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Abstracts



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# SCIS-2023

## CONTENTS

Plenary lectures .....	3
Invited talks .....	6
Oral talks.....	14
Poster presentations .....	33
Author index.....	61

# Plenary lectures

# Programming of the mechanical properties and magnetic response of magnetoactive elastomers

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Magnetoactive elastomers (MAEs) are composite materials consisting of soft polymer networks filled with magnetic microparticles [1-3]. Belonging to the class of smart materials, they are attracting ever-increasing interest nowadays. A complex magneto-mechanical coupling induced in these materials in magnetic fields gives us an effective tool to significantly alter and to control a number of physical properties of these composites by the application of a magnetic field. Among the most prominent effects observed in MAEs are magnetorheological and magnetodeformation effects, magnetically controlled dielectric and electric properties [1,2]. The high magnetic response of these materials is vital for many practical applications such as peristaltic systems, magnetic field sensors and soft robotics.

Rearrangement of magnetic particles in a soft polymer matrix caused by magnetic interactions in magnetic fields is the key reason of MAE's magnetic response. Its magnitude depends on the elastic modulus of the polymer matrix as well as the magnetic properties, concentration, and distribution of the magnetic particles. The softer is the matrix, the larger displacements of the particles from their initial equilibrium positions are available in magnetic fields, leading to larger magnetic effects. Anisotropic distribution of the magnetic particles produces larger magnetic response.

In this talk, we report on magnetically controlled properties of MAEs, discuss the possible ways to tune the mechanical properties of these composites and their magnetic response by altering properties of two main components, i.e., polymer matrix and magnetic particles. We demonstrate, how "magnetic activity" of the filler particles allows to use the magnetic field as a tool to produce anisotropic MAEs and how additional "thermal activity" of new polymer matrices allows to program magneto-mechanical coupling in a complex way by tuning temperature and magnetic field. Finally, prospects for practical application are discussed.

Financial support of the Russian Science Foundation (project No. 19-13-00340-II) is gratefully acknowledged.

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# Flexomagnetism: “bending horseshoe magnets” at nanoscale

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Films of magnetic materials are widely used in magnetic memory and spintronics. In epitaxial films the strain due to the lattice misfit with the substrate amounts to several percent, well above the strength limit of bulk materials that gives a way for strain engineering of material properties. With the advent of two-dimensional (2D) graphene-like materials, and, quite recently, the magnetic 2D materials found in 2017 [1,2], the idea of a thin film and its flexibility came to its ultimate limit and gave rise to the special strain-related fundamental and applied research areas of straintronics [3].

Among various types of deformation the *flexural* one is of special interest. Flexure or bending is a special type of deformation characterized by strain gradient. In contrast to the quite common flexoelectric phenomena (the strain-gradient induced electric polarization) the flexomagnetic effects [4,5] are nontrivial and occur only in media with special symmetry of magnetic ordering.

In this report the mechanism of flexomagnetism as well as major factors of flexomagnetic effect enhancement in van der Waals magnets is discussed. The vivid illustration of such a mechanism can be the decompensation of layer magnetizations in an antiferromagnetic bilayer material (fig.1): the exchange interaction in the stretched bottom layer is weaker than in the top one.

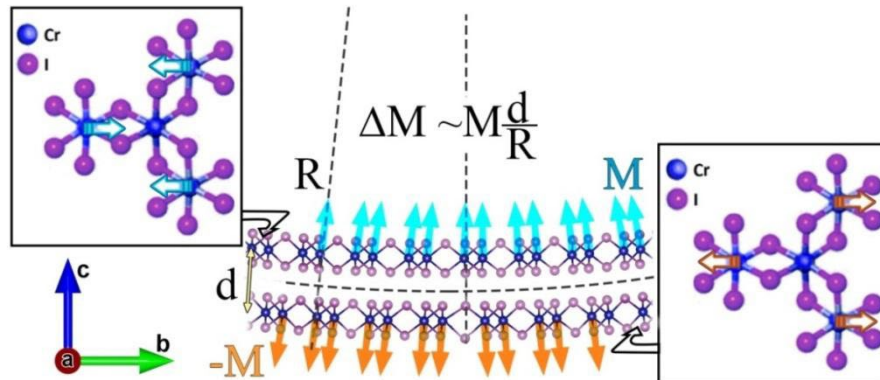


Fig. 1 The flexomagnetic effect in antiferromagnetic bilayer material:  $\mathbf{M}$  is a moment of a single ion in the antiferromagnetic sublattice,  $d$  is the distance between the middle lines of the top and bottom,  $R$  is the curvature radius that is inversely proportional to a strain gradient along  $c$ -axis. The top views of relative displacements of magnetic ions in the top and the bottom layers are shown in the insets.

A. Pyatakov and A. Kaminskiy acknowledge the support of Basis Foundation (Junior Leader Program).

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# Invited talks

# Low-temperature Peculiarities of Magnetoresistance and Hall Effect in Nanocomposites $(\text{CoFeB})_x(\text{LiNbO}_3)_{100-x}$ below the Percolation Threshold

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We present the results on magnetotransport properties of  $(\text{CoFeB})_x(\text{LiNbO}_3)_{100-x}$  film nanocomposites below the percolation threshold ( $x=40-48$  at.%) fabricated by ion beam sputtering of composite targets on silicon substrate. Magnetoresistance and Hall effect were studied at 3-250 K in magnetic fields up to 14 T.

The conductivity of nanocomposites with  $x \approx 44-48$  at.% in a wide temperature range is described by the relation  $\sigma \propto \ln T$ , characteristic for a strong tunneling coupling between granules [1]. For  $x < 44$  at.% this relation changes by the  $\ln \sigma \propto -(T_0/T)^{1/2}$  law, which is due to co-tunneling [1].

The samples with  $x \approx 44-48$  at.% demonstrate the anomalous Hall effect (AHE) with the scaling behavior  $\rho_{\text{AHE}} \propto \rho^n$ , where  $\rho_{\text{AHE}}$  is the AHE resistivity,  $\rho$  is the ordinary resistivity,  $n$  is the power-law index equal to  $\approx 0.4$ . This value  $n \approx 0.4$  is close to the index value corresponding to the tunneling AHE [2].

We observed the complicated non-monotonic behavior for the temperature dependence of magnetoresistance (MR). At  $T > 4$  K MR is negative and its absolute value exhibits minimum at  $\approx 40$  K. Above 40 K MR slightly increases with temperature that is unusual for MR of ferromagnetic materials. We attribute this anomaly with destroying superferromagnetic order. Below 40 K MR sharply increase with decrease of temperature. It was explained by resonance co-tunneling [3]. The unexpected behavior was observed below 4 K, where MR becomes positive and exhibits two minimums. It looks like a consequence of positive and negative contributions. In the presentation we discuss these peculiarities in the framework of existing theories of MR.

This work was financially supported by Russian Science Foundation, grant No. 22-19-00171.

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# Layered composite based on piezopolymer and magnetic elastomer for energy conversion

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Multilayered magnetoelectric materials are of great interest for investigations due to their unique tunable properties and giant values of the magnetoelectric effect (MEE). Despite the intense investigations in the field of multilayer multiferroics, many issues such as property modification still require more detailed investigations and thus remain the focus of the research. The flexible layered structures consisting of soft components can reveal lower values of the resonant frequency for the dynamic magnetoelectric effect occurring in the bending deformation mode. The use of polymeric components in magnetoelectric structures should be promising for the development of flexible electronics including sensors and energy harvesting devices or biomedical devices. For this reason, the investigations of layered structures based on magnetic elastomers (MAE) and piezoelectric polymers (PEP) are of especial interest.

The investigations of the MEE of the layered structure MAE-PEP for the cantilever configuration were carried out. The investigations included the measurements of the dynamic magnetoelectric effect, namely, the detection of the resonant amplification of the induced signal at the applied gradient alternating magnetic field. The application of the gradient magnetic field makes it possible to observe pronounced bending deformations of the samples. The investigations were aimed at searching for the influence of an external load, such as a DC magnetic bias field or mechanical pressure, on the resonant frequency and also on the induced signal. The transverse configuration of the magnetic and electric signals (opposite to the plane of the multilayer) was used.

The frequency dependence of voltage induced under the influence of AC magnetic field shows the main resonance peak and several resonance-like peaks with lower amplitude at sub-multiple frequencies. The appearance of resonance-like peaks at multiplied frequencies means that the acting force applies 2, 3, etc., times less frequently than at the main resonance. More rare application of the acting force leads to the lower induced signal. However, all resonances observed in this frequency range are associated with the first bending mode of the sample. The resonant frequency slightly changed with the changes of amplitudes of the AC magnetic field and had the tendency to decrease with the increase of iron particles concentration in the MAE layer.

Under the applied external DC magnetic field - bias field - the Young's modulus of the MAE increases due to the magnetorheological effect, as well as the density of materials as well as the mass distribution changes due to magnetodeformation. The induced electrical voltage depended on the permeability of the MAE and the bias magnetic field.

The mean value of the magnetoelectric effect can be calculated as the induced voltage divided by the thickness of the piezopolymer layer between the conductive plates and the value of the magnetic field amplitude at the center of the free edge of the sample. The maximum value of the MEE (mean value) reaches 0.77 V/cm\*Oe at the resonant frequency 60 Hz for the sample with MAE layer of 3 mm thickness and 77 mass% iron particle concentration.

Support by RSF, grant number 22-72-10137 is acknowledged.

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# Stress-dependent Magnetization Processes in CoFeSiBCr Amorphous Microwires

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Amorphous ferromagnetic materials in the form of microwires are of interest for the development of various sensors. This paper analyses the magnetization processes in  $\text{Co}_{71}\text{Fe}_5\text{B}_{11}\text{Si}_{10}\text{Cr}_3$  microwires and gives the reasons why they can be used as stress/strain sensors. The following properties: miniature dimensions, small coercivity, low anisotropy, and magnetostriction, along with tuneable magnetic structure, make them suitable for innovative applications, for example, for testing internal stress/strain conditions of polymer composite materials. The sensing operation is based on the generation of higher frequency harmonics of the voltage pulse induced during the re-magnetization of the wire [1].

The wires are prepared by the modified Taylor-Ulitovskiy method [2] and when quenched in water they typically have an amorphous structure without crystalline phases. However, in Co-based compositions with small magnetostriction a short-range crystalline anisotropy can prevail, and such wires exhibit magnetic bistability. This is confirmed by measuring the hysteresis loops and axial domain wall (DW) velocity (Fig.1) The DW velocity increases with increasing the applied tensile stress until they destroy the axial domain structure. For higher stresses, the circumferential anisotropy is formed and remagnetization takes place mostly by rotation. This leads to the generation of a voltage signal with a stress-controllable amplitude and duration. The frequency spectrum of this signal contains higher harmonics of the excitation frequency, and their amplitudes are stress-dependent. The strongest dependence on stress is demonstrated by higher-number harmonics (17-23 in Fig.1.).

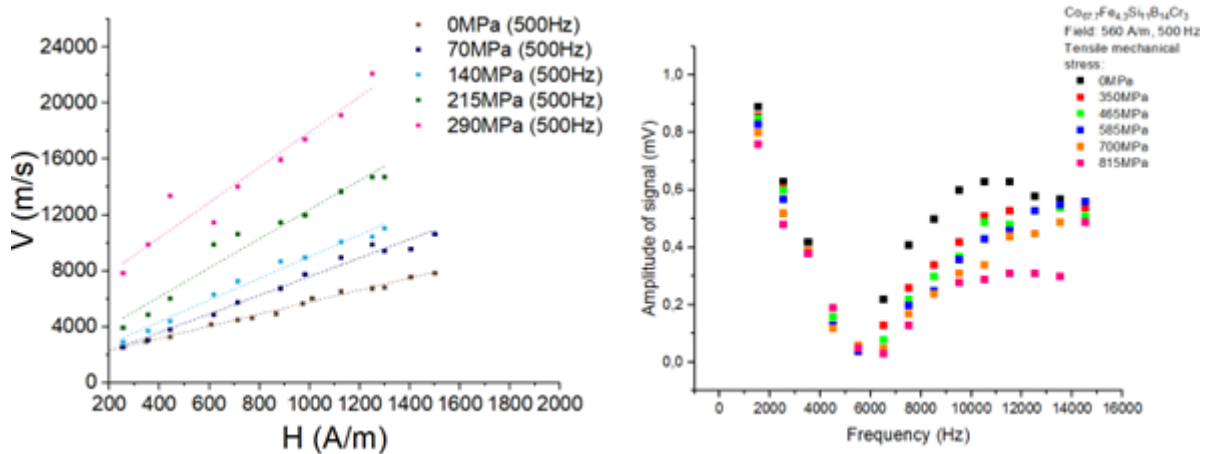


Fig.1. Domain wall velocity vs. driving magnetic field (left) and amplitudes of higher harmonics (right) for different tensile stress. Re-magnetization of the wire was done by plane coil creating a magnetic field of 325 A/m at its surface.

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# Magnetostrictive vs magnetostrainsome contributions of magnetic particles to the magnetoelectric response of piezopolymer-based composite films

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The conventional way of inputting the energy of an alternating magnetic field into a magnetoelectric transducing element of composite structure employs the magnetostriction effect (MSE) in the ferromagnetic component of the composite. The ferromagnetic grains generate the MSE-induced stress that is transferred either to the electrically neutral matrix and, by it, further to the piezoelectric component of the composite, or directly to the matrix provided the latter is piezoelectric as itself. A well-known example of easily commercially accessible and widely available ferromagnetic material of that kind are nano- or micropowders of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ , CFO).

This ferrite has a sufficiently strong spin-orbit interaction that entails both a relatively high magnetic anisotropy and a substantial MSE. Therefore, each CFO grain under application of external magnetic field that is not parallel to the axis of its easy magnetization, strives not only to undergo MSE-induced deformation but is also subject to a torque that tends to establish the grain easy axis along the direction of the applied field. Due to that, the particle experiences a magnetic strain qualitatively different from that imposed by MSE, see [1]. In the magnetoelectric composite, each CFO grain dwells in the environment that responds by electric polarization as soon as the mechanical state of the system (that it had under zero field) is perturbed by some additional stresses brought in by the exerted magnetization.

Evidently, both stress-inducing effects produce the electric polarization of the composite sample, so that any measurement delivers just the overall result. It is instructive to analyze the relative proportion of those contributions. It is the more interesting that, as the MSE and strainsome stresses are to different extent coupled to different components of the piezoelectric tensor, their actions might either enhance the total response or diminish it in comparison with partial contributions. Because of that, a number of situations would occur, especially when the CFO particles are anisometric.

The numerical modelling is performed for a test cell comprising several CFO particles embedded in the matrix possessing mechanical and electric properties of an archetypal polyvinylidene difluoride (PVDF) that is a conventional polymer with piezoelectric properties. The dependencies of the net polarization on the orientations of the magnetizing field, particle magnetic moment and electric anisotropy axis of the matrix are presented and analyzed.

Partial support by RSF grant # 21-72-30032 is gratefully acknowledged.

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## Biomimetic materials and tissue engineering

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Over the past decade, we have seen the emergence and transition to new modern trends, such as 3D and 4D printing, smart prostheses, biomimetic materials and bioprinting.

Biomimetic polymer materials are widely used in different medical applications, especially as scaffolds in tissue engineering. Reverse engineering approaches, which include the study of native tissue and polymer using high-resolution microscopy and CT, combined with 3D bioprinting methods, allows the formation of biomimetic anisotropic structures that repeat the architecture of native tissue.

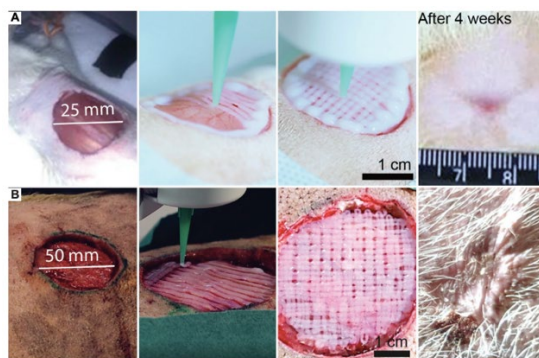


Figure 1 – In vivo bioprinting in animal experiments: (A) Rats and (B) minipigs. High levels of bioprinting fidelity have been demonstrated both in rats and in minipigs [5]

The in vivo experiments demonstrated that the employed original bioinks based on collagen hydrogel, platelet lysate, and dermal fibroblasts significantly improve the quality of wound healing processes in rat and minipig skin wounds. Further development and successful clinical applications of commercial in situ bioprinters are highly desirable.

SMP studies were funded by the Russian Science Foundation (RSF), project No. 21-73-20205; bio studies were funded by the Ministry of Science and Higher Education of the Russian Federation under the strategic academic Not acceptable leadership program “Priority 2030” (NUST MISIS).

