*ISSN 1063-7834, Physics of the Solid State, 2020, Vol. 62, No. 11, pp. 2063–2069. © Pleiades Publishing, Ltd., 2020.*
*Russian Text © The Author(s), 2020, published in Fizika Tverdogo Tela, 2020, Vol. 62, No. 11, pp. 1840–1846.*

## MAGNETISM

# Magnetoelectric Effect in Two-Layer Composites with a Graded Magnetic Phase

**V. N. Shut**[a, *], **V. L. Trublovsky**[a], **V. M. Laletin**[a], **and I. Yadroitsev**[b]

[a] *Institute of Technical Acoustics, National Academy of Sciences of Belarus, Vitebsk, 210023 Belarus*
[b] *Central University of Technology, Free State, Bloemfontein, 9300 South Africa*
** e-mail: shut@vitebsk.by*

Received June 18, 2020; revised July 8, 2020; accepted July 9, 2020

**Abstract**—Samples of a homogeneous ($x = 0$, 0.1, and 0.2) and multilayer ceramics with a gradient composition ($x = 0.2 \rightarrow 0.1 \rightarrow 0 \rightarrow 0.1 \rightarrow 0.2$) based on solid solutions of $(Ni_{1-x}Zn_x)Fe_2O_4$ nickel–zinc ferrites have been manufactured using the thick-film technology. After sintering in a two-step mode, the gradient samples exhibited a smooth non-uniform distribution of chemical elements (Zn, Ni) over the thickness. The longitudinal ($\alpha_{E33}$) and transverse ($\alpha_{E31}$) magnetoelectric effects in two-layer PZT–nickel ferrite composites have been studied. In the absence of an external magnetostatic field, the values of magnetoelectric coefficients were negligible. The maximum value of the longitudinal magnetoelectric coefficient for composites with the gradient magnetic phase was practically two times higher than value of $\alpha_{E33}$ for homogeneous structures.

**Keywords:** nickel–zinc ferrites, graded ceramics, magnetic properties, magnetoelectric effect

**DOI:** 10.1134/S1063783420110323

## INTRODUCTION

Recently, sustainable interest in magnetoelectrics (multiferroics), a class of simultaneously magnetically and electrically ordered materials, has been retained [1–3]. The interaction between the electric and magnetic subsystems of these materials is exhibited as the magnetoelectric (ME) effect. This effect consists in the appearance of electric field **E** (or polarization **P**) in a sample by the application of magnetic field **H** ($E = \alpha_E H$, direct ME effect) or in the appearance of magnetization **M** (or magnetic field **H**) by application of electric field $E$ ($H = \alpha_H E$, inverse ME effect). The presence of the mentioned effects in materials offers the extensive challenge of their application in different devices and facilities without the direct current flows and corresponding heat losses [4, 5]. However, for single-phase magnetoelectrics (such as $BiFeO_3$, $YMnO_3$, $Cr_2O_3$, etc.) low values of ME effects and low temperatures of their manifestation are typical, which made not possible to discuss their practical application [6, 7]. The situation was cardinally changed after the practical realization of the development of composite media consisting of two mechanically bonded phases: piezomagnetic (or magnetostriction) and piezoelectric. The key points by the development of composites with the high ME coefficients are the enhanced characteristics of separate components, formation of a perfect interface between the magnetic and piezoelectric phases, and the type of connectivity [1, 3, 8]. A new approach directed toward enhancement of characteristics of ME composites is the development of structures with a gradient composition (properties), for which doped elements are distributed not uniform, but according to a certain function. It was theoretically predicted that ME constants in layered composites with the 2-2 connectivity considerably increase by the use of structures with the gradient composition (properties) as a ferroelectric and/or magnetic component [9]. At the same time, all materials (in particular, ferrites) applied as the magnetic phase are not piezomagnetics. Their utilization is determined by the presence in these materials of a pseudo-piezomagnetic effect ($q = d\lambda/dH$, where $\lambda$ is the magnetostriction constant), occurring by simultaneous applying the biased constant ($H_{dc}$) and alternating ($H_{ac}$) magnetic fields. In this connection, enhancement in the composite characteristics can be determined by two reasons. First, in graded magnetics, the possibility of formation of internal magnetic field $H_{int}$ leading to the shift of the hysteresis loop and occurrence of spontaneous magnetization directed normally to the sample plane was predicted theoretically [10]. In this case, the ME effect can be manifested without applying the biased constant field. Second, under the action of alternating magnetic field $H_{ac}$ on a material with the transverse spontaneous magnetization, additional bending and rotational moments occur in a magnetic layer, which cause the increase in the electric response [11].

