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Presence of Inductivity in $(CoFeZr)_x(PZT)_{1-x}$ Nanocomposite Produced by Ion Beam Sputtering

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This paper presents the investigations of the electrical properties of the $(CoFeZr)_x(PZT)_{1-x}$ nanocomposite with the metallic phase content $x = 43.8$ at.%, which was produced by ion beam sputtering. Such preparation took place under an argon atmosphere with low oxygen content with its partial pressure $P_{O_2} = 2 \times 10^{-3}$ Pa. The measurements were performed using alternating current within the frequency range of 50 Hz–10^5 Hz for measuring temperatures ranging from 238 K to 328 K. The $(CoFeZr)_{43.8}(PZT)_{56.2}$ nanocomposite sample subjected to a 15 min annealing process in air at the temperature $T_a = 423$ K demonstrates a phase angle of $-90° \le \theta \le 0°$ in the frequency range 50 Hz–10^5 Hz. It corresponds to the capacitive type of conduction. In the frequency range 10^4–10^5 Hz sharp minima in selected conductivity vs. frequency characteristics occur, which corresponds to a current resonance phenomenon in RLC circuits. In case of a sample annealed at $T_a = 498$ K the inductive type of conduction with $0° \le \theta \le +90°$ occurs in a high frequency area. At the frequency f_r characterized by the phase angle $\theta = 0°$, the capacity value reaches its local minimum. It indicates a voltage resonance phenomenon in conventional RLC circuits. The $\theta = +90°$ crossing in the frequency dependence of phase angle corresponds to the current resonance phenomenon, which is represented by a strong local minimum in the conductivity vs. frequency characteristics.

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1. Introduction

Among a wide range of structural materials used in many fields of science and technology, there are nanocomposite materials with a metal–dielectric structure that deserve particular attention. They contain metallic or ferromagnetic alloy nanoparticles distributed in dielectric or ferroelectric matrices. The examples of such matrices are: Al_2O_3 [1–4], SiO_2 [5–7], CaF_2 [8–10] and ferroelectric PZT [11–13]. Such kind of materials can be produced by the ion beam techniques. The results of fundamental research of these materials demonstrate a large number of various physical and chemical properties [11, 14, 15]. The influence of surface on material properties is studied in [16–18]. The negative capacitance [19] and the shape memory [20] effects of the nanostructured materials are known as well.

In the present studies we have investigated electric properties of nanocomposite material containing $(Co_{45}Fe_{45}Zr_{10})$ ferromagnetic alloy nanoparticles randomly distributed in a (abbreviated as PZT) $(Pb_{81}Sr_4(Na_{50}Bi_{50})_{15}(Zr_{57.5}Ti_{42.5}))O_3$ ferroelectric matrix, fabricated by beam sputtering technique.

2. Experimental results and discussion

The fabrication method of nanocomposite films of $(Co_{45}Fe_{45}Zr_{10})_{43.8}(PZT)_{56.2}$ and structural characterization techniques are described in detail elsewhere [21, 22]. Sputtering was performed using a mixed argon–oxygen atmosphere under partial pressures of $P_{Ar} = 6.6 \times 10^{-2}$ Pa and $P_{O_2} = 2 \times 10^{-3}$ Pa, respectively. Targets consist of the ferromagnetic alloy plate $Co_{45}Fe_{45}Zr_{10}$ and ferroelectric PZT stripes. The $(CoFeZr)_x(PZT)_{1-x}$ nanocomposite layer was sputtered onto glass ceramic substrate 10 mm in length, 4 mm in width, and 1 μm in thickness for electric measurements. Chemical compositions of the fabricated layers were verified by microprobe X-ray analysis (EDX) with a scanning electron microscope (SEM, LEO 1455 VP) and the Rutherford backscattering method (RBS) with an accuracy of ≈1 at.% [23, 24].

Measurements of electrical parameters were made using alternating current in the frequency range 50 Hz–1 MHz, at temperatures T_p ranging from 238 K to 323 K with 5 K steps. Each measuring cycle was followed by a 15 min annealing process of the tested sample in air at T_a from 398 K to 598 K with a step of 25 K.

