_p does not depend on frequency but shows a temperature dependence – an increase in T_p causes an increase in resistance. It clearly indicates the metallic type of conduction in the tested nanocomposite.

Figure 6 demonstrates the frequency spectra of the phase shift angle φ and the capacitance C_p of first series sample with $(FeCoZr)_{73.2}(PbZrTiO_3)_{26.8}$ structure. The layer was annealed at air atmosphere in T_w = 573 K. Thermal treatment changed the behavior of the sample from resistive (similar to the Fig. 5) to capacitive (Fig. 6.a) for frequencies $f < 10^4$ Hz.

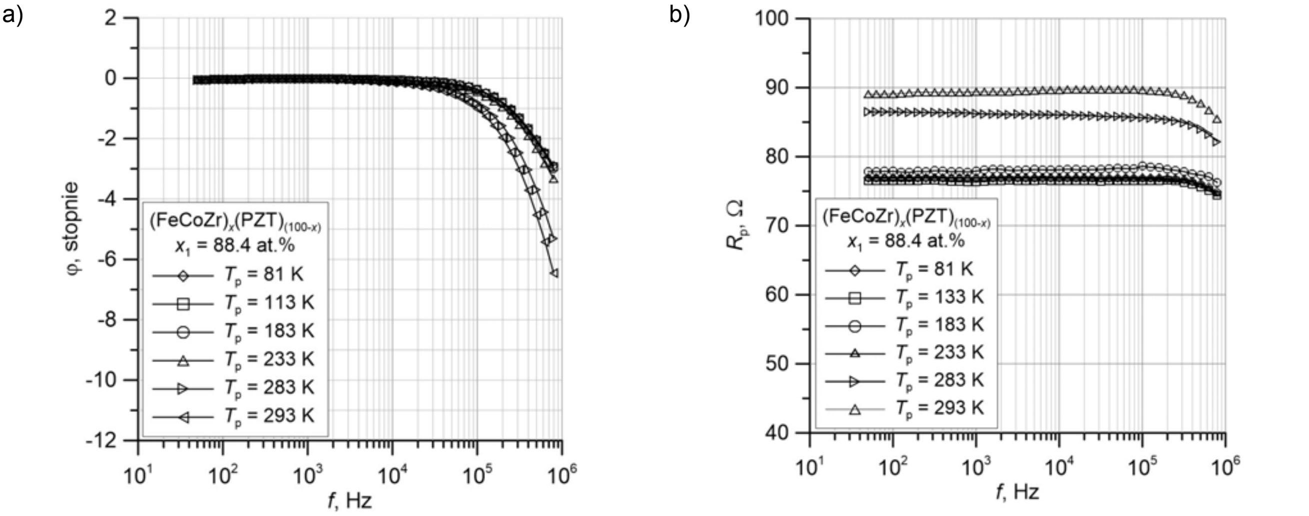


Fig.5. Frequency spectra of: a) phase shift angle *φ*, b) resistance R_p for selected measurement temperatures T_p obtained for $(FeCoZr)_{88.4}(PbZrTiO_3)_{11.6}$ sample

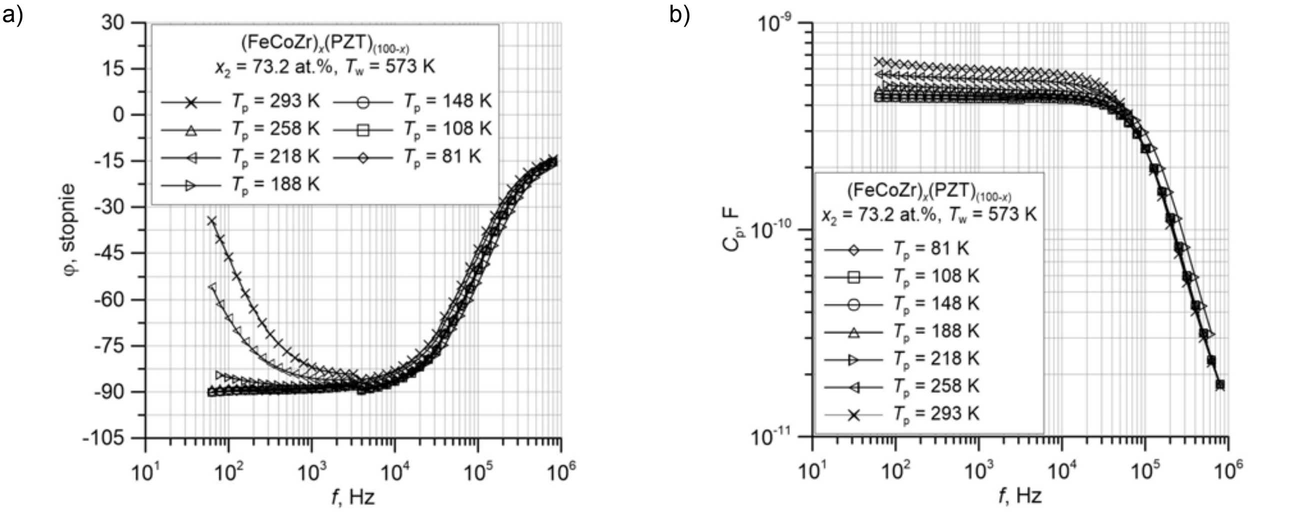


Fig.6. Frequency spectra of: a) phase shift angle *φ*, b) capacity C_p for selected measurement temperatures T_p obtained for $(FeCoZr)_{73.2}(PbZrTiO_3)_{26.8}$ nanomaterial annealed in $T_w = 573$ K

