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Study of magnetoelectric effect in composite film based on PVDF with addition of nanoparticles $SrFe_{12}O_{19}$

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Magnetoelectric (ME) properties of composite films based on PVDF piezo-polymer with addition of hexaferrite nanoparticles $SrFe_{12}O_{19}$ (10 wt.%) were studied. The developed complex of experimental equipment was presented to study electric and ME effects.

Keywords: magnetoelectric response, polyvinylidene fluoride, strontium hexaferrite, piezoelectric constant d_{33}.

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1. Introduction

Magnetoelectric (ME) composite materials including ferroelectric and ferro- or ferrimagnetic phases usually have higher values of ME coefficient vs. the natural materials, which makes them promising for a wide range of applications in biomedicine, electronics, logical elements, terahertz emitters and other multifunctional instruments [1–5]. ME interaction arises due to the connection between the corresponding ordering parameters — electric polarization P and magnetization M, and P may be switched by magnetic field H, and M may be controlled by electric field E. ME coupling is achieved via transmission of mechanical stresses, therefore the corresponding phases must have high piezoelectric and magnetostriction coefficients. The potential mechanism to transfer mechanical stresses to the ferroelectric phase includes rotation and/or displacement of ferromagnetic particles placed inside a ferroelectric matrix in the external magnetic field [6]. Due to the mechanical connection between the after phases this effect causes deformation of the piezoelectric component, which in its turn changes its electrical polarization. To achieve the reverse magnetoelectric effect, the same mechanism of indirect elastic deformation is used, which changes magnetization in the ferromagnetic phase as the external electric field is applied [7].

The most effective ME structure is so called architecture 0–3 — an elastic matrix with inclusions of ferroelectric and magnetic particles, due to the potential of using such materials in the industry and biomedicine. The important aspect is the understanding of the mechanisms of interaction between magnetic and electric phases, which will enable regulation of the composite properties at micro- and nanolevel. Recently the research interest has shifted towards composite materials based on polymer matrices. In particular, the PVDF (polyvinylidenfluoride) polymer family demonstrating the piezoelectric effect, is the basis for considerable scientific and technological achievements [8]. Among polymers, PVDF and its copolymers stir interest from the point of view of electroactive properties, even though they demonstrate lower piezoelectric and pyroelectric coefficients compared to piezoelectric ceramics, for example, lead zirconate-titanate. Nevertheless, they possess certain advantages. Among them — low dielectric permittivity and thermal conductivity, good compliance with air and water impedance, flexibility [9], higher strength and resistance to mechanical actions, chemical resistance, wide temperature range of use (from -30 to $+140^\circ C$) and high softening temperature [8].

Besides, PVDF is also biocompatible, which opens the opportuntiies of using it in biomedical applications [10–13]. It is known that the value of the ME effect in elastic polymer-bound composites of micron particles of lead zirconate-titanate and neodymium-iron-boron ($\sim 700\,mV/(cm \cdot Oe)$ [14]) is one order higher compared to the composites based on the piezoelectric polymer matrix and magnetic nanoparticles ($\sim 40\,mV/(cm \cdot Oe)$ [15,16]). However, polymer-bound composites do not meet the biocompatibility requirements. Therefore, the studies of composite multiferroid films based on a PVDF piezoactive matrix and a filler in the form of ferromagnetic nanoparticles for biomedical applications are relevant [2].

