

INSTITUTE OF PHYSICS POLISH ACADEMY OF SCIENCES

DOCTORAL THESIS

**Magnetoelectric properties of
ferromagnets/ferroelectrics layered
heterostructures**

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*A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy*

May 2014

Preface

This dissertation based on the experimental apparatus and data taken from previously published articles is the subject of a large international collaboration.

This work was carried out in the Institute of Physics Polish Academy of Sciences, in collaboration with the Scientific–Practical Materials Research Centre of Belarussian Academy of Sciences and International Laboratory of High Magnetic Fields and Low Temperatures in Wroclaw, Poland.

I am grateful to my supervisor, prof Henryk Szymczak, for theoretical and conceptual support of my thesis and co-supervisor, Aleksander Stognij, chief of group of ion-beam sputtering/deposition of Scientific–Practical Materials Research Centre of BAS, for preparation of the samples and guidance in field of surface science technology. I would like to thank prof Viktor Nizhankovski from International Laboratory of High Magnetic Fields and Low Temperatures in Wroclaw for sharing his knowledge and laboratory resources for performance of magnetoelectric and transport measurements.

Moreover, I would like to express my gratitude to the staff of Moscow State Technical University of Radio Engineering, Electronics, and Automation for sharing scanning electron microscopy and structural analysis of the samples as well as prof Valery Ketsko from Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences for synthesis of ferroelectric substrates and guidance in the area of inorganic chemistry.

I would like to say special thanks to prof Wojciech Paszkowicz for carrying out and help in interpretation of data of structural analysis and prof Vladimir Dyakonov for guidance and support during whole cycle of the work.

Abstract

ON3.2 - Group or spectroscopy and thermal properties of magnetics

Doctor of Philosophy

Magnetoelectric properties of ferromagnets/ferroelectrics layered heterostructures

by Andrei SAZANOVICH

This thesis presents the results of the investigations of structural, magnetic and magnetoelectric (ME) properties of ferromagnets/ferroelectrics layered heterostructures. The ferromagnetic (FM) constituents of the heterostructures, Co, Ni, NiFe or TbMnO₃, were grown on a ferroelectric (FE) PbZr_{1-x}Ti_xO₃ (PZT) or SrTiO₃ (STO) substrates. The structures were prepared using ion beam sputtering/deposition technique to assure the reproducibility and high quality of structure, stable mechanical contact between FM and FE layers without use of a chemical bounders. Special attention was paid to the structure of the interfaces between ferromagnetic and ferroelectric layers. To characterize the quality of the interface region, X-ray diffraction and scanning electron microscopy (SEM) measurements were carried out. The magnetic and magnetoelectric measurements have allowed to determine the influence of number, thickness and chemical composition of layers on the magnitude of ME response. The optimal configuration of the single layer structure of FM(2 μm)/PZT(80 μm)/FM(2 μm) was found.

Based on the single element structures, the two- and three-layered heterostructures connected to each other by ferromagnetic layers with epoxy glue were formed. The biggest value of ME response was found for three-layered permalloy based heterostructures (Py/PZT/Py)₃. These structures show a huge value of magnetoelectric effect of 250 mV/cm·Oe at room temperature and in low magnetic field. This effect is two orders of magnitude larger than the value reported for single-layered structures.

Streszczenie

List of Publications

The main findings and results of this thesis are described in the following papers:

1. A. Sazanovich, Yu. Nikolaenko, W. Paszkowicz, V. Mikhaylov, K. Dyakonov, Yu. Medvedev, V. Nizhankovskii, V. Dyakonov, H. Szymczak, *Magnetic and ferroelectric ordering in the $TbMnO_3$ film*, Acta Physica Polonica A, 125(1):128, 2014
2. A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bespalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, M. N. Smirnova, and V. A. Ketsko, *Effect of Cobalt Layer Thickness on the Magnetoelectric Properties of $Co/PbZr_{0.45}Ti_{0.55}O_3/Co$ Heterostructures*, Inorg. Mater., 49(10):1011, 2013
3. A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bespalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, and V. A. Ketsko, *Effect of Interfaces on the Magnetoelectric Properties of heterostructures $Co/PZT/Co$* , Inorg. Mater., 50(3):275, 2014
4. A. Stognij, N. Novitskii, A. Sazanovich, N. Poddubnaya, S. Sharko, V. Mikhailov, V. Nizhankovski, V. Dyakonov, and H. Szymczak, *Ion-beam sputtering deposition and magnetoelectric properties of layered heterostructures $(FM/PZT/FM)_n$, where FM -- Co or $Ni_{78}Fe_{22}$* , Eur. Phys. J. Appl. Phys., 63:21301, 2013

Publications not related to, and not included in the thesis:

1. A. Sazanovich, J. Pietosa, A. Pashchenko, E. Zubov, V. Dyakonov and H. Szymczak, *Influence of Nonstoichiometry on Magnetocaloric Effect in $(La_{0.7}Ca_{0.3})_{1-x}Mn_{1+x}O_3$* , Acta Physica Polonica A, 122(1):162, 2012

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Chapter 1

Introduction

1.1 From history and development of magnetoelectric phenomenon (ME)

The coupling between electric and magnetic fields in matter was initially discovered by Röntgen in 1888 [1], when he found that a moving dielectric placed in an electric field has become magnetized, and then was theoretically described by Curie in 1894 [2] on the basis of crystal symmetry considerations. This 'magnetoelectric' phenomenon has been passed many decades because of general weakness of the effect, poor theoretical background of the microscopic sources of the effect, the very limited number of compounds displaying it as well as technological difficulties in developing useful applications. The discovery of the phenomenon of ferroelectricity was made by Valasek in 1920 [3]. Fox and Scott [4] have also shown that ferroelectricity can produce magnetic order and vice versa. This has provoked interest in study and understanding of 'multiferroics' and 'magnetoelectric' materials.

Looking at the relationship between multiferroics and magnetoelectric materials W. Eerenstein and M. Opel [5, 6] have established, that the 'multiferroics' and 'magnetoelectric' terms overlap but incompletely. According to original definition, a single-phase multiferroic material is one that exhibits more than one 'ferroic' order parameter such as ferroelectricity, ferromagnetism and ferroelasticity. Magnetoelectric coupling, on the other hand, may exist whatever the nature of magnetism and electrical order parameters. Magnetoelectric coupling may arise directly as a product of interaction magnetic (electric) field and polarization (magnetization) of the material, or indirectly as a result of combination a few order parameters coupled via strain, like piezoelectricity and magnetostriction and so on.

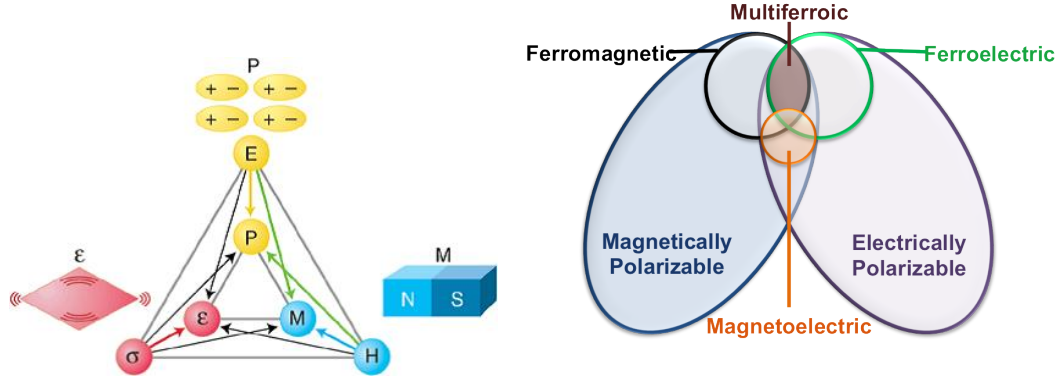


FIGURE 1.1: Right — coupling in multiferroic materials;
left — chart of materials for spintronics [5].

In the next few decades, numerous single phase ME materials were reported, in which the ME effect was caused by a direct coupling between dipole and spin moments on the atomic scale. This class of materials was named multiferroics, where the internal magnetic and/or electric fields are enhanced by the presence of multiple long-range ordering. These materials display at least two of the primary ferroic order parameters in one phase. In practice, the multiferroic material often incorporates (anti-) ferromagnetic and ferroelectric properties.

Unfortunately, the use of these materials for device applications was not successful mainly because most of them have low, much lower than room, the Neel or Curie temperatures. The magnetoelectric coefficient dramatically drops to zero as the temperature reaches the transition one, making difficult the practical application of such class of materials. Further investigations, especially in epitaxial layer thin films, were reported for the improved multiferroic BiFeO_3 , which attracts the attention being ferroelectric, ferroelastic and weakly ferromagnetic and having enhanced electric and magnetic ordering temperatures of about 1100 and 650 K, respectively. BiFeO_3 displays a huge magnetoelectric response of the order of few tens $\text{mV}/\text{cm}\cdot\text{Oe}$ [7–9].

But it was still small value for any practical usage. Going further, in order to obtain the material with a huge magnetoelectric response over a wide temperature range, two-phase systems were taken into account [5].

1.2 Magnetoelectric materials: classification

After brief historical introduction, the focus turns on the classification of magnetoelectric materials. They can be divided in single-phase and composite magnetoelectrics.

1.2.1 Single-phase magnetoelectrics

Single-phase multiferroics are the materials that show both ferroelectric and ferromagnetic order. Thus a multiferroicity is intrinsic property of the material. Khomskii classified the single-phase multiferroics in two big groups and other subgroups [10], according to the physical mechanism of ferroelectricity.

Type-I single phase magnetoelectrics: ferroelectric multiferroics.

Multiferroics of Type-I are the materials in which ferroelectricity and magnetism have different sources; usually they show large polarization values and ferroelectricity appears at much higher temperatures than magnetism. This difference in transition temperatures reveals that both orders involve different energy scales and mechanisms, which provoke the occurrence of weak magnetoelectric coupling. These materials are in turn separated in several subgroups:

1. *Ferroelectricity due to long pair*: in these materials, one of the cations (i. e. Bi^{3+} , Pb^{3+} , ...) has two electrons in the s orbital far from the core and without being part of any chemical bond. These electrons generate an electric dipole, which is the origin of ferroelectric order. Other cations (i. e. Fe^{3+} , Mn^{3+} , Ni^{2+} , ...) are responsible for magnetic properties. The most relevant example of this class is BiFeO_3 ;
2. *Ferroelectricity due to charge ordering*: charge ordering can occur in compounds having similar cations in the same structural site which have a different valence. After they become ordered both sites and bonds of the transition metals turn out to be inequivalent. This can lead in some cases to ferroelectricity [11]. Such example is TbMn_2O_5 ;
3. *"Geometric" ferroelectricity*: in hexagonal manganites (ABO_3 with $\text{A} = \text{Y, Lu, ...}$) ferroelectricity occurs because the tilting of the MnO_5 polyhedron provides a dense packing. As a result, the oxygen ions shift closer to the rather small A ions, leading to the formation of an electric dipole.

Type-II single phase magnetoelectrics: magnetic multiferroics.

Type-II multiferroics correspond to materials in which magnetism causes ferroelectricity and there is a strong coupling between them. They show small electric polarization values and ferroelectricity always appears at lower temperature than magnetic order (always antiferromagnetic ordering).

These are:

1. *Spiral magnets*: materials having atomic spin rotated across the lattice in a defined plane, this breaks the symmetry and allows ferroelectricity. However, ferroelectricity takes place in spiral magnets only when the so-called cycloidal spin arrangement sets, that is spins rotate in the plane of the propagation of the spiral. In this case, ferroelectricity arises in the plane of the cycloid and perpendicular to the propagation vector of the cycloid due to the so-called inverse Dzyaloshinsky-Moriya interaction [12, 13].
2. *Collinear magnets*: in these materials one-dimensional chains of up-up-down-down spins are formed due to the exchange striction. The distortion induced by up-up (down-down) or up-down (down-up) bonds is different, which provokes the formation of ordered electric dipoles. An example is CaCoMnO_3 [14], or E-type rare earth manganites, HoMnO_3 [15].

1.2.2 Composite magnetoelectrics

In opposition to single-phase magnetoelectrics, multiferroic order in such materials is not intrinsic but results from the combination of two, ferroelectric and ferromagnetic, materials. The ME effect in composite materials is known as a product tensor property, first proposed by van Suchtelen in 1972 [16], that results from the cross interaction between the two phases in the composite.

In composites, magnetoelectric coupling can occur via different interface mechanisms:

1. *Strain mediated coupling*: as illustrated schematically in Fig. 1.2, the ME effect is a result of the product of the magnetostrictive effect (magnetic/mechanical effect) in the magnetic phase and the piezoelectric effect (mechanical/electrical effect) in the piezoelectric phase.

The ME effect in such composite can therefore be described as follows:

$$\text{Direct magnetoelectric effect} = \frac{\text{Magnetic}}{\text{Mechanical}} \times \frac{\text{Mechanical}}{\text{Electric}}. \quad (1.1)$$

$$\text{Converse magnetoelectric effect} = \frac{\text{Electric}}{\text{Mechanical}} \times \frac{\text{Mechanical}}{\text{Magnetic}}. \quad (1.2)$$

Here, the application of either magnetic or electric external fields can result in changes of polarization and magnetization, respectively. This takes place in the case of CoFe_2O_4 columns embedded in a BaTiO_3 matrix [17] or in the LaSrMnO_3 film grown on the top of the (001) oriented BaTiO_3 single-crystal [18]. Multiferroic

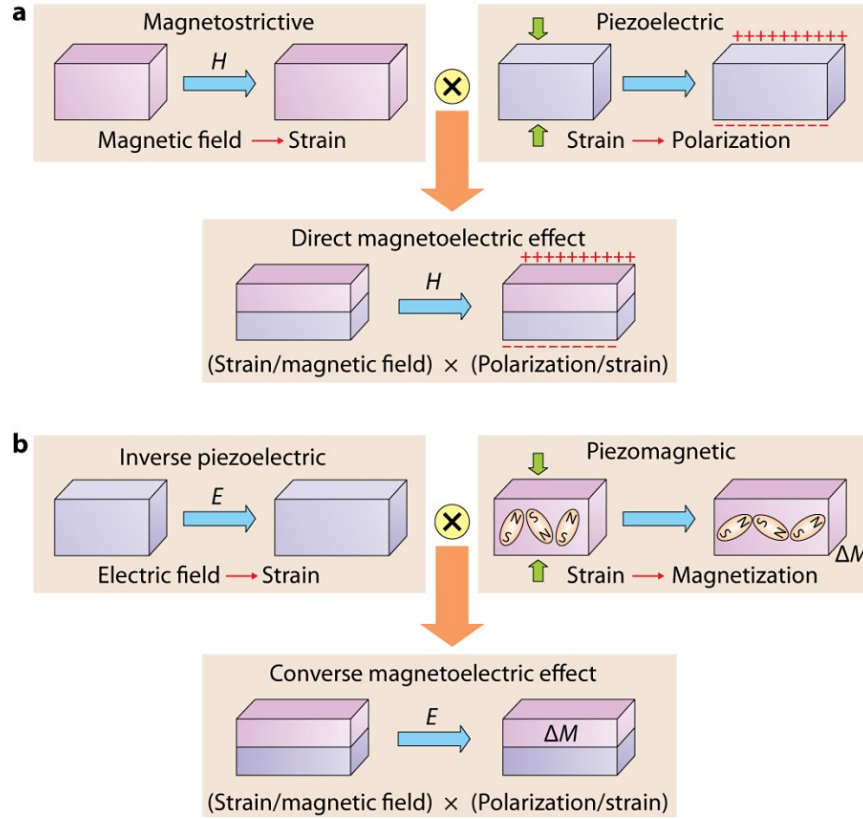


FIGURE 1.2: schematic illustration of strain-mediated ME effect in a composite system consisting of a magnetic layer (purple) and ferroelectric layer (pink). (a) — direct ME effect; (b) — converse ME effect

composites containing a rare earth-iron alloy are another important example [the most important: Terfenol-D ($\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$), in which a piezoelectric phase shows the giant magnetoelectric effect [19] due to the large magnetostrictive coefficient of the metallic alloy.

Many bulk ME composites have been found to exhibit such a strain-mediated ME effect above room temperature. Multiferroic ME films, in comparison with bulk ME composites, have some unique advantages. For example, ferroelectric/piezoelectric and magnetostrictive phases could be tuned and controlled at the nanoscale, representing a new scale for exploring ME coupling mechanisms.

2. *Charge mediated coupling*: the coupling occurs because the ferroelectrics accumulate charge at the interface, and the magnetic state of ferromagnet is sensitive to changes of the valence state of ferroelectrics ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$). Therefore, a change in the interfacial charge (produced by the electric switching of the ferroelectrics) would induce a change in the magnetization.
3. *Exchange bias mediated coupling*: exchange bias may exist at the antiferromagnetic/ferromagnetic interface. One of the origins of exchange bias can be the pinning

of the domain walls of the antiferromagnet, which display net magnetic moment, to the ferromagnetic domains of the ferromagnet. Taking advantage of that, in antiferromagnetic multiferroics, antiferromagnetic domain walls are coupled to ferroelectric domain walls. The changes in the ferroelectric domains configuration induced by application of an electric field in the antiferromagnet are converted in magnetization changes in the ferromagnet, resulting in magnetoelectric effect. For the instance, this is the case of permalloy (NiFe alloy) thin film grown on top of hexagonal manganite [20].

Note that all the discussed mechanisms that tend to increase of magnetoelectric coupling take place at the interface between the ferroelectric and ferromagnetic materials. If the contact area between them is large, the resulting magnetoelectric coupling is expected also to be large. The architecture of the composite will determine the contact area between the two materials. This is the reason why composites are also classified according to their architecture:

1. *Layered (horizontal) heterostructures*: these heterostructures are composed of n alternating layers of the ferroelectric and ferromagnetic materials, where n can be between two (bilayers) and larger numbers of layers (multilayers). For instance: the thin film bilayered structure of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ –ferromagnetics [21];
2. *Self-assembled nanocomposites with vertical geometry*: the prototypical vertical heterostructure consists of a magnetic spinel phase epitaxially embedded into the ferroelectric matrix. For instance: the BaTiO_3 – CoFe_2O_4 vertical composites [17].

Common connectivity schemes of ME composite nanostructures are shown in Figure 1.3: (a) — particulate nanocomposite films with magnetic particles embedded in a ferroelectric film matrix; (b) — horizontal heterostructure with alternating ferroelectric and magnetic layers; and (c) — vertical heterostructure with one-phase nanopillars embedded in a matrix of another phase.