Figure 1 presents selected results of the phase angle measurements performed for the nanocomposite film $(Co_{45}Fe_{45}Zr_{10})_{43.8}(PZT)_{56.2}$ annealed in air at $T_a = 423$ K. As can be seen from Fig. 1, in the whole frequency area, the phase angle value decreases from approximately 0° to −135° along with the increasing frequency. The nanocomposite sample demonstrates a capacitive type of conduction.

In frequency range from 50 Hz to 10^4 Hz the conductivity practically does not depend on measuring frequency (Fig. 2). In the frequency range 10^4–10^5 Hz sharp minima at selected conductivity vs. frequency characteristics occur. The frequencies corresponding to

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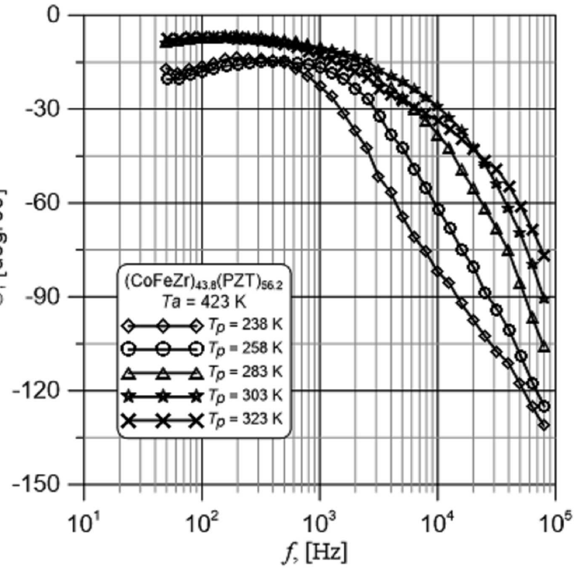

Fig. 1. Frequency dependences of phase angle Θ measured at selected T_p for the $(Co_{45}Fe_{45}Zr_{10})_{43.8}(PZT)_{56.2}$ nanocomposite sample annealed at $T_a = 423$ K for 15 min.

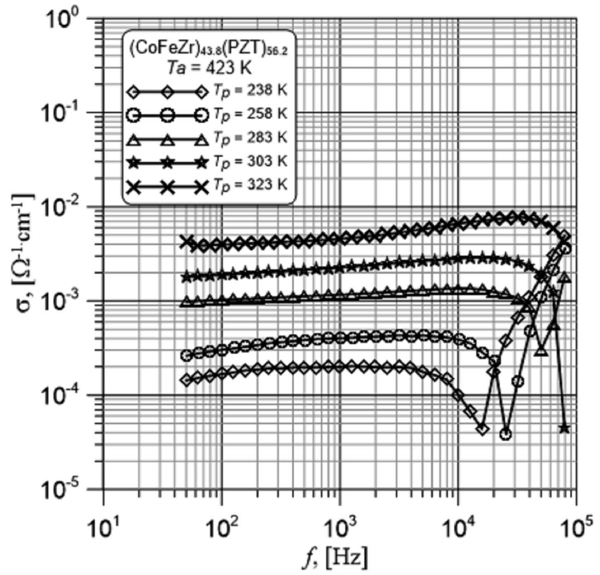

Fig. 2. As in Fig. 1, but for conductivity σ.

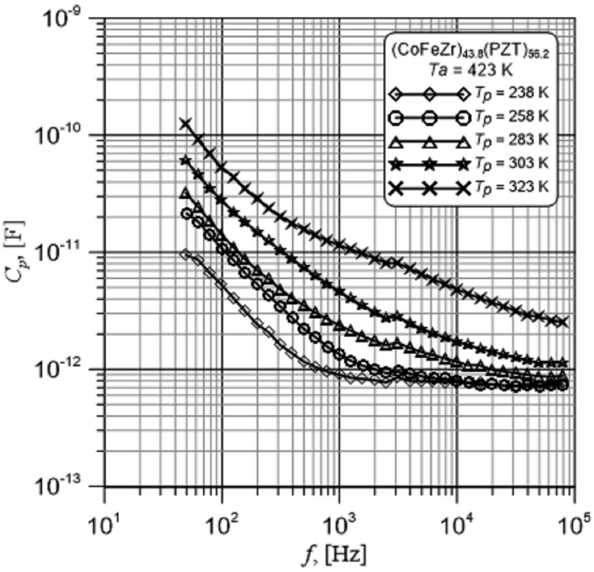

Fig. 3. As in Fig. 1, but for capacity C_p.