Polymer ME films of PVDF/ferromagnetic nanoparticles with controlled composite thickness type are manufactured by Dr. Blade method [2], in process of which the polymer solution is made with the mixed-in ferromagnetic nanoscale filler and dried (polymerized) as a thin layer on a flat substrate [9]. In process of manufacturing the important role is played by multiple technical parameters (type and quality of solvent, polymer drying temperature, molar weight of polymer base, method of filler dispersion etc.), since this determined the presence of pores therein[17] and homogeneity of filler distribution in the matrix volume. The composite structure forms a mechanical connection between the filler and the matrix. One of the key aspects is the understanding of the mechanisms of interaction between magnetic and electric phases, which will enable the regulation of the composite properties at the micro- and nano-scale [17]. Paper [6] develops model approaches to describe the impact of a separate magnetostriction effect of nanoparticles and rotation of nanoparticles in the matrix at the developed deformation of the matrix, which causes the piezoelectric effect. It is a combination and availability of two mechanisms that enable a higher piezoeffect value. In composites made by Dr. Blade method, the displacement of particles is rather restricted after polymerization, however, as the external magnetic field is applied, the particles try to turn and thus increase the mechanical stress in the matrix.

Both in theoretical [6] and experimental papers [2] the authors prefer ferromagnetic nanoparticles $CoFe_2O_4$ as a ferromagnetic filler, which have a rather high value of saturation magnetization, pronounced magnetocrystalline anisotropy and, accordingly, the highest value of magnetostriction coefficient ($\approx 200-220$ ppm) [18,19]. It is also promising to investigate a composite with nanoparticles of strontium hexaferrite $SrFe_{12}O_{19}$, which is a magnetically hard material with a high constant of magnetocrystalline anisotropy ($K = 0.35\,\mathrm{MJ/m^3}$) [20], which is the objective of this paper. Besides, nanoparticles $SrFe_{12}O_{19}$ as a filler for ME composite are studied to a less extent compared to cobalt ferrite nanoparticles. At the same time some papers specify the ability for co-existence of multiferroidal properties in single-phase hexaferrites [21]. This paper studies magnetic, ferroelectric and ME properties of composite films based on PVDF with addition of nanoparticles $SrFe_{12}O_{19}$. Besides, a developed complex of experimental equipment is presented to comprehensively study ME effects.

2. Test specimens and experimental procedure

To obtain nanoparticles (NPs) of strontium hexaferrite $SrFe_{12}O_{19}$ [22], iron nitrate and strontium nitrate were used taken in accordance with the required stoichiometric ratio. To obtain NPs, metal salts and citric acids separately from each other were dissolved in deionized water for 30 min while being continuously mixed. The ratio of citric acid to metal salts was 1 : 1. Then the solutions were mixed being continuously stirred intensely for 30 min. Then ammonia liquor (30%) was added to the solution to achieve the value of pH 7. The solution was heated at 135°C for 5 h with subsequent temperature increase to 250°C. At this temperature the self-combustion reaction occurred that released NPs. Further, the NPs were annealed in a furnace as the temperature increased at 5°C/min up to 950°C for 3 h on air. The prepared powder was ground in an agate mortar.

Composite films were produced by Dr. Blade method [9]. Particles were dispersed in dimethylformamide (DMF) using ultrasound (Elmasonic S15H, 35 W) for 30 min. PVDF powder was separately dissolved in DMF. The obtained solutions were mixed, adding a solution of particles to a solution with a polymer, and stirred until dissolved. Then the solutions were applied on a slide and evenly distributed by a wiper blade with a gap of $70\,\mu$m. The produced composites were placed into a dry-air sterilizer at 65°C and soaked for 12 h to evaporate the solvent and to form PVDF films.

Magnetic measurements were made using a vibration magnetometer (Lakeshore 7400 System) in the range of fields up to 13 kOe at room temperature (~ 295 K). Measurements of films with size of 5×5 mm were made as the external magnetic field was applied perpendicularly to the plane of the specimens. To analyze ME properties of composites, a specialized installation is required for electric polarization of the specimen and measurement of piezoelectric coefficient d_{33}, and also an ME coefficient a_{33}. The value of the ME effect is directly related to the piezoelectric properties of the ferroelectric phase [2]. Therefore, accurate measurement of the piezoelectric parameters matters. Their improvement can be achieved with the help of a process known as electric polarization, which includes applying electric field of high intensity (5 MV/m or more) to a specimen [23]. The electric polarization of specimens was carried out using a unipolar corona effect with the help of the installation we designed and assembled [23].