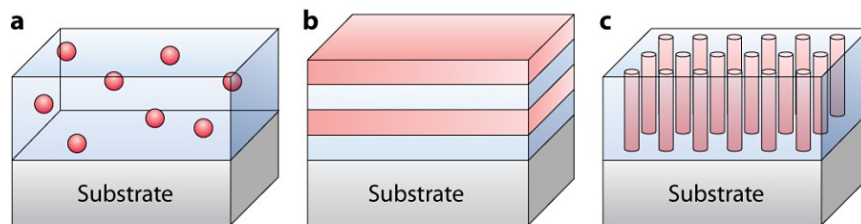


FIGURE 1.3: Common connectivity schemes of ME composite nanostructures.
 (a) — particulate nanocomposite; (b) — horizontal heterostructure; (c) — vertical heterostructure

1.3 Magnetoelectric effect: thermodynamics

It was shown that the origin of ME effect may be quite different. The general meaning of magnetoelectric effect is existence of coupling between magnetic and electric parameters inside a material.

Finding of the multiferroics with such coupling as well as interpretation of the magnetoelectric effect mechanisms becomes extremely important task. Such mechanisms are based on the influence of electric or magnetic fields, mechanical stresses applied, phase transitions and etc.

From the theoretical point of view, ME coupling may be described as some function linking electric, magnetic and toroidal parameters of the material. Here the toroidal order parameter is assumed as independent order parameter $\boldsymbol{\tau}$ originating only from the existence of magnetic toroidal moments.

Based on general thermodynamic formalism, let's define the Landau free energy function G in following way:

$$G = U - TS - \mathbf{E} \cdot \mathbf{P} - \mathbf{M} \cdot \mathbf{H} - \boldsymbol{\tau} \cdot \mathbf{T}, \quad (1.3)$$

where U is the internal energy per unit volume, T the temperature, S the entropy per unit volume, $\mathbf{E}$ the electric field, $\mathbf{H}$ the magnetic field, $\mathbf{P}$ the polarization, $\mathbf{M}$ the magnetization. The field $\mathbf{T}$ coupling to the toroidization $\boldsymbol{\tau}$ is related to the electric and magnetic fields through $\mathbf{T} = \mathbf{E} \times \mathbf{H}$. It is shown that the free energy of a system with magnetic toroidal moment must include a term proportional to the product $\boldsymbol{\tau} \cdot \mathbf{T}$.

Relations between electric and magnetic parameters are obtained by differentiation the free energy with respect to $\mathbf{E}$ and $\mathbf{M}$:

$$P = -\boldsymbol{\tau} \cdot \mathbf{H}, \quad (1.4)$$

$$\mathbf{M} = \boldsymbol{\tau} \cdot \mathbf{E}. \quad (1.5)$$

Here we have taken into account that the intrinsic components P and $\mathbf{M}$ do not depend on $\mathbf{H}$ and $\mathbf{E}$, respectively. This means that magnetoelectricity in the system originates only from the toroidal order.

An interesting relationship between $\boldsymbol{\tau}$ and $\mathbf{P}$, $\mathbf{M}$ can be obtained considering that

$$\begin{aligned}
\mathbf{P} \times \mathbf{M} &= -(\boldsymbol{\tau} \times \mathbf{H}) \times (\boldsymbol{\tau} \times \mathbf{E}) = (\boldsymbol{\tau} \times \mathbf{E}) \times (\boldsymbol{\tau} \times \mathbf{H}) = \\
&= -(\boldsymbol{\tau} \times \mathbf{E}) \times (\mathbf{H} \times \boldsymbol{\tau}) = -\boldsymbol{\tau} \times (\mathbf{E} \times \mathbf{H}) \times \boldsymbol{\tau} = -\boldsymbol{\tau} \times \mathbf{G} \times \boldsymbol{\tau}.
\end{aligned} \tag{1.6}$$

1.4 Strain-mediated magnetoelectric coupling

Magnetoelectric effect in two-phase system may be described as the product of two types of material properties, such as magnetostriction and piezoelectricity caused by mean mechanical strain [22, 23]. Magnetoelectric effect can be described as the induced electrical polarization under magnetic field or induced magnetization under electric field. The ME effect of such material can be evaluated by a parameter designated as the magnetoelectric voltage coefficient α_{ME} . The later can be defined by the electric field δE induced by an applied magnetic field δH ($\alpha_{ME} = \delta E / \delta H = \delta V / t \delta H$, where t is the thickness); or vice versa, by the magnetic field induced by an applied electric one.

Therefore, the composites from materials which themselves do not allow the ME effect can be used to generate ME behaviour. This is conveniently achieved by combining magnetostrictive and piezoelectric compounds, which interact via elastic force. A magnetic field applied to the composite will induce strain in the magnetostrictive constituent which is passed along the piezoelectric constituent, where it induces an electric polarization.

Here, a linear ME polarization is already induced by a weak ac magnetic field oscillating in the presence of a dc bias field. In the vicinity of electromechanical resonances a ME voltage coefficient of up to 90 V/cm·Oe is achieved [24], which exceeds the ME response of single-phase compounds by 3–5 orders of magnitude. Under applied alternating magnetic field, the magnetostrictive phase produces strain which is transferred on to the piezoelectric phase that converts strain into electric charge. On the other hand, under applied electric field, piezoelectric phase produces strain which is transferred on to the magnetostrictive phase that converts it into magnetic field. The former is called by the direct magnetoelectric effect and the later is called by the converse magnetoelectric effect. These materials are extremely promising for applications as sensors, actuator, transducer, storage devices, and various other devices. The interrelation between ferroelectricity and magnetism allows the magnetic control of ferroelectric properties and vice versa. A ferromagnetic and ferroelectric phase can be combined in several different ways, including naturally occurring composites, artificially designed composites, and in-situ sintered composites.

The ME response of the laminated composites is determined by four major aspects which will be discussed in the following:

- the magnetic, electric and mechanic coefficients of the constituents;
- the respective thickness and number of the piezoelectric and magnetostrictive layers;
- the type of bonding between the constituents;
- the orientation of both constituents and applied electric or magnetic fields (transverse or longitudinal effect).

The giant ME effect in the laminate composites has a very simple working principle. Application of magnetic field results in a shape change of the magnetostrictive layer; the magnetostrictive layer is elastically bonded with a piezoelectric one. The elastic–elastic coupling between layers then results in an induced shape change transmitted to the piezoelectric layer. In turn, a charge is generated across the piezoelectric layer by an applied magnetic field. This simple working principle has been manifested notably in more complex theories [25, 26]. The elastic–elastic coupling between layers is very important. An interfacial coupling parameter (k) has been introduced by Bichurin where the maximum ideal value is $k = 1$, and where real interfaces have values of $k < 1$. The higher the coupling parameter, the higher is the ME effect. In this regards, many coupling methods have been studied, including sintering, hot moulding, sputtering, and epoxy. Each method has its merit and working conditions, proper choice of these coupling methods can enhance the k factor. To achieve an optimum ME coefficient for a ME laminate, it is necessary to put the ME laminate under a critical or required DC magnetic bias [27–31]. This is because the magnetic phase is magnetostrictive, rather than piezomagnetic one. Demagnetizing field then results in a loss of magnetic remanence on removal of the field. Rather, these composite materials must be DC biased to the maximum point of slope on the ϵ – H (magnetostrictive strain–magnetic field) and the M – H curves. Because the demagnetization factor depends on geometry, the required DC bias to achieve the maximum value of α_{ME} strongly depends on the construction and geometry of the composite. It is thus equally important to talk about the composites mode of operation, as well as the materials constructed from them.

1.5 Horizontal heterostructures

Horizontal nanostructures (see Fig. 1.3 (b)) consisting of alternating layers of a ferroelectric and magnetic materials usually exhibit high value of ME effects. In such structures

different phases can be combined at the atomic level, and thus interface losses could be reduced significantly. By combining different phases with similar crystal lattices, epitaxial or superlattice composite films can also be designed, which facilitates the understanding of ME coupling at the atomic scale. Multiferroic ME films are therefore promising candidates for use in integrated magnetic/electric devices, such as sensors, microelectromechanical systems, high-density memories and spintronics.

Let's provide a simple physical model of the magnetoelectric ordering in two-phase laminate composite considering a simple three-layered schema of piezoelectric and magnetic phases with free boundary Fig. 1.4).

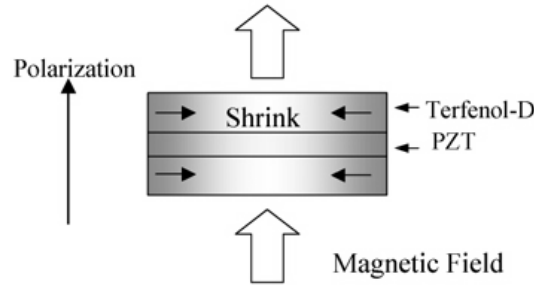


FIGURE 1.4: model of two-phase composite material.

It is known that Lead Zirconate Titanate (PZT) has a giant piezoelectric effect, is cheap and easy for obtaining and processing. So, it is probably the best candidate for piezoelectric constituent. Any magnetic material with large magnetostriction like Ni, Co, nickel ferrites (Permalloy, Permendur, Terfenol-D and ect.) may be used as magnetostrictive element. When a magnetic field is applied to this composite, the top and bottom ferromagnetic disks shrink or expand. This generates stresses in the sandwiched piezoelectric PZT disk. Hence, electric signals can be obtained when the composite is subjected to a magnetic field.

Theoretical models are available in the literature to account for the large ME effect of composites [32–34]. In the past, studies on ME composites have concentrated on estimation of the effective properties of the composite as a function of microstructure variables such as physical properties of individual phases, volume fraction, shape and connectivity. These models have their own advantages and disadvantages. Van den Boomgaard [33] assumed that if (1) the dielectric constant of the ferromagnetic phase and (2) Young's moduli for both the phases are equal and (3) there is perfect coupling between the phases, then the ME voltage coefficient is given by

$$\left(\frac{dE}{dH}\right)_{comp} = \left(\frac{dx}{dH}\right)_{comp} \left(\frac{dE}{dx}\right)_{comp} = m_v \left(\frac{dx}{dH}\right)_{FM} \left(\frac{dE}{dx}\right)_{piezo}, \quad (1.7)$$

where $(\frac{dx}{dH})$ is the change in dimension per unit magnetic field and $(\frac{dE}{dx})$ is the change in dimension per unit electric field. The subscript 'comp' stands for composite and m_v is the volume fraction of the ferromagnet. Using the maximum optimistic value of the parameters, $(\frac{dx}{dH}) = 5 \times 10^{-7} \text{ } Oe^{-1}$, $(\frac{dE}{dx}) = 102 \text{ V/m}$ and $m_v = 0.5$. The estimated maximum value of the ME voltage coefficient obtained is equal to $\frac{dE}{dH} = 5 \text{ V/cm} \cdot Oe$.

The estimated value of the ME response is very promising. It is important to note that modelling, producing or tuning of the composite structure, a few points should be taken into account:

1. *Thickness ratio effect.* Fig. 1.5 presents the theoretical expectation of the ME voltage coefficient as a function of thickness ratio $(\frac{t_{FM}}{t_{piezo}})$ for PZT/Terfenol-D structure [34].

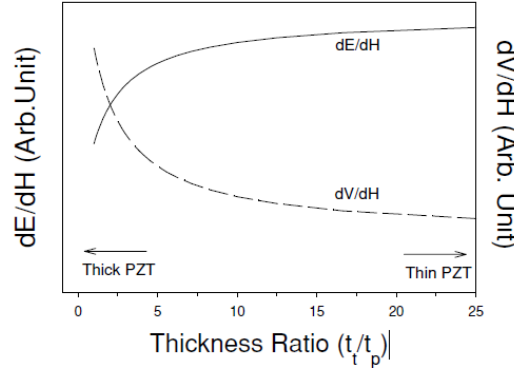


FIGURE 1.5: effect of thickness ratio of $(\frac{t_{FM}}{t_{piezo}})$ on magnetolectric coefficient in PZT/Terfenol-D structure.

This can be explained by the increase in compressive stress in the piezoelectric layer with decreasing thickness of PZT. The compressive stress in the PZT layer and the tensile stress in the FM layers can be derived from simple beam theory under plane stress conditions, as indicated in Eqs. 1.8 and 1.9 [35]:

$$\sigma_{FM} = \frac{E_{FM} E_{piezo} t_{piezo} \delta \varepsilon_0}{(1 - \nu)(2E_{FM} t_{FM} + E_{piezo} t_{piezo})}, \quad (1.8)$$

$$\sigma_{piezo} = \frac{2E_{FM} E_{piezo} t_{piezo} \delta \varepsilon_0}{(1 - \nu)(2E_{FM} t_{FM} + E_{piezo} t_{piezo})}, \quad (1.9)$$

where E , t , $\delta \varepsilon_0$, and ν are the elastic modulus, thickness, linear strain of the FM layer, and poisson's ratio (poisson's ratios of Terfenol-D and PZT are assumed to have the same value in these equations), respectively. As shown in these equations, the compressive stress in the piezoelectric layer is increased with decreasing thickness of the layer or with increasing thickness of the ferromagnetic layer. Since the

thickness of the FM is fixed by 1 mm, by decreasing the piezoelectric layer thickness, the compressive stress in this layer will be increased. The output voltage from the composite can be expressed by the following equations [34]:

$$V_{out} = 2 \times g \times t_{piezo} \times \sigma_{piezo}, \quad (1.10)$$

$$\frac{dE}{dH} = \frac{V_{out}}{H_{ac}} \times t_{piezo} = \frac{2 \times g \times \sigma_{piezo}}{H_{ac}} (V/cm \cdot Oe). \quad (1.11)$$

Therefore, a higher output voltage can be obtained when the compressive stress in the piezo layer is higher, i.e., than thinner this layer. From these equations, it can be seen that the output voltage from the composite is also directly proportional to the piezoelectric voltage constant g . Generally in PZT ceramics, the out-of-plane piezoelectric voltage constant is around 1/3 of in-plane constant.

2. *Magnetostriction direction dependence.* For such horizontal structure there are three magnetostriction directions as follow (see Fig. 1.6):

- magnetostriction along the thickness direction (denoted as Comp.T-T);
- composite with one constituent along the thickness magnetostriction direction, and with other one along with radial magnetostriction direction (denoted as Comp.T-R);
- magnetostriction along the radial direction (denoted as Comp.R-R).

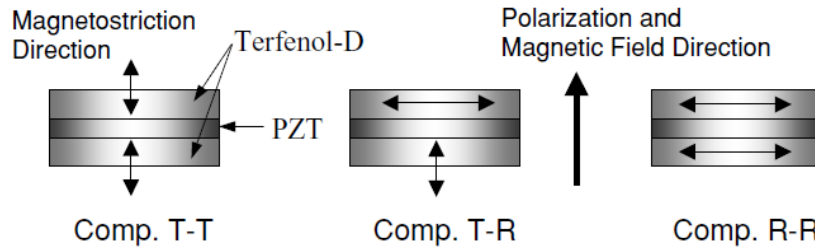


FIGURE 1.6: possible magnetostriction directions.

Commonly the configuration with the same magnetostriction directions of the ferromagnetic and piezoelectric phases has more superior ME property [24, 32].

3. *Magnetic field direction.* Dependence of the ME response on the magnetic field direction is an important factor. According to the theoretical calculations, these behaviors are basically related to the areal strain changing behavior of ferromagnet with changing applied magnetic field direction [34].

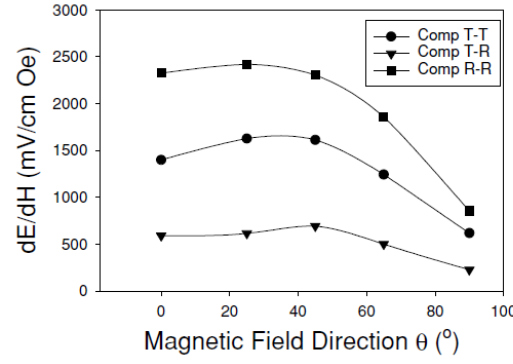


FIGURE 1.7: effect of magnetic field direction. It should be note, that the ME effect becomes bigger if the magnetostriction directions of top and bottom constituents are the same.

4. *Frequency of electromechanical resonance (ERM)*. Bichurin et al. [36] first developed a theory for the ME effect at electromechanical, ferromagnetic, and magnetoacoustic resonances in the composites. As the ME effect in the composites is due to mechanical coupling between the piezoelectric and magnetic phases, the ME effect would be greatly enhanced when the piezoelectric or magnetic phase undergoes resonance, i.e., electromechanical resonance for the piezoelectric phase and ferromagnetic resonance (FMR) for the magnetic phase. Mechanical oscillations of a medium are induced by either alternating magnetic or electric fields, and the wave length is tens meters and much larger than the composite sizes. One more resonance phenomenon is important. This is the ME interactions at the coincidence of the FMR and EMR, i.e., at the magnetoacoustic resonance (MAR). Coincidence of the FMR and EMR allows the energy to transfer between phonons, spin waves, and electric and magnetic fields. This energy transfer is found to be very efficient in the ferrite-PZT bilayer; ultrahigh ME coefficients are expected at MAR. This effect is important for miniature nanosensors and transducers at microwave frequencies [32].

Chapter 2

Aims

Over the last few decades a significant amount of works devoted to finding and manufacturing of novel materials with advanced magnetoelectric (ME) properties have been published.

It is known, that the magnetoelectric properties of the multiferroics based on induction of electric field in the sample by means of magnetic field and vice versa are very sensitive to changes of external conditions, such as temperature, electric and magnetic fields. The ME effect gives the opportunity both to control electric properties using magnetic field and to handle magnetic properties applying electric field. The ME effect depends on the coupling between electric and magnetic fields. Material, number and thickness of layers, chemical composition and configuration of the constituents as well as quality and stability of the interfaces radically affect on the value of ME response. Multilayered heterostructures, wherein a coupling between ferroelectrics and ferromagnet occurs by strain, allow to obtain the high value of magnetoelectric effect [24]. It should be noted that at present the film and laminated structures start to be a centre of attention of researchers because of their enhanced magnetoelectric properties, wide commercial accessibility and relatively low cost. Therefore the thin film multiferroic structures are perspective for practical application. Multiferroics studied in the present thesis being ferromagnetic/ferroelectric structures manifest simultaneously both magnetic ordering and spontaneous polarization. The combination of precise characterization of structural, magnetic and magnetoelectric properties of multiferroic structures using X-ray diffraction, scanning electron microscopy, magnetic and electric measurements allows to find out the dependence of magnetoelectric properties on both composition of heterostructures and optimal structure of constituents.

One of the aims of the thesis is looking for a new multiferroic materials with desired properties, broad availability and high reproducibility as well as a development of new

technology for obtaining of high quality hybrid thin film structures using dual ion-beam sputter technique [37–39]. The special attention will be given to an examination of structure and quality of the piezoelectric/ferromagnetic interface using the conversion scanning electron microscopy (SEM).

