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## THE DETERMINATION OF THE MAGNETOELECTRIC COUPLING COEFFICIENT IN FERROELECTRIC-FERROMAGNETIC COMPOSITE BASED ON PZT-FERRITE

### OKREŚLENIE WSPÓŁCZYNNIKA SPRĘŻENIA MAGNETOELEKTRYCZNEGO W FERROELEKTRYCZNO-FERROMAGNETYCZNYM KOMPOZYCIE NA BAZIE PZT I FERRYTU

In the present work, the magnetoelectric coupling coefficient, from the temperature dependences of the dielectric permittivity for the multiferroic composite was determined. The research material was ferroelectric-ferromagnetic composite on the based PZT and ferrite. We investigated the temperature dependences of the dielectric permittivity ( $\epsilon$ ) for the different frequency of measurement's field. From the dielectric measurements we determined the temperature of phase transition from ferroelectric to paraelectric phase. For the theoretical description of the temperature dependence of the dielectric constant, the Hamiltonian of Alcantara, Gehring and Janssen was used. To investigate the dielectric properties of the multiferroic composite this Hamiltonian was expressed under the mean-field approximation. Based on dielectric measurements and theoretical considerations, the values of the magnetoelectric coupling coefficient were specified.

*Keywords:* electric permittivity, magnetoelectric coupling coefficient, mean-field approximation, multiferroic composites

W niniejszej pracy określono współczynnik sprzężenia magnetoelektrycznego na podstawie pomiarów temperaturowych zależności przenikalności dielektrycznej, wykonanych dla multiferroikowego kompozytu. Materiałem badań był ferroelektryczno-ferromagnetyczny kompozyt powstały na bazie PZT i ferrytu. Przebadano temperaturowe zależności przenikalności dielektrycznej ( $\epsilon$ ) dla kilku różnych częstotliwości pola pomiarowego. Z pomiarów dielektrycznych określono temperaturę przemiany fazowej z fazy ferroelektrycznej do fazy paraelektrycznej. Do teoretycznego opisu temperaturowych zależności stałej dielektrycznej zastosowano hamiltonian Alcantary, Gheringa i Janssen. Do badania własności dielektrycznych multiferroikowego kompozytu, hamiltonian ten został przedstawiony w przybliżeniu średniego pola. Bazując na pomiarach dielektrycznych oraz teoretycznych rozważaniach określono wartość współczynnika sprzężenia magnetoelektrycznego.

### 1. Introduction

Multiferroics are materials that possess two or three forms of primary ferroic properties: ferroelectricity, ferromagnetism and/or ferroelasticity [1-2]. The current trend is to focus on ferroelectric-ferromagnetic materials. The electric, magnetic and elastic measurements give a lot of information about the properties of such materials [3]. Magnetic investigations allow to specify other interesting properties such as, for example, the concentration of magnetic ions [4]. Magnetic ferroelectrics may constitute the most interesting type of multiferroics because they may exhibit an unusually strong, so-called magnetoelectric coupling of magnetic and electric properties. Due to the interaction between the electric polarization and magnetic polarization, coexistence of ferroelectricity and ferromagnetism has the possibility to exhibit the magnetoelectric effect, that is electric polarization is changed by an external magnetic field, or magnetic polarization is changed by an external electric field [5-6].

In the present work, the magnetoelectric coupling coefficient, from the temperature dependences of the dielec-

tric permittivity for the ferroelectric-ferromagnetic composite PZT-ferrite was determined.

### 2. Experiment

The research material was ferroelectric-ferromagnetic PZT-ferrite type composite, which was prepared in the following manner. Ferroelectric ceramic powder (in amount of 90%) was based on the doped PZT type solid solution while magnetic component of the composite was nickel-zinc ferrite  $\text{Ni}_{0.64}\text{Zn}_{0.36}\text{Fe}_2\text{O}_4$  with ferromagnetic properties (in amount of 10%). The ferroelectric-ferromagnetic composite which was obtained in above way, it was marked further in our paper as PBZT-NZF.

The ferroelectric powder PZT type comprised of  $\text{Pb}_{0.90}\text{Ba}_{0.10}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 2.0\% \text{at. Nb}_2\text{O}_5$ . The initial constituents for obtaining PZT type powders included oxides:  $\text{PbO}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$ . The main component of the composite ceramic PZT type powder was synthesized using sintering of a mixture of simple oxides in solid phase (com-

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paction by free sintering) under the following conditions:  $T_{synth} = 1123$  K,  $t_{synth} = 2$  h. The second element of the composite with ferromagnetic properties (ferrite powder  $Ni_{0.64}Zn_{0.36}Fe_2O_4$ ) was synthesized using calcination under conditions of 1373 K/4 h.