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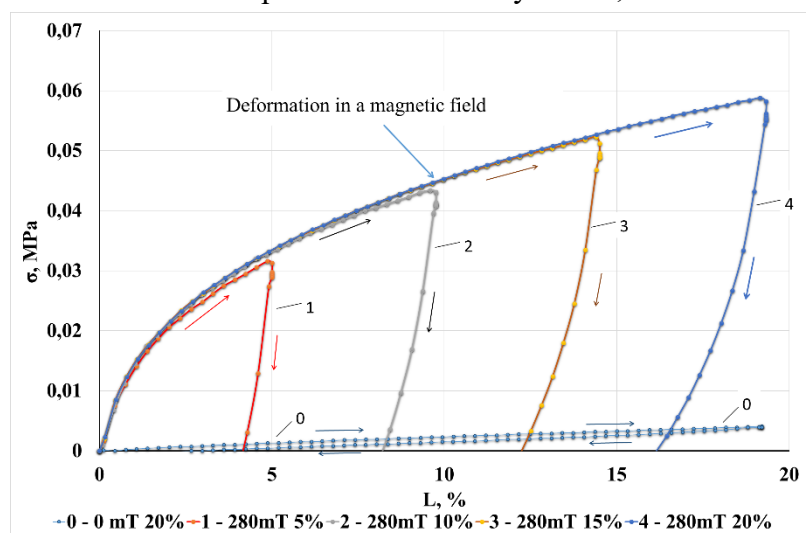
## Properties of Soft Magnetic Materials: from Experiment to Theory and Modeling

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Magnetoactive elastomer (MAE), a soft magnetic polymeric composite, has been in the focus of attention of Russian researchers for more than 25 years. A typical example of “smart material”, MAE possesses the capability to vary its parameters in magnetic fields reversibly. Nowadays, 12 properties, which may be changed in such a manner under the influence of external factors, are known. For instance, the capability to stiffen in magnetic fields is employed in controllable damping devices. Or, the way the material turns out of shape in homogeneous and non-homogeneous fields is used in micromotors. Alternatively, a multipolar magnetization pattern created in a strip of MAE filled with magnetically hard particles will give it the possibility to take complex shapes when placed in a magnetic field. This phenomenon may find use in soft grippers. In addition, the ability to change its conductivity in magnetic fields makes MAE a prospective material for employment in field sensors. The magnetic elastomer also exhibits the magnetopiezoresistive and magneto-optical effects. This set of properties is determined by the dipole interactions taking place among the magnetized particles filling the polymer matrix and capable of assembling reversibly into chain-like structures when influenced by a field. At the current moment, finding an adequate mathematical description for these properties is the key task.

Let's take the example of an MAE sample getting stiffer in magnetic field. The behavior of the material is clearly shown in the Figure demonstrating its stress-strain relationship. The measurements were carried out on a pull-test machine in the quasi-static regime using a cylinder-shaped specimen subjected to strain. As is suggested by the drawing, the stress-strain curve reveals a significant dependence on the strength of the magnetic field applied. For instance, line '0' shows the stress observed in the sample not influenced by a field, as a result of which its shape is practically that, which



would be seen in the classic Hook's law case. At the same time lines 1-4 correspond to different stress-strain relationships recorded at 280 mT and different strain degrees. The strain (load) move direction demonstrated by the sample is represented by the arrows. An important feature revealed by the curves is the magnitude of the residual deformation remaining in the sample still influenced by the field after load removal (the abscissa of the point at which the stress is zero and the curve intersects the x-axis). It is associated

with the shape memory of MAE and taken as the corresponding numerical characteristic. When the external influence is off, the sample will contract and regain its initial geometry. Such variations of properties appear as a result of the dipole interaction among the magnetized particles confined in the polymer and reversibly form chain-like structured under the influence of magnetic field. Giving these phenomena a description and modelling the processes taking place inside the magnetic elastomers is an important task of the present day.

# Modelling the effect of particle arrangement on the magnetoelectric response of polymer-based composite films

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Polymer composites materials capable of responding to an external magnetic field by generation of an electric field (multiferroics, MF) with prospects for tissue engineering do not require outstanding conversion characteristics. If their biocompatibility is granted, then quite moderate magnetoelectric efficiency of the films and scaffolds will do. However, a specific condition is the possibility to have the magnetoelectric effect at very low frequencies. For example, to accelerate osteogenesis of the stem cells adsorbed on such MF films, one may need the magnetic field – and, thus, the existence of surface electric field for the period from tens of seconds to many hours [1,2]. By those features the magnetoelectric units for tissue engineering differ greatly from industrial magnetoelectric transducers which work most at kHz or higher frequencies and do not need critically any substantial miniaturization.

As an attempt to understand the behavior of the materials of the afore-mentioned type, in our work we consider a model of the simplest scaffold—a thin film made of a three-component MF composite that is a polymer matrix filled with a mixture of piezoelectric and ferromagnet (or ferrite) micron-size particles. In particular, the films of this type are proposed for advanced muscle and bone engineering [3]. In the conventional Newnham classification of the magnetoelectric materials, this MF composite belongs to the 0-0-3 type.

The presence of a ferromagnetic phase, albeit the magnetic field has no direct effect on cell functioning, plays a key role. Indeed, in their vast majority, natural and artificial materials are ‘transparent’ for the magnetic field. Due to this, the field is experienced solely by the magnetic component of an MF film at a distance and independently of the presence of any organic substance (fabric, skin, etc.) in between. The driving mechanism of the magnetoelectric effect in question is the rotation of magnetically hard particles inside the matrix which, in turn, transfers the arisen mechanical stresses to the piezoelectric grains. The computer model of the MF film is built up as a periodic set of 2D cells each of which contains one piezoelectric and two ferromagnetic particles. The simulations are performed by means of finite element method on a single cell which, however, is incorporated in an infinite film by means of periodic boundary conditions. The problem of how the spatial arrangement of the particles and the orientation of the anisotropy axis of the piezoelectric one affect the magnetoelectric response is discussed. We argue that despite a quite particular scheme of the model, some important general conclusions may be drawn for the MF of the considered type [4].

Support by RSF grant # 21-72-30032 is gratefully acknowledged.

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# Oral talks

## PEGylated magnetic nanoparticles for water purification from methylene blue

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Organic dyes used in various industries cause water pollution [1]. Among the various types of dyes, methylene blue (MB) is a common industrial dye. Adsorption technique becomes one of the preferable methods to purify the wastewater containing dyes, as it is more economical, simpler and capable of efficiently treating dyes in more concentrated form than other conventional methods [2].

Here, iron oxide magnetic nanoparticles (NPs) were synthesised by a co-precipitation method and coated with varying concentrations of polyethylene glycol (PEG). An X-ray diffraction (XRD) analysis confirmed the inverse spinel structure of synthesized NPs (figure 1 (a)). The diffraction peak at about  $23^\circ$  for all coated samples is due to the reflex (032) for PEG. The magnetic properties of samples were investigated using a vibrating sample magnetometer (VSM). The saturation magnetization (MS) of samples coated with PEG decreased from 18 to 12 Am<sup>2</sup>/Kg as the amount of PEG loading increased from 0.6 g to 3.0 g (figure 1 (b)).

The coated NPs exhibit promise as potential candidates for sorption applications due to their water dispersibility, stability in aqueous environments, and significantly strong magnetic properties at room temperature.

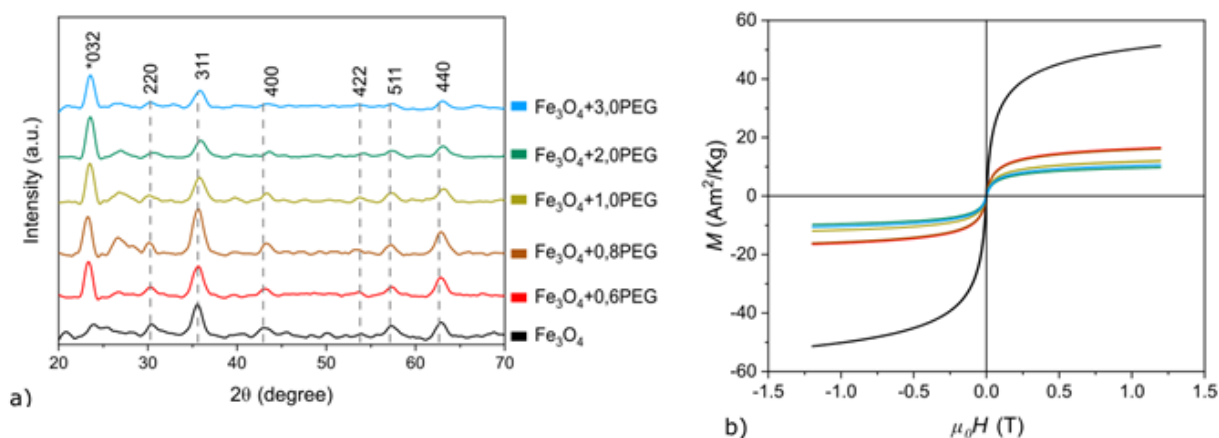


Fig. 1. a) XRD patterns of MNPs with different loading amount of PEG; b) room-temperature M-H loops of all samples.

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## **Biophysical regulation of cell behavior by PVDF-based magnetoelectric composites**

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The process of bone tissue repair of injuries resulting from trauma or disease is associated with a high risk of complications that significantly reduce the quality of life of patients. Therefore, the attention of researchers is focused on the search for new effective methods of treatment of such injuries. Tissue engineering is a rapidly growing field that aims to develop specialized 2D or 3D substrates capable of stimulating the repair of damaged tissues or replacing damaged areas of biological tissues. The key task in the development of such substrates is to ensure maximum similarity of mechanical properties of the substrates with native human tissue. The development of tissue engineering has led to the emergence of a group of so-called "biomaterials", which include biocompatible natural and synthetic polymers, such as polyvinylidene fluoride [1].

Polyvinylidene fluoride (PVDF) is a fluoroplastic with good mechanical and piezoelectric properties (similar to bone tissue properties). However, the low surface energy of PVDF negatively affects the adhesive properties of the polymer, which limits its use in biomedical applications [2]. There are various methods of PVDF surface modification (chemical etching, defluorination-sulfonation, plasma treatment, etc.), but the most optimal in terms of biomedical applications is plasma treatment [3].

The aim of this work was to study the effect of plasma treatment on mechanical and surface properties of PVDF-based composite materials, as well as on the adhesion and viability of mesenchymal stem cells cultured on the surface of magnetoelectric substrates. It was found that helium plasma treatment promotes the development of relief on the surface of the composite material, and there is a steady trend of increasing surface roughness with increasing treatment time (from 2-3 nm to 14-17 nm, after plasma treatment for 90s). The plasma-modified substrates had better hydrophilic properties: the average contact angle of the treated nanocomposites was less than 60°, whereas this value was more than 80° for the untreated substrates. Improved surface wettability of PVDF-based nanocomposites led to improved adhesion of stem cells, which in turn led to increased viability of cells cultured on magnetoelectric substrates. Thus, helium plasma surface modification of magnetoelectric nanocomposites can be used to improve the adhesive properties of the substrates without altering both their magnetic and structural properties, making these materials promising for biomedical applications such as bone tissue engineering.

The reported study was supported by the Russian Science Foundation № 21-72-30032.

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# Features of laser-induced demagnetization in van der Waals antiferromagnets FePS<sub>3</sub> and NiPS<sub>3</sub>

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Femtosecond laser pulses make it possible to induce and study the dynamics of various subsystems of the material on short time scales beyond thermodynamic equilibrium. Van der Waals magnetic crystals are interesting objects for studying the influence of magnetic ordering type on ultrafast laser-induced processes. These crystals can possess different types of quasi two-dimensional (2D) magnetic ordering with similar electronic and structural properties [1]. Transition metal thiophosphates MPS<sub>3</sub> (M = Fe, Ni, Mn, etc.) are promising objects for studying possibilities to control of magnetism by light in quasi-2D materials [2].

FePS<sub>3</sub> and NiPS<sub>3</sub> are antiferromagnetic van der Waals materials with Néel temperatures  $T_N=118$  K and 155 K, respectively. In both compounds within a layer, magnetic moments of  $M^{2+}$  ions form ferromagnetic zigzag chains coupled to each other antiferromagnetically. Yet, in FePS<sub>3</sub> magnetic moments are aligned perpendicular to the layers stacking direction [3], and FePS<sub>3</sub> can be described 2D-Ising model. The magnetic moments in NiPS<sub>3</sub> lie in plane of the layer [4], and 2D XY-model is suitable for describing its magnetic ordering.

We study how the type of magnetic order affects ultrafast laser-induced dynamics by comparing laser-induced demagnetization in these two compounds, i.e. laser-induced partial quenching of magnetic ordering. In the experiment, we used MPS<sub>3</sub> flakes obtained by exfoliation and deposited on a silicon substrate with 285 nm SiO<sub>2</sub>. The average thickness of our samples is 180 nm, the lateral size is  $\sim 85$   $\mu\text{m}$ . The measurement of laser-induced demagnetization was carried out using the pump-probe technique with pulse duration of 170 fs. In experiments laser-induced change in the intensity and rotation of the polarization plane of the reflected probing pulse were measured. In particular, changes of the probe polarization rotation were ascribed to the changes of linear dichroism commented to anisotropy of exchange coupling within atomic layers in these compounds [5].

In both NiPS<sub>3</sub> and FePS<sub>3</sub> below their transition temperatures  $T_N$  to the antiferromagnetic state, the laser pulse indeed induces an ultrafast partial decrease in the antiferromagnetic vector. To compare this process in the two compounds, we obtained the values of the critical exponent describing demagnetization degree change in a vicinity of  $T_N$  and the constants of the spin-lattice interaction from the data on ultrafast demagnetization. We show that the amplitude of the measured signal is governed by the derivative of the order parameter, which reveals laser-induced heating being the mechanism underlying demagnetization. The divergence of the demagnetization degree in a vicinity of  $T_N$  is found to agree well with the type of magnetic ordering of the studied compounds, 2D-Ising or 2D-XY. The characteristic demagnetization times in FePS<sub>3</sub> increase as the transition temperature is approached. We attribute this to the fact that the magnetic heat capacity of the system has a sharp maximum at  $T_N$ . In contrast to FePS<sub>3</sub>, the total heat capacity of NiPS<sub>3</sub> does not exhibit a sharp maximum near the transition temperature. As a result, the characteristic demagnetization times in NiPS<sub>3</sub> vary slightly near  $T_N$ .

Samples were provided by E. Coronado, S. Manas-Valero, and C. Boix-Constant (IC-Mol, Universidad de Valencia, Paterna, Spain). The work was partially supported by the RFBR grant No. 19-52-12065.

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# **Development of a Model for Predicting Efficient Catalysts for the Process of Urea Electrooxidation**

## **Smart Composites International School**

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Around 3 billion individuals worldwide face constraints in accessing safe water for drinking, cooking, and sanitation purposes, partially attributed to insufficient treatment of wastewater, which is laden with urea from agricultural and industrial activities. This raises the risk of irreversible damage to water bodies and greenhouse gas emissions. Electrochemical oxidation of urea can not only reduce the danger of eutrophication but also provide energy-efficient hydrogen and reduce nitrogen oxide emissions – potent greenhouse gases. Achieving target electrochemical reactions depends on the optimal catalyst. Therefore, developing a machine learning model to predict electrocatalyst reactions and optimize the reaction conditions can be a promising solution. This study aims to develop a neural network that can forecast the morphology of catalyst particles for selective urea electro-oxidation using input parameters, such as the catalyst composition and reaction conditions. Such a tool would be useful in optimizing various electrochemical processes that are economically and environmentally significant.

A training dataset of 6000 catalysts and reaction conditions was processed to produce descriptors containing geometric, kinetic, mechanical, thermodynamic, electronic properties, and molecular patterns. A variational autoencoder architecture was designed to predict catalyst composition and shape with an error  $<20\%$  and an  $R^2 \geq 80\%$ . The algorithm was optimized after validating the predicted data experimentally. The optimized algorithm would allow the identification of possible catalyst compositions for electrocatalytic processes (including urea electro-oxidation) and complement rational designs for directed particle design and fine-tuning. The future goal is to launch a digital service to help users select the appropriate catalyst type and morphology for a specific technology. This approach can help reduce the resources required for experimental screening and facilitate the efficient upscaling of processes to industrial capacity.

The work was carried out with the support of the State assignment No. FSER-2022-0002 within the framework of the national project "Science and Universities".