The essential objectives of the thesis are:

- analysis of methods and techniques of preparation and investigation of the new film structures with desired magnetoelectric properties;
- examination of size effect on the magnetoelectric properties of the ferromagnetic/ferroelectric heterostructures, where the mechanism of strain-mediated coupling exists. To achieve this goal the ferromagnetic films of metallic Ni and Co, alloy NiFe or TbMnO₃ manganite were grown on a ferroelectric PbZr_{1-x}Ti_xO₃ (PZT) or SrTiO₃ substrates, respectively;
- investigation of the influence of quality and stability of ferromagnetic/ferroelectric interface on the magnetoelectric properties of the heterostructures;
- study of the influence of number, configuration and chemical composition of ferromagnetic and ferroelectric layers in the new layered heterostructures on the value of ME effect;
- study of influence of resonance properties on the magnitude of magnetoelectric effect.

The main result of the thesis is expected to be clarification of the main factors responsible for an increase of magnetoelectric effect in new multiferroic heterostructures.

The aims and tasks of studies presented in the thesis are important for both the fundamental science and applications. Their realization gives opportunity to control the physical properties of multilayered structures by depositing ferromagnetic films with different magnetic properties and thickness on ferroelectric substrate.

Chapter 3

Experimental

Using standard ceramic processing technique, which included grinding and hot pressing into pellets of a few millimetres in diameter and 300–400 μm in thickness, ferroelectric PZT substrates with composition $\text{PbZr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ were prepared. The surface of the substrates prepared was abrasively ground to the desired thickness and then polished by a standard chemical–mechanical procedure to mirror. Small irregularities in the form of polishing-induced scratches and cavities were eliminated from the surface through a number of sequential cycles involving the deposition of smoothing layer similar in chemical composition to a ferromagnetic film. In each subsequent cycle, the thickness of the smoothing layer was reduced. The ferromagnetic film primarily deposited onto the PZT substrate was removed by high energy ion sputtering to a depth slightly exceeding the thickness of the film. This allowed to gain the flat ceramic surface with small number of discontinuities and nanoscale roughness (Fig 3.1).

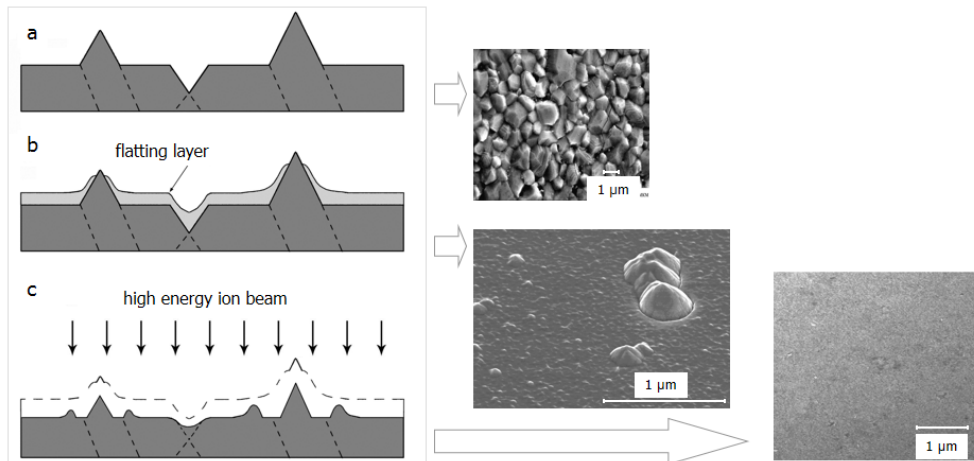


FIGURE 3.1: process of surface smoothing.

- (a) — initial surface of PZT ceramic;
- (b) — smoothing layer of a ferromagnetic film;
- (c) — cycle of high energy ion beam sputtering and final PZT surface image.

Ferromagnetic films were prepared by mean of ion-beam sputtering technique using the same sputtering system equipped by wide-aperture ion source with cold hollow cathode on the base of two-step self-contained low-pressure gas discharge. The main components of the vacuum sputter system are presented in Fig 3.2. The ferromagnetic films were formed by sputtering of targets by beam of Ar ions with energy of about 1600 eV and density of 0.25 mA/cm². The pressure in the camera was controlled by automatic system on the level of about 0.1 Pa. The substrates mount on rotated placeholders, which are enabled to rotate the substrates around both own axes and axe of rotator. Such technique together with wide-aperture ion source guarantees more uniform deposition of films.



FIGURE 3.2: ion-beam sputtering system.
Left — rotating placeholders;
right — deposition camera with wide-aperture ion source.

The FM/FE heterostructures obtained were polarized in external electric field at 150 °C for a few hours, followed by cooling in the field down to room temperature. To prevent degradation of the film during poling, the surface of the FM/PZT/FM samples was protected on both sides by gold film up to 0.4 μm in thickness (Fig. 3.3).

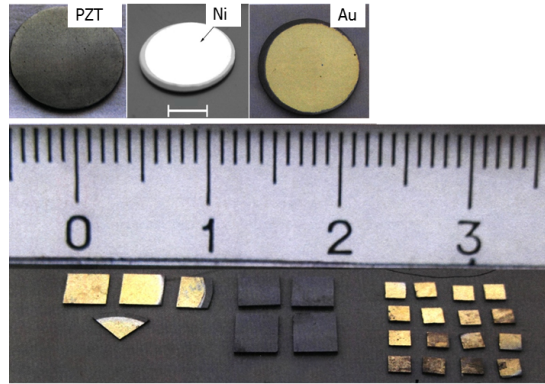


FIGURE 3.3: top — initial PZT surface, ferromagnetic (Ni) layer deposited, Au capping layer;
bottom — cut samples.

The surface and cross sections of the structures were examined by scanning electron microscopy (SEM) on a Helios NanoLab DualBeam (FIB/SEM) system (FEI, United States). Cross-sectional images of characteristic areas were obtained using focused ion

beams. Optical measurements were made on a Carl Zeiss NU-2E microscope. The films thickness during deposition and sputtering was determined using an MII-4 Linnik–Nomarski interference microscope and by analyzing cross-sectional SEM images. X-ray diffraction structural analysis of the samples was also performed.

Magnetic characteristics of the samples were investigated by vibrating magnetometry on universal automatized measuring setup "Liquid Helium Free High Field Measurement System" firm "Cryogenic LTD". Magnetic field dependences were measured in the range from -1 to +1 T at room temperature.



FIGURE 3.4: left — "Oxford Cryogenics" system with superconducting magnet; right — insert for magnetoelectric measurements.

Magnetoelectrical measurements at room temperature were carried out by measuring the voltage arising on the sample subjected to alternating and permanent magnetic fields. The magnetic field bias was produced by electromagnet while alternating field was produced by Helmholtzs coils. Magnetoelectric voltage coefficient α_E was determined as $\alpha_E = \frac{dU}{h \cdot dH}$, where dU is the alternating voltage, dH the magnetic field strength and h the PZT layer thickness [38].

Magnetoelectrical measurements of the heterostructures have been also performed at 4.2 K by measuring the electric charge induced by modulated magnetic field by means of special insert connected to Keithley electrometer (see Fig 3.4). The construction of the insert enables to perform measurement for various orientation of the sample in external magnetic field. Magnetic field was measured by conventional Hall sensor. Temperature was controlled by thermometer mounted directly on insert using a precision Lakeshore 340 temperature controller, which has provided a precision control of temperature in the sample space. Modulated magnetic field (0.01–0.015 T) was created using digital signal processor (Lock-In DSP). Its frequency was controlled by output

frequency of DSP [39, 40]. To avoid the influence of thermopower and temperature drift of the electric charges, the sample was electrically shielded and preliminary putted in the helium camera for 5–6 hours.

Measurements of magnetoelectric response were also carried out for ferroelectric substrates. It has been shown that the substrate doesn't contribute to the overall magnetoelectric signal of the structure. The measurements of capacity and dielectric losses have been done using high precision capacity bridge AH2550A in external magnetic fields of up to 8 T and over a temperature region of 4.2–300 K.

Chapter 4

Results

A magnetoelectric effect in ferromagnetic/ferroelectric composite heterostructures is strongly influenced by the state of interface between the ferromagnetic metal and ferroelectric ceramic layers. A quality of interface dramatically depends on adhesion between the composite layers, quality of layers surfaces and their connection method. The main drawbacks of an adhesive contact are relatively low thermal stability of properties of the resulting structures, poor reproducibility of characteristics from sample to sample and cutting-induced damage to samples during the fabrication of sensing elements (microscaling). An intermediate layer between ferromagnetic and ferroelectric materials becomes uncontrollable, since a presence of a glue layer at the metal/ferroelectric interface prevents to form the direct contact between components. This reduces significantly the interaction between ferromagnetic and ferroelectric subsystems resulting in decrease of reproducibility, controllability and the value of magnetoelectric effect.

To overcome these limitations, a sputtering deposition method has been applied. The ion-beam technique used allows to obtain the heterostructures, in which the ferromagnetic layer contacts directly with the ferroelectric substrate and to optimize the thickness of given structures.

Significant attention was paid to the size effect of piezoelectric and ferromagnetic constituents on the value of magnetoelectric response. It has been shown that the interface region plays a crucial role forming ME effect in such materials. By this reason, the technique of polling and smoothing of the surface of ferroelectric substrate as well as the protection of ferromagnetic layers deposited were applied.

The ferroelectric ceramic substrates were prepared using a standard technique of milling and hot pressing. After thinning by abrasive grinding to desired thickness, the substrate surface was polished by a standard chemical-mechanical procedure to mirror. In the final

step, the surface was smoothed to a submicron level by dual ion-beam sputter deposition as described previously. The ferromagnetic films were formed by means of ion-beam sputtering of targets by argon ions with energies of 1400–1600 eV using double ion-beam sputtering deposition setup equipped by wide-aperture ion sources with cold hollow cathode on the base of two-step self-contained low-pressure gas discharge (repeat). The samples were protected by gold capping layer and poled by a dc electric field of about 4 kV/mm at temperature of 150 °C for 2 hours, followed by cooling down to room temperature in the same field.

The quality of interfaces and layers deposited was examined by X-ray diffraction and high-resolution scanning electron microscopy techniques as well as by capacity measurements performed. This has allowed to select the most qualitative samples for following studies. Based on the structural analysis data, the crystal lattice parameters and internal stresses near interface regions were calculated. The performed calculations show that the entire relaxation of internal stresses takes place when the ferromagnetic layer thickness is of order 1 μm .

We have started our studies on the simple single-element structures of Co/PZT/Co, after more complex, multi-layered heterostructures were synthesised. Here, much attention has been compiled to structure, quality and optimal number of layers (interfaces) as well as finding and choosing appropriate candidates for ferromagnetic phase. Co, Ni and permalloy ($\text{Ni}_{78}\text{Fe}_{22}$) have been taken into account because of their high magnetostriction at room temperature and low magnetic fields applied.

In all the studies performed, the main objectives were chosen as to cover the widest spectrum of the factors, which affect the structure and, consequently, magnetoelectric properties of the heterostructures. Number and thickness of layers, configuration and chemical composition of the ferromagnetic and ferroelectric constituents, quality and stability of the interfaces were taken into account.

4.1 Paper I

A. Sazanovich, Yu. Nikolaenko, W. Paszkowicz, V. Mikhaylov, Yu. Medvedev, V. Nizhankovskii, V. Dyakonov, H. Szymczak, *Magnetic and ferroelectric ordering in the TbMnO₃ film*, Acta Physica Polonica A, 125(1):128, 2014

Investigation of magnetic and magnetoelectric properties of multiferroic TbMnO₃ film grown onto the ferroelectric SrTiO₃ substrate using magnetron sputtering technique has been performed. X-ray diffraction analysis showed minor offset in stoichiometric composition of the film and mismatch of lattice parameters of the film and the substrate. We concluded the film is compressively strained by the substrate resulting in the tetragonally distorted orthorhombic phase of TbMnO₃. The measurements of temperature dependences of both the electric polarization and dielectric constant of the TbMnO₃ film as well as temperature dependence of reciprocal susceptibility have helped to find out the phase transition points near 10 K and 40 K, corresponding to the antiferromagnetic ordering of the Tb³⁺ and Mn³⁺ moments, respectively. It has been shown that the charge ordering and ferroelectric phase appears below 30 K and significantly raises coming through 10 K.

Furthermore, series of anomalies of magnetic and electric properties of TbMO₃ near the magnetic and ferroelectric phase transitions were found that has allowed to control and manage these properties by the application of magnetic and/or electric fields.

The electric polarization depends strongly on both value and direction of magnetic field relative to the crystallographic axes. The magnetic-field-induced electric polarization in magnetic field $H \perp a$ exceeds one for magnetic field applied along the a axis. The significant increase of polarization is observed below 7 K, especially for $H \perp a$ direction, which may be associated with ordering of the Tb³⁺ moments. It should be noted that the temperature of ferroelectric phase transition slightly shifts towards high temperatures with applying or changing the direction of magnetic field.

The hysteretic behaviour in the TbMnO₃ film was observed at low temperatures. These measurements confirmed that an antiferromagnetic film exhibits an intrinsic ferromagnetic order at low temperatures. One of possible mechanism of the observed ferromagnetism is presumed to be the coupling between magnetization and film strain imposed by the substrate [42].

The TbMnO₃ multiferroic film grown onto the ferroelectric substrate shows relatively high value of magnetoelectric response of 8.2 $\mu\text{C}/\text{m}^2$ in magnetic field above 1 T and

about 15% of dielectric constant change below 40 K. The magnetoelectric and magneto-capacitive effects observed in this material can be used in novel magnetoelectric devices, in which the magnetic properties are electrically controlled and vice versa.

To archive these results, the technique of the measurement of magnetization, electric polarization and susceptibility of the film structures over a temperature range of 4.2–300 K and in magnetic fields up to 8 T was developed. This technique was successfully used in our further investigations of multilayered ferromagnet/ferroelectrics heterostructures.

4.2 Paper II and III

A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bepalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, M. N. Smirnova, and V. A. Ketsko, *Effect of Cobalt Layer Thickness on the Magnetoelectric Properties of Co/PbZr_{0.45}Ti_{0.55}O₃/Co Heterostructures*, Inorg. Mater., 49(10):1011, 2013

A. I. Stognij, N. N. Novitskii, S. A. Sharko, A. V. Bepalov, O. L. Golikova, A. Sazanovich, V. Dyakonov, H. Szymczak, and V. A. Ketsko, *Effect of Interfaces on the Magnetoelectric Properties of heterostructures Co/PZT/Co*, Inorg. Mater., 50(3):275, 2014

Ferroelectric PZT substrates with composition $\text{PbZr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ were prepared using processing and smoothing techniques described above (Sec. 3). Cobalt films were grown through ion-beam sputtering of the cobalt target by high energy argon ions in a residual vacuum of 0.1 Pa or better. To prevent degradation of the cobalt film during poling, the surface of the Co/PZT/Co samples was protected on both sides by gold film up to $0.4\ \mu\text{m}$ in thickness. After, the samples were polled by a dc electric field at temperature of 150°C for 2 h, followed by cooling down to room temperature in the same field.

Visual analysis of surface and cross section of the structures by scanning electron microscope has confirmed high homogeneity of surfaces and interfaces of the samples. It is important, that the interface region was smoothed and free from significant defects and impurities (Fig. 4.1).

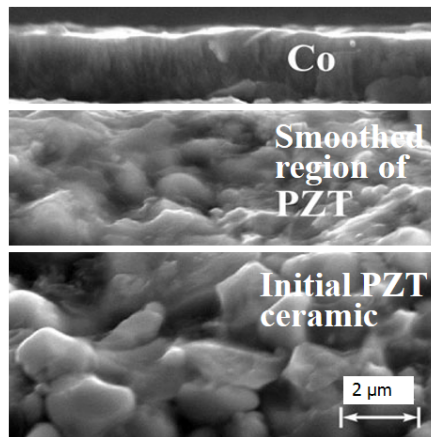


FIGURE 4.1: SEM image of Co/PZT interface region.

The X-ray diffraction measurements of the heterostructures with different thickness of Co layer show fluently increasing intensity of reflection from cobalt passing through a maximum at a thickness of $2\ \mu\text{m}$. This fact points at a relatively high structural

perfection of the ferromagnetic film on the ceramic substrate. This analysis has found that the substrate was in an elastically stressed state induced by cobalt film growth. Following the X-ray data we suggested, that, at the cobalt layer thickness more than $3\text{ }\mu\text{m}$, the PZT substrate is in a less elastic state in comparison with the heterostructures having cobalt layers of 1 and $2\text{ }\mu\text{m}$ in thickness. Therefore, the cobalt layers of $1.5\text{--}2.5\text{ }\mu\text{m}$ have a relatively perfect crystal structure and induce the highest elastic stress in the PZT substrates.

Magnetic measurements of cobalt films with various thicknesses grown on presmoothed PZT substrates have indicated that the maximum value of saturation magnetization appears at $2.5\text{ }\mu\text{m}$ of thickness of the film. These measurements together with the measurements of dependence of magnetoelectric coefficient on a thickness of ferromagnetic and ferroelectric constituents indicate that the largest value of the magnetoelectric response of $9.3\text{ mV/cm}\cdot\text{Oe}$ is observed at the thicknesses of cobalt layer of $2\text{--}3\text{ }\mu\text{m}$ and PZT component of about $100\text{ }\mu\text{m}$.

Such value of magnetoelectric response slightly differs in the magnitude of the ME effect reported for similar structures in which the functional layers are bonded by a foreign binder layer [32]. The key distinctive feature of the structures produced through ion-beam deposition/sputtering is that the good direct contact between ferromagnetic and ferroelectric phases makes the structures reproducible and stable during prolonged service under high thermal loads. It is important to note, that the volumes of piezoelectric and ferromagnetic phases do not need to be equal to form significant ME response. Our results show that the near interface region plays the determinative role in inducing of the magnetoelectric effect in such structures. This fact permits scaling up them by micro-electronic means in producing discrete miniature devices. FM/PZT/FM structures can be integrated into more complex structures, $(\text{FM/PZT/FM})_n$, which would be expected to exhibit a stronger ME effect.

4.3 Paper IV

A. Stognij, N. Novitskii, A. Sazanovich, N. Poddubnaya, S. Sharko, V. Mikhailov, V. Nizhankovski, V. Dyakonov, and H. Szymczak, *Ion-beam sputtering deposition and magnetoelectric properties of layered heterostructures (FM/PZT/FM)_n, where FM -- Co or Ni₇₈Fe₂₂*, Eur. Phys. J. Appl. Phys., 63:21301, 2013

Based on a technique of preparation of the single-layer Co/PZT/Co heterostructures, we have developed the method to scale up the structures to more complex multi-layered ones, which, potentially, should be allowed to obtain a stronger magnetoelectric effect.

Co/PZT/Co and Py/PZT/Py were chosen as initial heterostructures. The choice of lead zirconate titanate (PZT) as ferroelectric ceramic is conditioned by both high values of remanent polarization (10–40 $\mu\text{C}/\text{m}^2$) and relatively low temperature (550–650 °C) of perovskite phase formation [43]. Co and permalloy (Py) were chosen taking into account their high magnetostriction at room temperature and a data earlier obtained for the Co/PZT/Co structures [37, 41].

