Magnetic and electric properties of the lead free ceramic composite based on the BFN and ferrite powders

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Ferroelectromagnetic BaFe0.5Nb0.5O3 (BFN) ceramics and ferroelectromagnetic composites based on BFN powder and ferrite powder have been obtained in the presented work. The percentage of components in a two-phase composite was: biferroic powder BFN in the amount of 90%, and nickel–zinc ferrite Ni1−xZnxFe2O4 for x = 0.36 in the amount of 10%. The synthesis of the components of the BFN–ferrite composite was performed using the calcination method. Final densification of the synthesized powder was done using free sintering. For the obtained two-phase ceramic BFN–ferrite composite, the XRD, microstructure, EDS, dielectric, impedances, magnetic, Mössbauer and electrical hysteresis loop investigations were performed. The obtained results show correlations between the magnetic subsystem and the electrical subsystem of the ferroelectromagnetic composite. Such properties of the obtained composite give a possibility to use them in memory applications of a new type.

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1. Introduction

Ferroelectromagnetics are materials exhibiting magnetic properties (ferromagnetic, ferrimagnetic and anti-ferromagnetic) and electric properties (ferroelectric, ferrielectric and antiferroelectric), and belong to the group of multiferroics of miscellaneous applications [1,2]. Pb(Fe0.5Nb0.5)O3, Pb(Fe2/3W1/3)O3, Pb(Fe0.5Ta0.5)O3 as well as multicomponent materials obtained on their basis, can be included to multiferroics [3–8]. Since lead is the principal component of these materials, currently, for an increasing number of applications, lead-free materials of optimal parameters are being sought, capable of replacing the lead materials. BaTiO3, SrTiO3 and BiFeO3 altogether with Bi0.5Na0.5TiO3, K0.5Na0.5NbO3, Na0.5Bi0.5TiO3, BaFe0.5Nb0.5O3, Bi1.5Ti3FeO15, SrBi2Nb2O9 as well as composites and multicomponent compounds obtained on their basis, can be included to the group of lead-free materials [9–13].

Multiferroic composites may be divided into two-phase (with ferroelectric and magnetic properties — ceramic composites) and multiphase types, where aside from ferroelectric and magnetic phases, an additional, for instance, polymer phase (called ceramic–polymer composite) appears, however the composite acquires new properties.

In the research, a composite of ferroelectric and magnetic properties on the basis of ferroelectromagnetic BaFe0.5Nb0.5O3 BFN powder and ferromagnetic nickel–zinc ferrite, was obtained.
Its elementary ferroelectric and magnetic properties were analyzed, including a correlation between the magnetic and electric subsystems of this material.

The barium iron niobate: \( \text{BaFeO}_0.5\text{NbO}_0.5\text{O}_3 \) (BFN) is a ferroelectric material with a diffuse phase transition and high value of electric permittivity, and is also an anti-ferromagnetic insulator at \( T_N = -248 \, ^\circ\text{C} \) (25 K) with weak ferromagnetic behavior at \(-268 \, ^\circ\text{C} \) (5 K) [14–16]. This material is useful for high voltage capacitors and other applications [17]. The nickel–zinc ferrite \( \text{Ni}_{0.64}\text{Zn}_{0.36}\text{Fe}_2\text{O}_4 \) belongs to the so-called soft ferrites of high magnetic permeability and resistance values. The soft ferrites are applied in, inter alia, electric machines for transformation of electric energy (transformers), generation of electric energy (generators and alternators), transformation of electric energy into mechanical energy (electric motors), magnetic shielding, telecommunications filters, distance sensors, delay lines, EMI filters, etc.

2. Material and Methods

In order to obtain lead-free two-phase ceramic composite, ceramic powder of \( \text{BaFeO}_0.5\text{NbO}_0.5\text{O}_3 \) (BFN) chemical composition and of ferroelectromagnetic properties, as well as nickel–zinc \( \text{Ni}_{0.64}\text{Zn}_{0.36}\text{Fe}_2\text{O}_4 \) ferrite powder of ferromagnetic properties, was used. Fig. 1 shows images of the ferrite powder and microstructure of the fracture of a ceramic ferrite sample was carried out in the following conditions: \( T_s = 1150 \, ^\circ\text{C} \) and \( T_s = 2 \, \text{h} \). In case of sintering of compacts of the ferrite powder, a characteristic growth of the grains (of the shape similar to hexahedron) can be observed.