Composites being not required the application of external constant fields were called as self-biased magnetoelectric materials. Mandal et al. [11] studied two- and three-layer structures (PZT–$Ni_{1-x}Zn_xFe_2O_4$ and PZT–$Ni_{1-x}Zn_xFe_2O_4$–PZT, respectively). The ferritic layer gradient was formed by serial joint (bonding) of ceramic disks with various ratios Ni/Zn. These composites were characterized by the presence of the ME signal at $H_{dc} = 0$ and by the increase in its maximum value by the use of a graded magnetic subsystem. Similar results were obtained for other composites with the gradient magnetic phase [12–15]. Note that in the aforementioned works, the field dependences of the ME coefficient were symmetrical.

Interesting results and their another interpretation were presented in [16] by Menghui Li et al. In this work, two-layer magnetic structures were obtained by bonding of an amorphous Metglas and semicrystalline Metglas. The amorphous and semicrystalline Metglas exhibit considerably different magnetic hardness at a close saturation magnetization. Curves *M–H* for these samples were shifted over the *H* axis; the biased magnetic field was $H_{bias} \approx 2.7$ Oe. Such shift on the *M–H* curve was caused by interactions between the "soft" and "hard" magnetic phases. Symmetrical Metglas/PZT/Metglas composites based on these materials exhibit the high ME coefficient $\alpha_E = 12$ V cm$^{-1}$ Oe$^{-1}$ at the frequency $f = 1$ kHz by zero external magnetic field. It should be noted that the field dependences of the ME coefficient were strongly non-symmetrical.

The authors of [17, 18] reported on the presence of the biased magnetic field manifested themselves in the shift of the *M–H* curves and in the non-symmetrical field dependences of the ME coefficient. As a piezoelectric, AlN was used; as a magnetic component, $Ta/Cu/Mn_{70}Ir_{30}/Fe_{50}Co_{50}$ or $Ta/Cu/Mn_{70}Ir_{30}/Fe_{70.2}Co_{7.8}Si_{12}B_{10}$ multilayer structures were used obtained by HF-magnetron sputtering. Occurrence of $H_{bias}$ was determined by anisotropy of the exchange interaction between the $Mn_{70}Ir_{30}$ antiferromagnetic and $Fe_{50}Co_{50}$ ferromagnetic. The non-symmetrical dependence of the ME coefficient on the external field was observed in composites, in which the gradient magnetic phase was formed by electrodeposition of different metals [19]. The data on self-biased composites were systematized in [20] in detail.

Despite of promising theoretical predictions on characteristics of the graded composites, a number of publications dealing with them is not too large.—First of all, it is determined by the difficulty in technical fabrication of composites with spatially varying characteristics (composition) even for one piezoelectric or magnetic phase. Currently, the most of experimental works were performed on structure with a small number of layers (typically three) in conditions, for which the variation in parameters *q* and *d* is very sharp and occurs in a narrow spatial domain at the phase interface. Although in some cases, these works confirm theoretical predictions, there is a lot of unclearness and contradiction in a quantitative estimate of effects. Clearly, the development of structures with a smooth (ideally continuous) composition variation and the study of their integral characteristics will contribute to deeper understanding of the aforementioned effects.

The aim of this work is to fabricate a nickel–zinc ferrite $(Ni_{1-x}Zn_x)Fe_2O_4$-based ceramics with a gradient composition and to study the ME effect in the two-layer piezoelectric–graded ferrite composites.