The ferroelectric ceramic substrates were formed by standard technology of milling and pressing. After, the ceramic samples were thinned, polished and smoothed by repeated sputtering/deposition of a target with the same composition. The ferromagnetic films were formed by means of ion-beam sputtering of cobalt or Ni₇₈Fe₂₂ targets. Then, the heterostructures obtained were polarized in external electric field with strength of 4 kV/mm at 150 °C for two hours, followed by cooling in this field down to room temperature.

The magnetic measurements of Co and Py films deposited onto PZT and silicon substrates have allowed to determine the optimal thickness of ferromagnetic layers. The saturation magnetization of the ferromagnetic layer was found to depend on the substrate type. This is confirmed by the fact that the cobalt film of 3 μm thickness deposited onto the silicon substrate yields twice as large magnetic signal as the same film evaporated onto the ferroelectric substrate. The difference is explained by assumption that the film on ceramic surface is not continuous as compared with the same film on silicon. As a result, the discontinuities created by the ceramic substrate reduce the net magnetization of the whole film. Evidently that the smaller is the ceramic density, the smaller is the saturation magnetization of the film. It was found that the saturation magnetization change depends on thickness of ferromagnetic constituent. Together with the data of magnetoelectric measurements, it was found that the optimal thickness of ferromagnetic layers is of 2–2.5 μm , which is in agreement with X-ray data obtained before for Co films [37].

Further, the thickness optimization of ferroelectric PZT layer was made, which was realized by means of its thinning to such minimal thickness, at which the magnetoelectric interaction through the ceramic should be most effective. The transfer of elastic strains between ferroelectric and ferromagnetic phases, which plays a crucial role in formation of magnetoelectric interaction, was defined using the relative value of contact area of ceramic grains between themselves. Taking into account the structural data obtained by SEM, the average grain size was determined to be equal to 2–5 μm . It means that the distance through which the elastic interaction can be transferred is of about a few grains, that is within 10–20 μm . Unfortunately, during thinning ceramic plate down to 20 μm or less, the metal layer because of the accumulation of mechanical stresses in it bends the plate that results in its cracking and peeling. By this reason the thinning of ferroelectric plate has been realized down to safe thickness no less than 80 μm .

Having the data of optimal configuration of ferromagnetic and ferroelectric constituents, the multi-layered structures were produced. At first, the layered structures including only one elemental unit FM/PZT/FM with desired configuration of $\text{Co}(2\text{ }\mu\text{m})/\text{PZT}(80\text{ }\mu\text{m})/\text{Co}(2\text{ }\mu\text{m})$ or $(\text{Py}(2\text{ }\mu\text{m})/\text{PZT}(80\text{ }\mu\text{m})/\text{Py}(2\text{ }\mu\text{m}))$ were made. Such structure was formed in the following way. The metal layer of 2 μm thickness was deposited onto the one side of PZT plate of 400 μm thick. The opposite side of the ceramic plate was polished down to 80 μm , and the 2 μm thick metal layer was deposited onto this side. Based on this one-element structure the two- and three-element structures were formed. The one-element structures were connected to each other by ferromagnetic layers with epoxy glue. In the case of three-element structure, the medium ceramic layer was thinned down to 20 μm whereas the outer PZT layers had thicknesses of 80 μm . It is due to the fact that two adjacent ceramic layers thinned down to 20 μm have undergone the mechanical destruction because of the internal stresses arising in ferromagnetic layer (see Fig. 4.2).

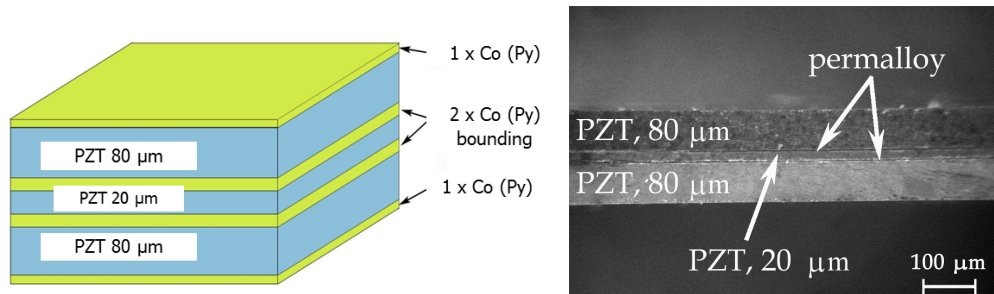


FIGURE 4.2: left — principal schema of multi-layered $(\text{Co(Py)}/\text{PZT}/\text{Co(Py)})_n$ heterostructure;
right — SEM image of three-layered $\text{Py}(2\text{ }\mu\text{m})/\text{PZT}(80\text{ }\mu\text{m})/\text{Py}(2\text{ }\mu\text{m})//\text{Py}(2\text{ }\mu\text{m})/\text{PZT}(20\text{ }\mu\text{m})/\text{Py}(2\text{ }\mu\text{m})//\text{Py}(2\text{ }\mu\text{m})/\text{PZT}(80\text{ }\mu\text{m})/\text{Py}(2\text{ }\mu\text{m})$, where the glue connections are marked by double inclined lines.

TABLE 4.1: The calculation results of maximal mismatch f^{max} , internal stresses σ^{max} and minimal ferromagnetic film thickness h_{min}

		Crystal lattice spacing of substrate, $\text{\AA}$	
		$a = 4.063$	$c = 4.106$
Crystal lattice spacing of HCP cobalt film, $\text{\AA}$	$a = 2.205$	$f^{max} = 0.622$	$f^{max} = 0.639$
		$\sigma^{max} = 65.6 \text{ GPa}$	$\sigma^{max} = 67.4 \text{ GPa}$
		$h^{max} = 0.25 \text{ }\mu\text{m}$	$h^{max} = 0.26 \text{ }\mu\text{m}$
	$c = 4.089$	$f^{max} = 0.006$	$f^{max} = 0.004$
		$\sigma^{max} = 0.633 \text{ GPa}$	$\sigma^{max} = 0.422 \text{ GPa}$
		$h^{max} = 0.002 \text{ }\mu\text{m}$	$h^{max} = 0.001 \text{ }\mu\text{m}$
Crystal lattice spacing of permalloy film, $\text{\AA}$	$a_{Ni} = 3.524$	$\sigma^{max} = 15.8 \text{ GPa}$	$\sigma^{max} = 17.1 \text{ GPa}$
		$h^{max} = 0.054 \text{ }\mu\text{m}$	$h^{max} = 0.058 \text{ }\mu\text{m}$
	$a_{Fe} = 2.860$	$\sigma^{max} = 42 \text{ GPa}$	$\sigma^{max} = 43.6 \text{ GPa}$
		$h^{max} = 0.012 \text{ }\mu\text{m}$	$h^{max} = 0.012 \text{ }\mu\text{m}$

The measurements of magnetoelectric response were performed on these multi-layered structures. The maximum value of magnetoelectric voltage coefficient of $250 \text{ mV/cm}\cdot\text{Oe}$ was achieved for $(\text{Py}/\text{PZT}/\text{Py})_3$ heterostructure. This is two orders larger value of effect than one reported for $(\text{Co}/\text{PZT}/\text{Co})_n$ [44]. The measurements of electric charge induced by altering magnetic field at different frequencies were also performed. It was found that magnetoelectric effect essentially depends upon frequency of alternating magnetic field and has a resonant behavior at low frequencies. Its maximum value is observed in the region of 50–150 Hz and a magnetic field range of $\pm 1.5 \text{ T}$.

The results of calculations of maximal mismatch f^{max} , internal stresses σ^{max} and minimal ferromagnetic film thickness h_{min} against combination of lattice spacing for Co, Py and Ni films and substrate were done (see Table 4.1). The performed calculations have shown that Co and permalloy are the most appropriate metals to form ferromagnetic layer onto $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ substrate. Here, the entire relaxation of internal stresses takes place when the ferromagnetic layer thickness is of the order of $1 \text{ }\mu\text{m}$. The obtained calculation results are in a good agreement with experimental data presented above.

Results of this work allow basing on single element cells to obtain, optimize and investigate the multi-layered heterostructures. We have obtained a huge value of magnetoelectric effect of $250 \text{ mV/cm}\cdot\text{Oe}$ for three-layered $(\text{Py}/\text{PZT}/\text{Py})_3$ structure at room temperature and low frequency of 100 Hz. These structures are perspective as a primary transforming element of sensor devices and can serve as the base for production of nonvolatile magnetoelectric sensors.

Chapter 5

Conclusions

The precise characterization of structural, magnetic and magnetoelectric properties of the ferromagnets/ferroelectrics heterostructures, especially their interfacial layers, is one of the main findings and results of the performed study.

The use of ion-beam sputtering/deposition technique has allowed to obtain ferromagnetic/ferroelectric layered heterostructures with direct, thermally stable contacts and the absence of chemical bounders between the layers. The essential role was established to play the process of chemical-mechanical polishing, smoothing of the ceramic surface and preliminary deposition of thin FM layer that forms high quality controllable interface between ferromagnetic film and ferroelectric ceramic substrate. X-ray structural analysis together with SEM investigations have found that the interface is continuous with no significant bulges, delaminations and free from impurities. This increases the interaction between ferromagnetic and ferroelectric subsystems resulting in increasing the magnetoelectric effect.

The particular attention has been paid to size optimization of ferromagnetic and piezoelectric constituents. Based on the results of X-ray diffraction measurements as well as the dependence of magnetization and magnetoelectric response on the thickness of both FM film and FE substrate, the optimal size of the ferromagnetic film equal to 2–2.5 μm was determined. The dependence of the ME effect on the PZT substrate thickness was found to be linear. The smaller was ceramics thickness, the biggest the ME effect was achieved. It was connected with the fact that the elastic strains can propagate most effectively through small enough distance between the layers. From the another hand, with thinning ceramic plate down to 20 μm , the metal layer because of the accumulation of mechanical stresses results to its cracking. For these reasons, the optimal thickness of FE substrate equal to 80 μm was selected.

Relying on the structural and size optimization of the single elements cells of $\text{Co}(2\ \mu\text{m})/\text{PZT}(80\ \mu\text{m})/\text{Co}(2\ \mu\text{m})$ or $(\text{Py}(2\ \mu\text{m})/\text{PZT}(80\ \mu\text{m})/\text{Py}(2\ \mu\text{m}))$, the multi-layered structures were formed. Combining with the number of element cells and the material of FM constituent, the biggest value of ME response was found for three-layered permalloy-based heterostructures $(\text{Py}/\text{PZT}/\text{Py})_3$. Such structures show the record value of magnetoelectric effect of $250\text{mV}/\text{cm}\cdot\text{Oe}$ at room temperature, at low magnetic field of a few hundreds of Oe and low frequency of 100 Hz. This effect is of the two orders of magnitude larger than the ME reported for single-layered structures. The layered structures with more than three ferroelectric layers are unpromising since each subsequent layer leads to decrease of mechanical strength of the overall structure and, as a result, the magnetoelectric effect does not increase. Also the cutting of this structure on chips by standard microelectronic device is significantly complicated.

It should be noted, that magnetoelectric effect essentially depends upon frequency of alternating magnetic field and has a resonant behaviour at low frequencies. Its maximum value is observed in the region of 50–150 Hz.

In frames of the thesis the new technology obtaining heterostructures with desired magnetoelectric properties was developed. The techniques and tools of investigation of magnetization, electric polarization and susceptibility of the film structures at low temperature and high magnetic fields were elaborated. It was found that main factors responsible for an increase of magnetoelectric effect in new multiferroic heterostructures are:

- producing of high quality, free of impurities interfaces between ferromagnetic and ferroelectric layers without use of any chemical bounders;
- determination of optimal thickness of ferromagnetic and ferroelectric constituents of $2\text{--}3\ \mu\text{m}$ and $20\text{--}80\ \mu\text{m}$, correspondently, at which the magnetoelectric interactions become the most effective;
- producing multi-layered heterostructures based on single element cells. It was established that three-layered structures show the bigger value of magnetoelectric response in contrast to single-layered ones. Replacing Co or Ni by permalloy has allowed to achieve a huge magnitude of ME effect equal to $250\text{mV}/\text{cm}\cdot\text{Oe}$. This value of magnetoelectric effect is of the two orders of magnitude larger than that known for multiferroic materials.

The materials studied are perspective as a primary transforming element of sensor devices and can serve as the base for production of nonvolatile magnetoelectric sensors. Furthermore, a number of drawbacks found must be still overcome. One of the main

problems here is the reducing mechanical strength of ceramics which does not permit to obtain thin ferroelectric layers. The solution of this problem is going to be the aim of our further investigations.

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Appendix A

Original publications

Magnetic and Ferroelectric Ordering in the TbMnO₃ Film

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(Received October 25, 2013; in final form December 9, 2013)

Measurements of magnetization and electric polarization performed for the TbMnO₃ film grown onto the single crystal [100] SrTiO₃ substrate using magnetron sputtering technique exhibit series of anomalies related to the magnetic and electric ordering of the Tb³⁺ and Mn³⁺ sublattices. The detailed temperature dependences of the electric polarization and dielectric constant of the TbMnO₃ film have shown that the ferroelectric phase appears below 30 K in magnetic field $H > 1$ T applied in-plane and out-of-plane of the film.

DOI: [10.12693/APhysPolA.125.128](https://doi.org/10.12693/APhysPolA.125.128)

PACS 75.47.Lx, 75.85.+t, 75.70.Ak, 77.55.Nv

1. Introduction

Among all of the known multiferroic materials, the TbMnO₃ manganite has attracted considerable scientific attention in the last years due to strong coupling between ferroelectricity and magnetism [1, 2]. The magnetoelectric and magnetocapacitive effects observed in the TbMnO₃ ferroelectric can be used in novel magnetoelectric devices, in which the magnetic properties are electrically controlled and vice versa.

In several works [2–5] the structural, electric, thermal, and magnetic properties of the TbMnO₃ single crystals as a function of temperature and magnetic field have been studied. According to a specific heat and neutron diffraction study of the TbMnO₃ single crystal, the anomalies observed at 7 and 41 K are attributed to the antiferromagnetic ordering of the Tb³⁺ and Mn³⁺ moments, respectively. Mn spins order in a sinusoidal incommensurate structure. A spontaneous electrical polarization in the single crystal samples was observed below 28 K, when the magnetic structure transforms from a sinusoidal incommensurate to a spiral antiferromagnetic one that testifies about very strong magnetoelectric coupling.

In works [6, 7] the magnetic properties of the TbMnO₃ thin films have been studied. Neutron scattering measurements [7] have shown the presence of an intrinsic ferromagnetic ordering in an antiferromagnetic multiferroic TbMnO₃ film at low temperatures. Since this antiferromagnet is piezomagnetic, the epitaxial strain was shown to induce a ferromagnetic moment in this film [6], whereas the electric polarization in the TbMnO₃ films was not investigated.

In this paper, the measurements of ferroelectricity and magnetization of the TbMnO₃ film have been performed that has allowed to observe the evolution of magnetic and electric properties of TbMnO₃ near the magnetic and

ferroelectric phase transitions as well as their control by the application of magnetic and/or electric fields.

2. Preparation and measurement techniques

The investigated TbMnO₃ film, 150 nm thick, was grown using magnetron sputtering of target onto [100] SrTiO₃ single crystal substrate in argon–oxygen gas atmosphere. The temperature of substrate was 650 °C and deposition time was 3 h.

Figure 1 presents X-ray diffraction structural analysis performed with low (16 h) and high (2 h) rate. It clearly shows diffraction peaks corresponding to cubic [100] oriented SrTiO₃ substrate (at $2\theta = 22.8$ and 46.5°) and slightly shifted to the left orthorhombic [001] TbMnO₃ film (at $2\theta = 23.8$ and 46.8°). The displacement of peaks corresponding to substrate and film could be justified by minor offset in stoichiometric composition of the film or mismatch of lattice parameters of the film and the substrate. Bulk TbMnO₃ has the orthorhombic perovskite structure, which has lattice parameters of 0.393 nm in-plane and 0.370 nm out-of-plane [8], while the film has the perovskite structure with an out-of-plane lattice parameter of 0.372 nm. Therefore, we conclude the film is compressively strained by the substrate resulting in the tetragonally distorted orthorhombic phase of TbMnO₃. To find out the origin of the peak of 37.5° the more detailed structural analysis must be performed.

The magnetic measurements were carried out using a commercial SQUID magnetometer in temperature range of 5–300 K in magnetic fields up to 5 T.

Electric polarization was measured both at fixed magnetic field and fixed temperature using Keithley 6423 electrometer at temperatures of 5–45 K and in magnetic fields up to 8 T. For measurements of the electric polarization, the silver contacts were plotted onto the widest faces of the rectangle 7×3 mm TbMnO₃ film. Magnetic field was measured by conventional Hall sensor, temperature was controlled by thermometer mounted directly on insert connected to precision Lakeshore 340 temperature controller. The magnetocapacitance measurements have

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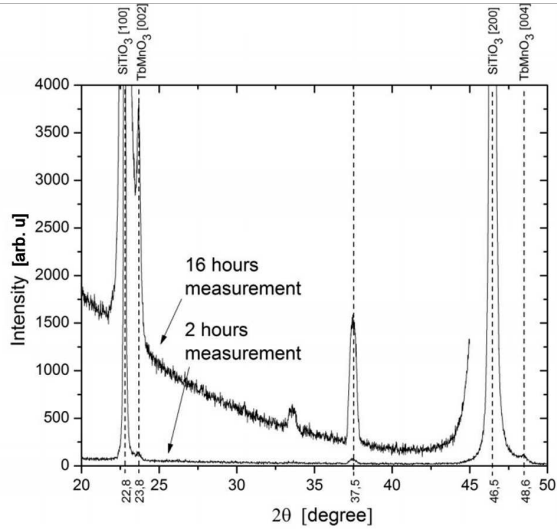


Fig. 1. X-ray diffraction spectra of $\text{TbMnO}_3/\text{SrTiO}_3$ film.

been performed by high precision bridge AH2550A with 1 kHz frequency.

3. Experimental results and discussion

Temperature dependence of susceptibility, M/H , of the TbMnO_3 film in magnetic field of 6 kOe is presented in Fig. 2. The diamagnetic contribution arising from the substrate measured in a separate experiment was subtracted from the raw magnetization. The M/H dependence shows a distinct anomaly at 45 K. This anomaly is close to the anomalies of $C(T)$ and $M(T)$ observed in the TbMnO_3 single crystal [2], which correspond to the magnetic phase transitions in Mn^{3+} sublattice.

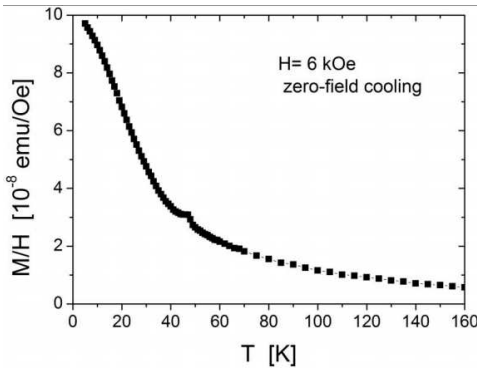


Fig. 2. Temperature dependence of M/H for the TbMnO_3 film with an anomaly near 45 K.

