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THE MAGNETOELECTRIC EFFECT OF A $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4 - \text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ MULTILAYER COMPOSITE

EFEKT MAGNETOELEKTRYCZNY W WARSTWOWYM KOMPOZYCIE $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4 - \text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$

The magnetoelectric effect in multiferroic materials has been widely studied for its fundamental interest and practical applications. The magnetoelectric effect observed for single phase materials like Cr_2O_3 , BiFeO_3 , and $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ is usually small. A much larger effect can be obtained in composites consisting of magnetostrictive and piezoelectric phases. This paper investigates the magnetoelectric effect of a multilayer (laminated) structure consisting of 6 nickel ferrite and 7 PFN relaxor layers. It describes the synthesis and tape casting process for $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$ ferrite and relaxor $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PFN). Magnetic hysteresis, ZFC – FC curves and dependencies of magnetization versus temperature for PFN relaxor and magnetoelectric composite were measured with a vibrating sample magnetometer (VSM) in an applied magnetic field up to 85 kOe at a temperature range of 10-400 K. Magnetoelectric effect at room temperature was investigated as a function of a static magnetic field (0.3-6.5 kOe) and the frequency of sinusoidal magnetic field (0.01-6.5 kHz). At lower magnetic field, the magnetoelectric coefficient increases slightly before reaching a maximum and then decreases. The magnetoelectric coefficient α_{ME} increases continuously as the frequency is raised, although this increase is less pronounced in the 1-6.5 kHz range. Maximum values of the magnetoelectric coefficient attained for the layered composites exceed about 50 mV/(Oe cm).

Keywords: Tape casting, Multilayer composite, Magnetic properties, Magnetoelectric effect

Materiały kompozytowe wykazujące efekt magnetoektryczny są obecnie szeroko badane zarówno dla celów poznawczych jak i aplikacyjnych. Szczególny nacisk kładzie się na kompozyty ferrytowo – relaksorowe, w których efekt magnetoektryczny jest znacznie większy niż w materiałach jednofazowych. W opracowaniu przedstawiono technologię wytwarzania wielowarstwowego kompozytu ceramicznego składającego się z magnetycznych warstw ferrytu $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$ rozdzielonych warstwami ferroelektryka $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$. Przedstawiono wyniki badań właściwości magnetycznych otrzymanego kompozytu. Badania te przeprowadzono przy użyciu magnetometru wibracyjnego w szerokim zakresie temperatur (10K-400K) w polu magnetycznym dochodzącym do 85 kOe. Wykonano pomiary efektu magnetoektrycznego w temperaturze pokojowej w zależności od częstotliwości zmiennego pola magnetycznego (0.01-6.5 kHz) oraz natężenia stałego pola magnetycznego (0.3-6.5 kOe). Współczynnik magnetoektryczny najpierw rośnie, osiąga maksimum a następnie lekko maleje ze wzrostem natężenia stałego pola magnetycznego. Współczynnik magnetoektryczny badanego kompozytu rośnie ze wzrostem częstotliwości sinusoidalnego zmiennego pola magnetycznego osiągając maksymalną wartość około 50 mV/(Oe cm).

1. Introduction

Magnetoelectric effect (ME) in multiferroic materials has been studied at great length for its fundamental usefulness and practical applications [1-8]. Defined as an induced dielectric polarization under an applied magnetic field, ME is generally characterized by the magnetoelectric voltage coefficient α_{ME} [1,2].

The magnitude of the magnetoelectric effect in multiferroics is determined by magnetostrictive deformation and the piezoelectric effect in the material. The magnetoelectric effect obtained for multiferroics is directly proportional to the piezomagnetic coefficient $\frac{d\lambda}{dH}$, where λ is magnetostriction and H is the magnetic field. The stress generated in the piezoelectric subsystem directly corresponds to the stiffness in the subsystem,

which results in effective mechanical coupling [1,2]. The stress causes an increase in the polarization of the domains oriented in the direction of tension and a decrease in the polarization of those oriented in the direction of compression. The change in polarization causes a bound electric charge to appear at the domain wall. These bound charges induce an electric field in grains [1,2].