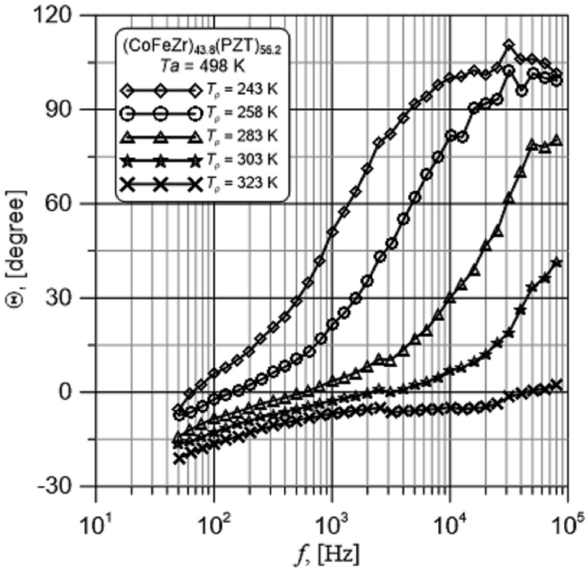

Fig. 4. As in Fig. 1, but for phase angle Θ and $T_a = 498$ K.

these minima, and those characterized by phase angle vs. frequency characteristics when crossing $\theta = -90°$ value were compared. The comparison have shown their matching, which confirms the occurring of current resonance phenomenon in the material.

Figure 3 presents capacitance vs. frequency characteristics for the selected measuring temperatures ranging from 238 K to 323 K. For the whole measurement frequency range the capacitance decreases by approximately two orders of magnitude.

The increase of annealing temperature from 423 K to 498 K causes the phase angle to increase up to positive values of $0° \leq \theta < 120°$, as shown in Fig. 4. Along with the measurement temperature decrease, the θ value increases more rapidly up to approximately 120°. The occurrence of positive phase angle values at alternating current is one of the effects of hopping charge exchange mechanism in the nanocomposite [11, 15, 25]. In our opinion, it can be related to the oxidation of metallic nanograins surface during the annealing process. The potential barriers, surrounding nanoparticles, occur.

As can be seen from the model of hopping conductivity presented in [11], every electron hops from one neutral potential well to another, stays there for a time period τ, which is about 10^{-13} s, and next it can hop to the third well in a direction determined by the external electric field or it can return to the first well, which takes the time $\tau_e \approx 10^{-3}$–10^{-4} s. In such case, the delay of electrons returning is equal to $2\pi f \tau_m$ and phase angle can reach values above $\theta = 3/2\pi$. Positive phase angle values occur, which corresponds to the inductive type of conduction. The time τ_m can be defined as:

$$\tau_m = \frac{1}{2\pi f_{\rm R}}, \quad (1)$$

where $f_{\rm R}$ — resonant frequency.

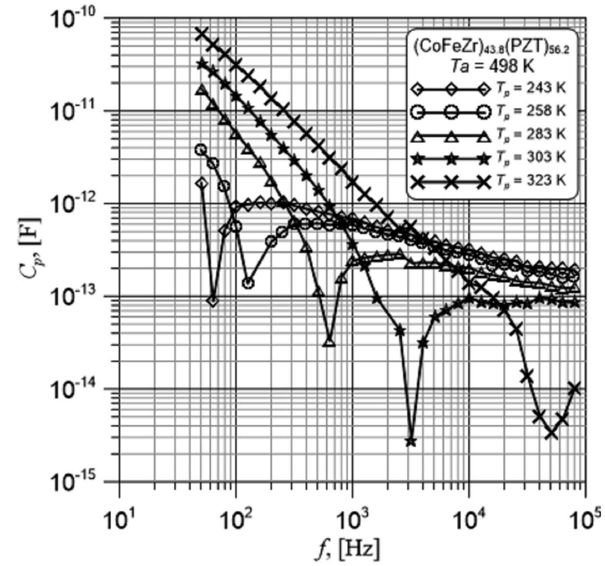

Fig. 5. As in Fig. 1, but for capacity C_p and $T_{\rm a} = 498$ K.