However, the $M/H(T)$ dependence did not detect the anomaly observed at 27 K in the single crystal [2] and connected with an occurrence of the ferroelectric phase, followed by an incommensurate to commensurate magnetic phase transition in the Mn sublattice.

The hysteretic behavior in the TbMnO_3 film was observed at low temperatures in the field range of ± 20 kOe. These measurements show that an antiferromagnetic

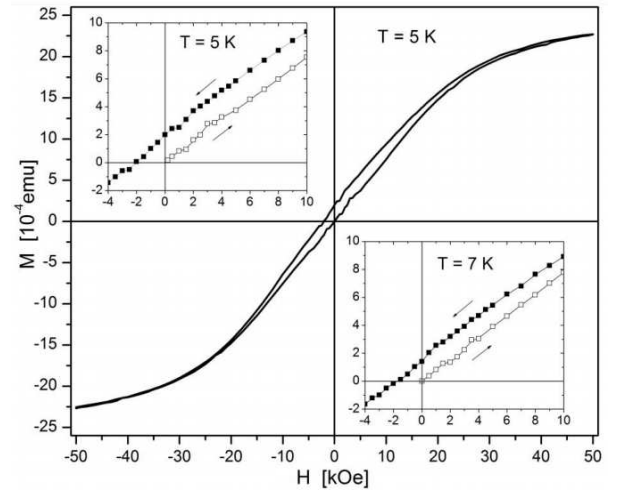


Fig. 3. Hysteresis loops at 5 K and 7 K.

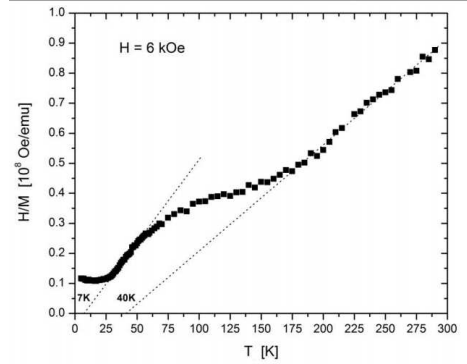


Fig. 4. Temperature dependence of reciprocal H/M susceptibility for the TbMnO_3 film in magnetic field of 6 kOe.

multiferroic TbMnO_3 film exhibits an intrinsic ferromagnetic order at low temperatures (Fig. 3).

This is in agreement with the polarized neutron reflectometry measurements data [7]. One of possible origin of the observed ferromagnetism in film is presumed to be the coupling between magnetization and film strain imposed by the substrate [6].

The measurements of temperature dependence of reciprocal susceptibility display the paramagnetic Curie-Weiss temperatures equal to about 7 K and 40 K for Tb^{3+} and Mn^{3+} ions, respectively (Fig. 4).

The electric polarization of the TbMnO_3 film as a function of temperature at different magnetic fields applied along the a (in-plane) and c (out-of-plane) configurations is presented in Fig. 5. Magnetoelectric measurements of SrTiO_3 substrate were performed in a separate experiment, and the contribution arising from the substrate was subtracted from the raw polarization. It is seen that the electric polarization appears below 30 K in applied magnetic field of $H > 1$ T that is related to the occurrence of the ferroelectric phase.

There is no more difference between ferroelectric signal and noise of substrate above 35 K. It is seen that

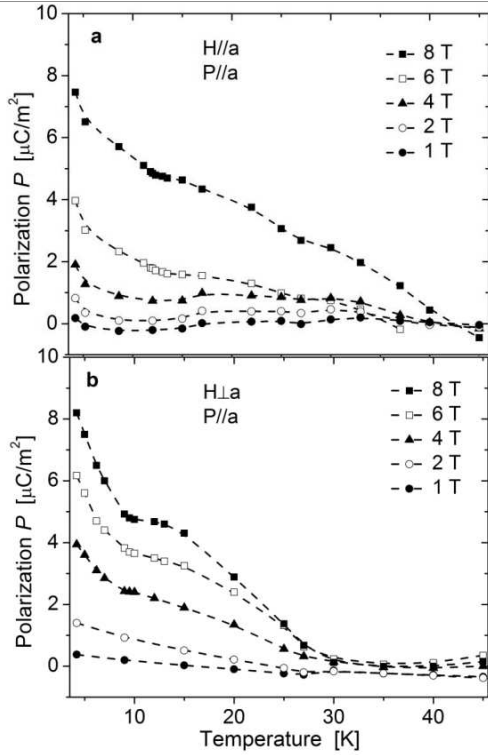


Fig. 5. Experimental electric polarization P vs. temperature at various magnetic fields applied along the in-plane (a) and out-of-plane (b) of the sample.

the electric polarization depends strongly on both value and direction of magnetic field relative to the crystallographic axes. The electric polarization value increases with decreasing temperature and as magnetic field is increased. The onset temperature of ferroelectric ordering (T_{FE}) in magnetic field $H \perp a$ (Fig. 5b) is almost independent of field in contrast to T_{FE} in magnetic field applied along the a axis (Fig. 5a) which shifts towards high temperatures with increasing magnetic field. The magnetic-field-induced electric polarization in magnetic field $H \perp a$ exceeds one for magnetic field applied along the a axis. The significant increase of polarization is observed below 7 K, especially for $H \perp a$ direction (Fig. 5). This data are in line with the measurements of dielectric properties (Fig. 4), where the saturation appears below 10 K.

We have also performed measurements of the dielectric constant at 1 kHz frequency as a function of temperature at magnetic fields applied perpendicular to the film plane.

Figure 6 presents the temperature variation of the dielectric constant, $\Delta\epsilon/\epsilon(0)$, in magnetic fields of 1 and 8 T applied perpendicular to the film plane. The dielectric constant value starts to be observed below 30 K that clearly shows the occurrence of ferroelectric ordering. The dielectric constant saturation below 10 K corresponds to an antiferromagnetic ordering of Tb^{3+} ions. The $\Delta\epsilon/\epsilon(T)$ behavior shows a slight magnetic field effect. These results are in agreement with early obtained data for the single crystal [4].

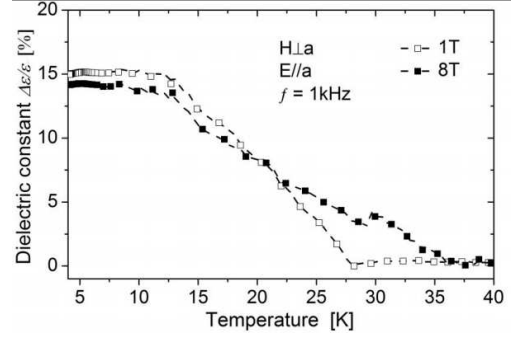


Fig. 6. Changes of dielectric constant, $\Delta\epsilon/\epsilon(0)$, vs. temperature at magnetic fields of 1 and 8 T for out-of-plane configuration.

4. Conclusions

In this paper, susceptibility and electric polarization measurements for the $TbMnO_3$ film have been carried out. The magnetic and ferroelectric phase transitions were determined from the anomalies of magnetic and electric properties as a function of temperature, respectively.

Magnetic field dependences of magnetization show a manifestation of the low temperature ferromagnetism in the antiferromagnetic $TbMnO_3$ film grown on [001] $SrTiO_3$ substrate. However, they do not display signs of a phase transition related to the onset of ferroelectricity observed in the $TbMnO_3$ single crystal. The measurements of temperature dependences of both the electric polarization and dielectric constant of the $TbMnO_3$ film have been performed. It has been found that the charge ordering and ferroelectric phase appears below 30 K and significantly raises coming through 10 K.

It should be noted that the temperature of ferroelectric phase transition slightly shifts towards high temperatures with applying or changing the direction of magnetic field.

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Effect of Cobalt Layer Thickness on the Magnetoelectric Properties of Co/PbZr_{0.45}Ti_{0.55}O₃/Co Heterostructures

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Received March 22, 2013

Abstract—We have studied the magnetic properties and determined the optimal range of thicknesses of cobalt films grown on PbZr_{0.45}Ti_{0.55}O₃ (PZT) ceramic substrates with smoothed surfaces. Using an ion-beam deposition–sputtering process, we have produced Co/PZT/Co heterostructures with smooth, thermally stable PZT/Co interfaces. The structures exhibit a reproducible magnetoelectric effect comparable in magnitude to that in known layered structures fabricated by splicing ferromagnetic and ferroelectric layers. A ferromagnetic layer of optimal thickness makes the largest contribution to the magnetoelectric effect. The structures can be used as elements of more complex, multilayer structures. The use of the ion-beam deposition–sputtering process allows one to scale up such heterostructures by microelectronic means in producing magnetoelectric devices.

DOI: 10.1134/S0020168513100117

INTRODUCTION

Layered composites of ferromagnetic metals and ferroelectric ceramics exhibit a giant magnetoelectric (ME) response, reaching a few units to hundreds of mV/(cm Oe), which is several orders of magnitude higher than that in single-layer materials [1–3]. This considerably extends the application area of ME materials and allows one to create high-sensitivity magnetic-field transducers and functional elements of ME control devices and devices for mutual conversion of magnetic and electrical quantities.

A significant role in determining this effect is played by the state of the ferromagnet/ferroelectric interface [4]. Interface smoothness means the absence of discontinuity zones, bulges, and delamination, which otherwise might impair metal–substrate bonding. Such regions may result, first, from a lattice mismatch, second, from a thermal expansion mismatch between the materials in contact, and, third, from submicron-scale discontinuity flaws of the ceramic surface. The second and third factors have a significant effect on the thermal cycling behavior of the material. The presence of pores due to poor contact between crystallites of a ceramic material and, accordingly, loose grain boundaries also considerably impedes mechanical interaction transfer.

The use of ion-beam sputter deposition allows one to obviate these drawbacks [4]. In combination with chemical–mechanical polishing of ceramic materials, this method allows one to produce a quality ferromag-

netic (FM)/ferroelectric (FE) interface, stable to thermal degradation, in contrast to previous results [1, 2, 5].

This article presents a continuation of a previous study in which Stognij et al. [4] obtained FM/PbZr_{0.45}Ti_{0.55}O₃ (PZT)/FM heterostructures with stable ME performance in the temperature range from –25 to +120°C, with an FM/FE interface smooth on a submicron scale. It was shown that the magnitude of the ME effect was influenced primarily by the ferromagnetic layer of optimal thickness, whereas the thickness of the PZT substrate had little effect on it.

EXPERIMENTAL

Ferroelectric PZT substrates with the composition PbZr_{0.45}Ti_{0.55}O₃ were prepared by a standard ceramic processing technique described elsewhere [6], which included grinding and hot pressing into pellets 8 mm in diameter and 400 μm in thickness. The surface of the substrates thus prepared was abrasively ground to the desired thickness and then polished by a standard chemical–mechanical procedure to mirror finish. Next, the substrates were placed in a dual ion-beam sputter deposition system described previously [7, 8]. The system enabled PZT surface profile smoothing followed by cobalt film growth in a single vacuum cycle [4].

To prevent degradation of the cobalt film during polishing, the surface of the Co/PZT/Co samples was pro-

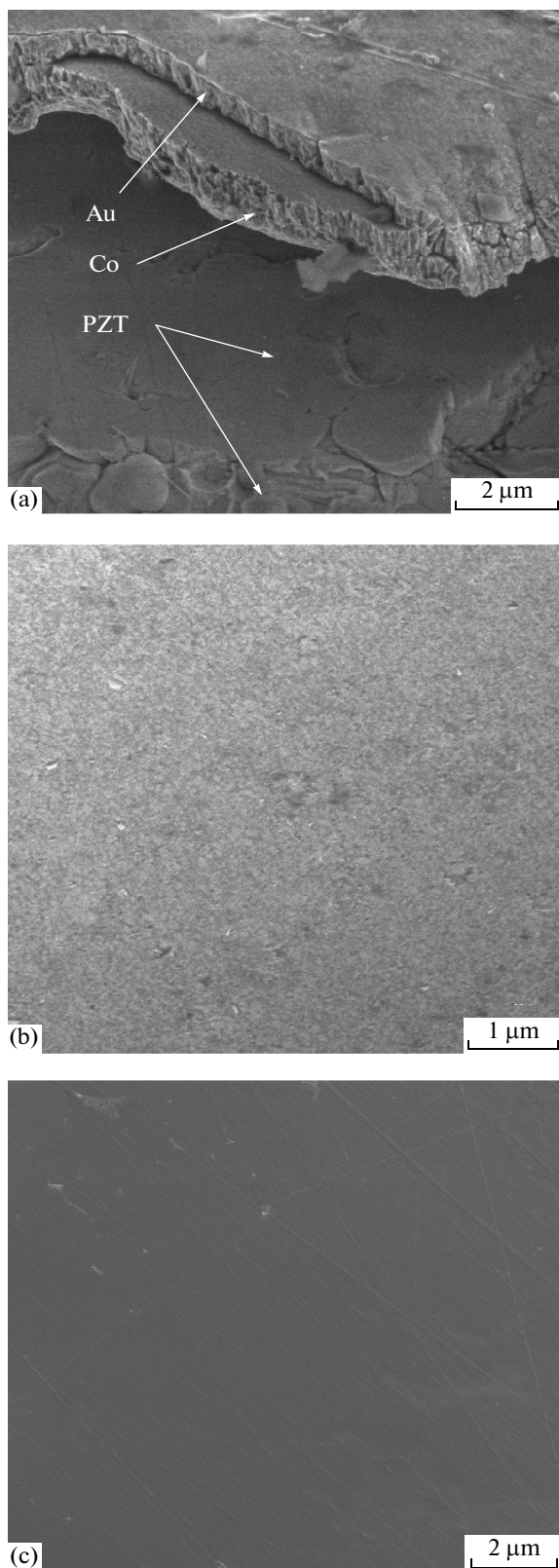


Fig. 1. (a) Cross-sectional fracture surface of a typical Au (0.4 μm)/Co (1.55 μm)/PZT (360 μm) heterostructure; (b) smoothed PZT substrate before metal deposition; (c) metal surface.

tested on both sides by gold film up to 0.4 μm in thickness.

The surface and cross sections of the structures were examined by scanning electron microscopy (SEM) on a Helios NanoLab DualBeam (FIB/SEM) system (FEI, United States). Cross-sectional images of characteristic areas were obtained using focused ion beams. Optical measurements were made on a Carl Zeiss NU-2E microscope. The thickness of the films during deposition and sputtering was determined using an MII-4 Linnik–Nomarski interference microscope and by analyzing cross-sectional SEM images.

The room-temperature ME performance of the structures was evaluated from the voltage induced across the sample by ac and static magnetic fields. The magnetic bias field was generated by electromagnets, and the ac field, by Helmholtz coils. The ME voltage coefficient (α) was determined from the induced ac voltage (dV) and ac magnetic strength (dH) under short-circuit conditions:

$$\alpha = dV/(hdH),$$

where h is the thickness of the PZT film [5].

RESULTS AND DISCUSSION

Figure 1a shows a Au/Co/PZT fracture surface of a Co/PZT/Co heterostructure. The gold film is continuous and protects the functional cobalt layer 1.5 μm thick from external influences. The interface region is smooth and free from impurities. Seen at the bottom of Fig. 1 are PZT crystallites, which are up to 2 μm in size on the fracture surface and have a planar shape and are densely packed on the surface of the structure. We were able to smooth the PZT surface (Fig. 1b) to a submicron level by a technique described previously [4].

Small irregularities in the form of polishing-induced scratches, cavities, and bumps were eliminated from the surface through three sequential cycles each involving the deposition of a smoothing layer similar in chemical nature to the substrate material and subsequent sputtering of the layer to a depth slightly exceeding the thickness of the deposit. At an average bump size of 0.4 μm , the thickness of the first deposited layer was half the bump height. In each subsequent cycle, the thickness of the smoothing layer was reduced by a factor of 2.

Ion-beam sputtering of the surface after the deposition of a smoothing layer occasionally opened grain-boundary cavities (dark areas in Fig. 1b) in the surface layer. Even though the total fraction of surface cavities at a particular distance from the surface does not exceed 2% of their area, the cavities prevent us from achieving a subnanometer smoothness of the FE substrate surface.

Proceeding from the above, the heterostructure surface was characterized by nanoscale roughness. This allowed us to examine the effect of cobalt and PZT layer thicknesses on the ME properties of the heterostructure on a submicron accuracy level.

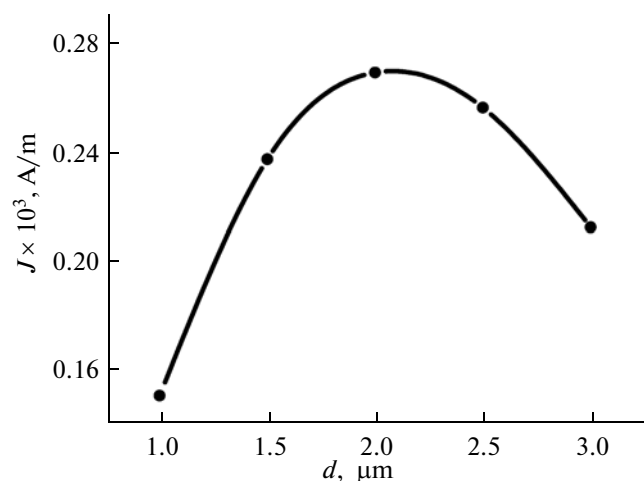


Fig. 2. Saturation magnetization as a function of cobalt layer thickness on smoothed PZT substrate surfaces.

Figure 1c shows the surface of a Co/PZT/Co heterostructure coated with a 0.4- μm -thick gold film. The gold conformally covers the surface of the cobalt layer, which is uniform in thickness (Fig. 1a). As seen in Fig. 1, the surface of the structure and the interfaces have a nanoscale roughness.

According to magnetic measurements on cobalt films of various thicknesses grown on presmoothed PZT substrates (Fig. 2), the ferromagnetic films 2–

2.5 μm in thickness have the highest saturation magnetization. The measured ME voltage coefficient α of the Co/PZT/Co layered samples at frequencies of 100 and 1000 Hz (Fig. 3a) indicates that the ferromagnetic film 2–2.5 μm in thickness makes the largest contribution to the ME effect.

The ME coefficient α is a weaker function of the FE layer thickness (h) (Fig. 3b) in comparison with the FM layer thickness (d). Nevertheless, the decrease in the magnitude of the ME effect with increasing FE layer thickness points to a nonuniform depth profile of the piezoelectric component of the effect.

The ME effect is due to an interplay between two contributions: the magnetoelastic contribution from the ferromagnetic film and the piezoelectric contribution from the dielectric substrate. In the case of the inverse ME effect, even though an external electric field poles the entire dielectric, the ME effect is only contributed by those regions of the FE that either are in mechanical contact with the FM or are located next to it. Thus, the ME effect develops near the interface, as confirmed by Figs. 3a and 3b.