## SAMPLES AND EXPERIMENTAL TECHNIQUES

The nickel–zinc ferrite powders were synthesized via a ceramic sintering technique using oxides ZnO and $Fe_2O_3$ (grade ChDA) and NiO (grade Ch) [21, 22]. We synthesized $(Ni_{1-x}Zn_x)Fe_2O_4$ powders of three compositions: $x = 0$, 0.1, and 0.2. The slip casting method was used to prepare ~27–28 μm-thick films from these powders. The homogeneous structures with fixed zinc concentration were combined from the films of the same compositions. To prepare the structure with the composition gradient ($x = 0.2 \rightarrow 0 \rightarrow 0.2$), the films of various compositions ($(Ni_{0.8}Zn_{0.2})Fe_2O_4 + (Ni_{0.9}Zn_{0.1})Fe_2O_4 + NiFe_2O_4 + (Ni_{0.9}Zn_{0.1})Fe_2O_4 + (Ni_{0.8}Zn_{0.2})Fe_2O_4$) were pressed in combination of two layers of each composition (Fig. 1).

Blanks 5.5 × 4.0 mm in size were cut down from the stacks. To decrease the diffusion processes at the boundaries between the layers with different compositions, we used the two-step mode of sample sintering. At the first step, the temperature increased for the maximum value of 1270°C (the heating rate was 350°C/h); then, it decreased to 1100°C, at which the samples were held for 3 h. The final thickness of the multilayer samples was ~260 μm. The ceramic samples have no visible deformation distortions.

To adjust all samples to the same thickness and to yield flatness of the surface, the homogeneous and graded magnetic ceramics was ground at one side to the thickness of 180 μm. In addition, in the case of

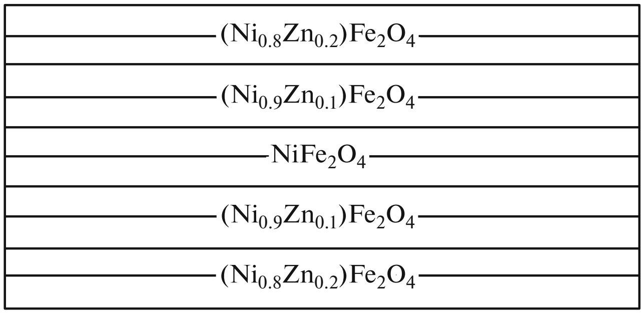

**Fig. 1.** Scheme of the structure with the "opposite" composition gradient ($x = 0.2 \rightarrow 0 \rightarrow 0.2$).

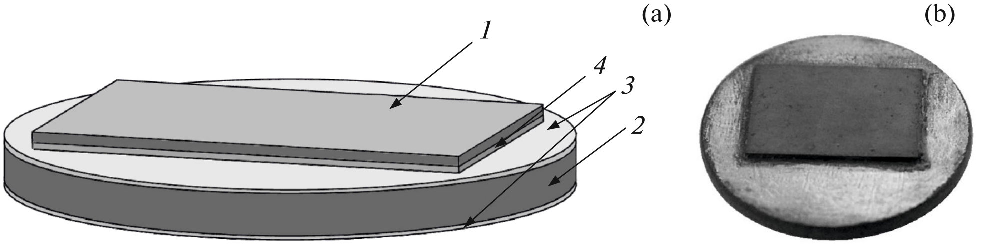

**Fig. 2.** (a) Scheme of the structure and (b) the ME composite picture: (*1*) $(Ni_{1-x}Zn_x)Fe_2O_4$, (*2*) PZT, (*3*) silver electrodes, and (*4*) bonding agent.