The \( \text{BaFeO}_0.5\text{NbO}_0.5\text{O}_3 \) (BFN) powder was obtained by means of a synthesis of oxides \( \text{Fe}_2\text{O}_3, \text{Nb}_2\text{O}_5 \) and barium carbonate \( \text{BaCO}_3 \), according to the following reaction: \( \text{BaO} + 0.25\text{Fe}_2\text{O}_3 + 0.25\text{Nb}_2\text{O}_5 \rightarrow \text{BaFeO}_0.5\text{NbO}_0.5\text{O}_3 \). The mixture of constituent powders of BFN was synthesized by calcination of the powders in 1250 °C for 4 h. The other component of the composite of strong ferromagnetic properties \( \text{Ni}_{0.64}\text{Zn}_{0.36}\text{Fe}_2\text{O}_4 \) ferrite powder was synthesized by calcination in 1100 °C for 4 h.

The composition of the composite was: 90% of BFN powder and 10% of ferrite powder. The constituent powders used for obtaining the composite were mixed in a Fritsch Pulverisette 6 planetary ball mill for 15 h (wet mixing) in ethyl alcohol.

The synthesis of the constituent powder’s mixture of the composite carried out in the following conditions: \( T_{\text{synth}} = 1250 \, ^\circ\text{C} \) and \( T_{\text{synth}} = 4 \, \text{h} \). For the purpose of the comparison, densification (sintering) of ceramics and the composite powder was carried out by free sintering (FS) method in the same conditions \( (T_s = 1350 \, ^\circ\text{C} \) and \( T_s = 2 \, \text{h} \). In case of the composite sample additional sintering was carried out in reduced temperature \( (T_s = 1300 \, ^\circ\text{C} \) and \( T_s = 2 \, \text{h} \). Electrodes were applied on the composite specimen surfaces by silver paste burning method for electrical tests.

X-ray tests of the crystallographic structure were performed on a Philips X’Pert diffractometer. Microstructure tests were carried out using a Hitachi S-4700 scanning electron microscope with EDS Noran Vantage system. Dielectric measurements were performed on a precision bridge of a QuadTech 1920 Precision LCR Meter for a cycle of heating (at frequencies of the measurement field from \( \nu = 0.02 \, \text{kHz} \) to 20 kHz), and magnetic properties measurements using a SQUID magnetometer (MPMS XL-7 Quantum Design) in the range of temperatures from \(-271 \, ^\circ\text{C} \) to 27 °C and magnetic field to 7 T and a magnetic Faraday scale in the range of temperatures from 27 °C to 827 °C.

Transmission Mössbauer spectra were obtained by means of a RENON MsAa-3 spectrometer with the velocity scale calibrated by the Michelson–Morley interferometer. Spectra were collected for the 14.41 keV resonant transition in 57 Fe applying commercial 57 Co(Rh) source kept together with the absorbers at room temperature. Mössbauer absorbers were prepared in the powder form. Data were processed within transmission integral approximation as implemented in the MOSGRAF suite. All shifts of the spectra are reported versus room temperature \( \alpha\text{-Fe} \).

3. Results and Discussion

The X-ray investigations are shown in Fig. 2. The pattern shows that at room temperature, the BFN ceramics is single phase monoclinic of perovskite structure (with the best fit to the model 00-057-0771 [18]) without the evidence of any additional phase. The X-ray diffraction patterns for the ferrite powder NiZnFe show a typical single phase cubic spinel. The X-ray analysis of the BFN–ferrite samples and the BFN ceramics exhibited the presence of

![Fig. 1 - SEM images powder Ni_{0.64}Zn_{0.36}Fe_2O_4 and crack of the ceramic Ni_{0.64}Zn_{0.36}Fe_2O_4 sample.](image-url)
strong maxima originating from the BaFe$_{0.5}$Nb$_{0.5}$O$_3$ (BFN) material, as well as weak reflections from the Ni$_{0.64}$Zn$_{0.36}$Fe$_2$O$_4$ ferrite component (Fig. 2), without the evidence of any additional phase.

The chemical compositions of the BFN-ferrite samples and the BFN ceramics were analyzed by means of X-ray spectroscopy with EDS energy dispersion. The EDS examination allowed to conduct qualitative and quantitative analyses of distribution of elements, consisting in an automatic scanning of the selected surface micro-areas (local analysis), as well as identifying the selected elements in an X-ray characteristic spectrum (the qualitative EDS analysis). The EDS analysis BFN-ferrite composite sample (Fig. 3) confirmed the assumed percentage of the individual components, and the presence of constituent elements originating from the two components (the ferrite powder and ferroelectric BFN-type powder).