Figure 4 shows the field dependences of the ME voltage coefficient α for a Co (2 μm)/PZT (280 μm)/Co (2 μm) structure at room temperature and frequencies of 100 Hz (Fig. 4a) and 1 kHz (Fig. 4b). They have a characteristic shape, like in the case of similar structures prepared by conventional splicing of FM

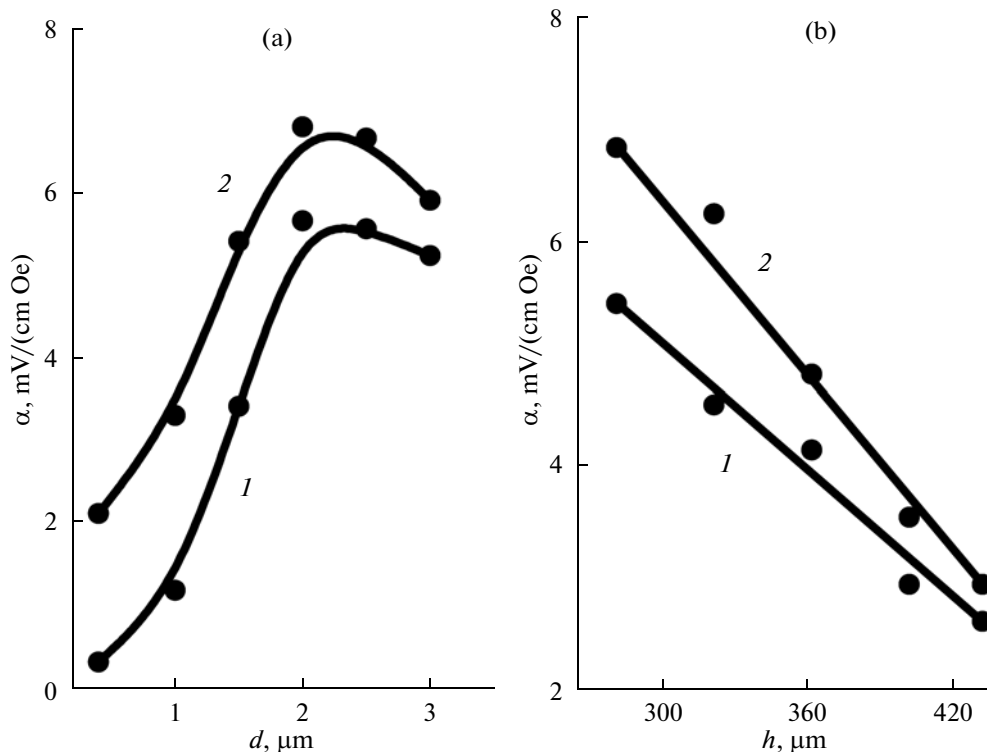


Fig. 3. ME voltage coefficient (a) as a function of cobalt layer thickness in a Co/PZT (360 μm)/Co heterostructure and (b) as a function of ceramic substrate thickness in Co (2.5 μm)/PZT/Co (2.5 μm) heterostructures in a magnetic field of 50 Oe at frequencies of (1) 100 Hz and (2) 1 kHz.

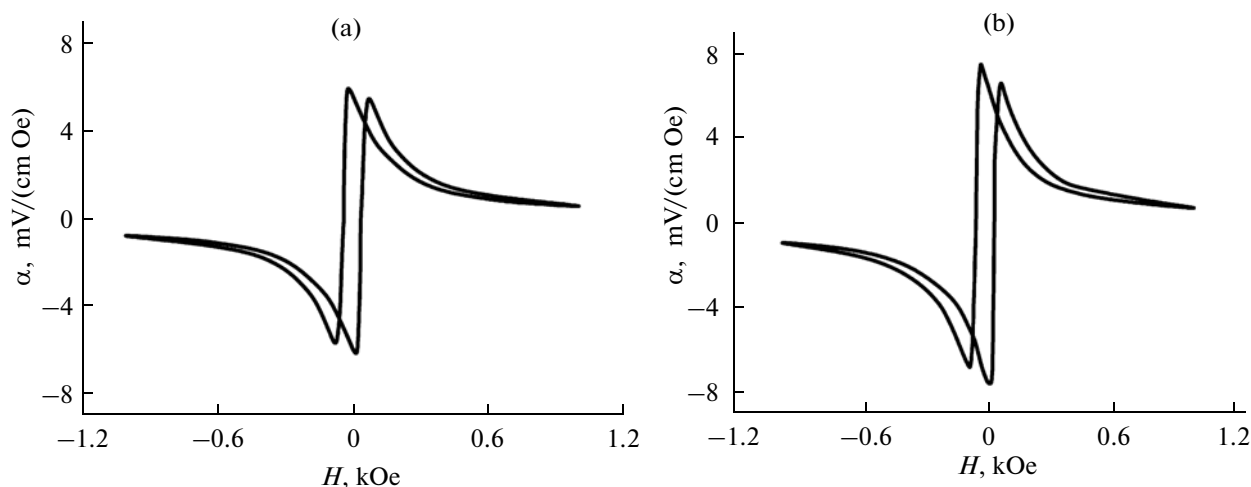


Fig. 4. Field dependences of the ME voltage coefficient for a Co (2 μ m)/PZT (280 μ m)/Co (2 μ m) structure at room temperature and frequencies of (a) 100 Hz and (b) 1 kHz.

and FE layers [1–3, 5]. These structures differ little in the magnitude of the ME effect from similar structures in which functional layers are bonded by a foreign binder layer [1–3, 5]. The key distinctive features of the structures produced through ion-beam deposition/sputtering are that direct contact between their constituent phases makes them reproducible and stable during prolonged service under high thermal loads. Another, no less important feature is the possibility of scaling up them by microelectronic means in producing discrete devices. FM/PZT/FM structures can be integrated into more complex structures, (FM/PZT/FM) $_n$, which would be expected to exhibit a stronger ME effect.

CONCLUSIONS

Chemical–mechanical polishing of PZT-based ferroelectric substrates in combination with an ion-beam deposition–sputtering process allows one to obtain Co/PZT/Co single-element structures with smooth interfaces and direct contact between the FM and FE phases. This allows one to optimize the thickness of the structures and obtain a stable ME effect. The largest contribution to the ME effect of Co/PZT/Co layered heterostructures is made by the ferromagnetic films of optimal thickness: 2–2.5 μ m. The ME effect is comparable in magnitude to that in known structures but differs from them in frequency, which approaches the line frequency, and enables the fabrication of such structures by microelectronic means, in particular, their miniaturization to discrete electronic crystals.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research and the Belarusian

Republican Foundation for Fundamental Research (project no. F12R-020).

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Translated by O. Tsarev

Effect of Interfaces on the Magnetoelectric Properties of Co/PZT/Co heterostructures

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Received September 30, 2013

Abstract—We have studied Co (film)/PZT (substrate)/Co (film) heterostructures with plane-parallel interfaces, produced by direct growth of cobalt films 0.5 to 3.5 μm thick on PZT surfaces smoothed to a subnanometer level (where PZT stands for a ceramic $\text{PbZr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ lead zirconate titanate ferroelectric substrate). The results demonstrate that they possess magnetoelectric properties comparable in magnitude to those characteristic of known structures but, in contrast to these latter, allow one to dispense with the condition that the volume fractions of the ferromagnetic and ferroelectric components be roughly equal. The interface is shown to play a key role in determining the magnetoelectric response of the heterostructures: above 9 mV/(cm Oe) (11.7 mV/A) in a magnetic field of 50 Oe (3980 A/m) at a frequency of 100 Hz and room temperature. The heterostructures are potentially attractive for use as nonvolatile sensors in household devices.

DOI: 10.1134/S0020168514030133

INTRODUCTION

Studies of the magnetoelectric (ME) effect in layered ferroelectric/ferromagnet structures are of both scientific and technological importance [1]. The use of ME devices will enable mutual instantaneous conversion of magnetic and electrical signals with no extra electric circuits and no standby power supply in household devices.

To date, the ME properties of layered ferroelectric/ferromagnet structures produced through mechanical contact followed by heat treatment, in particular with the use of organic fillers, have been studied in the greatest detail [2, 3]. This configuration ensures compact arrangement of ferromagnetic and ferroelectric components differing in physicochemical properties in samples, with the strongest ME interaction at roughly equal volume fractions of their components. The room-temperature ME coefficient in such structures is typically tens to hundreds of mV/(cm Oe) (mV/A) [2, 4].

The main drawbacks of the direct mechanical contact method are the relatively low thermal stability of the properties of the resulting structures, poor reproducibility of characteristics from sample to sample, and cutting-induced damage to samples in the fabrication of sensing elements (microscaling).

As shown by Poddubnaya et al. [5], ion beam sputter deposition is an attractive technique for producing metal/ferroelectric layered composite structures. For example, this method can be used to grow films of magnetic materials (metals, spinels, and ferrites) with bulklike properties on semiconductor and metal oxide substrates [6]. This method enables fabrication of a plane-parallel interface between a ceramic ferroelectric substrate and ferromagnetic metallic layers in heterostructures having thermally stable and reproducible properties [7]. In this case, layered heterostructures possess ME properties of practical interest [7–9] and are not damaged during microscaling of samples to minimal dimensions in cutting and cleavage processes [7, 9]. As shown previously [9], there is an optimal range of ferromagnetic layer thicknesses that ensures the best ME properties. This paper presents a continuation of previous work [9] concerned with the effect of layer and interface thicknesses on the ME properties of heterostructures where the volume of the ferromagnetic component is less than 0.01 of the volume of the ferroelectric component. Here, we examine Co/PZT/Co heterostructures (where PZT stands for a ceramic $\text{PbZr}_{0.45}\text{Ti}_{0.55}\text{O}_3$ lead zirconate titanate ferroelectric substrate 100 to 400 μm in thickness, and Co denotes a ferromagnetic film 0.5 to 3.5 μm in thickness).

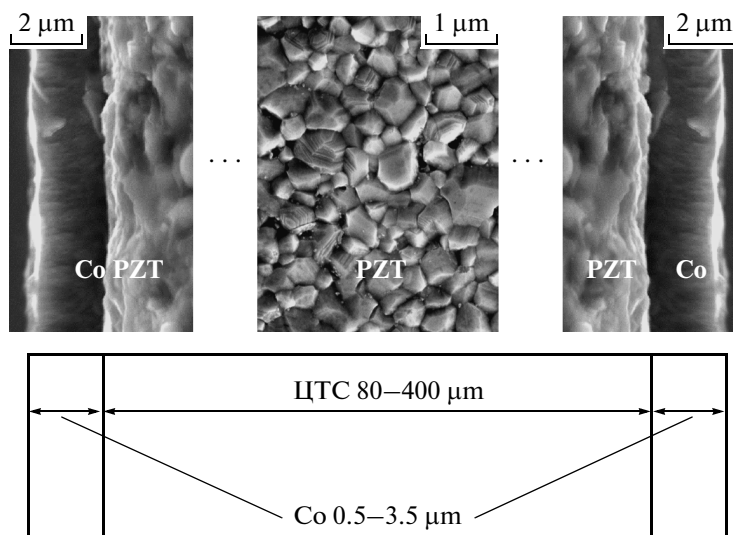


Fig. 1. Cross-sectional images of a Co(2 μm)/PZT/Co(2 μm) structure.

EXPERIMENTAL

Ferroelectric ceramics were produced by standard solid-state reactions [10] in the form of substrates 8 mm in diameter and 400 μm in thickness. After thinning by abrasive grinding to desired thicknesses, the substrate surface was polished by a standard chemical–mechanical procedure to mirror finish. In the final step, the surface was smoothed to a submicron level by dual ion-beam sputter deposition as described previously [7]. Cobalt films were grown through ion beam sputtering of a cobalt target by 1600-eV argon ions at a current density of 0.25 A/cm² in a residual vacuum of 0.1 Pa or better, as described elsewhere [8, 9].

The samples were poled by a dc electric field of 4 kV/mm at a temperature of 150°C for 2 h, followed by cooling to room temperature in the same field, as described by Petrov et al. [10].

Magnetoelectric measurements were performed at room temperature in static and ac magnetic fields, as described elsewhere [5, 10]. The magnetoelectric response was quantified by the ME voltage coefficient α . The ME voltage coefficient α (mV/(cm Oe) (mV/A)) was determined as $\alpha = dU/(h dH)$, where dU is the induced voltage, dH is the field strength, and h is the thickness of the PZT plate.

X-ray diffraction measurements were made on a DRON-3M diffractometer with CuK α radiation (scan step, 0.03°; counting time per data point, 3 s). The phases present were identified using Inorganic Crystal Structure Database (ICSD) data. Cross sections of the Co/PZT/Co structures were examined by scanning electron microscopy (SEM) using a Helios NanoLab system (FEI, United States).

RESULTS AND DISCUSSION

Figure 1 shows cross-sectional images of a typical heterostructure, Co(2 μm)/PZT/Co(2 μm), sequentially presenting cross-sectional SEM micrographs of the Co/PZT interfacial region, PZT ceramic proper, and PZT/Co interfacial region. According to Fig. 1, the cobalt film is free of pores and is in intimate contact with the surface of the ceramic grains in the substrate. Owing to the above-mentioned ion-beam surface smoothing procedure, the grains near the interface have a flat surface, also free of pores. The characteristic crystallite size of the ferroelectric ceramics does not exceed 1 μm. Shown at the bottom of Fig. 1 is a schematic representation of the heterostructures under consideration. Here, the cobalt film thickness ranges from 0.5 to 3.5 μm, and the thickness of the PZT ceramic substrate, from 100 to 400 μm.

Figure 2 shows X-ray diffraction patterns of Co/PZT(200 μm) samples. The thickness of the cobalt film is 0, 1, 2, and 3 μm in Figs. 1a, 1b, 1c, and 1d, respectively. The intensity of the 110 reflection from the uncoated PZT substrate is more than a factor of 5 higher than that of the 111 reflection (Fig. 2a). In the Co/PZT samples (Figs. 2b–2d), the intensity ratio of these reflections varies, suggesting that the substrate is in an elastically stressed state induced after cobalt film growth. In particular, this occurs even at a cobalt film thickness of 1 μm (Fig. 2b).

With increasing cobalt film thickness, the intensity of the 002 reflection from cobalt passes through a maximum at a thickness of 2 μm (Fig. 2c), which points to a relatively high structural perfection of the cobalt film on the ceramic substrate with respect to smaller and larger thicknesses. Indeed, a slight decrease in the intensity of the 002 reflection is

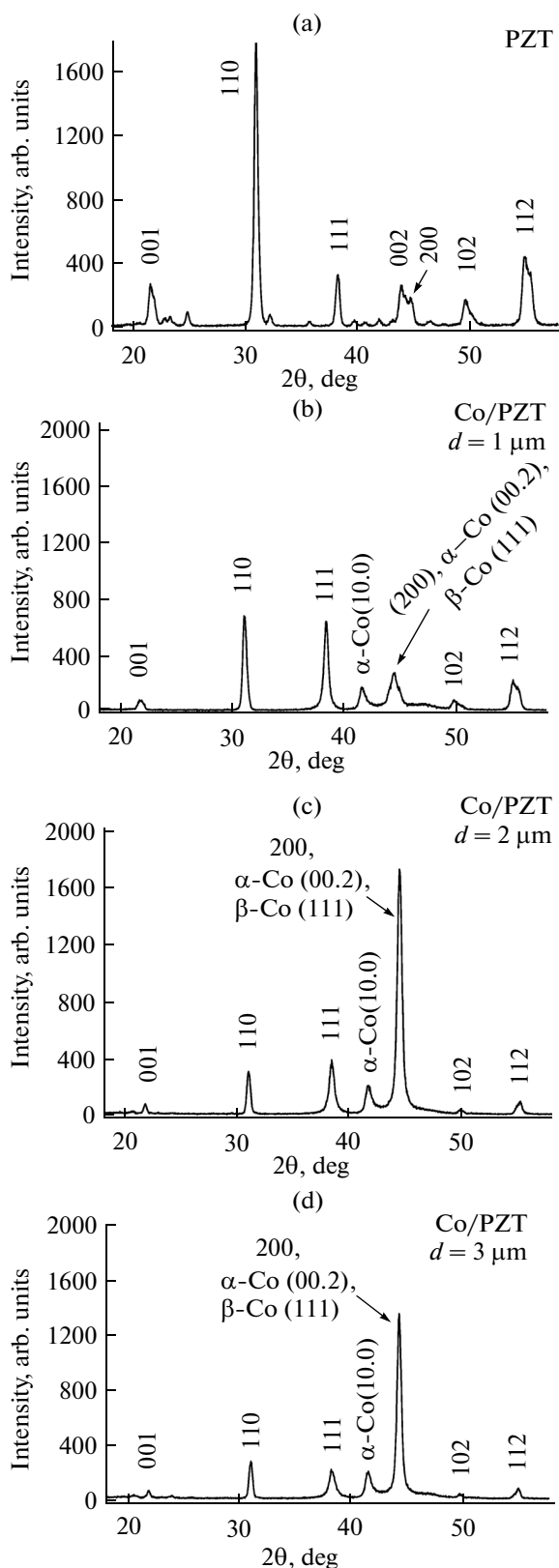


Fig. 2. X-ray diffraction patterns of Co/PZT samples at cobalt film thicknesses of (b) 1, (c) 2, and (d) 3 μm ; (a) uncoated PZT.

observed even at a cobalt film thickness of 3 μm (Fig. 2d), which points to a lower structural perfection of the cobalt film. In structures having cobalt layer thicknesses above 4 μm , large portions of the cobalt layer were observed to crack and spall off the substrate, so those structures are not considered here.

With increasing cobalt layer thickness, the intensity of the reflections from the PZT decreases, because the cobalt film shields the ceramic substrate from the X-ray beam (Fig. 2). Moreover, the relative intensity of the reflections varies, which is best illustrated by the example of two characteristic reflections from PZT: 001 and 110. A 1- μm -thick cobalt layer on the ferroelectric substrate reduces the intensity of the former reflection by a factor of 3.5 and that of the latter by about a factor of 2.5 (Figs. 2a, 2b). Upon a further increase in cobalt film thickness, the intensity of the 001 reflection from PZT decreases more gradually than that of the 110 reflection (Figs. 2c, 2d). This suggests, first, that the cobalt films in the thickness range under consideration are continuous, in agreement with SEM data (Fig. 1), and, second, that, at a cobalt layer thickness of 3 μm , the PZT substrate is in a less elastic state in comparison with the heterostructures having cobalt layers 1 and 2 μm in thickness.

The X-ray diffraction patterns presented in Fig. 2 are characteristic of the entire range of PZT thicknesses examined, 100–400 μm ; that is, their specific features are determined by the thickness of the cobalt layer rather than by that of the PZT substrate.