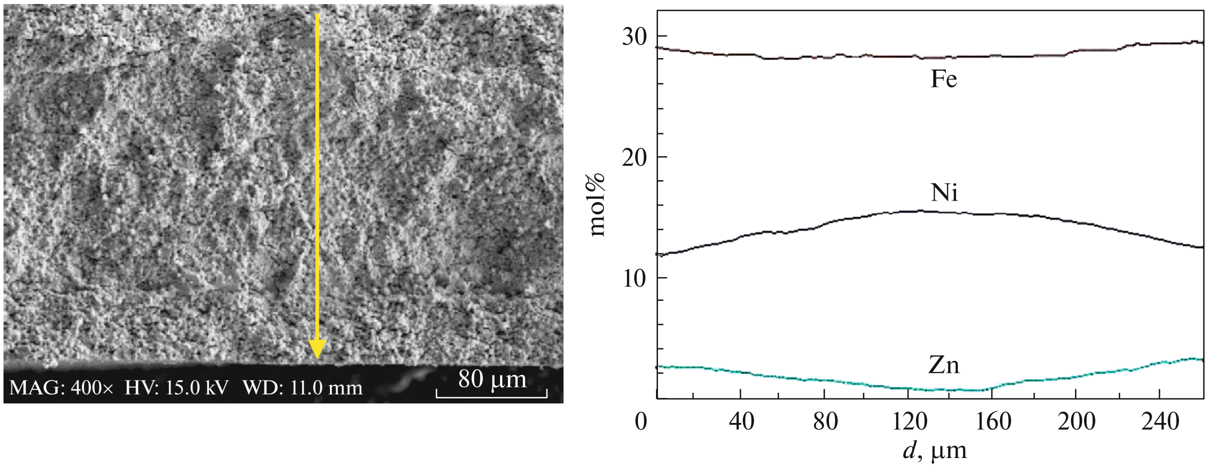

**Fig. 3.** Photomicrograph of the butt end (the arrow indicates the line, along which the measurements were performed) and the distribution of elements over the thickness of $(Ni_{1-x}Zn_x)Fe_2O_4$ graded ceramics ($x = 0.2 \rightarrow 0 \rightarrow 0.2$).

graded samples this procedure is necessary to yield a unidirectional gradient composition. As a piezoelectric, PZT ceramic disks of 8.9 mm in diameter and 0.62 mm in thickness were used. Tablets were coated with the silver electrodes and further polarized in a constant electric field. To form the composite, piezoelectric and magnetic materials were bonded according to the scheme shown in Fig. 2.

Studies of the microstructure and distribution of chemical elements were performed on a Hitachi S-4800 high-resolution scanning electron microscope with a QUANTAX 200 X-ray spectrometer.

The magnetoelectric signal was measured in two experimental modes. Transverse ME coefficient $\alpha_{E31}$ was determined in the case of constant $H_{dc}$ and alternating $H_{ac}$ magnetic fields are parallel to each other and to the main plane of the sample (normal to $P_S$). Longitudinal ME coefficient $\alpha_{E33}$ was determined in the case of the constant and alternating magnetic fields are parallel to each other and normal to the main plane of the sample (parallel to $P_S$).

## RESULTS AND DISCUSSION

Results of studies of the structure and characteristics of $(Ni_{1-x}Zn_x)Fe_2O_4$ nickel–zinc ferrites were described in detail in [21, 22]. All manufactured magnetic materials had a spinel structure. The unit cell parameter increased with the increase of the zinc concentration from $a = 8.34$ Å at $x = 0$ to 8.4 Å at $x = 0.2$. Samples exhibited the homogeneous structure with the grain size of 2–5 µm, which slightly changed with the variation in the zinc concentration. The dependences of the specific magnetization on the magnetic field induction $\sigma = f(B)$ were studied at room temperatures in the geometries of the parallel and normal directions of the magnetic field with respect to the film plane. In the homogeneous samples, the specific magnetization increases from $\sigma = 46$ A m$^2$ kg$^{-1}$ (at $x = 0$) to $\sigma = 67$ A m$^2$ kg$^{-1}$ (at $x = 0.2$). The magnetic hysteresis loops of the graded materials were symmetrical along both axes. No distortions such as necks were also observed.