# Composite polyvinylidene fluoride-( $\text{CoFe}_2\text{O}_4$ , $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$ ) filament for 3D printing

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A new class of "smart" materials, known as multiferroics, in which there is a pronounced, in particular, interrelation of magnetic and electrical subsystems, is being actively studied and has prospects for practical applications in power engineering, sensorics, microelectronics, and biomedicine [1, 2]. The magnetoelectric (ME) effect, is the appearance of electric polarization (P) induced by the magnetic field (H) and vice versa. One of the technologies for creating magnetoelectric multiferroics is the introduction of magnetic particles into the piezoelectric matrix. Composites obtained from piezopolymer polyvinylidene fluoride (PVDF) with incorporated magnetic nanoparticles (MNP) [1, 2] have demonstrated ME coefficient  $\alpha_{33}$  in the range  $5\text{-}20 \text{ mV} \times \text{cm}^{-1}\text{Oe}^{-1}$ .

In this work, we explore methods of 3D printing of PVDF-MNP composites, as additive manufacturing technologies can streamline production and reduce the number of required steps in fabricating parts and devices with ME effect. Composite filaments for fused deposition modeling (FDM) printing (layer-by-layer from the bottom up by heating and extruding thermoplastic filaments) were produced by extruding films obtained from polymers with different molecular weights ( $\sim 70\text{k}$  and  $\sim 500\text{k}$ ) as well as with different contents of and CFO ( $\text{CoFe}_2\text{O}_4$ ) and ZCFO ( $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$ ) MNPs (5-15 wt.%).

Our results showed that an optimal particle content of 10% improves the sample's crystallinity without negatively impacting the composite's mechanical properties. Additionally, utilizing a polymer with a lower molecular weight reduces the melting temperature and prevents cracking during cooling after printing.

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# Control of surface properties of magnetoactive elastomers by magnetic field

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"Intelligent" materials are the subject of active research and development in the 21st century. They are called intelligent because of the ability to change their properties in a controlled way with external influences, such as: pH, magnetic or electric field, temperature and light. Magnetoactive elastomers (MAEs) are good example of such materials. These are composite materials consisting of polymer matrix and magnetic microparticles. The particles are embedded into a soft polymer matrix, which they drag along with them when their position changes. As a result, deformation of the sample may occur [1], as well as a change in the structure of the near-surface layer of the material [2]. Since the surface structure affects the wettability of the sample, it is reasonable to study the hydrophobic properties of MAE.

Measurements were carried on the KRUSS EasyDrop device, which with the help of a camera captures the image of a drop on the substrate, where special software approximates the shape of the drop with a circle and determines the contact angle along the established liquid-substrate contact line. We use drops with a volume of 2  $\mu\text{l}$  and cylindrical neodymium magnets with a diameter of 6 mm and a height of 2 mm as the source of the magnetic field. An optical microscope was used to obtain images of the structure of the MAE surface.

In this paper, we compare isotropic and anisotropic composites based on polydimethylsiloxane with carbonyl iron concentrations of 50, 60, 75 and 80 wt. %, and also considered a material with an iron concentration of 70 wt.%, in which the surface of iron particles is modified with trimethylchlorosilane. The samples were synthesized with comb components replacing a silicone oil plasticizer. During the synthesis of anisotropic materials, a certain distribution profile of magnetic particles is formed.

It is shown that magnetoactive elastomers with filler particles modified with trimethylchlorosilane show greater sensitivity than materials with unmodified particles; anisotropic MAEs have more significant hydrophobic properties in a magnetic field; among the MAE on comb polymers, the greatest response to the magnetic field is achieved at a concentration of magnetic particles of 60 wt.%; at high concentrations of magnetic particles, the growth of the contact angle in the magnetic field is insignificant due to the reduced mobility of particles; with a decrease in the thickness of the MAE film, the response to the external magnetic field increases; susceptibility of the samples synthesized on comb polymers is less than MAE made with plasticizer.

The work was carried out with the financial support of the Russian Science Foundation (grant №. 19-13-00340-P).

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# **Wet Chemical Synthesis and Properties of Magnetic Nanomaterials and Composites**

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Magnetic nanomaterials and composites have received significant interest for application in various fields, including medicine, electronics, and environmental remediation. Among other methods for synthesis of nanomaterials, the wet chemistry has emerged as versatile technique for tailoring the properties of these materials, offering precise control over particle size, composition, morphology, and magnetic properties. In the lecture an overview of the wet chemical synthesis approaches employed for the preparation of magnetic nanomaterials and composites will be provided. Also, their unique properties and potential applications will be highlighted.

The wet chemical synthesis of magnetic nanomaterials involves a wide spectrum of routes that allow controlled nucleation and growth in a solution-based environment. Precursor selection, solvent composition, reaction temperature, and surfactant utilization are key parameters that influence the final properties. Through techniques such as co-precipitation, sol-gel, hydrothermal, and microemulsion methods, researchers can achieve tunable particle sizes ranging from a few nanometers to hundreds of nanometers, making it possible to tailor the materials for specific applications.

On the other hand, the magnetic properties of these nanomaterials are primarily governed by their composition, crystal structure, and size. Superparamagnetic behavior is a desired trait for biomedical applications like targeted drug delivery, hyperthermia-based cancer therapy and magnetic resonance imaging. Additionally, the controlled assembly of these nanoparticles into composites with graphene oxide, polymers, ceramics, or other materials can lead to synergistic effects, enhancing the overall performance of the resulting material. In electronics, magnetic nanomaterials find use in data storage, sensors, and spintronics. Environmental applications, such as water purification and pollutant removal, also benefit from the magnetic properties of nanomaterials. Magnetic nanocomposites can be designed to selectively adsorb contaminants from water sources, simplifying the separation process through magnetic collection.

In conclusion, wet chemical synthesis methods offer a versatile approach to tailoring the properties of magnetic nanomaterials and composites. By controlling synthesis parameters, researchers can create materials with desired sizes, shapes, and magnetic behaviors. These materials hold immense potential for diverse applications, spanning medicine, electronics, and environmental remediation, with ongoing research aiming to unlock their full capabilities and broaden their impact across various fields.

## **Growth of thin films using various deposition methods**

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Nanocomposite materials represent a basis for the development of novel devices or their components for a wide range of applications. This is due to their unique physicochemical properties that, when combined, result in a synergy that provides exceptional multifunctional characteristics, thus further stimulating development and implementation of nanocomposites in various fields. Thin films have played an important role in this direction. The controlled synthesis of thin films is a fundamental step in many applications and through precise manipulation of composition and microstructure an integration of novel functionality into/onto the existing systems can be achieved.

The growth and control of properties in thin film nanocomposites are governed by critical elements such as temperature, pressure, and precursor concentration that dictate the thickness, uniformity and crystallinity of the film. Furthermore, the selection of deposition method significantly influences mechanical, electrical, optical and other properties of the thin film. In the lecture, various aspects of the growth/appearance of thin films in chemical and physical systems will be given using selected examples, with focus on advanced integration techniques allowing growth monitoring and characterization at an atomic level.

In conclusion, it will be reflected upon the capacity of thin film nanocomposites to reshape our scientific and technological landscape.

# Dzyaloshinskii–Moriya interaction in epitaxial iron garnet films and 2D CrI<sub>3</sub> based materials

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Multiferroics, materials with several coexisting types of ordering, particularly magnetoelectrics, have attracted great research interest since the beginning of this century due to the promising practical applications, especially after the synthesis of materials (including composites) which exhibits a strong magnetoelectric effect at room temperature [1]. There is a tendency at present to consider magnetoelectric phenomena within a domain and even a domain wall [2]. Iron garnets are the most popular magnetoelectric materials for research due to relative simplicity of visualization of their domain structure [3]. However, the magnetoelectric effect in these crystals is weak, and one must apply large electrical voltages to observe substantial changes. Recently it has been demonstrated that the nature of the magnetoelectric effect in epitaxial iron garnet films is connected to the strain gradient induced by the mismatch of lattice constants of the substrate and the film [4]. Thereby it seems promising to research the magnetoelectric effect and its connection to bending deformations, which are hypothetically able to affect at the intensity of the magnetoelectric effect, in 2D materials.

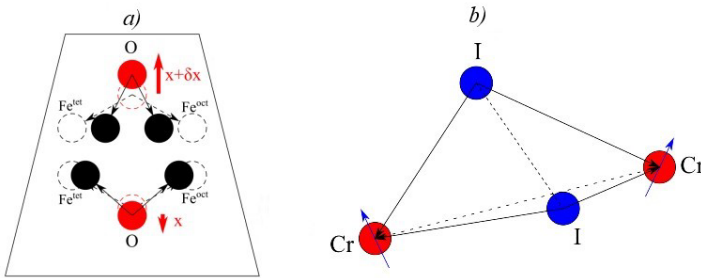


Figure 1. The effect of inhomogeneous deformation on the crystal lattice of iron garnet (a) and CrI<sub>3</sub> (b)

to a strong deformation of the parallelograms of two Cr and two I, which transforms the parallelogram into a tetrahedron (see Fig. 1).

The proposed mechanism can occur in nanostructures with large curvature values, such as nanotubes.

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## Electroreduction of polychloromethanes to C2 products

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Dichloromethane is widely used as a solvent for paints, as a solvent in chemical and pharmaceutical industries, for polyurethane production and metal degreasing. However, its extensive use and improper disposal can lead to groundwater and surface water pollution. When dissolved in water, dichloromethane inhibits the growth of living organisms. Dichloromethane is classified as a probable human carcinogen and can disrupt liver and kidney functions. Additionally, it may contribute to the ozone layer depletion when released into the atmosphere. Traditional methods of dichloromethane removal from water have limitations. For example, employing adsorption to remove dichloromethane from water requires several phases of regeneration and partial replacement of the sorbent materials. An electrochemical approach for water purification from dichloromethane allows for complete removal of the pollutant even at low concentrations. Moreover, electroreduction of dichloromethane makes it possible to obtain ethane and ethylene that are used in the production of many organic compounds.

The aim of this study is to determine the optimal conditions for the electrochemical reduction of dichloromethane to ethane and ethylene. The reaction was conducted in a divided H-cell with anion exchange membrane; in protic and aprotic media; silver was used as working electrode material. Reaction product's concentrations were determined using an Agilent 7890b gas chromatograph. The following parameters were varied: electrode surface, solvent, concentration of dichloromethane, and electrolyte concentration. Conditions ensuring significant Faraday efficiency in the formation of C2 products have been selected. To enhance the efficiency of the target reaction, an optimal methodology for the synthesis of silver nanoparticles was identified and nanomodified silver electrodes were produced.

The research was carried out within the state assignment № FSER-2022-0002 within the framework of the National Project "Science and Universities".



# Magnetic field induced modulation of Goos-Hänchen effect in magnetophotonic crystals

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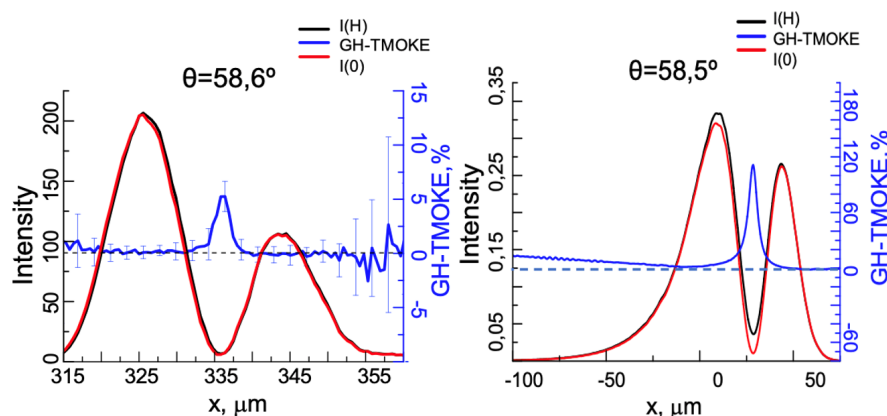
Nowadays, one of the main topics in modern nanophotonics is the study of optical effects in nanostructures that allow light to be controlled by external influences. These include the Goos-Hänchen effect (GH) [1]. Under the GH effect the reflected light beam experiences a lateral shift along the interface in comparison with the position predicted by the geometric optics. The GH effect can be enhanced by surface electromagnetic waves, for example, Bloch surface waves (BSW), which propagates in photonic crystals. It is worth mentioning that magnetic field is also a powerful tool for tunability of the GH shift in magneto-optical structures [2].

In this work, we investigate magnetic field induced modulation of the GH effect in the magnetophotonic crystal (MPC) due to the excitation of BSWs. Experimental observation of the intensity modulation under the GH effect in the MPC has not been carried out before, which proves the relevance of the work.

MPC consists of 14 periodic layers of SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> with thickness of 132 nm and 93 nm, refractive indexes 1,46 and 2,1, respectively. The waveguide layer of Bi:YIG with thickness of 1059 nm lies on the top of the MPC. Simulation and experimental measurements of the angular dependence of the GH effect was obtained. BSW was excited with laser beam with wavelength of 675 nm near the resonant angle of incidence 58,5°. The largest calculated and experimental GH shift was observed near the resonant incident angle and equaled of 34,5 μm and 33,2 μm, respectively. The value of the magnetic field induced modulation of the spatial distribution of the reflected beam intensity, which we called GH-TMOKE, has been defined by following equation:

$$\frac{I(x,H) - I(x,0)}{I(x,H) + I(x,0)} \times 200\% \quad (1)$$

The modulation of the intensity was caused by the displacement of the resonant incident angle when a magnetic field applied. Thus, it leads to the modulation of the intensity profile of the GH effect. Fig. 1 shows that the largest simulated GH-TMOKE is 120% and experimental value – 7%.



In conclusion, the GH effect and the GH-TMOKE have been investigated in the MPC with BSW excited.

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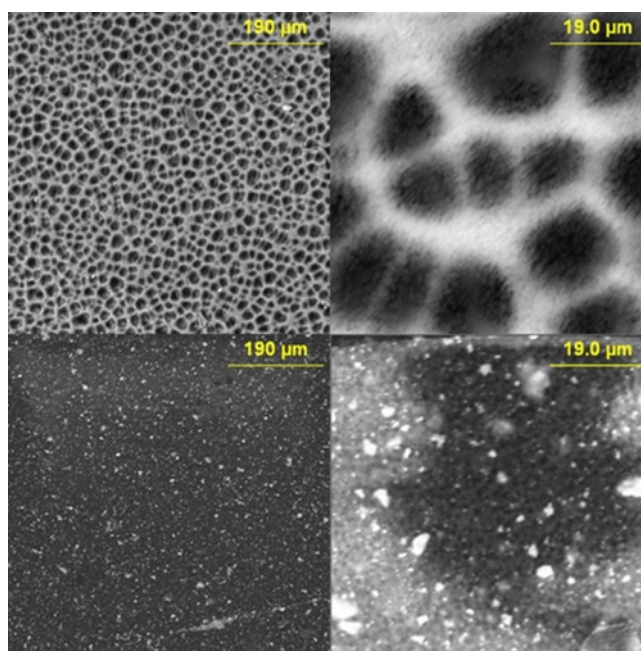
## Novel Hybrid Membranes based on PVDF/BiFeO<sub>3</sub> for Efficient Catalysis

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The creation of stimulus-sensitive smart materials for catalytic applications that are capable of efficiently decomposing organic pollutants is currently a relevant task [1]. Hybrid functional materials that combine and merge the properties of 2-3 materials represent a particular advantage. The most interesting material is BiFeO<sub>3</sub> (BFO) multiferroic bismuth ferrite, which possesses spontaneous polarization, magnetoelectric coupling, and a narrow forbidden zone, making it highly promising for use as a smart photocatalyst. However, these catalysts may affect pollutants in water in the form of particles and limit the possibility of their secondary processing. Therefore, composite materials based on polymers that possess non-toxicity, biocompatibility, and chemical inertness offer significant advantages in this area. Among them, polyvinylidene fluoride (PVDF) is an excellent choice as a matrix for BFO due to its properties.



**Fig.1. SEM images of a polymer-inorganic membrane: pure and PVDF/BFO 10%**

New two-phase polymer-inorganic composite films consisting of the piezoelectric polymer polyvinylidene fluoride (PVDF) and the nanocrystalline semiconductor multiferroic BiFeO<sub>3</sub> (BFO) were synthesized using the non-solvent-induced phase inversion method (NIPS).

Samples were investigated using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), photoluminescence microscopy, and X-ray diffraction analysis (XRD). Photo-, piezo-, and piezophotocatalytic experiments were conducted on a model dye MC (methylene blue).

The study was supported by a grant from the Russian Science Foundation (project no. 22–73-10091) [1] Orudzhev F. et al., *Polymers.*, 2023, T. 15- №. 1. – C. 246.