The ME effect observed for single-phase materials like Cr_2O_3 , BiFeO_3 and $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ is usually small. Much larger ME effects can be obtained in composites consisting of two functional phases: magnetostrictive, in which a strain is produced by applying a magnetic field, and piezoelectric, in which a change in electric polarization is produced by an applying stress. The reported values for ferrite/relaxor composites are 10-100 times higher than the magnetoelectric coefficient for single – phase multiferroics [6-8].

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From a practical point of view nickel ferrite is frequently used in magnetoelectric composites, because it possesses good dielectric and magnetic properties and high magnetostriction [9,10]. As a piezoelectric phase, the ferroelectric relaxor $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) has often been employed in several applications because it has good ferroelectric properties [11]. PFN is a member of an enormous perovskite-like family of ferroelectrics with the general formula $\text{A}(\text{B}'\text{B}'')\text{O}_3$, which is characterized by wide isomorphism. Earlier examinations have revealed that PFN is a biferroic with ferroelectric and antiferromagnetic properties in the same phase [11].

In the present work we report on our investigation of new magnetoelectric composites based on $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$ ferrite as a magnetostrictive phase and $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ relaxor as a ferroelectric phase. The composite was prepared as a multilayer tape cast and cosintered laminate. The magnetic and magnetoelectric properties of the composite are presented.

2. Experimental

The $\text{Ni}_{0.30(1)}\text{Zn}_{0.62(1)}\text{Cu}_{0.08(1)}\text{Fe}_{2.00(2)}\text{O}_{4.00(2)}$ ferrite was prepared using the standard solid-state reaction method. The high-purity oxides Fe_2O_3 , NiO , ZnO and CuO were weighed in stoichiometric proportions, ball-milled in isopropyl alcohol, dried, pelletized and calcined at 900°C for 4 h.

The $\text{Pb}(\text{Fe}_{0.50(1)}\text{Nb}_{0.50(1)})\text{O}_{3.00(1)}$ was synthesized with the "wolframite" method. Wolframite FeNbO_4 was prepared by ball-milling Fe_2O_3 and Nb_2O_5 in stoichiometric proportions in isopropyl alcohol for 8h. After drying, the powder was pressed into pellets and calcined at 1000°C for 4h. The reaction product was then mixed by ball milling with PbO , dried, pelletized and calcined at 800°C for 4h in a covered crucible, and 1 mol.% MnO_2 was introduced to the batch in order to improve its resistivity. For all reactions, the materials were placed in an alumina crucible, topped with a second alumina crucible, and then placed inside the furnace.

The crystal structures and stoichiometry of the synthesized materials were tested by standard X-ray powder diffraction using $\text{CuK}\alpha$ radiation (TUR – M61 diffractometer). X-ray diffraction analysis of the synthesized powders confirmed their single phase compositions.

The ferrite and relaxor tape were fabricated as follows: ferrite and relaxor powder were mixed with binder solutions and solvent to make slurries for tape casting. These slurries were prepared by ball-milling for 4 h with inorganic (powders) and organic components mixed in carefully chosen proportions. The following composition for the organic part was chosen as optimal: fish oil – 2.1%, polyvinyl butyral – 16.7%, polyethylene glycol – 4.2%, dibutyl phthalate – 4.2%, toluene – 35.4%, isopropyl alcohol – 37.5%. The polyvinyl butyral (PVB) was used as a binder, fish oil as a dispersant, polyethylene glycol and dibutyl phthalate as plasticizers, and toluene and isopropyl alcohol as solvents. Tape casting was done with a table top tape caster (TTC-1200, Richard E. Mistler, Morrisville, US) with a 20 cm wide doctor blade on moving polyester carrier film. The doctor blade was run with a blade gap of $500\ \mu\text{m}$ to fabricate the tapes, which has a dry thickness of $110\text{--}150\ \mu\text{m}$ after tape casting and drying. The

fabricating process of the ferrite $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$ tape has been described in detail elsewhere [9].