**Transverse ME effect in two-layer piezoelectric–$(Ni_{1-x}Zn_x)Fe_2O_4$ structures.** Note that at first, the $(Ni_{1-x}Zn_x)Fe_2O_4$ magnetic material structures with

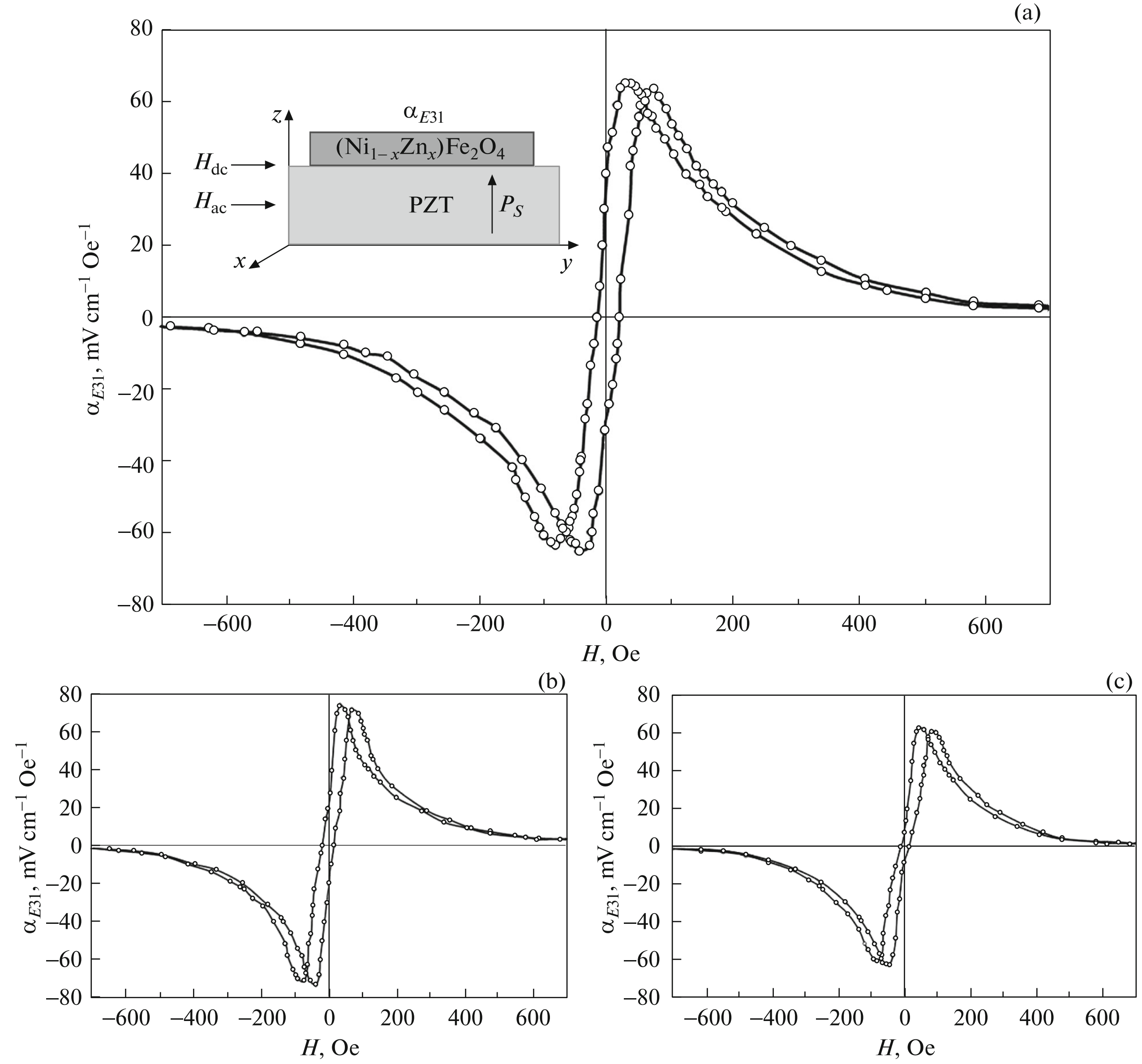

**Fig. 4.** Field dependences of transverse ME coefficient $\alpha_{E31}$ at various compositions of the magnetic phase: (a) $NiFe_2O_4$, (b) $(Ni_{0.8}Zn_{0.2})Fe_2O_4$, and (c) graded ferrite.

the stepwise variation of the composition ($x = 0.2 \rightarrow 0.1 \rightarrow 0 \rightarrow 0.1 \rightarrow 0.2$) were manufactured. After sintering, the zinc concentration was smoothly changed from ~0.3 mol % in the center to ~2.3 mol % at the sample edge (Fig. 3). The nickel concentration was 13 mol % in the center and 10.9 mol % at the edge by the total thickness of ~260 μm [22]. Therefore, the used two-step sintering mode makes it possible to reach compromise of yielding ceramic synthesis and keeping the regularly inhomogeneous distribution of chemical elements. Further, samples were ground to the thickness of 180 μm. Thus, the variation of the zinc concentration over the thickness in the graded ferrites used by fabrication of magnetoelectric composites was 0.3–2.3 mol %.