# **New Functional Agents of Hybrid Imaging – Micro/Nano Microbubbles Based on Amphiphilic Polymers for Reproductive Medicine**

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The issues of reproductive medicine bear significance and relevance as resolving the demographic obstacle is one of the primary objectives of contemporary Russia. Identifying and resolving problems pertaining to reproductive health represent a crucial step towards elevating medicine to cutting-edge levels, given that tubal-peritoneal factor of infertility, as a leading cause of female infertility, contributes to a range of 30% to 50%. Recently, we developed a prototype contrast agent for imaging women's pelvic organs, namely microbubbles comprising an air core and shell, encompassing protein and amphiphilic copolymers. Additionally, we generated a model for the female reproductive system for evaluating the contrast agent's effects, which does not have any global parallels. Presently, clinical use of just one contrast agent (Sonovue) is permissible in the Russian Federation whose capacity to use ultrasound imaging of cavities is not certified. Moreover, its analogues are not produced in Russia. Our developed contrast agent surpasses all its global analogues in terms of efficiency. It offers non-invasive assessment of the causes underlying female infertility by utilizing safe biocompatible materials, allowing timely and effective treatment. Our researchers' contrast agent for ultrasound can have greater applications, for instance, identifying bloodstream contrasts and lowering the toxic influence of clinically implemented procedures. Moreover, we analyzed the potential of multifunctionalization of microbubbles like the inclusion of therapeutic medications within their structure for photodynamic and sonotherapy as well as gold and magnetite nanoparticle introduction for optoacoustic and magnetic resonance imaging.

The work is supported by the Russian Science Foundation grant No. 21-73-10254 "New functional hybrid imaging agents based on amphiphilic polymers for reproductive medicine"

# Hydrogen Bond-Mediated Activation of Piezo- /Photo-Catalytic Properties in Calcium Nitrate-Doped PVDF Nanofibers

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With the increase in industrial capacity, there has been a rise in pollution and toxicity levels, including organic compounds. One promising method for purification is piezo-/photocatalytic processes, which utilize two types of natural energy: solar energy for photocatalysis and mechanical energy for piezocatalysis [1].

In this work, a composite polymer membrane based on the organic piezoelectric material polyvinylidene fluoride (PVDF) with the addition of inorganic calcium nitrate  $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$  was synthesized by electrospinning [2]. The obtained sample was investigated using SEM, XRD, RAMAN, FTIR, XPS, PL, and DSC. The results demonstrated that doping with the salt led to structural and phase changes, in particular, a transition from  $\gamma$ - to  $\beta$ -polymorph. It was found that the hydrated salt and polymer form a hydrogen bond  $-\text{C}-\text{F}\dots\text{H}-\text{O}-\text{H}$ . Addition of the salt leads to a change in the electronic structure of the polymer and photoresponse due to narrowing of the band gap. It is worth noting that neither the polymer nor the salt is photosensitive materials.

The catalytic properties were studied during the decomposition of the model dye methylene blue (MB) under irradiation with both visible and UV-visible light, and ultrasound with a frequency of 18 kHz was used as a source of mechanical stress. The composite material showed high photocatalytic activity.

The results showed that under UV-visible irradiation, piezophotocatalysis exhibited the highest activity in MB decomposition (93% in 30 minutes), while in the absence of light irradiation, piezocatalysis occurred (79.1% efficiency in 60 minutes), and photocatalysis showed 89% efficiency in the same time period. When using a visible light source, the activity of photocatalysis and piezophotocatalysis was 80% and 90%, respectively.

Experiments with scavengers of reactive oxidizing-reducing species allowed us to suggest that the hydrogen bond acts as a transport bridge for the migration of photo-generated electrons in the composite structure, leading to the limitation of recombination and enhancement of catalytic properties.

*The research was carried out with financial support from the Russian Science Foundation (project No. 22-73-10091).*

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# Synthesis and piezo photocatalytic properties of a PVDF fiber membrane modified with an iron-containing organometallic framework

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PVDF (polyvinylidene fluoride) is a multifunctional polymer that has proven itself as an effective matrix for nanoparticles with photocatalytic (FC) properties, whose composites successfully decompose organic dyes [1]. Iron-containing organometallic frameworks Benzene-1,3,5-iron tricarboxylate (Fe-BTC) represent an interesting class of porous crystalline materials with a band gap of  $\approx 3.2\text{eV}$  [2-4], which makes them very interesting candidates for the role of photocatalysts. In this work, using the method of electrospinning at a constant voltage of 50 kV, composites based on PVDF with the addition of Fe-BTC were synthesized, the structure (Fig. 1a) and piezophotocatalytic (PPC) properties (Fig. 1b) of PVDF/Fe-BTC with different contents were studied (Fig. 1b). filler.

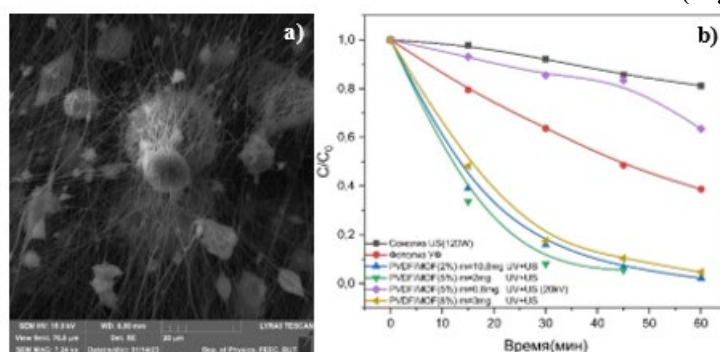


Figure 1. a) – SEM image of PVDF/Fe-BTC nanofibers, b) – PPC decomposition curves of methylene blue.

PPC experiments were carried out using an ultrasonic bath with a power of 120 watts and a frequency of 40 kHz. As sources of ultraviolet and visible light, a high-pressure mercury lamp with a power of 250 watts (Phillips) and a metal halide lamp with a power of 70 watts (Osram) were used. An organic dye, methylene blue (MB), with a concentration of 1 mg/l was used for decomposition. The degree of decomposition was determined using an optical spectrophotometer CФ-2000. In Fig. 1b shows the decomposition efficiency, which was 97.8%, 94.5% and 95.3% for composites with a percentage of Fe-BTC of 2%, 5%, and 8%, respectively.

The research was carried out with the support of the grant of the RHSF number 22-73-10091.

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# Optical properties of 0D and 2D lead halide perovskite nanostructures doped with Yb<sup>3+</sup> and Mn<sup>2+</sup> ions *via* anion-assisted approach

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The development of lead halide perovskite (LHP) nanostructures has revolutionized technologies requiring efficient and adjustable light emitters. LHP nanocrystals (NCs) exhibit high photoluminescence quantum yield (PL QY) due to their tolerance for defects [1]. Quantum confinement, particularly in 2D LHP nanoplatelets (NPLs), enhances their radiative properties, making them ideal for advanced light-emitting diodes and lasers [2].

LHP offers spectral tunability across the visible range by adjusting the halide composition during synthesis or employing anion exchange. Doping at the B-site position in the perovskite structure allows for fine-tuning the band-edge PL position or introducing additional emission bands through dopants [3]. Synthetic methods for doped LHP have been developed, but they often require high temperatures, limiting control over morphology and hindering the formation of desired nanostructures. To address this, post-synthetic doping of LHP with predetermined morphology can be employed [4]. Therefore, there is an urgent need to develop universal, non-destructive, and efficient methods for doping LHP nanostructures with varying chemical compositions and morphologies.

In this study, we propose a universal method for creating LHP nanostructures with multiple emission bands through anion-assisted cation doping in a nonpolar solvent at room temperature. By introducing Yb<sup>3+</sup> and Mn<sup>2+</sup> precursors to pre-synthesized perovskite nanostructures, we successfully synthesized near-infrared emitting Yb<sup>3+</sup>-doped CsPbCl<sub>x</sub>Br<sub>3-x</sub> and FAPbCl<sub>x</sub>Br<sub>3-x</sub> NCs and NPLs. We also achieved double-wavelength emission with Mn<sup>2+</sup> doping and triple-wavelength emission with Mn<sup>2+</sup>-Yb<sup>3+</sup> co-doping in CsPbCl<sub>x</sub>Br<sub>3-x</sub> nanoplatelets. Doping occurs by simultaneous incorporation of guest cations and halogens onto the surface and may be followed by further migration of the guest cations inside a nanostructure. The process dynamics depends on the type of doping ion, and the composition and morphology of the pristine perovskite nanomaterial.

The proposed method offers a versatile approach to create targeted perovskite-based nanomaterials for photonics and optoelectronics. By utilizing this doping method, it becomes possible to engineer perovskite nanostructures with distinct and desirable optical properties, opening up new avenues for their application.

The study was carried out with the support of the Russian Science Foundation, project No. 21-73-10131.

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## Synthesis and characterization of PVDF-CFO composite films

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Multiferroics can exhibit segmentelectricity, ferromagnetism, segment elasticity, and ferrothoroidal properties for a single phase. The coexistence of at least two ferroic properties, such as ferroelectric and ferromagnetic, in a composite magnetoelectric (ME) structure, has attracted attention because of the potency of such devices in various applications such as sensors, transducers, multistate memory devices, switching, and filters [1].

Among electroactive polymers, PVDF is a semi-crystalline polymer that has five crystalline phases:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ . The  $\beta$ -phase has a trans-conformation (TTT), where fluorine and hydrogen atoms are on opposite sides of the polymer chain structure. This structure exhibits the total characteristics of a nonzero dipole moment. The  $\beta$ -phase includes electroactive properties of the polymer and exhibits segmentelectric, piezoelectric, pyroelectric properties [1].

In this work, composite films of different thicknesses were fabricated and characterized in terms of their structural, morphological, and magnetic properties. The PVDF-CFO composite films were synthesized by the doctor blade method and characterized by various methods including X-ray diffraction (XRD), scanning electron microscopy (SEM), scanning atomic force microscopy, and vibrating sample magnetometry analysis.

Cobalt ferrite nanoparticles were synthesized by the hydrothermal method. The hydrothermal method allows controlling the size of  $\text{CoFe}_2\text{O}_4$  particles only by adjusting the reaction time at low temperatures, which is also vital for obtaining appropriate values of saturation magnetization  $M_s$  and coercivity  $H_c$  for its practical application [2].

The thickness of the films obtained ranged from 15,28 to 58,1 micrometers (58,1; 47,4; 26,23; 20,29; 15,28). The film synthesis method used allows to uniformly distribute particles CFO in the polymer matrix, but does not allow achieving monodispersity, as evidenced by the formation of nanoparticle agglomerates. As a result of measurements, it was found that when the thickness of the composite film decreases, the size of spherulites and pores on the surface decreases. XRD results showed that the obtained composite films are dominated by alpha phase, but beta phase is also present and clear peaks from CFO are visible. Measurements of magnetic properties proved that we synthesized a magnetic polymer, so we can conclude that the composite film is a multiferroic as it has piezoelectric and magnetic properties. An initial study of the surface revealed that with increasing film thickness, there is an increase in adhesion, a decrease in deformation and an increase in the Young's modulus.

**Acknowledgement:** This work was supported by the Russian Science Foundation, grant 21-72-30032. We acknowledge the Centre for development of gifted children (Kaliningrad) for provision of XRD and SEM measurements.

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# Combination NIPS/TIPS Synthesis of $\alpha$ and $\alpha/\gamma$ - $\text{Fe}_2\text{O}_3$ /PVDF Composite for Efficient Piezocatalytic Degradation of Rhodamine B

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The development of smart materials that respond to stimuli and efficiently break down organic pollutants is currently an important objective [1, 2]. A particular advantage lies in hybrid functional materials that combine the properties of 2-3 materials.  $\alpha/\gamma$ - $\text{Fe}_2\text{O}_3$  is a highly promising material due to its magnetic properties, and narrow forbidden zone, making it an ideal smart photocatalyst [3]. However, the use of these catalysts may result in pollutants in water taking the form of particles, limiting the possibility of secondary processing. Therefore, composite materials based on polymers that possess non-toxicity, biocompatibility, and chemical inertness offer significant benefits in this field. Among these, PVDF is an excellent choice as a matrix for  $\alpha/\gamma$ - $\text{Fe}_2\text{O}_3$  due to its properties.

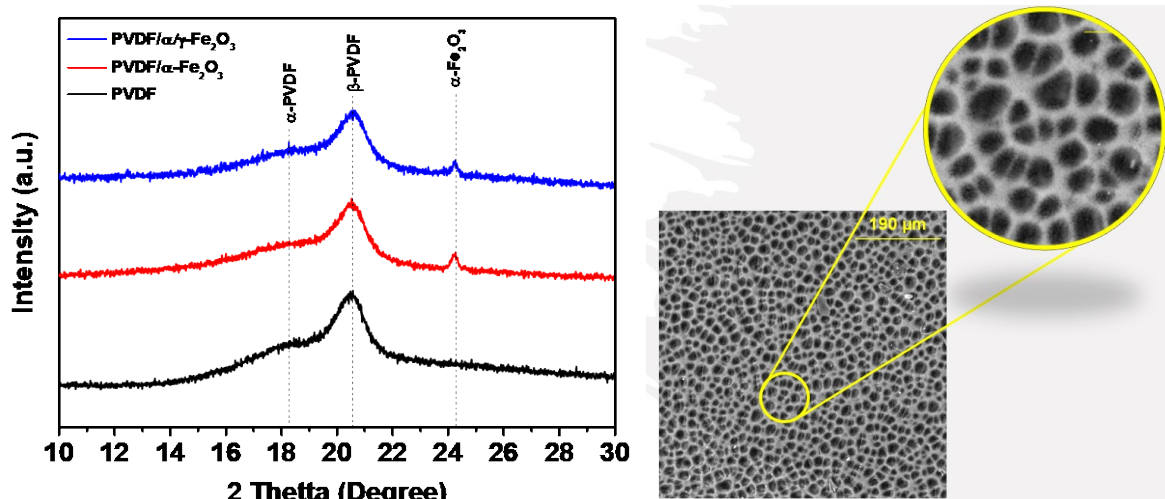


Fig.1. XRD spectra and SEM images of PVDF,  $\alpha$ - $\text{Fe}_2\text{O}_3$ /PVDF and  $\alpha/\gamma$ - $\text{Fe}_2\text{O}_3$ /PVDF membranes.

New two-phase polymer-inorganic composite films consisting of the piezoelectric polymer polyvinylidene fluoride (PVDF) and the nanocrystalline  $\alpha/\gamma$ - $\text{Fe}_2\text{O}_3$  were synthesized using the non-solvent-induced phase inversion method (NIPS).

Samples were investigated using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction analysis (XRD). Piezocatalytic experiments were conducted on a model dye Rhodamine B.

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# Poster presentations

## Effect of carbon addition on the piezophotocatalytic properties of PVDF nanofibers

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Polyvinylidene fluoride (PVDF) is a piezoelectric polymer that is one of the most attractive candidates for use as a piezocatalyst due to its high piezoelectric response and good wear resistance [1]. The polymer has at least five crystalline phases  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ . The polarization of PVDF is explained by the presence of polar crystalline phases, such as  $\beta$ -phase and  $\gamma$ -phase, among which  $\beta$  shows the largest electric dipole moment [2]. One way to increase the polarization of a polymer is to add various fillers to it [3]. One of the most popular materials for modifying PVDF is carbon [4–5].

In this work, we synthesized and studied nanofiber composites based on PVDF and various amounts of carbon flakes (0.5 wt % - PVDF0.5C and 1.5 wt % - PVDF1.5C) [5].

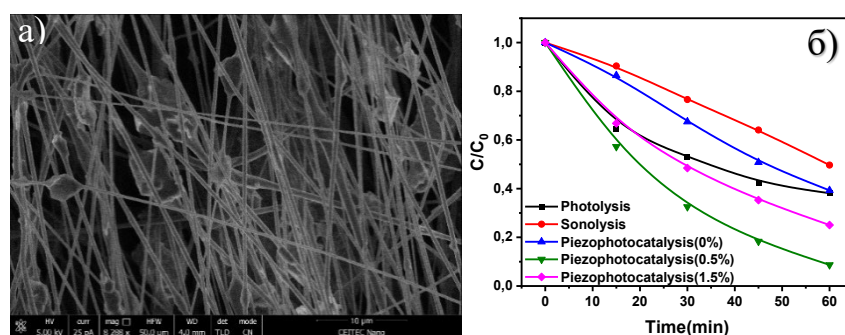


Figure 1. – a) SEM image of a composite based on PVDF and carbon flakes, b) Curves of piezophotocatalytic decomposition of MC (1 mg/l, 20 ml) depending on the exposure time to ultraviolet light.

The samples were studied by scanning electron microscope (SEM), infrared Fourier spectroscopy (FTIR), X-ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy (XPS).