The zero crossing in the frequency dependence of phase angle and sharp minima in Fig. 5 indicate a voltage resonance phenomenon. For the resonant frequency $f_{\rm R}$, characterized by the reverse phases of the inductive and capacitive components (−90° and +90°), the voltage compensation takes place

$$U = i_0 \left(\omega_{\rm R} L - \frac{1}{\omega_{\rm R} C}\right) \quad (2)$$

or

$$\omega_{\rm R} L - \frac{1}{\omega_{\rm R} C} = 0, \quad (3)$$

where i_0 — amplitude of forcing current, C — capacity, L — serial circuit inductivity, $\omega_{\rm R} = 2\pi f_{\rm R}$ — resonant pulsation.

The impedance meter used in the research does not allow to determine capacitive and inductive parameters at the same time, that is why voltage compensation was demonstrated by the minima in the capacitance vs. frequency characteristics. We think that a precise setting of resonant frequency allows capacitance value to reach zero.

As can be seen in Fig. 6, a similar phenomenon observed for the sample annealed at $T_{\rm a} = 423$ K, is observed for the nanocomposite sample annealed at 498 K. Current resonance phenomena at the frequency area of 10^4–10^5 Hz occurs. With the measuring temperature T_p growth from 243 K to 323 K the conductivity increases 10 times.

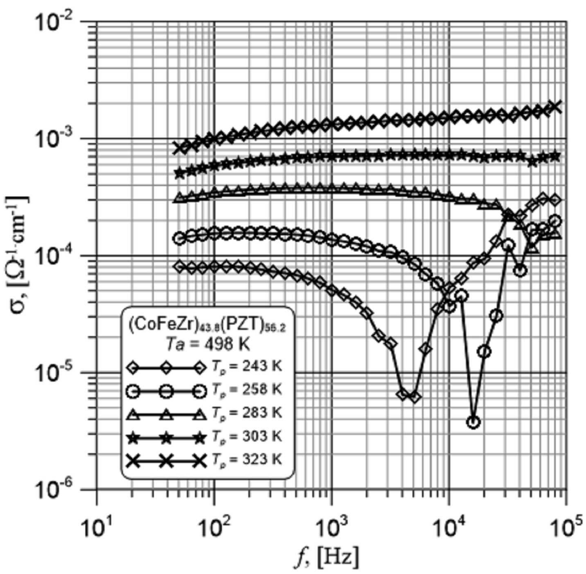

Fig. 6. As in Fig. 1, but for conductivity σ and $T_{\rm a} = 498$ K.

The equivalent circuit of the nanocomposite annealed at $T_{\rm a} = 498$ K can be illustrated as both serial RLC circuit, which corresponds to the voltage resonance, and parallel RLC circuit, which corresponds for current resonance phenomenon, respectively.

3. Conclusion

Frequency and temperature dependences of phase angle, conductivity and capacitance have been measured for the $(CoFeZr)_x(PZT)_{1-x}$ nanocomposite annealed for 15 min in air at $T_{\rm a} = 423$ K and 498 K.

It has been established that the phase angle of the nanocomposite sample with $x = 43.8$ at.% annealed at $T_{\rm a} = 423$ K demonstrates negative values ranging from $-90° \le \theta \le 0°$ in the frequency area 50–10^5 Hz. It indicates a capacitive type of conduction in the nanocomposite. When $\theta(f)$ characteristics pass $\theta = -90°$ value, we observe sharp minima in the conductivity vs. frequency characteristic at the same frequencies of measurement. It can be explained by the occurrence of current resonance phenomenon in the tested material.

The increasing of annealing temperature to $T_{\rm a} = 498$ K causes the phase angle increase up to positive values of $0° \le \theta < 120°$. The type of electric conduction in the material is defined as inductive. The occurrence of positive phase angle values is one of the effects of hopping charge exchange mechanism, which appears in the nanocomposite. It can be also explained by the additional oxidation of metallic nanograins surface, which is reflected in potential barriers surrounding these nanograins. The current and voltage resonance phenomena occur in the material. These phenomena can be described as a combination of serial and parallel RLC circuits.

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