The field dependences of transverse ME coefficient $\alpha_{E31}$ are shown in Fig. 4 (the magnetic field is directed normal to the polarization axis). They exhibit a typical pattern: the ME coefficient increases with the increase in the constant magnetic field, reaches the maximum and then decreases to zero.

The ME signal is directly proportional to the pseudo-piezomagnetic coefficient $q = d\lambda/dH$, and, therefore, $H$-dependence in principle follows the slope of $\lambda$ on $H$. For nickel–zinc ferrite, it was theoretically calculated that $q$ grows linearly with the

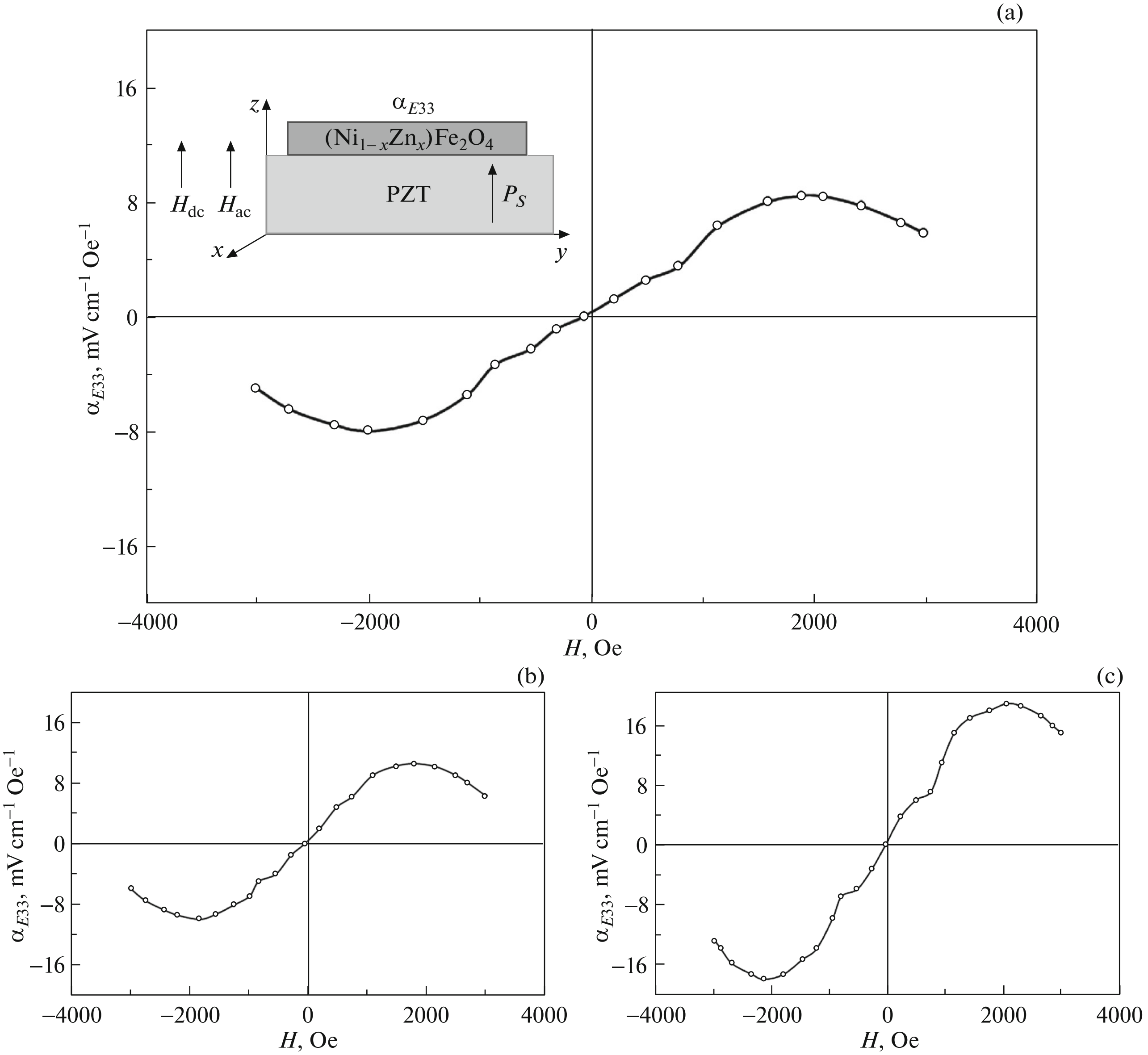

**Fig. 5.** Field dependences of longitudinal ME coefficient $\alpha_{E33}$ at various compositions of the magnetic phase: (a) $NiFe_2O_4$, (b) $(Ni_{0.8}Zn_{0.2})Fe_2O_4$, and (c) graded ferrite.

increase of the zinc concentration in the range $x = 0$–0.3, and further decreases at $x > 0.3$. In general, experimental studies of two-layer composites confirm this tendency [23]. However, quite wide spreads of characteristics are typical for the ceramic sintering route. They can be caused by variations in characteristics of the piezoelectric and magnetoelectric phase along with different coupling coefficients at the structure layer interfaces in different samples. In our experiments, the magnetoelectric coefficient increased by the increase of the zinc concentration ($\alpha_{E31}$ = 65.4 mV cm$^{-1}$ Oe$^{-1}$ at $x = 0$; ($\alpha_{E31}$ = 73.1 mV cm$^{-1}$ Oe$^{-1}$ at $x = 0.2$). By substituting the homogeneous ferrite by graded one, the ME signal was slightly lower: $\alpha_{E31}$ = 63.6 mV cm$^{-1}$ Oe$^{-1}$. In two-layer structures, the piezomagnetic coefficient is determined as $q = q_{11} + q_{12} = d\lambda_{11}/dH + d\lambda_{12}/dH$, where $\lambda_{11}$ is the magnetostriction constant in the direction parallel to magnetic field $H$ and $\lambda_{12}$ is that normal to $H$. In two-layer structures, the external magnetic field excites two modes of mechanical stresses: the in-plane stress caused by magnetostriction and stresses caused by the bending strain due to the structure asymmetry. Bending stresses have a component in the direction of longitudinal stresses (in-plane component) and decrease the entire intensity of the ME interaction [11]. By design of composites with the gradient magnetic phase, two options of the structure formation are possible: negative gradient of $q$ by decreasing of $q$ from the PZT–ferrite interface, and the positive gradient. In the second case, the positive gradient of $q$ is resulted in occurring of a bending moment directed oppositely to the bending strain caused by the structure asymmetry. As a result, the ME coefficient increases. In our experiments, the teo-layer composite exhibits the positive gradient of $q$. However, the ME coefficient does not increase. This phenomenon can be explained by the dependence of the intensity of the ME interaction on the ferrite volume fraction with respect to piezoelectric one. The strongest influence of the gradient structure occurs in the case of the ferrite volume fraction is more than 20–30%. In the case of the ferrite volume fraction is less than 20%, the ME coefficient decreases sharply and its value is independent of that the magnetic subsystem is homogeneous or gradient and also is independent of the gradient direction of $q$ [9]. In our samples, the ferrite/PZT volume fraction ratio was ~0.12.