During piezophotocatalytic experiments, it was found that the degree of decomposition of the dye methylene blue (MB) was 60.79%, 91.33%, 74.96% for PVDF, PVDF0.5C and PVDF1.5C, respectively. It is shown that with a mass load of graphite flakes of more than 0.5%, the piezophotocatalytic activity decreases, while the piezocatalytic activity increases.

The research was carried out with the support of the grant of the RHSF number 22-73-10091.

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# Exploring the Photocatalytic and Magnetic Properties of Zinc-Doped Cobalt Ferrite Nanocomposites with PEG and PVDF

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Dye pollutants in wastewater discharge from various industries such as textile, leather, cosmetics, digital printing, and plastics are harmful to the ecosystem because of their toxicity. Photocatalysis is a promising dye degradation technique to overcome this challenge [1,2].

This work focused on studying composites of magnetic  $\text{CoFe}_2\text{O}_4$  nanoparticles (NPs) and zinc-doped cobalt ferrite NPs coated with polyethylene glycol (PEG) and embedded into polyvinylidene fluoride (PVDF) membrane, which are promising photocatalysts due to their high chemical stability, low production cost, and unique properties. Spinel ferrites, such as  $\text{CoFe}_2\text{O}_4$  nanoparticles (NPs) are magnetic materials that have high chemical stability, high Curie temperature, and its low production cost [3]. Their magnetic properties can be enchanted by doping with other transition metal cations such as zinc. PEG with long polymer chains is highly soluble in water and largely non-toxic. In this study PEG coating of nanoparticles was used to improve homogeneity of NPs distribution in membrane. PVDF is a chemically stable, lightweight polymer with piezoelectric and dielectric properties, which frequently used photocatalysis as support for catalyst and recently it was shown its intrinsic photocatalytic properties [4,5].

Spinel ferrites NPs used as photocatalyst materials exhibit a high degradation efficiency of organic contaminants and a broad absorption band in the visible range.

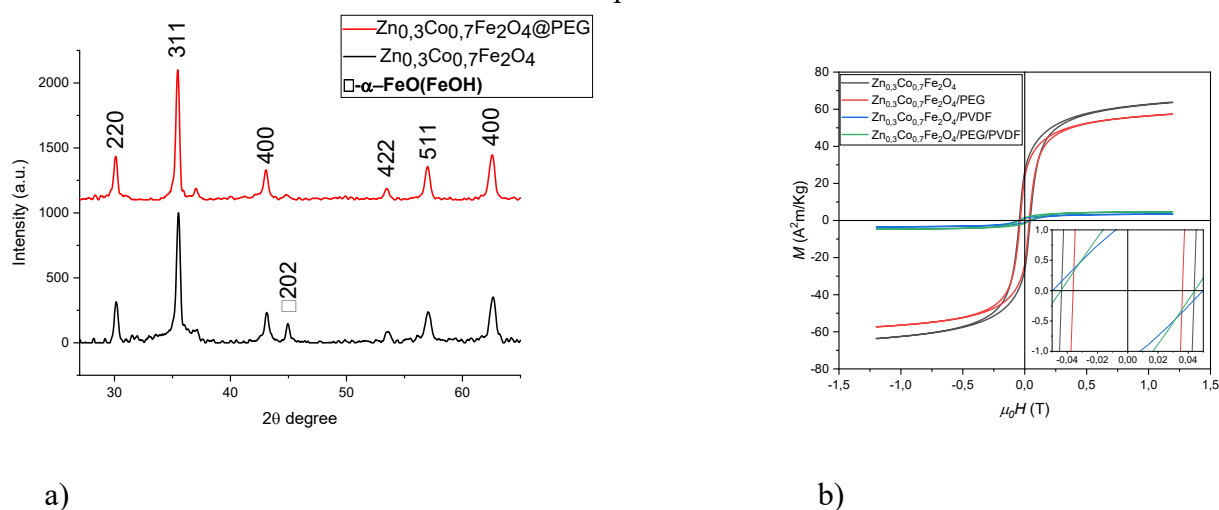


Fig. 1. a) XRD patterns of MNPs; b) room-temperature M-H loops of all samples.

This work was supported by the Russian Science Foundation under grant no. 22-22-20124.

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# Growth of high-entropy BaFe<sub>12-x</sub>(Ti<sub>x/4</sub>Mn<sub>x/4</sub>In<sub>x/4</sub>Ga<sub>x/4</sub>)O<sub>19</sub> single crystals and study of their properties

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This work is devoted to the development of a technology for growing high-entropy bulk single crystals with a magnetoplumbite structure. In the original matrix, some iron atoms are replaced by titanium, manganese, indium, and gallium. It was found that the magnetic properties of ferrites can be significantly changed by partial or complete replacement of iron cations with dopants. Thus, by changing the degree of iron substitution, we get the opportunity to control the magnetic properties of the material for a specific task. When iron is replaced by four elements at once, the value of the entropy of mixing increases. Due to this, substitution to higher concentrations of substituting elements relative to compositions with one substituent is possible.

Single crystals were grown by the method of spontaneous crystallization from solution. The solvent used was sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in an amount of 26.6 mole percent. The choice of sodium carbonate as a solvent is due to the fact that sodium is not incorporated into the crystal structure of hexagonal ferrites. The initial components for the preparation of the mixture were powders of iron oxide (Fe<sub>2</sub>O<sub>3</sub>), manganese (Mn<sub>2</sub>O<sub>3</sub>), titanium (TiO<sub>2</sub>), indium (In<sub>2</sub>O<sub>3</sub>), gallium (Ga<sub>2</sub>O<sub>3</sub>) and barium carbonate (BaCO<sub>3</sub>) having the qualification of analytical grade.

The mixture obtained was placed in a platinum crucible and heated to a temperature of 1300°C. After melting, the resulting solution was kept at the maximum temperature for 24 hours. Isothermal exposure is necessary for good homogenization of the solution. The furnace was cooled at a rate of 4.5°C/h to a temperature of 1000°C below which the cooling rate was not controlled. Separation of crystals from the solvent was carried out by boiling in an aqueous solution of nitric acid.

The crystal structure and elemental composition of the obtained single crystals were studied using X-ray powder diffraction and energy dispersive X-ray fluorescence spectroscopy (EDS). The magnetic properties were studied using a Versa Lab Quantum Design (PPMS) magnetometer in the temperature range of 50–300 K. The chemical formulas, as well as the crystal lattice parameters of the obtained single crystals, are presented in Table 1.

Table 1. Crystal lattice parameters and magnetic characteristics of the obtained single crystals.

№	Chemical formula of crystals	Lattice parameters		T <sub>c</sub> , K	H <sub>s</sub> , Am <sup>2</sup> /kg (T=300K)	H <sub>s</sub> , Am <sup>2</sup> /kg (T=50K)
		a, Å	c, Å			
1	BaFe <sub>12</sub> O <sub>19</sub>	5.897	23.219	-	71.09	100.6
2	BaFe <sub>10.20</sub> Ti <sub>0.22</sub> Mn <sub>0.76</sub> In <sub>0.58</sub> Ga <sub>0.23</sub> O <sub>19</sub>	5.929	23.369	-	52.21	83.8
3	BaFe <sub>8.71</sub> Ti <sub>0.44</sub> Mn <sub>1.16</sub> In <sub>1.25</sub> Ga <sub>0.44</sub> O <sub>19</sub>	5.954	23.529	-	48.72	49.64
4	BaFe <sub>7.14</sub> Ti <sub>0.57</sub> Mn <sub>1.77</sub> In <sub>1.79</sub> Ga <sub>0.73</sub> O <sub>19</sub>	5.979	23.693	233.4	-	23
5	BaFe <sub>5.6</sub> Ti <sub>0.64</sub> Mn <sub>2.48</sub> In <sub>2.52</sub> Ga <sub>0.76</sub> O <sub>19</sub> .	6.000	23.795	171.1	-	16

# Influence of synthesis conditions on the structural and magnetic properties of cobalt ferrite nanoparticles doped with zinc and nickel

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Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanoparticles are considered one of the most promising metal-oxide nanomaterials because of their unique magnetic properties, such as high saturation magnetization and magnetic anisotropy. From this reason, it has been successfully used in many applications such as biomedical drug delivery, magnetic resonance imaging, biosensors, etc. The morphostructural features formed during synthesis of nanoparticles determine their magnetic properties, which must be tailored to each specific application. Consequently, an important task of current research is to optimize the synthesis processes of nanoparticles to obtain them with desired properties. On the other hand, the substitution of  $\text{Co}^{2+}$  in cobalt ferrite with other transition metals allows additionally tailor magnetic properties.

This work focuses on the synthesis and characterization of cobalt oxide nanoparticles substituted by  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  metal ions, synthesized by the sol-gel method at different pH levels (2, 7 and 10) and two distinct metal-to-chelating agent (citric acid) ratios. As a result, we produced nanoparticles with compositions of  $\text{CoFe}_2\text{O}_4$ ,  $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$ ,  $\text{Ni}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$  under various conditions. X-ray diffraction (XRD) was used to investigate structural properties of samples. Magnetic properties were studied by Vibrating-sample magnetometer (VSM) at room temperature ( $\sim 300$  K). Crystal sizes were calculated by Scherrer equation.

Specifically, we discovered that the maximum saturation magnetization values were observed in samples synthesized at a pH of 2 (acidic) across all compositions (Fig. 1a). Among these, the nanoparticles with a composition of  $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$  exhibited the highest saturation magnetization, reaching  $80 \text{ Am}^2/\text{kg}$ . Concurrently, the coercivity value for these samples was minimal, at  $35 \text{ mT}$  (Fig. 1b). Our findings contribute to a deeper understanding of effect of synthesis parameter of these mixed ferrite nanoparticles on their magnetic properties and their potential applications in various fields.

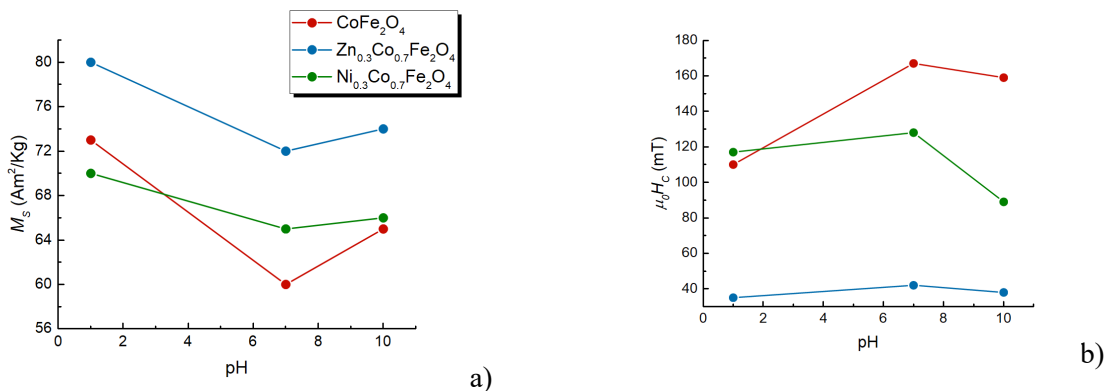


Fig.1. Dependence of saturation magnetization (a) and coercivity (b) measured at room temperature for nanoparticles  $\text{CoFe}_2\text{O}_4$  (red),  $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$  (blue),  $\text{Ni}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$  (green) synthesized with different pH.

Acknowledgments: This work was supported by the Russian Science Foundation grant No. 21-72-30032.

## **Study of the properties of a piezoelectric composite based on PVDF with different percentages of PZT particles**

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Currently, the lead zirconium titanate (PZT) despite its toxicity is actively used in many areas of the industry (electronics, sensors, etc.) and today it has one of the highest piezo responses between piezoceramics [1], while polyvinylidene fluoride (PVDF), which is non-toxic, biocompatible and flexible piezoelectric material, is also widely used in the industry (sensors, drug delivery), however, it has a rather low piezo response [2]. The aim of this work is to create a composite material with an optimal ratio of PVDF and PZT, which will allow one to obtain a less toxic flexible material with a sufficiently high piezo response.

In this study, a series of thin films were fabricated by the doctor blade method with different percentages of PZT particles in a PVDF polymer matrix from 0% to 30% in 5% increments.

The samples were characterized by differential scanning calorimetry, scanning electron microscopy, X-ray diffractometry [3]. The value of the  $d_{33}$  constant was also measured. The piezoelectric signal was measured using an STM32 F103C8T6 microcontroller and an oscilloscope using a periodic mechanical load.

The result of this work was the selection of the optimal ratio between PZT and PVDF to obtain a composite with high sensitivity and stability of the received signal.

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# Enhancing Crystallinity in CoFe<sub>2</sub>O<sub>4</sub>-PVDF Composites through Annealing with Optimized Temperature Regimes

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In recent years, the study of composite materials comprising cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) nanoparticles embedded within a polyvinylidene fluoride (PVDF) matrix has garnered significant attention in the fields of nanotechnology and biomedicine [1-2]. These multifunctional composites exhibit remarkable magnetic and piezoelectric properties, rendering them highly promising candidates for a wide range of applications, including sensors, actuators, energy harvesting, data storage, and biomedical devices. In the field of biomedicine, these composites have the potential to be employed in drug delivery systems, tissue engineering scaffolds, and implantable devices, among others. The synergistic coupling of the intrinsic properties of cobalt ferrite nanoparticles and the PVDF matrix is crucial for the realization of advanced functional materials with tailored properties and enhanced performance.

PVDF is known to exhibit several crystal phases, including the non-polar  $\alpha$ -phase, the polar  $\beta$ -phase, and the  $\gamma$ -phase. The  $\beta$ -phase, in particular, possesses strong piezoelectric properties, which are highly desirable for various applications. Therefore, understanding and controlling the formation of these crystal phases is of paramount importance for optimizing the performance of CoFe<sub>2</sub>O<sub>4</sub>-PVDF composites.

In this work, we present a comprehensive experimental investigation of the crystallinity of the PVDF matrix in CoFe<sub>2</sub>O<sub>4</sub>-PVDF composites, employing differential scanning calorimetry (DSC) as a powerful and reliable analytical tool. The crystallinity of PVDF is a critical factor influencing the piezoelectric response of the composite material, as it directly affects the alignment and ordering of the polymer chains. By systematically varying the processing parameters and nanoparticle loading, we elucidate the interplay between the CoFe<sub>2</sub>O<sub>4</sub> nanoparticles and the PVDF matrix, and its impact on the crystalline phases and overall piezoelectric performance of the composite. Our findings provide valuable insights into the optimization of CoFe<sub>2</sub>O<sub>4</sub>-PVDF composites for diverse applications, including those in biomedicine, paving the way for the development of next-generation multifunctional materials.

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# Catalytic Activity of PVDF fibers with embedded $\text{Fe}_3\text{O}_4$ nanoparticles

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In this work, the electrospinning method was used to synthesize and study the catalytic properties of PVDF nanofibers with embedded  $\text{Fe}_3\text{O}_4$  nanoparticles. PVDF is an organic piezoelectric material with ferroelectric properties that is widely used in mechanical energy collection and water treatment [1, 2].  $\text{Fe}_3\text{O}_4$  is a material with high electronic conductivity, which increases the rate of transfer of photoinduced charge carriers [3]. The resulting membrane is a non-woven mat of oriented PVDF fibers with  $\text{Fe}_3\text{O}_4$  nanoparticles included in them. A micrograph of this membrane is shown in Fig. 1a. The fibers have a non-uniform diameter. It can be seen that some of the particles form large agglomerates within the fibers.

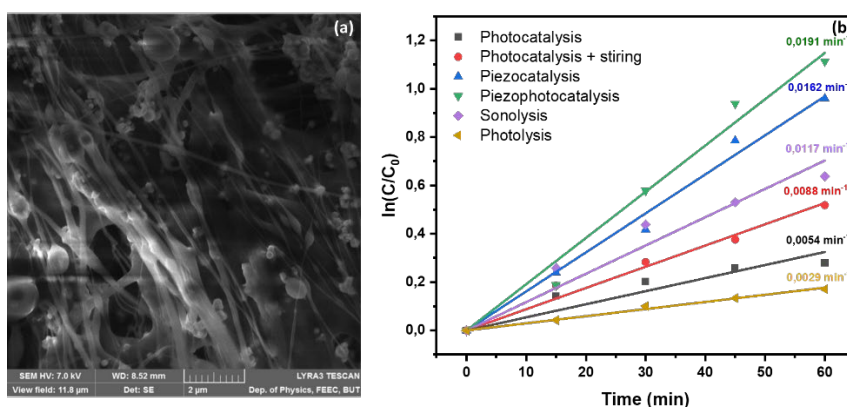


Fig. 1a) SEM-image of PVDF nanofibers with embedded  $\text{Fe}_3\text{O}_4$  nanoparticles. b) Semilog anamorphoses of methylene blue decomposition of methylene blue with PVDF/ $\text{Fe}_3\text{O}_4$ .