The synthesized ceramic PBZT-type powder constituted 90%, while the ferrite (NZF) powder – 10%, of the PBZT-NZF composite. After proportionally weighing and mixing components, synthesizing was carried out using sintering of the mixture of simple oxides in a solid phase (compaction by a free sintering method) under the following conditions:  $T_{synth} = 1323$  K and  $t_{synth} = 4$  h. Compaction of the synthesized composite powder (sintering) was carried out using free sintering of compacts under the following conditions:  $T_s = 1523$  K and  $t_s = 2$  h. For the dielectric investigations silver electrodes were spread on the polished surfaces of the ceramic specimens by a paste burning method.

The dielectric measurements were performed on a capacity bridge of a BR2817 type, with a heating rate of  $0.5^\circ/\text{min}$  for several different frequencies of the measurement's field. Complex research of the ceramic PBZT-NZF composites are presented in work [7].

### 3. The theoretical model

In order to determine the magnetoelectric coupling coefficient, the theoretical model was used. In this model, we divided the ferroelectromagnetic system into two separated subsystems, namely the magnetic subsystem and the ferroelectric subsystem. Meanwhile, we introduce the coupling form as a medium to connect the two subsystems. Following Alcantara and Gehring [8] and Janssen [9], the Hamiltonian can be written in three parts as follows:

$$H = H^m + H^e + H^{me}, \quad (1)$$

where:  $H^m$  is the Hamiltonian of the magnetic subsystem,  $H^e$  is the Hamiltonian of the ferroelectric subsystem and  $H^{me}$  is the coupling interaction between the two subsystems.

We use Ising model [10] to describe the magnetic subsystem. The Hamiltonian of the magnetic subsystem  $H^m$  comprises four origins, namely the coupling of the nearest neighbors and the next nearest neighbors, magnetic static energy, and single-ion anisotropy energy. The Ising Hamiltonian has the following form:

$$H^m = \sum_{\langle i,j \rangle} J_1 S_i S_j - \sum_{[i,k]} J_2 S_i S_k - \sum_i h S_i - D \sum_i S_i^2, \quad (2)$$

where:  $J_1, J_2$  represent the nearest and next nearest exchange integral, respectively,  $h$  is the external magnetic field along spin ordered direction.  $D$  is the uniaxial single – ion anisotropy constant, and  $S_i, S_j, S_k$  are the Ising spins at sites  $i, j, k$ , respectively.

We use Diffour model [11] to describe the ferroelectric subsystem. The Diffour model includes a potential energy term and the enharmonic potential, which is called a double-well potential. The Hamiltonian of the ferroelectric subsystem  $H^e$  is composed of three parts. The first part is the kinetic and potential energy of the particle. The second one is the nearest

neighbor electric interaction, and the third one is electric static energy. This Hamiltonian has the following form:

$$H^e = \sum_i \left( \frac{p_i^2}{2m} - \frac{a}{2} u_i^2 + \frac{b}{4} u_i^4 \right) - \sum_{\langle i,j \rangle} U u_i u_j - \sum_i E u_i, \quad (3)$$

where:  $m$  is the mass,  $p_i$  is the particle momentum,  $u_i$  is the electric displacement at site  $i$ ,  $a, b$  represent the double-well potential parameters.  $U$  indicates polarization interaction coupling parameter and  $E$  denotes external electric field, which is parallel to the polarization direction.

For the coupling interaction between these two subsystems, we introduce the coupling mechanism proposed by Gao [12-13], and apply it to the ferroelectric ferromagnets by making simple change the following form:

$$H^{me} = \sum_{k \langle i,j \rangle} g u_k^2 S_i S_j, \quad (4)$$

where:  $g$  is the magnetoelectric coupling coefficient indicating the intensity of the magnetoelectric coupling,  $u_k$  is the electric displacement at site  $k$ , and  $S_i, S_j$  is the spin – pair correlation that directly affects the electric displacement  $u_k$ .

To investigate the dielectric properties of the multiferroic materials the Hamiltonian should be expressed under the mean – field approximation. After mathematical transformations, we have got the following equation:

$$\varepsilon(h, T) = \frac{1}{-\bar{a} + 3b(\sigma + p^2) - z_1 U}, \quad (5)$$

where:  $\varepsilon$  is the dielectric permittivity and  $\sigma$  is the fluctuation of the electric displacement.

Due to the presence of the magnetoelectric coupling both the polarization  $p$  and the dielectric constant  $\varepsilon$  are the function of the spin-pair correlation  $\langle S_i S_j \rangle$ . If we consider only the linear term of  $\langle S_i S_j \rangle$ , then the Equation 5 can be written in the following form:

$$\varepsilon(h, T) = \varepsilon_0 \left( 1 + \alpha \langle S_i S_j \rangle \right) \quad (6)$$

where:  $\varepsilon_0 = \left( -a + 3b(\sigma_0 + p_0^2) - z_1 U \right)^{-1}$  is the dielectric constant in the absence of the magnetoelectric coupling,  $\alpha = 2z_2 g \varepsilon_0$  is taken as a normalized magnetoelectric coupling factor, where  $z_2$  is the number of the spin-pair correlation that will directly influence a given ferroelectric particle.