The next step was to stack and laminate the composite. Three basic parameters in lamination (temperature, pressure and dwell time) have to be controlled. In our study, eleven alternate layers of the ferrite and the relaxor were used to form a multilayer composite, which was laminated at 40°C under $10\text{--}15\ \text{MPa}$ of pressure. Following the stacking and lamination, the multilayer composite was sintered at 950°C for 2h and then allowed, along with the furnace to cool down to approximately $200^\circ\text{C}/\text{h}$.

Magnetization measurements performed using a vibrating sample magnetometer from a Quantum Design PPMS6000 system were taken in the external magnetic field up to 85 kOe in the temperature range $10\text{--}400\ \text{K}$. A magnetic field of $H=50\ \text{Oe}$ was applied for the zero-field (ZFC) and field-cooled (FC) magnetization profiles, both of which were acquired at increasing temperature. The same field value was to cool the sample prior to FC measurements. Magnetic hysteresis curves ($M(H)$) were measured at 10K, 100K, 223K, 293K, 343K, and 393K. The direction of the applied magnetic field was parallel to the layers. The magnetoelectric effect was evaluated at room temperature by dynamic lock-in method, which has been described previously in the literature [12]. The induced voltage between sample surfaces was measured with a lock-in amplifier (Stanford Research System, model SR 830) with input resistance of $100\ \text{M}\Omega$ and a capacitance of $25\ \text{pF}$. The lock-in amplifier was used in differential mode, while the DC and AC magnetic field were measured with a Hall probe SM 102.

3. Results and discussion

Figure 1 presents the temperature dependence of the magnetic susceptibility for PFN (a) and laminated composite (b) (T_N – Neel temperature for PFN).

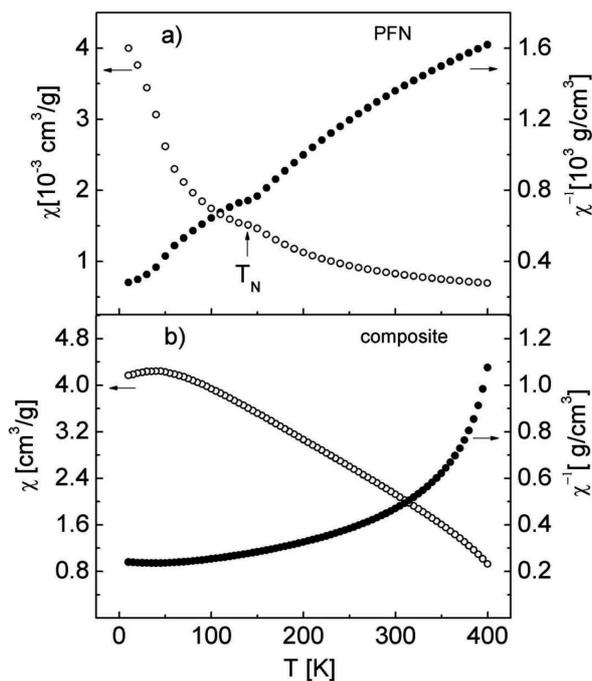


Fig. 1. Temperature dependence of the magnetic susceptibility $\chi(T)$ and $\chi^{-1}(T)$ for PFN (a) and laminated composite (b) (T_N – Neel temperature for PFN)

The temperature courses of the magnetic susceptibility for PFN relaxor indicate the local maximum occurs at temperature $T_N = 140$ K, which may be related to the presence of magnetic phase transition (Fig. 1a). The anomaly at temperature T_N can be ascribed to the paramagnetic (PM) to antiferromagnetic (AFM) phase transition. The temperature profile of the magnetic susceptibility for laminated composite (Fig. 1b) shows a dependence typical of such composite materials, i.e. it consists of a dominant signal from the ferrimagnetic (ferrite) and a weak signal from the paramagnetic (antiferromagnetic) phase (relaxor). The magnetic susceptibility for composite is the sum of magnetic susceptibility for PFN and ferrite. Experimental error in this case can be estimated as 10^{-4} cm³/g.