The specimens were placed onto a flat grounded electrode, which was heated to maintain a the constant temperature of specimens during polarization. To develop the corona effect, a positive potential of 30 kV was applied to electrodes with a small radius of curvature. In this installation, medical needles were used with their tips located at a distance of 6.5 cm from the surface of the grounded electrode. The schematic diagram of the installation and its photograph are shown in Figure 1.

The piezoelectric response of the material is characterized by piezoelectric constants d_{ij}, which relate the values of mechanical stress s and electrical polarization P [24]:

$$\mathbf{P} = \mathbf{d} \cdot \mathbf{s}.$$

For the direct piezoelectric effect the indices, i and j specify the directions of electric voltage measurement and application of the mechanical stress, respectively. Non-zero values of d_{ij} depend on the crystal symmetry group [24]. For PVDF polarized along the third axis, only d_{31}, d_{13} and d_{33} are not equal to zero [24]. One of the effective methods for specification of material piezoelectric properties is direct measurement of d_{33}. The coefficient d_{33} of the specimen was measured by the quasi-static method by measuring the charge induced on the specimen under low-frequency force, and the value of the induced force and capacitance of the specimen [24]. Measurement of the value of longitudinal ME coefficient α_{33}, at which the direction of the external magnetic field matches the direction of specimen polarization, was carried out using a dynamic method on the installation developed and assembled within the study [25]. Constant magnetic field of displacement H_{DC} with value of up to 10 kOe, where the specimen was placed, was created using electromagnets of vibration magnetometer (7400 System VSM; Lake Shore Cryotronics Inc). Alternating magnetic field H_{AC} with value of 1.5 Oe and frequency of 770 Hz, directed along the constant magnetic field, was created using Helmholtz coils. The V_{out} generated on the specimen surface was detected using a synchronous amplifier SR 830 (Stanford Research Systems). The value of ME coefficient was calculated using formula

$$\alpha_{33} = V_{out}/(t \cdot H_{AC}),$$

where t — sample thickness.

The schematic measuring circuit and photograph of the installation are shown in Figure 2.

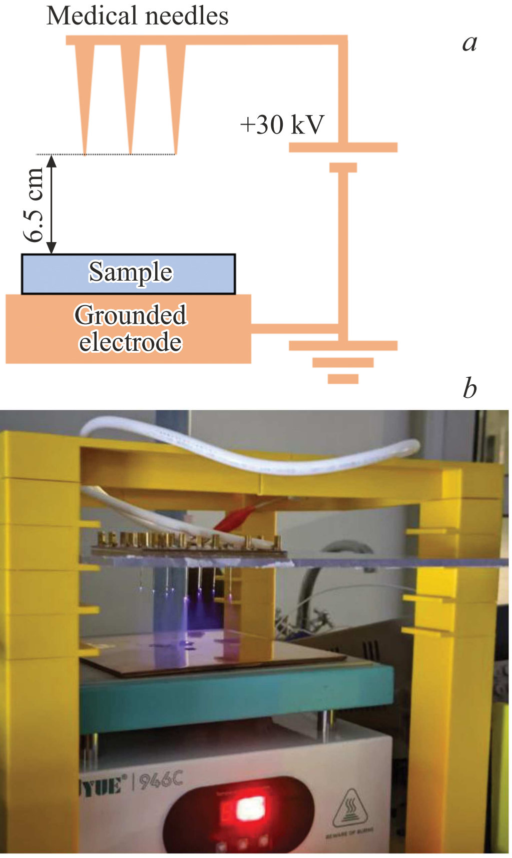

Figure 1. Installation for electric polarization of specimens: *a*) schematic diagram; *b*) photo.