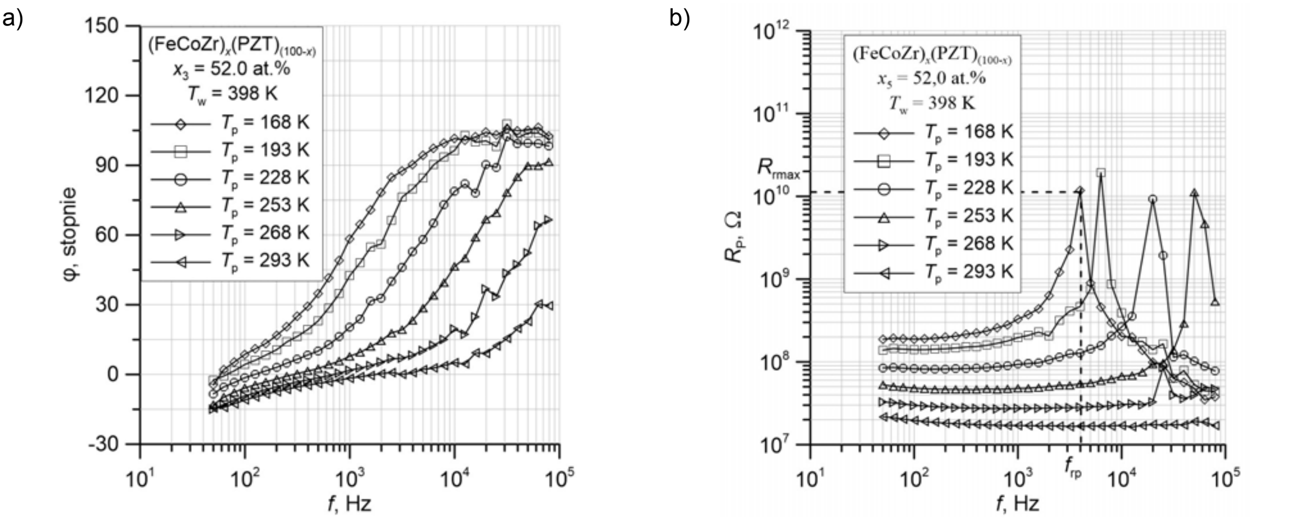


Fig.7. Frequency spectra of: a) phase shift angle *φ*, b) resistance R_p for selected measurement temperatures T_p obtained for $(FeCoZr)_{52.0}(PbZrTiO_3)_{48.0}$ nanocomposite annealed in $T_w = 398$ K

The material behaves as an ideal capacitor (phase shift angle φ ≈ -90 °) at temperatures lower than 258 K. After exceeding $f = 10^4$ Hz, the angle φ increases with the increase of frequency f. Similar behavior of $\varphi(f)$ is in accordance with the impedance model of metal-dielectric nanocomposites below the threshold x_c developed in [8]. The sample's capacity C_p in the frequencies $f < 10^4$ Hz shows weak dependencies on frequency and temperature. After exceeding $f = 10^4$ Hz, the capacity demonstrates a strong frequency dependence (C_p decreases by more than one order of magnitude). Such changes in nanomaterials are related to the additional oxidation of the $Fe_{45}Co_{45}Zr_{10}$ metallic alloy nanoparticles as a result of thermal treatment by using open system. The type of electrical conduction in this case considered to be dielectric.

Figure 7 demonstrates the inductive properties of the $(FeCoZr)_{52.0}(PbZrTiO_3)_{48.0}$ sample from the second series annealed at $T_w = 398$ K (below the percolation threshold). These kind of properties are accompanied by positive values of φ in the entire frequency range (Fig. 7.a). The exceptions are fragments of the characteristics for temperatures $T_p \geq 268$ K in the low frequency range. The dependencies of $\varphi(f)$ passes through the value of $\varphi = +90$ °, which indicates the inductive nature of the nanocomposite. Increasing the temperature T_p shifts $\varphi(f)$ spectra to the area of higher frequencies.

Few local peaks of the resistance (R_{rmax}) corresponding to certain frequencies f_{rp} in Figure 7.b could be observed. It is related to the phenomenon of current resonance in thin metal-dielectric nanocomposites, which was investigated in [9]. The resonant frequencies f_{rp} coincide with the frequencies at which φ = + 90 ° (see Fig. 7.a). This fact corresponds to the theory of resonances in conventional *R*, *L*, *C* circuits. The increase in temperature T_p causes a decrease in the resistance R_p related to the dielectric type of conduction in the tested nanocomposite. The inductive properties of nanomaterials with a similar structure are related to the oxidation of most nanoparticles of the metallic phase during synthesis (increased content of oxygen ions) and during the thermal processing of the sample in air. Metal oxides constitute an additional potential barrier, which significantly weakens the conductivity in nanolayers [10].

Conclusions

The study presented the AC electrical properties of granular metal-dielectric nanocomposites with the structure of $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$. The nanostructures of two series with different metallic phase contents *x* were investigated.

It was found that nanocomposites above the percolation threshold exhibit resistant properties in the entire range of measurement frequencies. The heat-treated samples above the percolation threshold typically show capacitive character at frequencies $f < 10^5$ Hz. It is related to the partial oxidation of FeCoZr metallic nanoparticles during annealing in open system. The annealed nanocomposites below x_c demonstrate the inductive character associated with the oxidation of majority of metallic nanoparticles due to the peculiarities of synthesis methodology and the annealing process. In this case, the phenomenon of current resonance was also observed. It corresponds to the theory of resonances in conventional *R*, *L*, *C* circuits.

The obtained measurement results indicate the possibility of using $(FeCoZr)_x(PbZrTiO_3)_{(100-x)}$ films as an alternative solution for passive SMD components. The nanocomposites are also characterized by the simplicity of construction, an efficient technological process which allow to obtain series of samples with different parameters, and a huge application potential in micro / nano electronics.

Acknowledgements

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