Figure 2 shows a comparison of the magnetic hysteresis loops for PFN (a) and laminated composite (b). The magnetic hysteresis loops for PFN (Fig. 2a) at higher temperature are typical for paramagnetic materials, because the magnetization linearly increases with magnetic field. At lower temperatures, especially at $T=10$ K, the magnetization increases nonlinearly because below $T_N \sim 140$ K the relaxor PFN has an antiferromagnetic ordering. The hysteresis loops for composite (Fig. 2b) measured at higher temperatures are typical of a mixture of soft ferrite with a significant amount of paramagnet (relaxor); there is an abrupt increase up to the saturation field of ferrite and a further linear increase. While the profiles measured at lower temperatures, especially at $T=10$ K, show a slightly

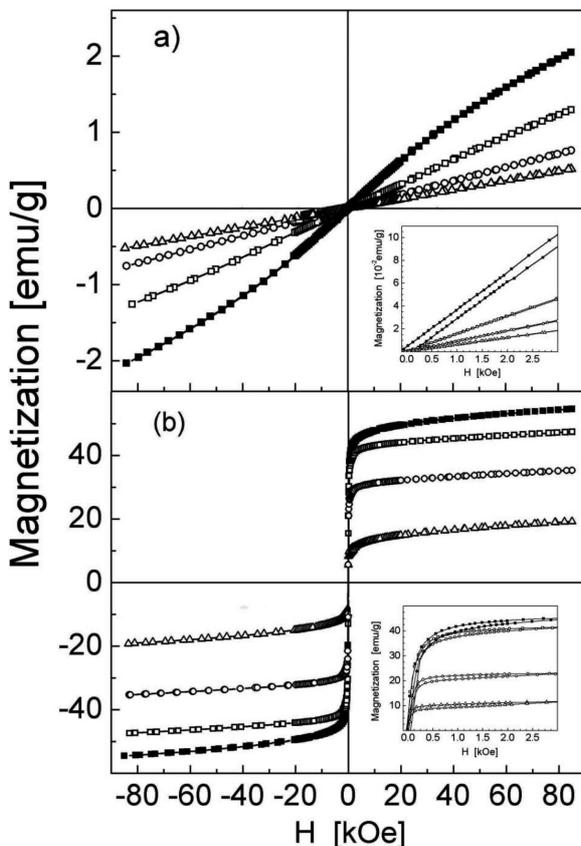


Fig. 2. $M(H)$ profiles measured up to 85 kOe at temperature 10 K (black squares), 100 K (open squares), 223 K (open points) and 393 K (open triangles) for PFN (a) and laminated composite (b). Closer inspection of the low field parts of the hysteresis loops is presented in the insets

distinct shape due to the evolution of the magnetic properties of the relaxor phase, the mixture becomes antiferromagnetic below T_N . Experimental error in this method can be estimated as $2 \cdot 10^{-5}$ g/cm³.

