Ferroelectric and ferromagnetic properties of the \((1-x)\)NiZnFeO\(_4\) – \((x)\)Pb(Fe\(_{1/2}\)Nb\(_{1/2}\))O\(_3\) composite

INTRODUCTION
According to the thermodynamic terminology of the multiferroics, they are some ferroics of II and III order which have simultaneously at least two spontaneously ordered subsystems among the states: ferromagnetic FM, ferroelectric FE, ferroelastic FES and ferrotoroidal FT \([1\div3]\). Possible application of the multiferroics depend, first of all, on a degree of mutual coupling of particular subsystems (magnetic, electric and elastic) \([4]\).

Materials showing simultaneous electric (FE – ferroelectric, AFE – antiferroelectric or FIE – ferritelectric) and magnetic ordering (FM – ferromagnetic, AFM – antiferromagnetic or FIM ferrimagnetic) are called ferroelectromagnetics (FEM) \([5]\). In the ferroelectromagnetics both magnetic and electric properties can be controlled by external factors, such as: a magnetic field, an electric field, stress or temperature \([6]\). If a multiferroic material is the ferromagnetic and the ferroelectric at the same time, then it will be characterized by magnetic response to a variable electric field, or inversely, a polarization change in the external magnetic field. This effect can be strengthened by making composite based on the ferrites and the ferroelectric materials (multiferroics, biferroics, ferroics). According to the classification, made by D. Khomsky, the multiferroic materials can be divided into multiferroics of type-I and type-II \([5]\). \(\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3\) (PFN) is one of the well-known ferroelectromagnetic materials. It has a structure of the perovskite type of the ABO\(_3\) general formula, where A positions of the unit cell are filled with big ions of lead Pb, whereas B positions are filled alternately with (in a random way) ions of iron Fe and niobium Nb \([7, 8]\). According to the classification of D. Khomsky \([5]\) PFN belongs to multiferroics of type-I, in which ferroelectricity is connected with a displacement of ferroelectrically active ions \(d^0\) (Nb) from the centre of regular octahedrons – \(O\), whereas magnetism is connected with presence of ions \(d^0\) (Fe). Such a situation in the „mixed” perovskites is a polarization source which co-exists with the magnetic ordering (antiferromagnetic). However, coupling of those subsystems in PFN is weak. The multiferroics with the strong coupling of the magnetic and electric subsystems are included into the multiferroics of type-II, where magnetism causes ferroelectricity formation, but the spontaneous polarization is relatively low (about \(10^{-2}\) \(\mu\)C/cm\(^2\)). Ferroelectricity in those multiferroics occurs only if they show the magnetic ordering. \(\text{TbMnO}_3\) and \(\text{TbMn}_2\text{O}_3\) are the examples of the materials from this group \([5]\).

Technology and results of comprehensive examinations of the ferroelectromagnetic composite based the NiZnFeO\(_4\) nickel-zinc ferrite and the \(\text{PbFe}_{1/2}\text{Ni}_{1/2}\text{O}_3\) multiferroic with the general formula of \((1-x)\)NiZnFeO\(_4\)-(\(x\))PFN, for \(x = 0.6\) (a ratio of the component content 40:60) are presented in this work.

Ferrite NiZnFeO\(_4\) \((\text{Fe}_{2}\text{Ni}_{0.63}\text{Zn}_{0.37}\text{O}_5)\) belongs to the soft ferrite of the work frequency range \((50\div1000\ \text{MHz})\) and it is used, among others, for signal treatment (in telecommunication filters, distance sensors, pulse transformers, in delay lines), for damping EMI (while damping broad-band electromagnetic interferences in EMI filters, in current-compensated chokes), for broad-band transformers, elements, which do not require usage of higher power levels, higher frequencies. Recently, soft nickel-zinc ferrites with high permeability and high Curie temperature have been widely studied both for scientific reasons and for LTCC (low temperature co-fired ceramics) applications \([9, 10]\).