Therefore, cobalt layers 1.5–2.5 μm thick on PZT substrates have a relatively perfect crystal structure and induce the highest elastic stress in the PZT substrates. As shown earlier [8, 9], they have the highest saturation magnetization among samples with cobalt layer thicknesses from 0.5 to 3.5 μm on PZT substrates, which is, however, several times lower than the saturation magnetization of bulk cobalt of Co films of comparable thickness on silicon substrates. Excellent magnetic characteristics and elastic action of a magnetic layer on a ferroelectric substrate are among the key conditions for effective ME interaction in inhomogeneous materials (including the heterostructures under consideration) [1].

Figure 3 shows the magnetoelectric voltage coefficient α as a function of cobalt layer thickness d in the range 0.5 to 3 μm at room temperature in a magnetic field of 50 Oe (3980 A/m) at a frequency of 100 Hz for Co/PZT/Co heterostructures with PZT substrate thicknesses of 100 (curve 1), 280 (curve 2), and 400 μm (curve 3). The magnetoelectric voltage coefficient α has a maximum at $d = 2$ –2.5 μm , increases by more than a factor of 5 relative to $d = 1$ μm , and rises from 2.4 to 9.3 mV/(cm Oe) (from 3 to 11.7 mV/A) as the PZT substrate thickness decreases from 400 to 100 μm .

The nearly inverse proportionality of α to the PZT substrate thickness stems from the fact that the electrical capacitance of a dielectric layer is inversely proportional to its thickness. At the same time, the nonlinear

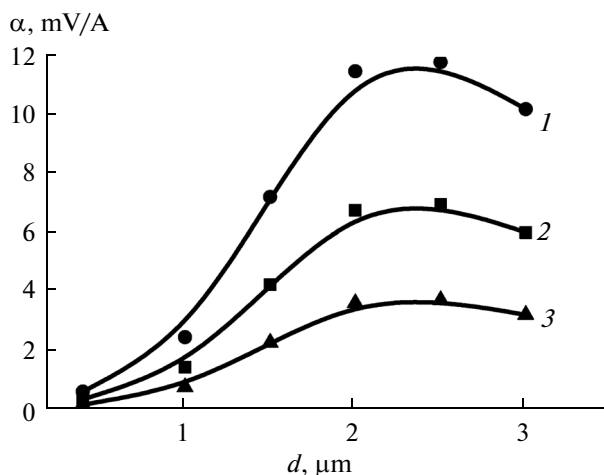


Fig. 3. Magnetolectric voltage coefficient α as a function of cobalt layer thickness d for Co/PZT/Co heterostructures in a magnetic field of 50 Oe (3980 A/m) at a frequency of 100 Hz. The PZT substrate thickness is (1) 100, (2) 280, and (3) 400 μm .

variation of α with d cannot be understood in terms of the existing ideas of inhomogeneous ME materials [1–4, 10, 11]. It is generally believed that effective ME interaction in inhomogeneous ME materials occurs at roughly equal volume fractions of their ferroelectric and magnetic components, or even when the latter slightly prevails. In the Co/PZT/Co heterostructures under consideration, the volume of the ferromagnetic component is less than 0.01 of the volume of the ferroelectric component. Moreover, there is a maximum in α as a function of cobalt layer thickness (Fig. 3). The α values obtained are comparable to those reported for inhomogeneous ME materials under normal conditions [1, 2, 4, 5, 10, 11]. It is, therefore, reasonable to assume that the ME interaction in the heterostructures under consideration is determined by the state of the ferromagnet/ferroelectric interface region, because this interaction has an interfacial nature. Clearly, the ferromagnet should have good magnetostrictive properties, but in the case of a thin ferromagnetic layer the way it is bonded to the substrate plays a decisive role in ME interaction.

Discarding the condition that the volume fractions of the components of inhomogeneous ME materials be roughly equal considerably extends the possibilities of producing layered heterostructures by methods common in microelectronics, including ion beam sputter deposition [6]. Dispensing with the use of foreign materials for ensuring contact between magnetic and ferroelectric components markedly enhances the strength of ME layered heterostructures and improves the stability of their properties, in particular after cutting and cleavage in the fabrication of sensing elements for microsensors.

CONCLUSIONS

It has been shown that the magnetolectric properties of Co/PZT/Co heterostructures grown by ion beam sputter deposition of cobalt layers directly on a presmoothed surface of a ceramic PZT substrate are determined by the ferromagnet/ferroelectric interface region. A ferromagnetic cobalt film 2–2.5 μm thick ensures a room-temperature magnetolectric response above 9 mV/(cm Oe) (11 mV/A) in a magnetic field of 50 Oe (3980 A/m) at a frequency of 100 Hz. The heterostructures studied can be fabricated and microscaled by methods common in microelectronics and are potentially attractive for use as sensing elements of magnetolectric sensors operating under normal conditions in household devices.

ACKNOWLEDGMENTS

This work was supported through the F10 GCST-002 (Poland–Belarus) project and by the Russian Foundation for Basic Research (grant no. 13-08-12402).

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SPELL: 1. heterostructures, 2. inhomogeneous

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DOI: 10.1051/epjap/2013120541

Ion-beam sputtering deposition and magnetoelectric properties of layered heterostructures (FM/PZT/FM)_n, where FM – Co or Ni₇₈Fe₂₂

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Ion-beam sputtering deposition and magnetoelectric properties of layered heterostructures (FM/PZT/FM)_n, where FM – Co or Ni₇₈Fe₂₂

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Received: 10 December 2012 / Received in final form: 17 May 2013 / Accepted: 25 June 2013

Published online: 7 August 2013 – © EDP Sciences 2013

Abstract. Magnetoelectric properties of layered heterostructures (FM/PZT/FM)_n ($n \leq 3$) obtained by ion-beam sputtering deposition of ferromagnetic metal (FM), where FM is the cobalt (Co) or permalloy Ni₇₈Fe₂₂, onto ferroelectric ceramic based on lead zirconate titanate (PZT) have been studied. The polished ferroelectric plates in thickness from 400 to 20 μm were subjected to finished treatment by ion-beam sputtering. After plasma activation they were covered by the ferromagnetic films from 1 to 6 μm in thickness. Enhanced characteristics of these structures were reached by means of both the thickness optimization of ferroelectric and ferromagnetic layers and obtaining of ferromagnetic/ferroelectric interfaces being free from defects and foreign impurities. Assuming on the basis of analysis of elastic stresses in the ferromagnetic film that the magnetoelectric effect forms within ferromagnetic/ferroelectric interface, the structures with 2–3 ferromagnetic layers were obtained. In layered heterostructure (Py/PZT/Py)₃, the optimal thickness of ferromagnetic film was 2 μm , and outer and inner ferroelectric layers had 20 μm and 80 μm in thickness, respectively. For such structure the maximal magnetoelectric voltage coefficient of 250 mV/(cm Oe) was reached at a frequency 100 Hz in magnetic field of 0.25 T at room temperature. The structures studied can serve as energy-independent elements detecting the change of magnetic or electric fields in electronic devices based on magnetoelectric effect.

1 Introduction

In the last few decades great attention is paid to composite structures, where the magnetoelectric effect (ME) is generated as a property of a magnetostrictive and a piezoelectric compounds originated by strain-mediated indirect magnetoelectric coupling [1–8]. A linear ME polarization is induced by a weak *ac* magnetic field oscillating in the presence of a *dc* field. These structures with a high ME voltage coefficient are perspective for application in sensor devices. Operated by static and alternating magnetic fields [7,8], they do not require the measuring current circuits and emergency power supply in contrast to conventional Hall sensors [9–16]. This opens the real opportunities for application of ME effect in electronics and production of magnetoelectric sensors.

A magnetoelectric effect in ferromagnetic/ferroelectric composite heterostructures is strongly influenced by the state of interface between the ferromagnetic metal and

ferroelectric ceramic layers. In known lamination composites exhibiting a magnetoelectric effect, a stable contact between ferroelectric and ferromagnetic layers is achieved through mechanical connection using adhesive [9,17]. A quality of interface dramatically depends on adhesion between the composite layers, quality of layers surfaces and connection method. The drawback of such structures is that the intermediate layer between ferromagnetic and ferroelectric materials becomes uncontrollable, since a presence of glue layer at the metal/ferroelectric interface prevents to form the direct contact between components. This reduces significantly the interaction between ferromagnetic and ferroelectric subsystems resulting in decrease of the reproducibility and controllability of magnetoelectric effect.

The above fabrication method of composite structure also does not allow to perform the heterostructure optimization consisting in fitting of thicknesses of ferromagnetic and ferroelectric layers, at which the magnetoelectric interaction becomes most effective and can approach the maximum. There are two factors that suppress the

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optimization of geometrical sizes of multilayer structures, namely, the existence of mechanical stresses in metallic film and insufficient strength of ferroelectric layer leading to its destruction caused by metallic layer. Therefore, the multilayered ferromagnetic/ferroelectric structures have not been optimized up till now.

One of the methods of such structure formation was found to be the sputtering deposition which allows to produce inhomogeneous structures based on a ferromagnetic metal and dielectric oxide [17,18]. Therefore, the goal of this work is both obtaining of layered heterostructures using an ion-beam sputtering deposition and studying of their magnetoelectric properties. The ion-beam technique used allows to obtain the heterostructures, in which the ferromagnetic layer contacts directly the ferroelectric one and to optimize the thickness of given structures.

Co/PZT/Co and Py/PZT/Py were chosen as initial heterostructures. The choice of lead zirconate titanate PZT as ferroelectric ceramic is conditioned by both high values of remanent polarization ($10\text{--}40\text{ }\mu\text{C}/\text{m}^2$) and relatively low temperature ($550\text{--}650\text{ }^\circ\text{C}$) of perovskite phase formation [19].

2 Experimental

The ferroelectric ceramic tablet with 8 mm in diameter and $400\text{ }\mu\text{m}$ in thickness was prepared using standard technology of milling and hot pressing [20]. The cross-section micrograph of ceramic sample $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ is shown in Figure 1. The sample was a high-density material of single crystal grains assembly with the grain size of $1\text{--}2\text{ }\mu\text{m}$. The grains had the crystallographic faceting. The ceramic samples have been thinned to required size and their surfaces were treated by standard mechanochemical polishing to obtain a mirror surface.

The ferromagnetic films were formed by means of ion-beam sputtering of cobalt or $\text{Ni}_{78}\text{Fe}_{22}$ targets by argon ions with energies of $1400\text{--}1600\text{ eV}$ using double ion-beam sputtering deposition setup equipped by wide-aperture ion

sources with cold hollow cathode on the base of two-step self-contained low-pressure gas discharge [21].

Then, the heterostructures obtained were polarized in external electric field with strength of $4\text{ kV}/\text{mm}$ at $150\text{ }^\circ\text{C}$ for two hours, followed by cooling in this field down to room temperature [22].

The analysis of samples was performed by high-resolution scanning electron microscopy realized on double-beam complex DualBeam (FIB/SEM) systems of Helios NanoLab (FEI Company, USA).

Magnetic characteristics of the samples were investigated by vibrating magnetometry on universal automated measuring setup “Liquid Helium Free High Field Measurement System (firm ‘Cryogenic LTD’, London, UK)”. Magnetic field dependences were measured in the range from -1 to $+1\text{ T}$ at room temperature.

Magnetoelectrical measurements at room temperature were carried out by measuring the voltage arising on the sample subjected to alternating and permanent magnetic fields. The magnetic field bias was produced by electro-magnet while alternating field was produced by Helmholtz’s coils. Magnetoelectric voltage coefficient α_E was determined as $\alpha_E = \frac{dU}{(h \cdot dH)}$, where dU is the alternating voltage, dH the magnetic field strength and h the PZT layer thickness [20].

Magnetoelectrical measurements have been also performed at 4.2 K by measuring the electric charge induced by modulated magnetic field by means of special insert connected to Keithley electrometer [23]. Magnetic field was measured by conventional Hall sensor. Temperature was controlled by thermometer mounted directly on insert using a precision Lakeshore 340 temperature controller, which has provided a precision control of temperature in the sample space. Modulated magnetic field ($0.01\text{--}0.015\text{ T}$) was created by special coil mounted in the sample volume using Lock-In DSP (digital signal processing). Its frequency was controlled by output frequency of DSP.

3 Results and discussion

The principal problem in the process of formation of metal/ferroelectric heterostructure originates at the deposition of metal film onto the surface of polycrystalline ceramic sample. This is connected with both metal and ceramic crystal lattices spaces mismatch and absence of high-quality treatment of ceramic material surface. The polycrystalline ceramic sample is an ensemble of disoriented single crystal grains with voids between them. A considerable quantity of impurities can be contained in these discontinuities. All this defines a high imperfection of ceramic surface. The metal film sputtered onto the surface starts to expand such discontinuities, and as a result of considerable mechanical stresses localized there the film is broken off.

To solve this problem the repeated deposition of metal film was performed. To do this, the metal film of $0.2\text{--}0.3\text{ }\mu\text{m}$ thickness primarily deposited onto the PZT substrate is mechanically removed from substrate in the imperfect places. Then, the film of thickness required is

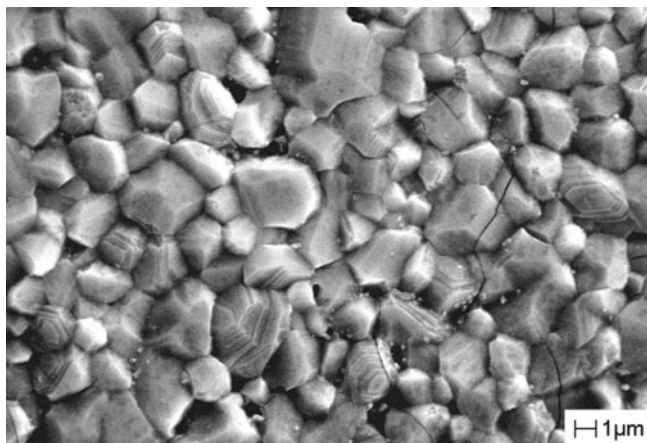


Fig. 1. Cross-section micrograph of initial ceramic sample $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$.

deposited onto the substrate by ion-beam sputtering of ferromagnetic metal targets at the same regimes. At thicknesses of less than 1 μm , the continuity and uniformity of ceramic surface coating are not reached. In the films thicker than 3 μm both the loss of high luster and formation of nonuniform island structure because of accumulation and relaxation of mechanical stresses are observed.

The metal film in regions of direct contact with single crystal grain surface undergoes mechanical stresses caused by both the film and grains crystal lattice mismatch and difference in thermal expansion coefficients. The removal of the initially deposited film leads to reduction of net uncontrollable interface area because the ceramic grains slightly coupled with surface are removed from surface together with the film and impurities. The film on defectless parts of interface has better adhesion, therefore, it can partly remain there at second ion-beam sputtering deposition. The controllable interface area will increase in comparison with initial state. An increase of ferromagnetic/ferroelectric interface continuity enhances adhesiveness of magnetic film to ceramic substrate in defect regions. After second deposition of the metal film, the sample surface has high luster typical for quality metal films.

As a result of this process, along with increasing interface area a mechanical contact between magnetic and ferroelectric layers of structure is enhanced that leads to increase of magnetoelectric effect.

Figure 2 shows the focused ion-beam (FIB) layer-by-layer analysis of Co (2 μm)/PZT (80 μm)/Co (2 μm) structure obtained by the above-mentioned way. It presents how the overgrowth of metal film on the ceramic grain occurs. In the beginning, the deposited film forms the fine-crystalline interface. As deposition proceeds the surface becomes plane and the film becomes smooth. At the end of deposition the average film thickness amounts to 2 μm .

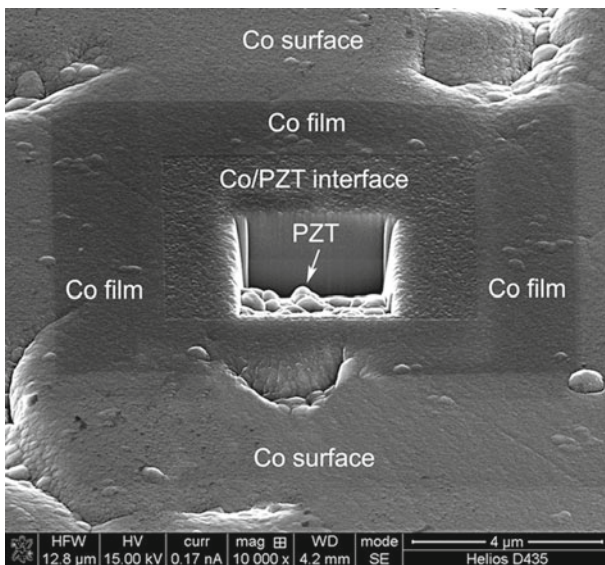


Fig. 2. FIB cross-section micrograph of Co (2 μm)/PZT (80 μm)/Co (2 μm) structure.

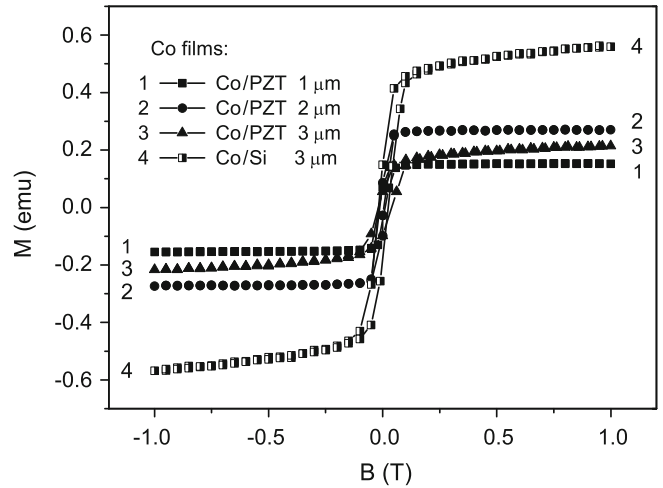


Fig. 3. The hysteresis loops of cobalt films with different thickness deposited onto the PZT substrates (curves 1, 2, 3) and cobalt film with 3 μm thickness deposited onto the silicon substrate (curve 4).

So it can be concluded that the interface formed has a high enough quality.

Both the real surface of ceramic sample and magnetic characteristics of cobalt and permalloy layers on such surface versus thickness have not been investigated in detail. Some tentative investigations were performed in [24]. They have allowed to optimize the thickness of cobalt and permalloy films deposited on PZT surface and treated by mechanochemical polishing to optical luster. Saturation magnetization was chosen as optimization parameter.

Cobalt films with thicknesses of 1, 2 and 3 μm were obtained by the above-mentioned method onto mechanically polished substrates of ferroelectric ceramic $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$. The magnetic measurements data (Fig. 3) evidence that the magnetization of films increases with thickness (curves 1, 2). The optimal cobalt film thickness must be within 1.5–2.5 μm , when the saturation magnetization is reached. The thinner cobalt films have deformed and have broken off because of the internal stresses. The films thicker than 3 μm after deposition were peeled off.