Figure 3 shows a comparison of the ZFC-FC profiles measured at 50 Oe for PFN (a) and laminated sample (b). The ZFC and FC magnetizations for PFN (Fig. 3a) increase as the temperature decreases. Below $T \sim 50$ K the ZFC-FC magnetizations rapidly increase and diverge significantly. The deviation that results from the ZFC and FC curves overlapping is typical of spin glass phases and was reported for PFN [13]. At low temperature a spin-glass state coexists when long-range antiferromagnetic order occurs in the relaxor perovskite PFN. The ZFC and FC dependencies for laminated composite (Fig. 3b) diverge at the relatively high temperatures of 350 K, indicating that coercivity varies considerably with temperature. Going to the low temperatures, ZFC and FC magnetizations increase and reach their maxima between 60 K and 80 K. However, the dependence of the ZFC profile of the laminated sample shows a wide plateau between 200 K and 300 K. At the lowest temperatures – below ~ 60 K – the ZFC and FC magnetizations of the composite are strongly reduced due to a significant increase of the coercive field at low temperatures, which reaches the value of the order of the applied field, i.e. 50 Oe. Experimental error in this method can be estimated as $2 \cdot 10^{-5}$ g/cm³.

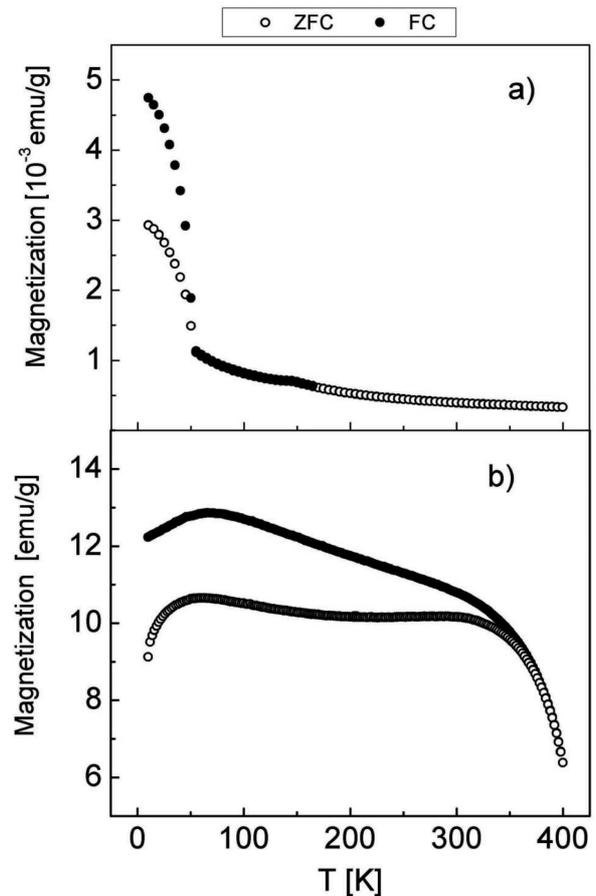


Fig. 3. ZFC (open points) and FC (black points) profiles of magnetizations measured at 50 Oe for PFN (a) and laminated composite (b)

Figure 4 plots the magnetoelectric coefficient α_{ME} determined for $\text{Ni}_{0.3}\text{Zn}_{0.62}\text{Cu}_{0.08}\text{Fe}_2\text{O}_4$ – PFN composite versus the

bias magnetic field H_{DC} . The AC and DC magnetic fields were applied perpendicular (closed and open circles) and parallel (closed and open triangles) to the sample surfaces. At lower magnetic field, the α_{ME} coefficient increases slightly before reaching a maximum at $H_{DC} = 750$ Oe and then decreases. The increase in the α_{ME} coefficient can be attributed to the improvement of the magnetostrictive properties and piezomagnetic coefficient of the composite.