The efficiency of catalysis was checked by the decomposition of methylene blue (MB) with  $C=2.5\text{mg/L}$ . The light source was a 250 W high pressure mercury lamp (Philips) and a 70 W metal halide lamp (Osram). The source of mechanical action is an ultrasonic bath at 40 KHz. Figure 1b shows the decomposition rate constants MB. The decomposition efficiency was 67.2, 24.4, 62.7, and 40.5% for piezophotocatalysis, photocatalysis, piezocatalysis, and stirred photocatalysis, respectively. Also, for comparison, experiments on photolysis and sonolysis were carried out. Their efficiency was 16.7 and 48.9%, respectively.

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# Study of the piezoelectric response of PVDF-based composite films

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Magnetolectric composites are capable of producing a direct magnetolectric effect (electric polarization under the influence of a magnetic field) as well as the inverse one (to change the magnetization in response to an applied electric field). The reason for this coupling is the mechanical interaction of the ferromagnetic and piezoelectric phases of the composite. The materials of that kind provide the conversion rate several orders of magnitude greater than the single-phase magnetolectrics [1]. This implies a wide use of the composites of that kind as core elements for magnetic or electric fields sensors [2, 3], energy collection devices [3], smart supports for tissue engineering [4], etc. As the piezoelectric polymers of the PVDF family are well biocompatible, they fit very well the requirements for the piezo phase of the magnetolectric composites destined for constructing “smart scaffolds” for e.g. animal/human bone regeneration. Indeed, a support capable of inducing surface charges in response to an applied magnetic field enables one both to enhance the precipitation rate of the osteogenic stem cells from the environment and to create more favorable conditions for the cell differentiation and, then, proliferation.

To get a PVDF-based composite with good electric characteristics, it is necessary to have a polymer with maximal concentration of its piezoactive isomer (so called  $\beta$ -phase) and also to make this piezoelectric phase oriented. These characteristics might be modified both at the stage of manufacturing and at the stage of post-processing the obtained material [4]. Due to a number of external and internal factors, which affect the synthesis, the actual values of the magnetolectric parameters of the resulting samples (we prepare films) are predictable only by the order of magnitude. For a more precise characterization, each sample needs to be tested as itself.

One of the key properties that is crucial for the interpretation of experiments as well as essentially involved in theoretical modelling [5] is the effective constant  $d_{33}$  of the prepared composites. In the present work we report the dependence of parameter  $d_{33}$  of home-made magnetolectric PVDF-based films on the concentration of cobalt ferrite nanoparticles and the parameters of the electric poling of the film.

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# Thermomagnetic Treatment of the Magnetostrictive Component of Magnetolectric Composites

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Currently, studies of the magnetolectric (ME) effect in structures using magnetostrictive and piezoelectric materials are being actively carried out. In such structures, the ME effect is the result of the interaction of the magnetostrictive and piezoelectric phases, i.e., electric polarization is induced by an external alternating magnetic field in the presence of a bias field. One of the most important tasks is to increase the sensitivity of various sensors, where the ME composite is used as a sensitive element. Studies carried out in this direction show that it is possible to increase the magnitude of the ME effect when the amorphous structure of a magnetostrictive material passes into a partial nanocrystalline state during heat treatment [1].

An experimental study of heat treatment in terms of the ME coefficient is carried out on magnetostrictive-piezoelectric ME structures. As the magnetostrictive phase of the ME composite, we used the amorphous alloy AMAG493. Metglas were subjected to heat treatment in a muffle furnace. The wafers were placed in the heating area and heated to a predetermined temperature for 15 min. Then, Metglas was kept at a given temperature for 60 min, and then the plates were cooled to room temperature. After Metglas heat treatment, six plates of magnetostrictive material were glued to each PZT plate (piezoelectric material), three plates on each side. And then samples were dried for 24 h.

Figure 1 shows the experimental values of the ME voltage coefficient in the resulting composite structures. The measurements were carried out using a lock-in amplifier MFLI.

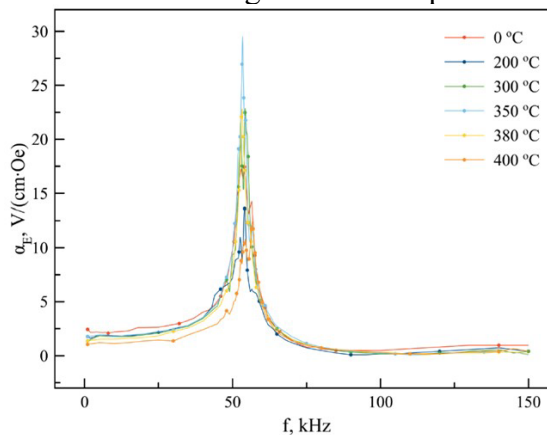


Figure 1. The dependence of the ME voltage coefficient on frequency.

As can be seen from the Figure 1, during the heat treatment of the magnetostrictive component, a significant increase in the value of the ME voltage coefficient is observed. The maximum value of the ME coefficient for samples after heat treatment at a temperature of 350 °C was 29.52 V/(cm·E) at a longitudinal resonance frequency of 53.4 kHz, without heat treatment, the resonance value of the ME coefficient on these samples was 17.44 V/(cm·E). As a result of the experiment, we note that the increase in the value of the ME voltage coefficient due to heat treatment was ~70%. Further research will be aimed at studying the process of nanocrystallization in amorphous magnetic alloys.

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# Angular dependence of the microwave magnetoelectric effect in the ferroelectric-ferromagnetic structure

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Recently, interest has arisen in conducting experiments to study the influence of the magnetic anisotropy of a single crystal of yttrium iron garnet (YIG) on the microwave magnetoelectric effect (ME).

It is necessary to take into account the crystallography of ferrite in layered structures of the ferroelectric-ferromagnet type. The ME effect in the region of ferromagnetic resonance (FMR) consists in the shift of the resonance line under the action of an electric field and is called the microwave ME effect. The cubic anisotropy of YIG single crystals affects the frequency and width of the FMR line, and in layered structures with lead zirconate titanate (PZT) it affects the shift of the resonance line [1].

In the experiment, a YIG disk with an arbitrary crystallographic plane, for example, (111), and a PZT plate are placed in a microwave field  $\vec{h}(t)$  along the OZ axis and a magnetic field  $\vec{H}$  along the OY axis (Fig. 1). If the condition  $\vec{h}(t) \perp \vec{H}$  is satisfied, FMR arises, and coupled magnon-phonon modes are excited in the two-layer structure. By rotating the structure along the OZ axis by an angle  $\varphi$ , due to the crystalline magnetic anisotropy, one can find the orientation of the magnetic field with the highest value of the ME constant  $\mathbf{A}$  and a narrow FMR line, which is planned to be studied in detail in this work within the framework of the theory of two-magnon scattering [2].

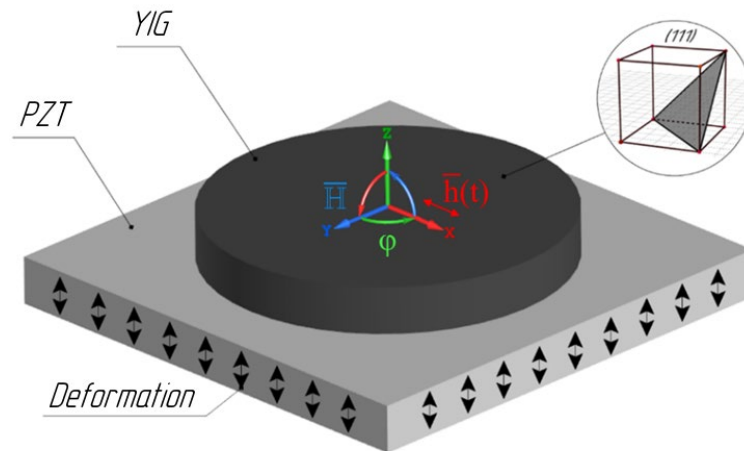


Figure 1. Variant of layered ferrite-ferroelectric structure.

It is planned to study the factors that affect the most important parameters of ME resonators based on YIG and PZT, as well as discuss the experiment and perform a calculation explaining the mechanism of the appearance of the angular dependence, which will improve the characteristics of microwave devices based on the ME effect.

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# FORC -analysis of magnetic behaviour in magnetic polymer-based composites

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First Order Reversal Curve (FORC) analysis is on top of popularity to describe magnetic interactions in ferromagnetic materials [1]. The measurement of sets of FORCs provides detailed information from different paths of magnetization, which enables the determination of the Switching Field Distribution (SFD) and interaction fields for all the phases that contribute to the hysteresis loop [2].

This work provides deepen analysis of magnetic behaviour within FORCs study for different magnetic polymer-based composites containing: (i) hard magnetic nanoparticles (CFO), (ii) hard magnetic nanoparticles with additional piezoelectric inclusions BaTiO<sub>3</sub> (BTO) and (iii) mixture hard magnetic nanoparticles (CFO) and magnetic soft ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles. For each composite sample, 150 FORC curves were measured at room temperature on a LakeShore vibrating magnetometer.

It was shown that for the composites with only CoFe<sub>2</sub>O<sub>4</sub> nanofiller, two magnetic phases are present, due to the distribution of particles in the matrix in such a way that finely dispersed nanoparticles remagnetize in a near-zero external magnetic field creating a magnetically soft phase, and nanoparticles knocked into aggregates remagnetize in high fields and have a wide range of switching fields, which indicates the presence of a strong dipole–dipole interactions between the aggregates.

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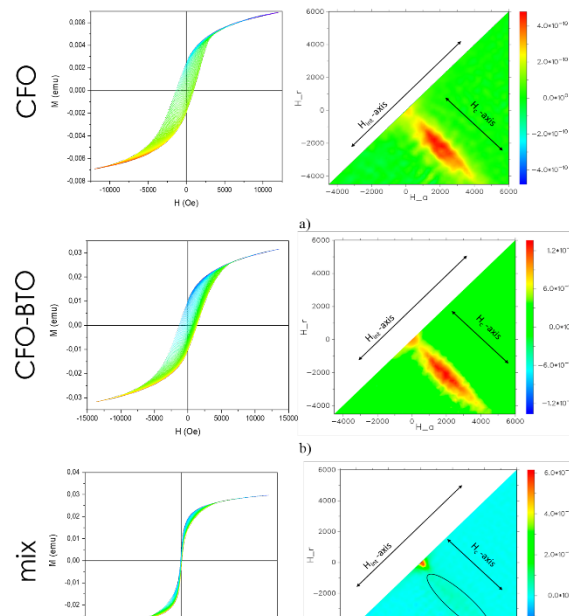


Figure 2. FORC-curves and FORC-diagrams for nanocomposites

## The synthesis of iron-cobalt nanowires of calibrated size in polymer matrices and the study of the magnetic hyperthermia effect.

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The study of ferromagnetic nanostructures currently represents significant scientific interest due to the wide range of potential applications. The heating of nanostructures is used in many industries, including biomedical research, environmental science, and new materials. This method is based on the conversion of magnetic energy into thermal energy, which allows it to be used for various technological processes.

The use of ferromagnetic nanostructures as therapeutic agents has shown promise for biomedical applications, such as the destruction of cancerous tumors. The introduction of such structures into the body at the site of oncology and subsequent heating with a variable magnetic field for a certain period of time allows for controlled therapy. The necessary magnetic parameters, in particular coercive force ( $H_c$ ), are achieved by regulating the composition and aspect ratio of the nanowires (NW). The dependence of the magnetic properties and heating power of an array of NWs on their aspect ratio (diameter-to-length ratio) was studied.

Arrays of  $Fe_{0.92}Co_{0.08}$  NWs were obtained in PETP track membranes. Matrices with loosely oriented pores (average slope of 10 degrees) of two different diameters – 100 nm and 65 nm, with pore densities of  $1,2 \cdot 10^9$  pores/cm<sup>2</sup> and  $4,5 \cdot 10^9$  pores/cm<sup>2</sup>, respectively, were used. The synthesis of nanoparticles was carried out by electrochemical deposition using a two-electrode scheme in a potentiostatic mode. The electrolyte used contained  $Fe^{2+}$  and  $Co^{2+}$  ions in the required ratio.

The magnetic properties were studied using vibrational magnetometry. The heating of NWs was carried out using an infrared camera and a variable magnetic field generator.

A nonlinear change in coercive force along the length of NWs was detected in samples of both diameters. The heating power increases with the length of NWs and also has higher values in samples with a diameter of 100 nm. The highest heating temperatures (55 °C) and the highest heating efficiency ( $SAR = 4709$  W/g and  $ILP = 0.030$  nH·m<sup>2</sup>/kg) were demonstrated by samples with the largest diameter (100 nm) and the greatest length (5.2 μm). Moreover, the use of multiple matrix samples increases the heating temperature of the system, while all heating efficiency indicators remain approximately the same as compared to a single sample.

But based on biomedical considerations, the most suitable sample can be considered to be the one heated to 42 °C (diameter 100 nm, length 4.2 μm), with  $SAR = 3302$  W/g and  $ILP = 0.021$  nH·m<sup>2</sup>/kg.

# The property specifics of the CrFeCoNi(Al,Ti) high-entropy alloys produced by additive manufacturing

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In 2004, a new class of materials called high-entropy alloys was introduced [1]. The first alloy discovered in this category was CrFeCoNiMn, which exhibits exceptional strength-ductile properties at cryogenic temperatures (achieving up to 1 GPa strength and 60% elongation at 77 K) [2]. However, the mechanical properties of this alloy weaken significantly at high temperatures and do not surpass those of conventional austenitic steels. To enhance the alloy suitability for high-temperature applications, aluminum and titanium have been added as alloying elements, resulting in the development of the AlCoCrFeNiTi alloy. This new alloy boasts a tensile strength of 590 MPa and elongation of over 40% at 700°C [3]. However, further research is needed to optimize the composition for desired property combinations. Furthermore, most studies on HEA materials have focused on small workpieces, whereas industrial applications often require the production of larger items.

The use of additive manufacturing (AM), or 3D printing, allows for the fabrication of large parts. This technique is becoming increasingly popular due to its ability to create complex geometries while saving time and feedstock material. Powder bed fusion (PBF) is a commonly used AM technique that utilizes metal powder as the stock material for printing solid parts. However, the production of new materials presents challenges for manufacturers of metal powders, who typically provide only conventional alloy compositions. To address this limitation, there is a growing trend in the AM field towards using metal powder blends or in situ printing to build solid parts [4],[5].

The focus of this study is to explore the feasibility of using a powder bed fusion (PBF) technique to produce CrFeCoNi(Al,Ti) alloys. This involves utilizing blends of aluminum, titanium, and CrFeCoNi powders to create solid parts and analyzing the characteristics of the printed material. The elemental distribution in the printed alloys was examined both in their as-built state and after undergoing various heat treatments using scanning electron microscopy (SEM) methods. The evolution of phase composition in response to changes in the chemical composition of the CrFeCoNi(Al,Ti) alloys was also analyzed using X-ray diffraction and SEM techniques. Additionally, the microhardness and tensile mechanical properties of the alloys were evaluated before and after undergoing heat treatment at 800°C.

The results of the structural and phase investigations showed that the chemical heterogeneity in the materials led to the formation of new phases that affected their mechanical characteristics. This is more obvious for the PBF CrFeCoNiAlTi alloy compared with the PBF CrFeCoNiAl alloy. High-temperature annealing at 1200°C was found to be an effective post-treatment process for the printed alloys, as it homogenized the material. In contrast, annealing at a lower temperature of 800°C initiated the partial decomposition of the initially formed face-centered cubic structure into the body-centered cubic structure.

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## Magnetolectric Magnetic Field Sensors

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Magnetolectric (ME) composites are functional materials that are created on the basis of various physical effects and, along with semiconductor materials, determine the progress of electronic materials science today. The ME effect in composites, as is known, consists in the induction of electric polarization in an applied external magnetic field or, conversely, in magnetization by an external electric field, and is the result of the interaction of the electric, magnetic, and elastic subsystems of the composite. Compared to single-phase materials, composites show a giant ME response at room temperature and are ready for practical applications. The required high values of the ME coefficients can be obtained by choosing components with high piezoelectric and piezomagnetic modules. At present, a large number of works are known that are devoted to the wide study of ME composites with the aim of their application in magnetic field sensors [1].

As known, most of the studies of ME magnetic field sensors were carried out on the basis of such components as piezoelectric PZT, PMN-PT, lithium niobate and magnetic Terfenol, and Metglas in the linear ME effect mode. At the same time, it should be noted that in recent years, original works have appeared in which new approaches were used and high characteristics of sensors were obtained. In particular, the magnetostrictive component was replaced by a NdFeB magnet [2], then a miniature and highly sensitive MEMS structure [3], and NEMS and nanoresonator [4] for biomedicine were proposed, and a nonlinear regime and new components such as piezoelectric AlN and soft magnetic Ni [5] were used. In addition, new possibilities for developing sensors on the basis of the  $\Delta E$ —effect have been discussed [6].