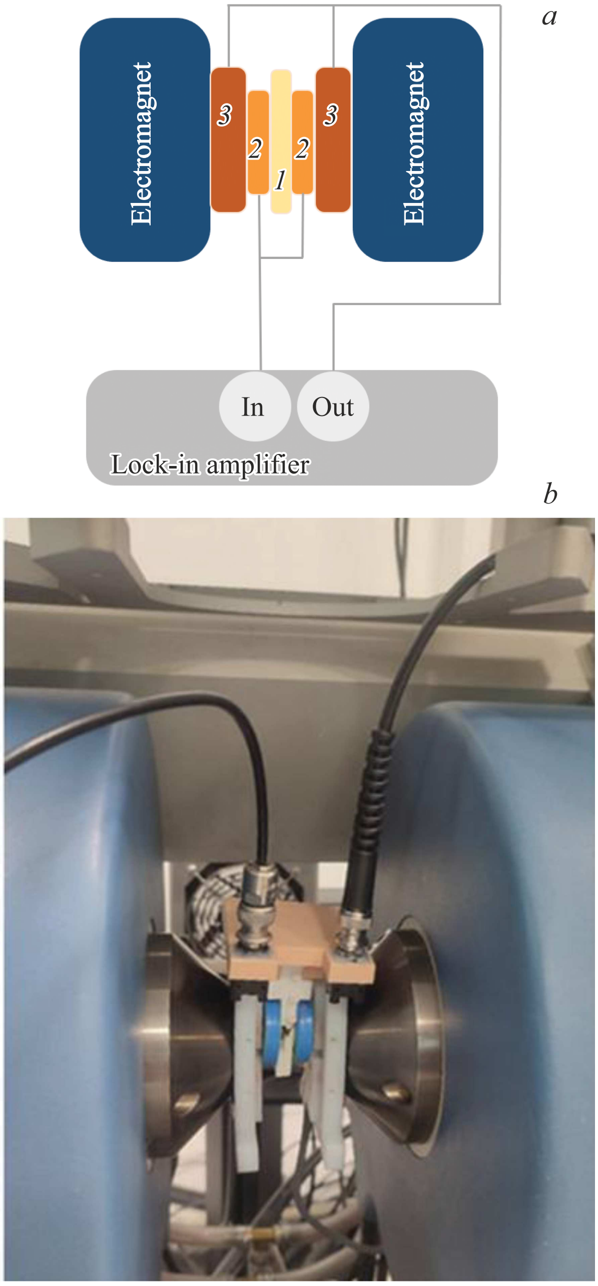

Figure 2. *a*) Schematic measuring circuit (*1* — specimen, *2* — pins, *3* — Helmholtz coils) and *b*) photograph of the installation to measure magnetoelectric coefficient.

3. Experimental results and discussion

Figure 3 presents magnetic hysteresis loops for powder of nanoparticles $SrFe_{12}O_{19}$ and composite with nanoparticles $SrFe_{12}O_{19}$/PVDF. Both materials are characterized by high values of coercive force: $H_c = 5.9$ and 6.3 kOe, respectively. Values H_c for both materials are close, which implies a significant effect of the uniaxial anisotropy of the particles [20]. A slight increase of H_c-value in the composite

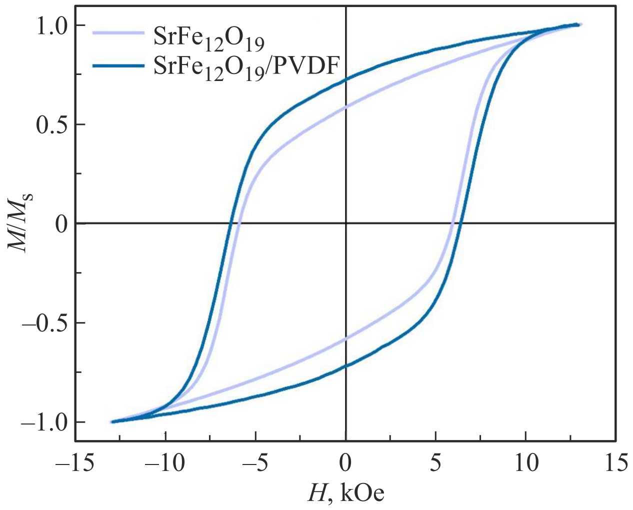

Figure 3. Magnetic hysteresis loops for powder of nanoparticles $SrFe_{12}O_{19}$ and composite with nanoparticles $SrFe_{12}O_{19}$/PVDF (normalized to saturation magnetization M_s.