**Longitudinal ME effect in two-layer piezoelectric–($Ni_{1-x}Zn_x$)$Fe_2O_4$ structures.** By studying the longitudinal ME effect $\alpha_{E33}$, the external constant and alternating magnetic fields were directed parallel to the vector of the spontaneous polarization of PZT and to the magnetization gradient (or composition gradient). Just this configuration of the external field with respect to the gradient direction of magnetization (composition) is optimum for occurring of new effects in the system. As it was mentioned above, no shifts and distortions of the hysteresis loops were observed in our graded ferrites. This confirms the absence of the internal magnetic field or a low value of $H_{int}$. Therefore, in the absence of the external magnetic field the ME coefficient is negligible (Fig. 5). In two-layer composites, low ME signals can occur because of the structure asymmetry and hysteresis phenomena. The field dependences of $\alpha_{E33}$ are practically symmetrical, which also confirms the absence of the internal magnetic field in ferrites.

The maximum value of the ME coefficient considerably grows by using the graded materials as a magnetic subsystem as compared with homogeneous structures ($\alpha_{E33} = 18.9$ mV cm$^{-1}$ Oe$^{-1}$ for the graded structure; $\alpha_{E33} = 8.4$ mV cm$^{-1}$ Oe$^{-1}$ for the homogeneous sample with $x = 0$; $\alpha_{E33} = 10.5$ mV cm$^{-1}$ Oe$^{-1}$ for the homogeneous sample with $x = 0.2$). Here, it should be noted that the longitudinal and transverse ME effects were studied in the same composites, i.e., for two experimental geometries, the magnetic, piezoelectric, and mechanical characteristics of materials along with the coupling coefficients between layers were identical. Therefore, the increase in the longitudinal ME coefficient in the graded structures occurs in the absence of the internal magnetic field. Our results do not allow to claim that the increase in $\alpha_{E33}$ is solely determined by the presence of the magnetization gradient. Probably, additional mechanical stresses occur in such composites because of the presence of the gradient in elastic properties caused by the regularly inhomogeneous variation in the composition.

As a rule, the transverse signal is studied in composites including graded structures. This is determined by that its value is more than two times larger as compared with the longitudinal signal ($\alpha_{E31} > 2\alpha_{E33}$) and it is revealed at smaller external magnetic fields. The author of [2] reported on the multiple increase in $\alpha_{E33}$. They presented the results of the study of the PZT–compositionally graded $Ni_{1-x}Zn_xFe_2O_4$–PZT symmetrical structure. By substituting the homogeneous nickel ferrite by graded one, the maximum value of $\alpha_{E33}$ increased by more than 10 times. In this case, composites did not reveal a considerable ME interaction in the absence of external biased field $H_{dc}$, which agrees with our obtained results.

## CONCLUSIONS

Samples of a homogeneous ($x = 0$, 0.1, and 0.2) and multilayer ceramics with a gradient composition based on solid solutions of ($Ni_{1-x}Zn_x$)$Fe_2O_4$ nickel–zinc ferrites were prepared using the thick-film technology. The variation of the zinc concentration over the thickness in the graded samples was 0.3–2.3 mol %. Two-layer PZT–$NiFe_2O_4$, PZT–($Ni_{0.8}Zn_{0.2}$)$Fe_2O_4$, and PZT–graded ($Ni_{1-x}Zn_x$)$Fe_2O_4$ composites were manufactured. The longitudinal and transverse magnetoelectric effects in the obtained composites were studied. In the absence of the external magnetic field, the ME coefficient values were negligible. No increase in the maximum value of the transverse ME coefficient was observed by substituting of the homogeneous ferrite by the graded one. The maximum value of the longitudinal ME coefficient was practically two times higher in composites with the graded magnetic phase as compared with homogeneous structures ($\alpha_{E33} = 18.9$ mV cm$^{-1}$ Oe$^{-1}$ for the graded structure; $\alpha_{E33} = 8.4$ mV cm$^{-1}$ Oe$^{-1}$ for the homogeneous sample with $x = 0$; $\alpha_{E33} = 10.5$ mV cm$^{-1}$ Oe$^{-1}$ for the homogeneous sample with $x = 0.2$). The field dependences of $\alpha_{E33}$ are practically symmetrical, which confirms the absence of the internal magnetic field in ferrites. Probably, additional mechanical stresses occur in these composites because of the presence of the gradient in elastic properties caused by the regularly inhomogeneous variation in the composition.

## FUNDING

This work was partially supported by the Belorussian Foundation for Basic Research, project no. F20MS-026.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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*Translated by N. Podymova*