An aim of this work was to obtain the \((1-x)\)NiZnFeO\(_4\)-(\(x\))PFN ferroelectromagnetic composite and to improve the coupling of the magnetic and electric sub-systems.

EXPERIMENT
The test material was the \((1-x)\)NiZnFeO\(_4\)-(\(x\))Pb(Fe\(_{1/2}\)Nb\(_{1/2}\))O\(_3\) ferroelectromagnetic composite, for \(x = 0.6\), consisting of the zinc-nickel ferrite of high magnetic permeability and high resistance (NiZnFeO\(_4\)) (Fig. 1) and the synthesized \(\text{PbFe}_{1/2}\text{Ni}_{1/2}\text{O}_3\) (PFN) ferroelectromagnetic powder. In the further part of the work the composite was marked as NZF-PFN.

The columbite method (a two stage synthesis of the \(\text{Fe}_{1/2}\text{Ni}_{1/2}\text{O}_3\) components) by powder calcination was used to obtain the synthesizedPFN \([11]\). In the first stage, the \(\text{FeNbO}_4\) iron niobate was obtained according to the \(\text{Fe}_2\text{O}_3\text{+Nb}_2\text{O}_5\rightarrow 2\text{FeNbO}_4\) reaction (synthesis conditions: \(T_{\text{synthI}} = 1000^\circ\text{C}\) and \(t_{\text{synthI}} = 4\) h), whereas in the second stage the final product was obtained in a form of the synthesized \(\text{PbFe}_{1/2}\text{Ni}_{1/2}\text{O}_3\) powder according to the reaction: \(\text{FeNbO}_4\text{+}2\text{PbO} \rightarrow 2\text{PbFe}_{1/2}\text{Ni}_{1/2}\text{O}_3\) (synthesis conditions: \(T_{\text{synthII}} = 800^\circ\text{C}\) and \(t_{\text{synthII}} = 3\) h). The nickel-zinc ferrite was

Fig. 1. SEM image of the ferrit powder
Rys. 1. Zdjęcie SEM proszku ferrytu NiZnFeO\(_4\)
applied. Measurements of the magnetoelectric coefficient in tandem with a power supply (Dacpol Service, Poland). The surfaces of the pellets onto which conductive electrodes had been applied. Measurements of the magnetoelectric coefficient were performed by recording voltage output (V) as a function of magnetic field $H_{\text{AC}}$. The $\alpha_{\text{ME}}$ coefficent was calculated from the voltage output by the following relation (1):

$$\alpha_{\text{ME}} = \frac{V}{H_{\text{AC}} \cdot d}$$

where V is the voltage generated due to the magnetoelectric effect, $H_{\text{AC}}$ is the amplitude of the sinusoidal magnetic field and d is the thickness of the sample as presented here [12, 13] for both the single phase and composite magnetoelectric media. The induced voltage between sample surfaces was measured using the SR 830 lock-in amplifier with an input resistance of 100 MΩ and capacitance of 25 pF. The lock-in amplifier worked in the differential mode. The Hall probe system SM 102 (Asonik, Poland) was employed to measure the DC and AC magnetic fields.

RESULTS

At room temperature the X-ray diffraction patterns show a typical single phase cubic spinel for the ferrite powder NiZnFeO4 (Fig. 3). The diffraction peak of PFN component was identified as a tetragonal perovskite structure with a $P4_{mm}$ space group without pyrochlore phase. The X-ray analysis of the NZF-PFN composite showed that besides the peaks coming from the component phases (PFN and ferrite NiZnFeO4) there was also a low quantity of a foreign pyrochlore phase, which was formed during the technological process (Fig. 3).

The EDS examinations of the NZF-PFN composite and its particular components (Fig. 4), showed presence of characteristic maxima coming from the elements constituting the compounds in question. The examinations also confirmed a similar percentage composition of the components in the examined compounds according to the stoichiometric calculations.