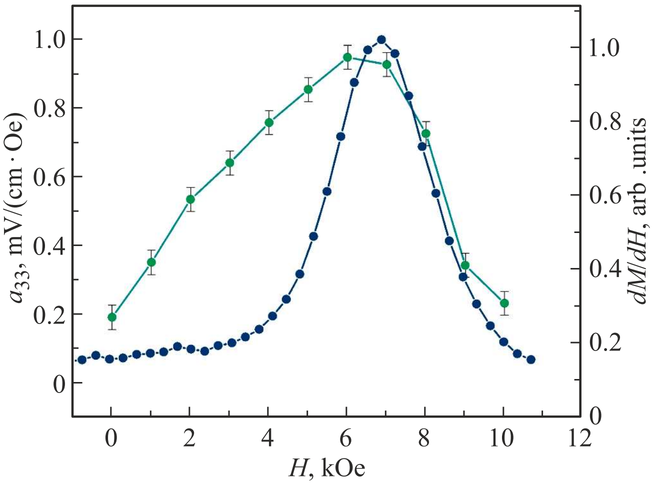

Figure 4. Dependence of the averaged value of longitudinal ME coefficient a_{33} and differential magnetic susceptibility dM/dH of composite $SrFe_{12}O_{19}$/PVDF on external constant magnetic field.

may be caused by the formation of large-size agglomerates and more complex domain structure.

To study ferroelectric properties of manufactured composite, the values of ferroelectric coefficient d_{33} were experimentally obtained for the initially fabricated composite and after electrical polarization. Seven samples of 10 × 10 mm were cut from the large area composite film. According to the results of measurements of 7 samples, the averaged value of the coefficient d_{33} was 2 ± 1 pC/N in the initial state before electric polarization and $d_{33} = 23 \pm 2$ pC/N after electric polarization. The increase of the value of d_{33} by more than 10 times is due to the rotation of easy axes of polarization of ferroelectric domains in PVDF when exposed to external electric field of high intensity (around 7 MV/cm) [26].

The longitudinal ME coefficient of the composite film $SrFe_{12}O_{19}$/PVDF was measured on the same series of 7 samples. The average thickness of the specimens was $39 \pm 1\,\mu$m. The field dependence of the averaged value of the longitudinal ME coefficient is shown in Figure 4. The averaged longitudinal ME coefficient reaches a maximum of 0.94 mV/(cm · Oe) at the value of constant magnetic field 6.00 kOe, close to the value of 6.75 kOe, where the maximum value of magnetic susceptibility of specimens is observed (for comparison, Figure 4 presents the differential magnetic susceptibility). It can be assumed that in this interval of fields the maximum gradient of the change of the magnetostriction coefficient change in the external magnetic field is observed.

4. Conclusion

Magnetoelectric properties of the composite made of piezoactive matrix PVDF with introduced nanoparticles $SrFe_{12}O_{19}$ with mass fraction of 10% were analyzed. It was found that the value of the piezoelectric coefficient d_{33} increases more than tenfold when the composite is electrically polarised using the corona effect method. The maximum value of ME effect for the polarized composite reaches 0.94 mV/(cm · Oe) at the external magnetic field, which corresponds to the maximum value of differential magnetic susceptibility of the composite. This means that ME effect in the composite is caused by magnetostrictive stresses in the matrix.

The results of the paper elucidate the mechanisms of phase interaction in polymer composites with architecture 0–3, which can be used to optimize the composition of such composites and to obtain the improved characteristics for specific applications.

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Conflict of interest

The authors declare the absence of conflicts of interest.

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