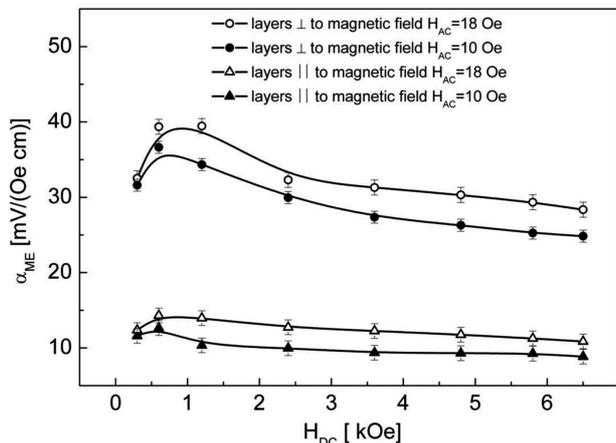


Fig. 4. Magnetoelectric coefficient α_{ME} determined for laminated composite is plotted versus the bias magnetic field H_{DC} . The frequency of the H_{AC} magnetic field equals $f = 1$ kHz. Values of amplitude H_{AC} are presented

Figure 5 shows the dependence of the magnetoelectric coefficient versus frequency. The magnetoelectric coefficient α_{ME} increases continuously as the frequency is raised, although this increase is less pronounced in the 1-6.5 kHz range. The AC and DC magnetic fields were applied perpendicular (closed and open circles) and parallel (closed and open triangles) to the sample surfaces. Magnetoelectric coupling between magnetostrictive phase and relaxor phase increases with the frequency of the AC magnetic field rising up to a value corresponding to the resonance magnetoelectric effect, and then decreases [14,15]. However, the resonance effect is observed at frequencies much higher than those applied in this work (several dozen to a few hundred kHz higher) [14,15].

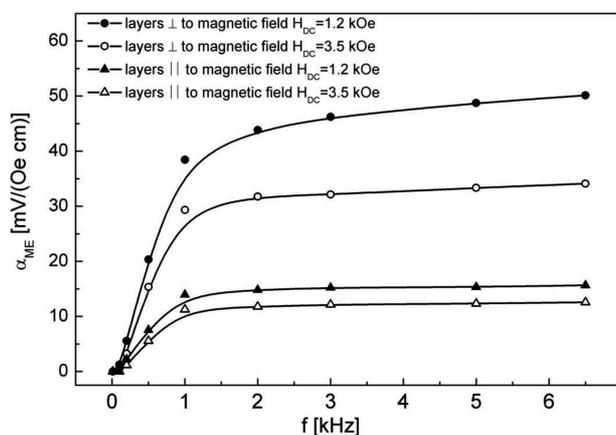


Fig. 5. Magnetoelectric coefficient α_{ME} versus frequency of H_{AC} magnetic field for laminated composite. Values of bias magnetic field H_{DC} are presented

4. Conclusion

A magnetoelectric composite consisting of a solid solution containing ferrimagnetic ferrite $Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe_2O_4$ and ferroelectric relaxor $Pb(Fe_{0.5}Nb_{0.5})O_3$ was prepared as multilayer tape cast laminate.

Temperature courses of the magnetic susceptibility for PFN indicate the local maximum at temperature $T_N = 140$ K. The anomaly at temperature T_N is attributed to the paramagnetic to antiferromagnetic phase transition. At moderate and high magnetic fields the sample reveals properties typical of a mixture of ferrimagnetic and para/antiferromagnetic phase. Here the properties are affected by a small amount of additional phase of the higher magnetocrystalline anisotropy observed in the laminated sample. The additional phase is likely of a carbide type (e.g. cementite-like) which could be created at the ferrite/relaxor interface from the carbon included in the organic additives. The bifurcation of field and zero-field cooled magnetizations observed for PFN and laminated composite implies spin-glass behavior.

At lower magnetic fields, the magnetoelectric coefficient increases slightly before reaching a maximum at $H_{DC} = 750$ Oe and then decreases. The magnetoelectric coefficient α_{ME} increases continuously as the frequency is raised, although this increase is less pronounced in the 1-6.5 kHz range.