In spite of the long mixing and milling in the planetary ball mill, the NZF-PFN composite microstructure shows high heterogeneity. It confirms the non-simultaneous and non-uniform growth of the grains of the PFN powder and NiZnFeO4 ferrite. Bigger grains grow quicker at the expense of smaller grains what is visible in the SEM microstructural images of the composite specimen fracture (Fig. 5). The NiZnFeO4 ferrite powder grains are characterized by rectangular boundaries in a shape of polygons, whereas the PFN ferroelectric powder grains have irregular edges on the grain boundaries (Fig. 5b).
Fig. 4. EDS microanalysis of element for PFN and NiZnFeO₄ powders and NZF-PFN composite
Rys. 4. Wyniki mikroanalizy EDS pierwiastków dla PFN, NiZnFeO₄ oraz kompozytu PFN-NiZnFeO₄

Fig. 5. Fracture of composite NZF-PFN samples: a) magnification ×5000, b) magnification ×25000
Rys. 5. Przełamanie próbek kompozytu NZF-PFN: a) pow. ×5000, b) pow. ×25000

The temperature examinations of the \( M(T) \) relationship of the NZF-PFN composite have shown high values of magnetic susceptibility (Fig. 6), decreasing with an increase in temperature. The \( M(T) \) curve is typical for ferro/ferrimagnetic behaviour with the Curie temperature near 400°C. In the temperature range from 80°C to 120°C an anomaly, connected with a slight inflexion of the \( M(T) \) course, is observed. That behaviour can show an influence of the electrical sub-system on the magnetic properties of the NZF-PFN composite. Above 400°C the NZF-PFN composite is the paramagnetic.

Magnetic hysteresis loops \( M(H) \) for the NZF-PFN composite, made at –271°C, –173°C and 27°C are presented in Figure 7. The \( M(H) \) courses are characteristic for magnetically soft materials. At –271°C the NZF-PFN composite shows a narrow magnetic loop with high saturation. Spontaneous magnetization at this temperature is \( M_S = 36.42 \, \text{emu/g} \), magnetization remanence \( M_R = 18.24 \, \text{emu/g} \), whereas the coercion field value is about \( H_C = 0.11 \, \text{T} \). With an increase in temperature the spontaneous magnetization value decreases and at 27°C it is \( M_S = 27.84 \, \text{emu/g} \), whereas the magnetization remanence equals \( M_R = 7.98 \, \text{emu/g} \). With an increase in temperature the magnetic hysteresis loop image narrows, and the coercion field value decreases to the value of \( H_C = 0.03 \, \text{T} \). Similar results of the magnetic examinations were obtained by the authors in article [14], but the values of magnetization were lower.

Examinations of the dielectric properties of the NZF-PFN confirmed presence of a few maxima of electric permittivity in the \( \varepsilon(T) \) relationship – Figure 8. The first maximum present at a lower temperature is connected with the ferroelectric-paraelectric phase transition (coming from PFN). The second maximum (strongly diffused), present at a higher temperature, is connected to an increase in activation mechanism of electric conductivity. In the \( \varepsilon(T) \) diagram anomalies can be also seen in the area of the magnetic – paramagnetic phase change (about 390°C), visible for lower frequencies of the measurement field. Like in the PFN ceramics, the phase transition from paraelectric to ferroelectric phase shows a diffused character (Fig. 8b) in the NZF-PFN composite. The maximum of the \( \varepsilon_m \) electric permittivity value in the phase transition is about 12 times lower comparing to the PFN ceramics [e.g. 15]. The characteristic maxima present in the area of the magnetic phase transition in the NZF-PFN composite show an influence of the magnetic subsystem on its dielectric properties. Dielectric losses decrease with an increase in the frequency of the measurement field. It is visible in the tan(\( \delta \)) temperature relationships of the NZF-PFN composite (Fig. 9). However, values of the dielectric losses are rather high. The temperature increase (above 100°C) results in their rapid increase, which is particularly visible for low frequencies of the measurement fields.
Fig. 7. Magnetic hysteresis loops for NZF-PFN composites at temperatures: a) –271°C, b) –173°C and c) 27°C