The saturation magnetization of the ferromagnetic layer was found to depend on the substrate type. This is confirmed by the fact that the cobalt film of 3 μm thickness deposited onto the silicon substrate yields twice as large magnetic signal (Fig. 3 curve 4) as the same film evaporated onto the ferroelectric substrate (Fig. 3 curve 3). The difference in magnetization of the cobalt films deposited onto the ceramic and silicon substrates is explained by that the film on ceramic surface is not continuous as compared with the same film on silicon. As a result, the discontinuities created by the ceramic substrate reduce the net magnetization of the whole film. Evidently that the smaller is the ceramic density, the smaller is the saturation magnetization of the film.

The saturation magnetization change also depends on the ferromagnetic metal thickness. Figure 3 evidences that the 3 μm cobalt film (curve 3) isn't magnetized to saturation as compared with the 2 μm film (curve 2).

The reason is that the film with such and more thickness becomes granular. The granular films are known to be magnetized harder than the continuous films.

The similar results were obtained for the permalloy films. The saturation magnetization of these films deposited onto the silicon and ceramic substrates is also differed. In this case, the optimal thickness must be less than $2.5 \mu\text{m}$.

In the next stage, the thickness optimization of ferroelectric layer in the form of ceramic plate was made. The real ceramic surface represents the totality of single crystal grains oriented in a random way along the surface. The mechanochemical polishing of surface up to its optical homogeneity and optical luster has been carried out. The ferroelectric layer thickness optimization was realized by means of its thinning to such minimal thickness, at which the magnetoelectric interaction through the ceramic should be most effective.

The initial thickness of ceramic plate is $400 \mu\text{m}$. The magnetoelectric interaction between ferroelectric and ferromagnetic phases was shown to be the most effective when the ferroelectric layer thickness is of $20 \mu\text{m}$ and less. Figure 1 shows the cross-section micrograph of initial ceramic sample $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ obtained by high-resolution scanning electron microscopy. The regularly shaped crystallites with average grain size of $2\text{--}5 \mu\text{m}$ are distinctly seen in the micrograph. The intercrystalline spaces in some regions of sample are comparable with grain size (of about $1 \mu\text{m}$). The maximal distance through which the elastic interaction can be transferred, as is seen in figure, is of $4\text{--}5$ grains, that is within $10 \mu\text{m}$.

The transfer of elastic strains between ferroelectric and ferromagnetic phases plays a crucial role in formation of magnetoelectric interaction. The transfer of mechanical stresses through the ceramic is known to be defined by the relative value of contact area of ceramic grains between themselves (the larger the contact area, the stronger elastic interaction between contacting grains). The grains are not touched to each other tightly, and the spaces between them are of the same order as grain sizes. For this reason, there is quite a definite maximal thickness of ferroelectric layer, at which the elastic strains aren't increased with further increasing thickness of ferroelectric layer. Thus, the transfer of elastic strains can propagate most effectively through small enough distance within several grains as it follows from Figure 1. The piezoelectric contribution due to elastic interaction between the grains will most probably have a linear dependence and will not saturate with thickness of ferroelectric layer.

With thinning ceramic plate down to $20 \mu\text{m}$ or less, the metal layer because of the accumulation of mechanical stresses in it bends the plate that results in its cracking and peeling. For this reason, the mechanical strength of ceramic plate drops. By this reason the thinning of ferroelectric plate has been realized down to thickness no less than $80 \mu\text{m}$.

The geometric sizes optimization of both ferroelectric and ferromagnetic layers was followed by the optimization of layered structure using the magnetoelectric effect mea-

surements data. At first, the layered structures including only one elemental unit FM/PZT/FM were made. Such structure was formed in the following way. The metal layer of $2 \mu\text{m}$ thickness was deposited onto the one side of PZT plate of $400 \mu\text{m}$ thick. The opposite side of the ceramic plate was polished down to $80 \mu\text{m}$, and the $2 \mu\text{m}$ thick metal layer was deposited onto this side.

Thus, we had determined that the multilayered structure should be such as $\text{Co}(2 \mu\text{m})/\text{PZT}(80 \mu\text{m})/\text{Co}(2 \mu\text{m})$ or $(\text{Py}(2 \mu\text{m})/\text{PZT}(80 \mu\text{m})/\text{Py}(2 \mu\text{m}))$, which are determined by elastic stresses.

On the base of given one-element structure the two- and three-element structures were formed in the following way. The one-element structures were connected to each other by ferromagnetic layers with epoxy glue. In the case of three-element structure, the medium ceramic layer was thinned down to $20 \mu\text{m}$ whereas the outer PZT layers had thicknesses of $80 \mu\text{m}$. It is due to the fact that two adjacent ceramic layers thinned down to $20 \mu\text{m}$ have undergone the mechanical destruction because of the internal stresses arising in ferromagnetic layer. As a result the two-element structure has the form: $\text{Co}(2 \mu\text{m})/\text{PZT}(80 \mu\text{m})/\text{Co}(2 \mu\text{m})$ or shortly $(\text{Co}/\text{PZT}/\text{Co})_2$ and three-element structure is $\text{Co}(2 \mu\text{m})/\text{PZT}(80 \mu\text{m})/\text{Co}(2 \mu\text{m})/\text{PZT}(20 \mu\text{m})/\text{Co}(2 \mu\text{m})$ or in a short form $(\text{Co}/\text{PZT}/\text{Co})_3$. The glue connections are marked by double inclined lines.

Figure 4 shows the cross-section micrograph of three-element $(\text{Py}/\text{PZT}/\text{Py})_3$ heterostructure. The interlayer border between ferromagnetic film and ferroelectric substrate is distinctly observed. This is evidence of good enough quality of optimized heterostructures obtained by ion-beam technique.

Figure 5 shows a top view of cross-section split of the two-element $(\text{Py}/\text{PZT}/\text{Py})_2$ heterostructure. The interlayer border between the ferromagnetic film and ferroelectric substrate is distinctly observed. This is evidence of good enough quality of optimized heterostructures obtained by ion-beam technique.

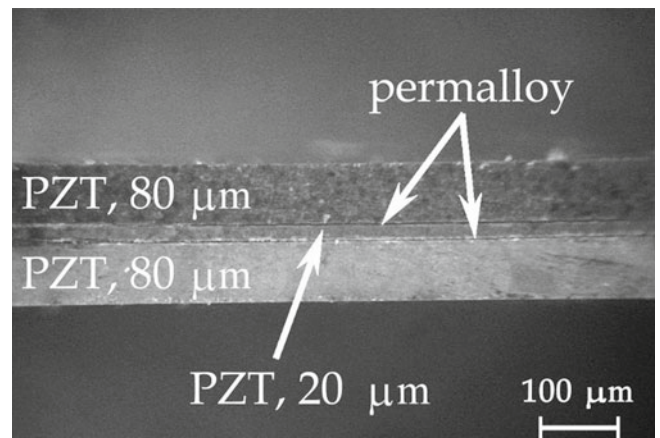


Fig. 4. Cross-section micrograph of $(\text{Py}/\text{PZT}/\text{Py})_3$ heterostructure.

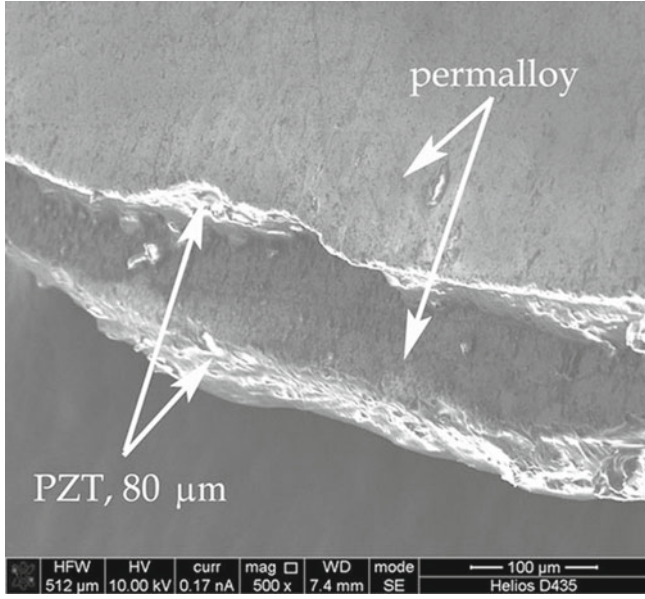


Fig. 5. Top view of cross-section split of (Py/PZT/Py)₂ heterostructure.

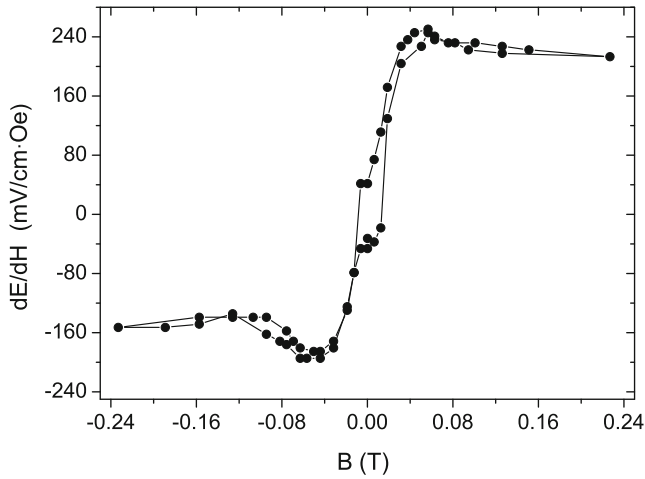


Fig. 6. Room temperature longitudinal magnetoelectric voltage coefficient of (Py/PZT/Py)₃ heterostructure versus magnetic field at frequency of 100 Hz.

Measurements of magnetoelectric voltage coefficient versus magnetic field for three-element (Py/PZT/Py)₃ structures have been carried out at both room and helium temperatures. The results of measurements at frequency 100 Hz in a magnetic field range of ± 0.25 T at room temperature are shown in Figure 6 for longitudinal configuration when magnetization and polarization are parallel to each other and are aligned perpendicular to the surface. The maximum magnetoelectric voltage coefficient is equal to 250 mV/(cm Oe) in magnetic field of 0.05 T.

In our recent researches of the (Co/PZT/Co)_n structures obtained by ion-beam sputtering technique we have achieved the value of ME response in at least two orders as larger as the magnetoelectric parameters of the structures produced by electrolytic deposition or mechanical

gluing of the components, keeping the Q (quality) factor value of about 1000 characterized for bulk composite materials [17,21].

In Figure 7, the magnetic field dependences of electric charge induced by alternating magnetic field at different frequencies are presented. The measurements were performed in a magnetic field range of ± 1.5 T at 4.2 K in transverse configuration (magnetization is oriented along the surface and polarization aligned perpendicular to it). Figure 7 shows that magnetoelectric effect essentially depends upon frequency of alternating magnetic field and has a resonant behavior at low frequencies. Its maximum value is observed in the region of 50–150 Hz.

To estimate the internal stresses arising in metal film and breaking it off as well as its minimal thickness, at which the stresses are not able to break off the film, the accommodation model based on elasticity theory [25] has been used. According to this model, a stress state occurring in metal film is determined by mismatch value:

$$f = \frac{d_s - d_0}{d_s}, \quad (1)$$

where d_0 is the space of film in the bulk structure and d_s is the space of substrate at room temperature. At sufficiently small values of f ($\sim 10^{-3}$) the epitaxial film deforms elastically until its space along the interface becomes equal to one of the substrate.

This model can be applied to the PZT/Co interface. It is known that the PZT ceramic based on lead titanate PbTiO₃ has the tetragonal crystal structure (pseudo-cubic lattice with a small elongation) with the unit cell parameters of $a = 4.063$ Å and $c = 4.106$ Å [26]. Cobalt crystallizes in hexagonal close-packed lattice with $a = 2.505$ Å and $c = 4.089$ Å [27]. At any combination of crystal lattice parameters of ferromagnetic film and ceramic substrate, the f mismatch value considerably exceeds the limits at which internal stresses occurring will disrupt the thin magnetic film.

One can estimate the value of internal stresses appearing in the metal film because of crystal lattice deformation using the following formula [28]:

$$\sigma^{\max} = \frac{E}{2} \times \frac{d_s - d_0}{d_s} = \frac{E}{2} f^{\max}, \quad (2)$$

where E is the Young modulus of metal film.

The internal stresses reduce with increasing film thickness. Therefore one can estimate the minimal thickness of metal film, at which the mechanical stresses are not capable to tear off the film. To do this, Formula (2) should be written for maximal elastic stresses as follows:

$$\sigma^{\text{elast}} = \frac{E}{2} \times \frac{f^{\max}}{n} = \frac{E}{2} f^{\text{elast}}, \quad (3)$$

where n is the number of atomic planes in transient layer of cobalt. It is assumed that to create the maximal elastic stresses the mismatch value should be equal to $f^{\text{elast}} = 0.001$ [28].

The thickness of transient layer is equal to

$$h_{\min} = n d_0 = \frac{f^{\max}}{f^{\text{elast}}} d_0, \quad (4)$$

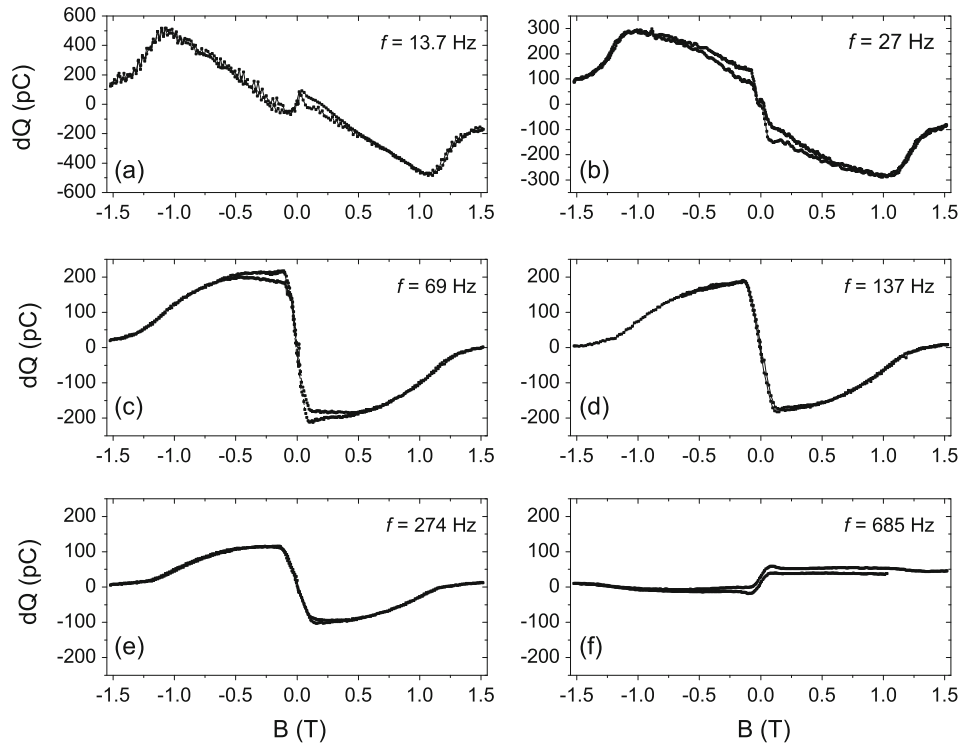


Fig. 7. Magnetic field dependences of electric charge induced in $(\text{Py}/\text{PZT}/\text{Py})_3$ heterostructure by alternating magnetic field at different frequencies in transverse configuration at 4.2 K.

Table 1. The calculation results of maximal mismatch $f^{\max}$, internal stresses $\sigma^{\max}$ and minimal ferromagnetic film thickness $h_{\min}$ using Equations (1), (2) and (3), respectively, depending on combination of lattice spacing for cobalt film and substrate.

		Crystal lattice space of ferroelectric substrate, Å	
		$a = 4.063$	$c = 4.106$
Crystal lattice space of HCP cobalt film, Å	$a = 2.205$	$f^{\max} = 0.622$ $\sigma^{\max} = 65.6 \text{ GPa}$ $h^{\max} = 0.25 \mu\text{m}$	$f^{\max} = 0.639$ $\sigma^{\max} = 67.4 \text{ GPa}$ $h^{\max} = 0.26 \mu\text{m}$
	$c = 4.089$	$f^{\max} = 0.006$ $\sigma^{\max} = 0.633 \text{ GPa}$ $h^{\max} = 0.002 \mu\text{m}$	$f^{\max} = 0.004$ $\sigma^{\max} = 0.422 \text{ GPa}$ $h^{\max} = 0.001 \mu\text{m}$

where d_0 is the crystal lattice space of film in the growth direction, that is perpendicular to interface.

The calculation results of maximal mismatch $f^{\max}$, internal stresses $\sigma^{\max}$ and minimal ferromagnetic film thickness $h_{\min}$ against combination of lattice spacing for film and substrate are represented in Table 1. For cobalt, nickel and iron the tabular values of elastic modulus E equal to 211 GPa, 207 GPa and 200 GPa, respectively, were used [29].

The performed calculations have showed that the entire relaxation of internal stresses takes place when the ferromagnetic layer thickness is of order $1 \mu\text{m}$. The obtained calculation results are in a good agreement with experimental data presented above.

4 Conclusion

This work shows that the ion-beam sputtering deposition technique combined with mechanochemical polishing

and plasma activation of ferroelectric substrates allows to form the structures consisting of ferromagnetic layers with thickness from 1.5 to $2.5 \mu\text{m}$, PZT layers with thickness from 20 to $100 \mu\text{m}$ and interface. The given structure is the unit section of complex structures formed as a result of their gluing to each other by epoxy adhesive.

We report that by two orders larger the value of magnetoelectric voltage coefficient was achieved replacing cobalt with permalloy. The most room temperature magnetoelectric voltage coefficient equaling $250 \text{ mV}/(\text{cm Oe})$ at frequency of 100 Hz in magnetic field of 0.05 T was observed for triple-layered Py/PZT/Py structure with 80, 20 and $80 \mu\text{m}$ of thickness of PZT layers and $2 \mu\text{m}$ of ferromagnetic interlayers. It exceeds the magnetoelectric parameters of the structures produced by other alternative methods [21].

The structures obtained are perspective as a primary transforming element of sensor devices [9] and can serve as the base for production of nonvolatile magnetoelectric sensors.

The main problem to obtain the layered structures possessing magnetoelectric effect is reduced mechanical strength of ceramic which does not permit to obtain thin ferroelectric layers. The solution of this problem being in the deposition of thick ferromagnetic film on thin ferroelectric layers will be the aim of our further investigations.

The layered structures with more than three ferroelectric layers are unpromising as each subsequent layer leads to decrease of mechanical strength of the overall structure, and in this case the magnetoelectric effect does not increase. Also the cutting this structure on chips by standard microelectronic device is significantly complicated.

This work was supported by F10 GCST-002 (Poland-Belarus). The authors are grateful to Dr. A.V. Bepalov and Dr. O.L. Golikova (Moscow State Institute of Radiotechnics, Electronics and Automation) for experiment assistance and valuable discussions.

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