### 4. Results and discussion

Temperature characteristics of  $\varepsilon(T)$  for ferroelectric-ferromagnetic PBZT-NZF composite as well as pure PBZT ceramics are shown in Figure 1. The maximum occurrence on the presented characteristic are connected with the phase transition from ferroelectric to paraelectric phase. The phase transition has a broadened character, which is typical for multicomponent materials [14]. The magnetic element in PBZT-NZF composite leads to the decrease of the maximum value of electric permittivity and the considerable dispersion of phase transition. This dispersion of phase transition may be explained by the phenomenon of dipole relaxation. This is due to the inability of the electric dipoles to be in space with the frequency of applied electric measurement's field.

Moreover the magnetic elements in PBZT ceramics leads to the considerable dispersion of the phase transition. The discussed dispersion could be a consequence of the impact of magnetic properties on the electric system, widely described by the other authors [15].

Using the Equation 6 and the experimental results (Fig. 1), we attempted to determine the magnetoelectric coupling coefficient  $g$ .

The experimental and theoretical results are shown in the Figure 2. Solid lines show the results of approximation.

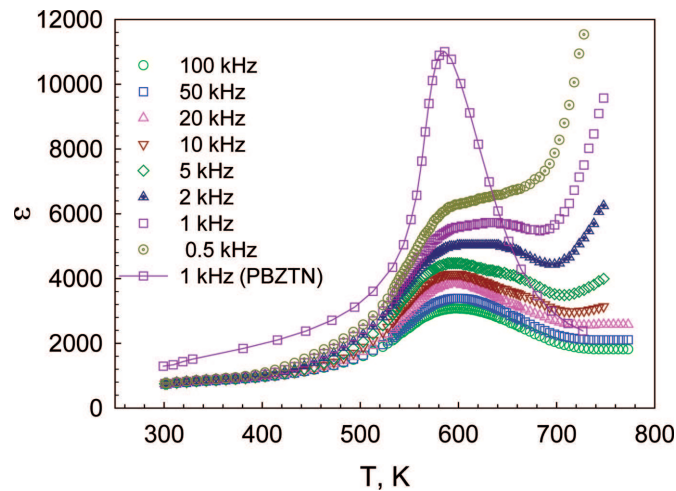


Fig. 1. Temperature dependences of the dielectric permittivity for the PBZT-NZF and pure PBZT (for different frequencies of measurement's field)

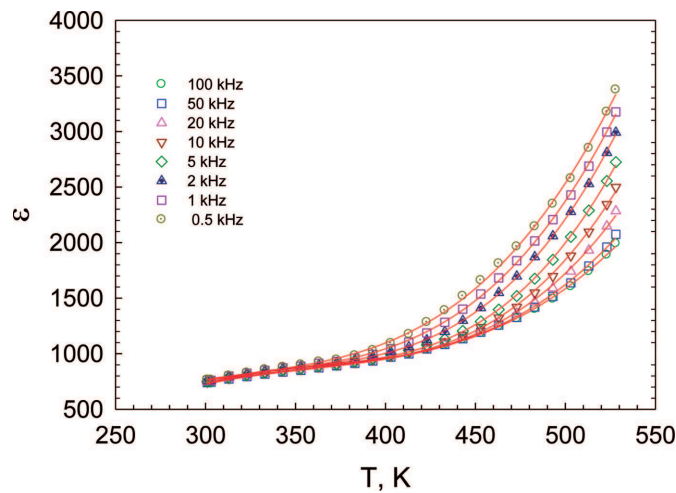


Fig. 2. Temperature dependences of the dielectric permittivity in the low region of temperature for the PBZT-NZF composite. Solid lines present the approximation results

Results of calculations of the magnetoelectric coupling coefficient, presented in CGS unit system, are shown in Table 1.

The calculations show, that the value of the magnetoelectric coupling coefficient increases with increasing frequency,

from  $g = 0.0254$  for  $f = 0.5$  kHz to  $g = 0.0372$  for  $f = 100$  kHz. The magnetoelectric coupling coefficient shows the dispersion, which results from dispersion of the dielectric permittivity.

TABLE 1

Values of the magnetoelectric coupling coefficient, calculated for different frequency of measurement's field

$f$ [kHz]	0.5	1	2	5	10	20	50	100
$g$ [unitless]	0.0254	0.0275	0.0298	0.0328	0.0347	0.0360	0.0368	0.0372

## 5. Conclusions

In the present work, we have investigated the dielectric permittivity and the magnetoelectric coupling in multiferroic ceramics.

We attempted to determine the magnetoelectric coupling coefficient, from the temperature dependences of the dielectric permittivity for the ferroelectric-ferromagnetic composite.

Based on dielectric permittivity measurements and theoretical considerations, the values of the magnetoelectric coupling coefficient were specified.

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