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REFERENCES

- [1] M. Fiebig, Revival of the magnetoelectric effect, *J. Phys. D: Appl. Phys.* **38**, R123 (2005).
- [2] R. Grössinger, G.V. Duong, R. Sato-Turtelli, The physics of magnetolectric composites, *J. Magn. Magn. Mater.* **320**, 1972 (2008).
- [3] Y.K. Fetisov, K.E. Kamentsev, A.Y. Ostaschenko, Magnetolectric effect in multilayer ferrite – piezoelectric structures, *J. Magn. Magn. Mater.* **272-276**, 2064 (2004).
- [4] D. Bochenek, P. Niemiec, R. Zachariasz, A. Chrobak, G. Ziółkowski, Ferroelectric-ferromagnetic composites based on PZT type powder and ferrite powder, *Arch. Metall. Mater.* **58**, 4, 1013-1017 (2013).
- [5] R. Zachariasz, J.A. Bartkowska, D. Bochenek, P. Niemiec, Internal friction in the ferroelectric-ferromagnetic composites, *Arch. Metall. Mater.* **58**, 4, 1327-13330 (2013).
- [6] J. Kulawik, P. Guzdek, D. Szwagierczak, A. Stoch, Dielectric and magnetic properties of bulk and layered tape cast $CoFe_2O_4 - Pb(Fe_{1/2}Ta_{1/2})O_3$ composites, *Compos. Struct.* **92**, 2153 (2010).
- [7] M. Venkata Ramanaa, N. Ramamanohar Reddy, G. Sreenivasulu, K.V. Siva Kumar, B.S. Murty, V.R.K. Murthy, Enhanced magnetolectric voltage in multiferroic particulate $Ni_{0.83}Co_{0.15}Cu_{0.02}Fe_{1.9}O_{4-\delta}/PbZr_{0.52}Ti_{0.48}O_3$ composites – dielectric, piezoelectric and magnetic properties, *Cur. Appl. Phys.* **9**, 1134 (2009).

- [8] S.A. Solopan, O.I. V'yunow, A.G. Belous, A.I. Tovstolytkin, L.L. Kovalenko, Magneto-electric effect in composite structures based on ferroelectric/ferromagnetic Perovskites, *J. Eur. Ceram. Soc.* **30**, 259 (2010).
- [9] P. Guzdek, J. Kulawik, K. Zaraska, A. Bieńkowski, NiZnCuFe ferrite applied for LTCC microinductor, *J. Magn. Magn. Mater.* **322**, 2897 (2010).
- [10] P.A. Joy, S.K. Date, Effect of sample shape on the zero-field-cooled magnetization behavior: comparative studies on NiFe_2O_4 , CoFe_2O_4 and $\text{SrFe}_{12}\text{O}_{19}$, *J. Magn. Magn. Mater.* **222**, 33 (2000).
- [11] D. Bochenek, P. Guzdek, Ferroelectric and magnetic properties of ferroelectro-magnetic $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ type ceramics, *J. Magn. Magn. Mater.* **323**, 369 (2011).
- [12] G.V. Duong, R. Grössinger, M. Schoenhardt, D. Bueno-Basques, The lock-in technique for studying magnetoelectric effect, *J. Magn. Magn. Mater.* **316**, 390 (2007).
- [13] G.M. Rotaru, B. Roessli, A. Amato, S.N. Gvasaliya, C. Mudry, S.G. Lushnikov, T.A. Shaplygina, Spin-glass state and long-range magnetic order in $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ seen via neutron scattering and muon spin rotation, *Phys. Rev. B* **79**, 184430 (2009).
- [14] U. Laletsin, N. Padubnaya, G. Srinivasan, C.P. Devreugd, Frequency dependence of magnetoelectric interactions in layered structures of ferromagnetic alloys and piezoelectric oxides, *Appl. Phys. A* **78**, 33 (2004).
- [15] D.V. Chashin, Y.K. Fetisov, K.E. Kamentsev, G. Srinivasan, Resonance magnetoelectric interactions due to bending modes in a nickel-lead zirconate titanate bilayer, *Appl. Phys. Lett.* **92**, 102511-1 –102511-3 (2008).