The phase transition taking place in the NZF-PFN composite are also confirmed on the temperature relationships of mechanical losses $Q^{-1}$ and Young’s modulus $Y$ (Fig. 10), determined by the internal friction method [16]. In the diagrams distinct changes of the $Y$ values in a form of the $\Delta_{\text{PCE}}$ minimum, correlating with the maximum of the $P_{\text{PCE}}$ internal friction (the $Q^{-1}$ maximum diffused at about 100°C) can be observed.

Fig. 8. Temperature dependences on dielectric permittivity $\varepsilon$ for NZF-PFN composite

Rys. 8. Temperaturowe zależności przenikalności elektrycznej $\varepsilon$ dla kompozytu NZF–PFN

Fig. 9. Temperature dependences on the $\tan\delta$ for NZF-PFN composite

Rys. 9. Zależności tangensa kąta strat dielektrycznych $\tan\delta$ od temperatury $T$ dla kompozytu NZF–PF
Such behaviour of the $P_{MC}$ peak connected with the rapid increase in the Y Young's modulus value above the $A_{FCE}$ minimum shows that the phase transition takes place (ferroelectric ↔ paraelectric). Similar regularities are observed at higher temperature, where there is the subsequent Y minimum ($A_{FCE}$), overlapping with the internal friction maximum ($P_{ECM}$).

Temperature of the $Q^{-1}$ maxima correspond rather well to temperature of the $\varepsilon$ electrical permittivity maxima (Fig. 8a) and the magnetic phase transition in the $M(T)$ diagram (Fig. 6). Those anomalies can confirm an influence of the magnetic subsystem on the electrical properties and inversely.

The results of the magnetoelectric coefficient measurements for NZF-PFN composite are plotted versus the effect decreases with the increase in bias magnetic field $300÷2000$ Oe and above strongly decreases with increase in DC field in the range of obtained using measurement or theoretical calculations for frequency dependencies of the magnetoelectric coefficient, and then decreases [18]. However, the field rising up to the value corresponding to the resonance for a ferroelectric phase increases with the frequency of AC magnetic magnetoelectric coupling between a magnetostrictive phase and constant maximum level in the range of $6÷10$ kHz. In general, frequencies changing from 10 Hz to 6 kHz and reach an almost constant maximum level in the range of 6÷10 kHz. In general, magnetoelectric coupling between a magnetostRICTive phase and a ferroelectric phase increases with the frequency of AC magnetic field rising up to the value corresponding to the resonance magnetoelectric effect, and then decreases [18]. However, the frequency dependencies of the magnetoelectric coefficient obtained using measurement or theoretical calculations for magnetoelectric composites by others authors are similar to our dependencies [19, 20]. The authors suggested, that the magnetoelectric coefficient in the low frequency region depended on the composite composition and conductivity of the ferrite phase.

SUMMARY

The X-ray examinations of the $(1-x)$NiZnFeO$_3$–(x)Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ composite showed a slight quantity of the pyrochlore phase besides the main composition phases (coming from PFN and NZF), and the examinations of the magnetic properties showed their significant increase (comparing to PFN).

The conducted comprehensive examinations of the dielectric, magnetic, magnetoelectric and elastic properties showed characteristic anomalies, present in the phase transition area of the electric sub-system (ferroelectric ↔ paraelectric) and in the area of the magnetic sub-system phase transition (ferromagnetic ↔ para-magnetic). These characteristic changes visible in the temperature relationships $M(T)$, $\alpha(T)$, $Q^{-1}(T)$ and $Y(T)$ can confirm a mutual influence of the magnetic and electric sub-systems. In the future possibility of controlling of electric and magnetic properties by both an external electric and magnetic factor can be used for building magnetoelectric transducers.

REFERENCES