Further, of note are the results of the group of Prof. D. Viehland, who significantly advanced our knowledge of ME magnetic field sensors and their capabilities. Dong et al. showed that L-T mode in the structure Terfenol-PMN-PT has extremely high magnetic field sensitivity: at room temperature, an output ME voltage with a good linear response to magnetic field  $H_{ac}$  was found over the range of  $10^{-11} < H_{ac} < 10^{-3}$  T. Then, a number of articles was published in which the authors of this group applied new ideas: the use of push–pull and bimorph structures to increase a ME effect and sensitivity by reducing the vibrational and thermal noises, and the transition to higher signal processing frequencies, which made it possible to significantly increase the sensitivity of sensors and achieve a pico-Tesla sensitivity of a sensor at room temperature. The sensitivity limit was about 20 pT/Hz<sup>1/2</sup> or  $2 \times 10^{-16}$  C/Hz<sup>1/2</sup> at 1 Hz, and about 2 fT/Hz<sup>1/2</sup> at 78 kHz in the EMR range. Extremely low values of the equivalent magnetic noise of 6.2 pT/Hz<sup>1/2</sup> at a frequency of 1 Hz were obtained on a heterostructure consisting of a PMN-PT bimorph doped with 1% Mn and longitudinally magnetized Metglas layers. As the frequency increased to 10 Hz, the equivalent magnetic noise significantly decreased and amounted to  $<1$  nT/Hz<sup>1/2</sup>.

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## Modeling of magnetoelectric microwave devices

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Many studies of the ME effect have been carried out in the microwave range in connection with the possibility of creating new electronic devices. One of the main microwave ME effects is the shift of the FMR line in an electric field, on the basis of which the operation of magnetoelectric microwave devices is based [1, 2].

Despite significant progress in the field of ME research in composite materials, there are problems that prevent the transition from fundamental research to the development of devices - it is necessary to develop the basis for designing these devices based on the obtained composite ME materials. Currently, there are only a few models of such devices. As follows from information sources, as a result of research, the experimental samples obtained have insufficient sensitivity, low speed, small tuning range, relatively large dimensions, and are not technologically advanced.

Therefore, with a deep and comprehensive study of the features of the processes during the formation of ME structures and directly ME composite materials, as well as the development of physical principles for creating microwave devices based on the studied composites, it is necessary to carry out computer and theoretical modeling to develop and create new ME microwave devices.

In turn, the appearance on the market of ME microwave devices based on the ME effect will contribute to the development of domestic electronics. An analysis of the materials of foreign and domestic scientific and technical literature shows that over the past decade there has been a steady growing interest in ME devices in a wide frequency range.

In this work, it is planned to simulate magnetoelectric microwave devices, such as a two-section microstrip filter, a phase shifter, and a circulator.

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# Enhancement of magneto-optical activity enabled by Goos-Hänchen effect in magnetoplasmonic crystals

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Magneto-optical Kerr effects play an important role in modern nanophotonics. Since the values of magneto-optical effects are smaller than 0.1% for common magneto-optical active materials, enhancing these effects is a major challenge in modern magneto-optical research. Nanosystems with combined magnetic and plasmonic properties are promising for this purpose.

This work was dedicated to the experimental study and numerical simulation of the magnetic-field-induced modulation of the Goos-Hänchen effect in the one-dimensional all-nickel magnetoplasmonic crystal (MPC), resulting in an increase of the modification of the reflected light intensity.

The study utilized the MPC — a one-dimensional nickel periodic grating that supports the excitation of surface plasmon-polaritons (SPPs). SPPs are coupled oscillations of electrons and light propagating at the metal/dielectric interface [1]. The work is based on two effects. The Goos-Hänchen effect (GH) is the longitudinal displacement of the reflected light beam relative to the position determined by the geometric optics [2]. This effect is enhanced by the excitation of SPPs and can be modulated by adding magnetic materials. The second effect is the transverse magneto-optical Kerr effect (TMOKE), characterized by changes in the phase and intensity of the light reflected from a magnetized medium.

The experimental results are confirmed by numerical simulations (Ansys Lumerical FDTD). When SPPs are excited, both the experimental and simulated GH effect, which is a distance between the non-resonant reflected and shifted beam, reaches of 15.3  $\mu\text{m}$ .

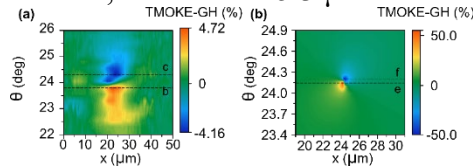


Figure 1. 2D map of the angular dependence of the TMOKE-GH:  
(a) – experimental results, (b) – numerical simulations.

When applying an external magnetic field to the MPC, the spatial distribution of the reflected beam intensity  $I(x)$  changes that we called combined TMOKE and GH effect (TMOKE-GH), which is defined by following equation:

$$\text{TMOKE - GH} = 2 \cdot \frac{I(x, H) - I(x, -H)}{I(x, H) + I(x, -H)} \cdot 100\% \quad (1)$$

In the range of light incident angles ( $\theta=23.3^\circ-24.3^\circ$ ) corresponding to SPP excitation, the maximum experimental value of the combined TMOKE-GH effect is observed. It reaches 4.7% and -4% (Figure 1(a)). The maximum simulated values of the TMOKE-GH are 55.5% and -50% (Figure 1(b)). The observed values of the combined TMOKE-GH exceed the conventional measurements of TMOKE: for a Gaussian beam, by a factor of 2.6, and for a plane wave source — by 5.9.

Thus, this study demonstrates that the combined effect of TMOKE-GH is superior to the conventional TMOKE. This discovery has the potential to enhance the functionality of magnetoplasmonic devices, such as sensors and light modulators.

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# Theoretical investigation of ring-shaped magnetoelectric composites Metglas/PZT/Metglas

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The direct magnetoelectric (ME) effect, which is a reaction of electric polarization to an applied magnetic field, can be used in the design of various devices, including contactless current sensors. ME composites of disk, square or rectangular geometry are suitable only for detecting magnetic fields of a fixed direction. In practice, vortex magnetic fields are more common, for example, in electrical cables. A ring-shaped ME structure is ideal for detecting vortex magnetic fields of current-carrying cables.

In [1], the resonant mode of electromechanical oscillations in a ring-shaped piezoelectric structure was investigated and a corresponding mathematical model was given. This theoretical model was adapted to the studied ring-shaped ME structure Metglas/PZT/Metglas and an expression for the output voltage (1) was obtained.

$$U = \frac{{}^m\nu q_{11} d_{31} {}^p c^D {}^p t}{\varepsilon_{33} \varepsilon_0 {}^m s_{11} (c - \rho R^2 \omega^2)} h_1 \quad (1)$$

In Figure 1, one can see the dependence of the output voltage on the frequency for two structures differing in the number of Metglas layers.

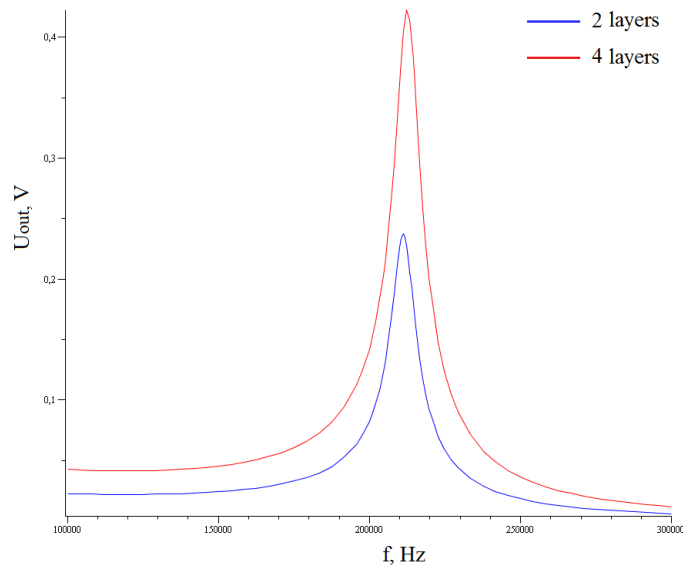


Figure 3. Dependence of the output voltage on the frequency.

As can be seen from Figure 1, with an increase in the number of Metglas layers by 2 times, the output voltage increased almost 2 times, while the resonant frequency changed slightly. The obtained theoretical model correlates well with the experiments conducted in [2].

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# Comparison of magnetic nanoparticles $Fe_3O_4$ modified with Sodium Dodecyl Sulfate and with Polyacrylic Acid for Methylene Blue Adsorption

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Dyes are widely used in various industries, including dyestuffs, paper, textile, cosmetic and others, leading to significant water contamination. Most of the dyes are toxic and have mutagenic and carcinogenic effects influencing the health of human, plants, and aquatic beings [1,2]. Among them, methylene blue (MB) is a cationic dye commonly used for dyeing of cotton, wood, and silk. Therefore, the treatment of effluent containing such dye is of interest owing to its harmful impacts on receiving waters. Magnetic nanoparticles (MNPs) have been extensively studied as suitable adsorbents with large surface area and small diffusion resistance for the separation and removal of such dyes [3].

In this study, sodium dodecyl sulfate-coated  $Fe_3O_4$  MNPs ( $Fe_3O_4@SDS$  MNPs) and polyacrylic acid-bound iron oxide MNPs ( $Fe_3O_4@PAA$  MNPs) were selected as inexpensive and efficient solid supports for the removal of MB from aqueous solutions [4]. The MNPs were synthesized by classical coprecipitation method followed by surface modification to obtain stable aqueous suspensions of MNPs coated by different surfactants. The synthesized MNPs were characterized using XRD (X-Ray diffraction), SEM (scanning electron microscope) and VSM (vibrating-sample magnetometer).

Several effective experimental parameters on the performance of dye adsorption, such as pH, amount of surfactant and  $Fe_3O_4$  MNPs, adsorption time were investigated to find optimal conditions for MB adsorption. The removal percent and absorbed amount of MB were determined by spectroscopic method of the sample solution at the wavelength (664 nm) corresponding to the maximum in the light absorbance of MB.

Thus, modified MNPs are an efficient and easy-to-use method for removing cationic dyes from water.

This work was supported by the Russian Science Foundation under grant no. 22-22-20124.

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# Investigation of Magnetic Properties in Cobalt-Doped Nickel Ferrite Nanoparticles: A Comprehensive Study Using Advanced Characterization Techniques

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In this study, we present a detailed investigation of the magnetic properties of equisized 6-nm cobalt-doped nickel ferrite nanoparticles. The nanoparticles were synthesized by thermal decomposition method with varying cobalt content, allowing us to explore the influence of cobalt doping on the magnetic behavior of these materials. The structural characteristics of the nanoparticles were examined using X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM), confirming the successful incorporation of cobalt into the spinel structure keeping the same particle size and morphology. The magnetic properties were thoroughly investigated, that provided a comprehensive understanding of the magnetic behavior of the cobalt-doped nickel ferrite nanoparticles. Our findings reveal a significant enhancement in the magnetic properties (saturation magnetization and anisotropy) with increasing cobalt content, suggesting the potential of these nanoparticles for various applications in magnetic storage, spintronics, and biomedical fields [1-3].

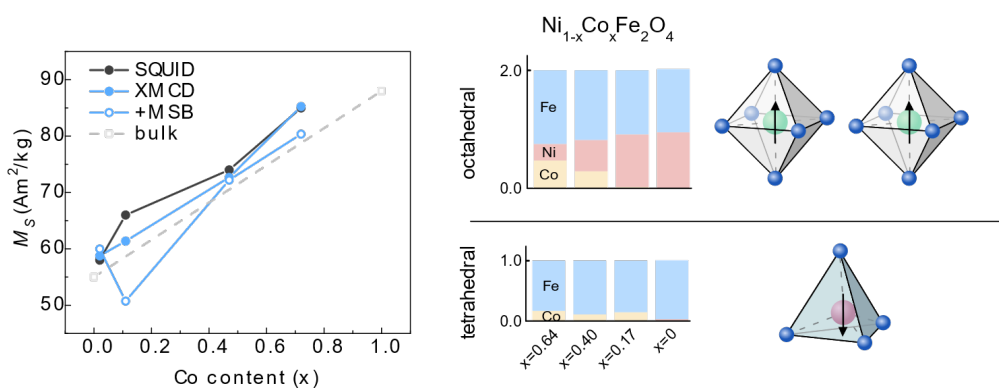


Figure 1. Dependence of saturation magnetization as functions of Co content in  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  nanoparticles measured by a set of experimental techniques and a schematical representation of distribution of Fe, Ni and Co cations in octahedral and tetrahedral sites of the spinel ferrite structure with different cobalt content.

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## Effect of bismuth ferrite nanoparticle concentration on the magnetic and structural properties of PVDF-based composites

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Multiferroic materials with ferroelectric and ferromagnetic properties are applicable in various fields, including biomedicine [1]. There are just few natural materials that possess multiferroic properties, among them the most frequently studied is bismuth ferrite ( $\text{BiFeO}_3$ ) with perovskite crystal structure. Bismuth ferrite possess weak ferrimagnetic properties and one of the important tasks is to increase it by varying magnetic structure of bismuth ferrite itself or by creating composite materials. On the other hand, polymer-based multiferroics have some advantages over their inorganic counterparts, such as low density, flexibility, and ease of processing [2].

In this work, we synthesised  $\text{BiFeO}_3$  nanoparticles by the sol-gel method and we focus our research on studying the effect of  $\text{BiFeO}_3$  nanoparticle concentration on the magnetic and structural properties of polyvinylidene fluoride (PVDF)-based composites. PVDF can exist in several crystalline phases, among which the  $\beta$ -phase exhibits the highest piezoelectric activity, making it more favorable to produce multiferroic composites. One approach to enhance the formation of  $\beta$ -phase is adding of  $\text{BiFeO}_3$  nanoparticles which may act as nucleating agents during the solvent casting process of composite formation [3].

The composite consisting of PVDF matrix with the inclusion of  $\text{BiFeO}_3$  nanoparticles was characterized using Scanning Electron Microscopy (SEM) for microstructural features, X-ray Diffraction (XRD) to investigate its structural properties, and Vibrating Sample Magnetometry (VSM) to evaluate its magnetic properties. At the next stage of research, we plan to produce bismuth ferrite nanoparticles doped with other transition cations to enhance their magnetic properties thus increasing multiferroic properties of derives composite samples.

**Acknowledgement:** This work was supported by the Russian Science Foundation, grant 21-72-30032. We acknowledge the Centre for development of gifted children (Kaliningrad) for provision of XRD measurements.

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# Tailoring Magnetic Properties of Cobalt Ferrite Nanoparticles with Bi-Modal Size Distribution

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Ferrimagnetic particles have attracted significant attention due to their unique magnetic properties and potential applications in various fields, such as magnetic hyperthermia, magnetic biomedical imaging, or perform as a nanocomposite magnet [1,2]. Understanding the magnetic properties of ferrimagnetic particles is crucial for tailoring their performance in technological applications. One strategy for tuning magnetic properties is to mix particles with different chemical compositions or sizes.

In this work, the cobalt ferrite magnetic nanoparticles (MNPs) were synthesized with different reaction times ranging from 8 to 12 hours using a hydrothermal method and sodium dodecyl sulfate (SDS) surfactant[3]. Transmission electron microscopy revealed two distinct fractions of particles with different sizes. X-ray diffraction was employed to determine the crystal structure. As well, we have performed detailed characterization of magnetic properties using vibrating sample magnetometer, inter alia, we used techniques as First Order Reversal Curves (FORCs), Isothermal Remanent Magnetization (IRM), and Direct Current Demagnetization (DCD) [4].

Our results showed that as the synthesis time increased from 8 hours to 12 hours, the coherent scattering region of X-rays remained constant, while the size of fine particles had increased over time, which increased the dipole interaction, besides, microstrain decreased in the system. At the same time, the coercive force increased from 698 Oe to 1573 Oe. This can be explained by an increase in the crystallinity of the system and the approach of a fraction of fine particles from superparamagnetic to blocked state.

The results provide valuable insights into the correlation between the structural and magnetic properties, enabling the performance of ferrimagnetic particles with tailored magnetic interactions.

This work was financially supported by the Russian Science Foundation (grant No. 21-72-30032). We would also like to acknowledge the Center for Gifted Children (Kaliningrad, Russia) for providing the opportunity to conduct X-ray diffraction measurements.

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# **Influence of modification of the surface of the fabric filler on the physical and mechanical properties of the silicone composite material**

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In this work, silicone modified with an electrically conductive carbon filler (carbon nanotubes) was chosen as the PCM matrix. Previously, we studied this matrix for changes in the value of resistivity during deformation. Carbon fabric, as the basis of a flexible and electrically conductive membrane shell, is used to reinforce a nanocomposite material. However, after curing, the silicone as a matrix had poor adhesion to the carbon fabric used as a reinforcing filler. To increase the adhesion between the silicone binder and the carbon fabric, a surface modifier was used - a solution of 3-aminopropyltriethoxysilane (APTES). However, the effect of surface modifier concentration on the change in tensile strength has not been studied. The results of the study will be presented in this paper. The objects of study were PCM samples based on Aspro A-60 carbon fabric (Aspro, Russia). Carbon tissue was pre-treated with a solution of APTES (Acros Organics, Belgium) in chloroform with concentrations: 5; 10; 15; 20; 25 and 30%. Silicone (WACKER, Germany) with a concentration of 1 wt % of a conductive concentrate based on single-wall carbon nanotubes MATRIX 601 (OCSiAl, Russia) was used as a matrix for PCM to impart electrically conductive properties to the material. The removal of the solvent from the surface of the fibrous material was carried out in a drying oven at a temperature of 80°C for 2 hours.

The PCM samples were plates 110 × 20 mm in size, with a thickness of 0.2...0.5 mm. Mechanical tensile testing of PCM samples was carried out at least 24 hours after gluing under quasi-static loading conditions on a Eurotest T-50 universal testing machine (S.A.E. IBERTEST, Spain). The load was created at a constant speed of 5 mm/min. Five samples of PCM were tested for each selected concentration of APTES solution according to GOST 25.601-80 [1].

APTES pretreatment of carbon fabric has a significant effect on the tensile strength of PCM samples. The concentration of the APTES modifier of the properties of the composite is different, as follows: at 5%, an increase in the tensile strength by 4 times is observed; at 10%, an increase in tensile strength was noted: 6 times (maximum); from 15 to 30% - there is a decrease in the ultimate strength of PCM samples, up to the values of untreated APTES carbon fabric.

## Acknowledgements

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# Composite polyvinylidene fluoride-( $\text{CoFe}_2\text{O}_4$ , $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$ ) filament for 3D printing

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A new class of "smart" materials, known as multiferroics, in which there is a pronounced, in particular, interrelation of magnetic and electrical subsystems, is being actively studied and has prospects for practical applications in power engineering, sensorics, microelectronics, and biomedicine [1, 2]. The magnetoelectric (ME) effect, is the appearance of electric polarization (P) induced by the magnetic field (H) and vice versa. One of the technologies for creating magnetoelectric multiferroics is the introduction of magnetic particles into the piezoelectric matrix. Composites obtained from piezopolymer polyvinylidene fluoride (PVDF) with incorporated magnetic nanoparticles (MNP) [1, 2] have demonstrated ME coefficient  $\alpha_{33}$  in the range  $5\text{-}20 \text{ mV} \times \text{cm}^{-1}\text{Oe}^{-1}$ .

In this work, we explore methods of 3D printing of PVDF-MNP composites, as additive manufacturing technologies can streamline production and reduce the number of required steps in fabricating parts and devices with ME effect. Composite filaments for fused deposition modeling (FDM) printing (layer-by-layer from the bottom up by heating and extruding thermoplastic filaments) were produced by extruding films obtained from polymers with different molecular weights ( $\sim 70\text{k}$  and  $\sim 500\text{k}$ ) as well as with different contents of and CFO ( $\text{CoFe}_2\text{O}_4$ ) and ZCFO ( $\text{Zn}_{0.3}\text{Co}_{0.7}\text{Fe}_2\text{O}_4$ ) MNPs (5-15 wt.%).

Our results showed that an optimal particle content of 10% improves the sample's crystallinity without negatively impacting the composite's mechanical properties. Additionally, utilizing a polymer with a lower molecular weight reduces the melting temperature and prevents cracking during cooling after printing.

This work was supported by the Russian Foundation for Basic Research (RFBR) according to the research project No. 21-72-30032

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## Radioisotope Power Supply for Perspective Electronic Devices Based on ZrO<sub>2</sub> Nanoparticles

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At the present stage of electronics development there is a tendency to reduce the size and power consumption of radioelectronic devices, Subvolt nanoelectronics and microsystems technology is gaining more and more mass. Accordingly, the requirements to power supplies are changing: the power requirements are decreasing, but the service life and size become critical, and most importantly - scalability to the low size range, if possible - flexibility and transparency, as well as - cost-effectiveness and manufacturability. The main of these requirements, in particular, the service life of autonomy are satisfied only by radioisotope power sources.

The working idea of this work is to use radiolysis and high chemical activity of the nanoparticle surface to convert chemical energy into electric energy.

The aqueous surface of nanoparticles with a radioactive core is actually a nanoreactor of ions and radicals. In this work, ZrO<sub>2</sub>-based nanoparticles with a small content (3 mol%) of Y<sub>2</sub>O<sub>3</sub> were taken as the core. [1]

The study was performed in the scope of the RO-JINR project No. 366 / 2021 item 81, RO-JINR grant No. 367 / 2021 item 27, Poland-JINR cooperation Projects PPPB/168-26/1128/2021, PPPB/120-25/1128/2022, PPPB/120-26/1128/2022, Serbia - JINR cooperation Projects № 178 2021 items 7 and 8, JINR-Belarus Cooperation Program, Order No. 529, paragraphs 22 and 23, JINR-Vietnam Cooperation Program Order 906 items 4.

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# Green emissive N-doped carbon dots functionalized with L-cysteine for pH and Hg-ion sensing by change in both photoluminescence and circular dichroism signals

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## 1. Introduction

The detection of heavy metals is of great interest due to their impact on the ecological systems and biological objects, including human health [1]. Thus, the development of nanomaterials with sensory properties has attracted scientific attention because of the demand for low-cost colloidal probes with high sensitivity. Carbon dots (CDs) are promising candidates for these applications as they demonstrate unique optical properties as bright emission, biocompatibility, and ease of fabrication.

## 2. Methods

### 2.1 Sample synthesis

The CDs were synthesized by the solvothermal synthesis method from citric acid and urea in dimethylformamide. Precursor mixtures were heated at 180°C in Teflon-lined stainless-steel autoclaves for 8 h. After the reaction, the autoclave was naturally cooled down to room temperature. To remove unreacted precursors and molecular fluorophores, the filtered solutions were transferred to a dialysis tube with a molecular weight cut-off of 3500 Da and left for dialysis for 24 h. The conjugation of CDs with L-cysteine molecules was performed by carbodiimide coupling (EDC/NHS reaction).

### 2.2 Characterization

The absorption and PL spectra of the solutions were measured on a spectrophotometer UV-3600 (Shimadzu, Japan) and spectrofluorometer Cary Eclipse (Varian, USA), respectively. Circular dichroism absorption spectra were collected on a J-1500 (Jasco, Japan) spectrophotometer.

## 3. Results

The obtained CDs are N-doped particles with emission observed in the 400-600 nm spectral region. The emission and circular dichroism signals of CDs demonstrate a clear dependence on pH in aqueous solution in the range from 2.0 to 10.0. The photoluminescence peak excited at 450 nm shifts from 531 to 537 nm and shows an increase in the intensity with increasing of pH. In addition, the circular dichroism spectrum of CDs shows two extrema at 220 and 263 nm for pH=6. With an increase in the pH of the medium, the negative peak shifts from 269 to 256 nm.

When mercury ions are added, the photoluminescence peak excited at 450 nm demonstrates a decrease in intensity, until complete quenching upon the addition of 100 µL of a 0.01 M Hg<sup>2+</sup> solution. In addition, with an increase in the concentration of mercury ions, the intensity of the positive and negative peaks in the spectra of circular dichroism decreases. Moreover, an additional peak appears at 245 nm.

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## Studying of polyvinylidene fluoride polymer-based composite films with cobalt ferrite magnetic particle inclusions

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Research focused on the creation and characterization of composite film materials is crucial for the advancement of smart materials and technology. Composites consisting of a polymer matrix with particles possess unique properties and have applications in numerous fields, including electronics, optics, energy and biomedicine [1]. In particular, composite film materials based on the polyvinylidene fluoride (PVDF) polymer with cobalt ferrite  $\text{CoFe}_2\text{O}_4$  (CFO) particles have potential applications in biomedicine. PVDF exhibits piezoelectric properties and CFO is a ferromagnetic material. Such composites can be utilized in the creation of biosensors, drug delivery systems and tissue engineering [2].

This study focuses on the synthesis and characterization of composite films based on the polymer PVDF (polyvinylidene fluoride) with inclusion of CFO magnetic particles. The investigation aimed to explore the physical properties of the composite films with varying concentrations of CFO cobalt ferrite (0%, 5%, 10%, and 15%). The composite films were fabricated using the doctor blade method. The effects of the particles concentration on the physical properties of the films were systematically examined using DSC (differential scanning calorimetry), XRD (X-ray diffraction), SEM (scanning electron microscopy), and EDX (energy-dispersive X-ray spectroscopy) techniques.

The results indicated that the addition of CFO cobalt ferrite influenced the thermal behavior and crystallinity of the PVDF composite films. The melting temperature and crystallinity of the films were found to change with increasing particles concentration. XRD analysis confirmed the successful formation of the composite structure, with distinct diffraction peaks corresponding to both PVDF and CFO phases. SEM imaging revealed the morphology of the composite films, showing a uniform dispersion of CFO particles within the PVDF matrix. The EDX analysis provided elemental mapping and compositional information, confirming the presence and distribution of cobalt, iron, and fluorine elements in the composite films.

These findings contribute to the advancement of composite film materials and their potential applications in various fields. The use of the doctor blade method for film fabrication offers a scalable and cost-effective approach for producing PVDF-CFO composite films. This study provide valuable insights into the synthesis and characterization of PVDF-CFO composite films. The combination of DSC, XRD, SEM, and EDX techniques allows for a comprehensive understanding of the physical and structural properties of the films. The obtained results open up new possibilities for the development and utilization of composite film materials in diverse applications, including biomedical fields.

It should also be noted that the composites obtained are spherulites of the PVDF polymer, around which magnetic particles are located, prompting modeling studies were carried out. The objectives of the model are to understand the size control and dispersion of particles in the composite matrix, as well as the magnitude of the magnetoelectric effect.

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## Modeling of hybrid noble-ferromagnetic mesoscale particles optical properties

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Hybrid nanomaterials made of noble and ferromagnetic metals offer new opportunities to improve treatment methods of oncological diseases. Several methods like magnetic hyperthermia, magneto-mechanical induction of cell death and photothermal therapy (PTT) can be combined for efficiency improving with the use of such materials [1]. Most experimental works use ferromagnetic particles of a certain shape, coated with noble metals for excitation of plasma resonance and effective transformation of electromagnetic energy into thermal energy [2]. When the energy of the incident light coincides with the resonance frequency of free electrons, a localized plasmon resonance is observed in the metallic nanoparticles (NP), the excitation of which leads to an increase in the absorption of the incident light increasing the heat output. The conditions of resonance excitation depend on the composition of the material, the size and morphology of the NP, as well as the dielectric constant of the environment. The energy absorbed by plasmon NP's can be released either by photon re-radiation (luminescence), or by phonon generation (heat), which can be used for selective anti-tumor therapeutic effects [3]. Hybrid mesoscale structures, such as nanotubes, nanodiscs and nanorods, are also magnetoanisotropic, which allows them to turn in the direction of magnetic field and mechanically destroy cancer cells.

Thus the mesoscale NP's main advantage are the large surface area relative to volume, which is important for drug delivery and PTT; high magnetic anisotropy and magnetization value due to the use of transition metals, resulting in higher heat emission values and enhanced optical effect; biocompatibility due to the selected cover layer (Au, Ti2O3, SiO2 etc) [3].

This works aims to determine the optimal design of hybrid mesoscale structures made of noble and ferromagnetic metals using the modeling of their optical properties in Lumerical software package.

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# Author index

## A

Abdurakhmanov C.....	31
Abdurakhmanov M.....	34, 35, 41, 47
Aga-Tagieva S.....	51
Aga-Tagiyeva S.....	19, 42, 59, 64
Albino M.....	61
Alekhina Iu.....	8
Amirov A.....	45
Amirov K.....	24, 67
Antipova V.....	20
Arkipova E.....	21

## B

Bakhtiyorov A.....	14
Barmir R.....	33
Belyaev V.....	72
Bichurin M.....	49, 50, 54, 55, 58

## C

Cherkasova N.....	43
Chicea D.....	68

## D

Dmitrieva A.....	23, 29
Doroshkevich A.....	68

## E

Ershov P.....	24, 37, 45, 46, 63, 67, 70
Evlashin S.....	53
Evstigneeva S.....	9

## F

Fedyanin A.....	30, 56
Fesik S.....	66
Fomkina A.....	23
Frolov A.....	30, 56

## G

Gavrilov D.....	44
Gorin D.....	33
Gorshenkov M.....	64
Granovsky A.....	7
Gulakhmedov R.....	35, 41
Gulkin D.....	56
Guryanova L.....	46
Gyulakhmedov R.....	31, 34, 47

## I

Ignatov A.....	16, 45, 48
Isaev A.....	38
Ismailova A.....	25
Ivasheva E.....	49

## J

Jovanović S.....	26
Jovanović Z.....	27

## K

Kafarov R.....	50, 55
Kalashnikova A.....	21
Kaminskiy A.....	5, 28
Karshieva S.....	12
Kazbanov V.....	45
Keruchenko M.....	45
Khairtdinova D.....	52
Khashirova S.....	24, 67
<u>Kolesnikova V</u> .....	51, 64
Komarova S.....	52
Korepanova E.....	20
Koudan E.....	12
Kovaleva P.....	12
Kramarenko E.....	4, 25
Krivoshapkina E.....	23, 29
Krotkova E.....	29
Kuntu D.....	21
Kuritskiy M.....	45
Kuzminova Y.....	53

## L

Leontev V.....	54
Levada K.....	20
Levin A.....	12
Litvin A.....	36
Lobanov D.....	14
Lobekin V.....	55
Lutsenko O.....	9

## M

Magomedov K.....	19, 42, 59
Magomedova A.....	38
Makarín R.....	8
Makarova A.....	56
Makarova L.....	8, 51
Mardare D.....	68
Markov I.....	58

# SCIS-2023

Mita C.....	68
Musorin A.....	30
Musov Kh.....	24, 67
Muzzi B.....	61
Myasnikov N.....	28

## N

Nerovnaya A.....	30, 56
Ni V.....	59
Nikolaev S.....	7

## O

Omelyanchik A....	19, 24, 37, 42, 44, 46, 51, 59, 61, 63, 64, 67
Orudzev F.....	19, 42
Orudzhev F.....	31, 34, 35, 38, 41, 47

## P

Panina L.....	9, 52
Peddis D.....	61
Perov N.....	8
Petrov S.....	12
Petrukhin D.....	63
Popov V.....	56
Pshenichnikov S.....	20
Pyatakov A.....	5, 28

## R

Rabdanova A.....	31, 34, 35, 38, 41, 47
<u>Raikher Yu.....</u>	11, 16, 48
Rodionova V.....	16, 19, 20, 24, 37, 42, 44, 45, 46, 48, 51, 59, 61, 63, 64, 67, 70, 72
Romanenko E.....	23
Rudakovskaya P.....	33
Rylkov V.....	7

## S

Salnikov V.....	37, 42, 46, 51, 63, 64
Sangregorio C.....	61
Savin V.....	45
Selimov B.....	31
Selimov D.....	34, 35, 41, 47
Semenukha O.....	66

Senatov F.....	12
Sharipova M.....	56
Shelukhin L.....	21
Shishkovsky I.....	53
Shuaibov A.....	31, 34, 35, 41, 47
Sitnikov A.....	7
Skurlov I.....	36
Sobola D.....	35, 41, 47
Sobolev K.....	20
Soboleva I.....	30, 56
Sokolova A.....	36
Stepanov G.....	14
Stolbov O.....	11, 16, 48
Storozhenko P.....	14
Studnev K.....	68

## T

Tashkinov M.....	24, 67
Tatarinov D.....	36
Tatarinova A.....	68
Timkina Y.....	36
Trofimov E.....	43

## U

Ushakova E.....	69
-----------------	----

## V

Vedernikova A.....	69
Vindokurov I.....	24, 67
Vinnik D.....	43
Voronina S.....	66
Vorontsov P.....	24, 37, 46, 67, 70
Vorontsov S.....	20, 70

## Y

Yudanov N.....	9
----------------	---

## Z

Zhansitov A.....	24, 67
Zhivulin V.....	43
Zimina A.....	12
Zinnyatullina D.....	72