Fig. 4 presents microstructural SEM images of the BFN ceramics samples and the BFN-ferrite composite fractures sintered at 1350 °C. The BFN ceramic microstructure is
characterized by a compact structure with densely packed grains (Fig. 4a) with sparse (intergranular) closed pores. A mixed character of the fractures, i.e. on the edges and across the grains, is present in this material, whereas in the BFN–ferrite composite, larger BFN powder grains (of a bigger number of walls) surround smaller grains of magnetic ferrite (of tetrahedron sections) — Fig. 4b.

Reduction of sintering temperature by 50 °C in the BFN–ferrite composite reduces the excessive growth of the grains (Fig. 5), and the fracture (with prevalence) occurs after the edges of grains. The microstructure of this two-phase composite is characterized by smaller grains, in comparison with a composite obtained in a higher temperature (1350 °C). Bigger and properly crystallized BFN grains (of inhomogenous size), as well as tiny ferrite grains (of tetrahedron sections), in the microstructural image, are visible.

The temperature diagrams of electric permittivity (Fig. 6) illustrate a diffuse character of the phase ferroelectric–paraelectric transition in the BFN and BFN–ferrite composite [14]. The high values of electric permittivity in a very wide temperature interval are due to a disorder in the distribution of B-side ions in the perovskite unit cell. This may lead to the appearance of composition fluctuations and, as a consequence, to different local Curie temperatures in different regions of the ceramics. It creates a diffuse phase transition in BFN.

High values of electric permittivity in BFN might be also related to a formation of layers (metal–semiconductor junction) at a near-electrode surface, which equal to the sum of capacity of the sample’s material and capacity of the created near-electrode surfaces [19]. The near-electrode surfaces can form in a majority of materials with a perovskite-type structure, increasing at the same time values of electric permittivity.

The analysis of dielectric properties of the two-phase BFN–ferrite composite revealed a significant increase of the maximal value of electric permittivity. Besides, the BFN–ferrite composite exhibits an increase of diffuse of phase transition and frequency dispersion (a shift of phase transition temperature with an increase of the frequency of measurement field — towards higher temperatures). These changes of temperature progressions ε(T) of the BFN–ferrite composite might evidence the influence of magnetic subsystems on dielectric properties. Other factor influencing the character of transitions is also the increase of electrical conductance in higher temperatures. The reduction of temperature of the BFN–ferrite composite sintering (1300 °C), decreases the values of electric permittivity (Fig. 6c).

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The BFN ceramics and the BFN–ferrite composite dielectric losses are substantial, and their temperature graphs tan(θ) are similar (Fig. 7). In lower temperatures (up to about 150 °C), with an increase of the frequency of measurement field, an increase of dielectric loss values occurs. The quantity of dielectric loss for BFN is close to the results presented by the authors [20]. Yet, in case of the BFN–ferrite composite, dielectric loss is lower (Fig. 7b). The reduction of temperature of the BFN–ferrite composite sintering (1300 °C) insignificantly reduces the values of dielectric loss (Fig. 7c).

Fig. 8 shows dependences of impedance of BFN ceramic sample and BFN–ferrite composite sample sintered at temperature 1300 °C and 1350 °C, for measurement frequencies: 100 kHz and 1 MHz. The characteristic behavior of curves Z(T) for ferroelectric materials was observed. With increased temperature, value impedance systematically increases, and subsequently after broad of maximum, it decreases violently. The BFN ceramics show the maximum of value of impedance at higher temperature, in comparison with composite BFN–
ferrite samples. The higher temperature of sintering, the BFN–ferrite composite (1350 °C) shifts the maximum value of impedance towards lower temperature. With the increased frequency of measuring field reduction of value impedance is observed. It is associated with the occurrence of the frequency dispersion effect characteristic for ferroelectric materials.
The variation of the real $Z'$ part of impedance as a function of frequency at different temperatures is shown in Fig. 9, varying from 150 to 350 °C for the BFN ceramic (Fig. 9a) and for the BFN–ferrite composite (Fig. 9b). Inset: these figures shows part of graph of $Z'(T)$ at high frequency range. The real $Z'$ parts of impedance decrease with an increase in frequency and temperature. 

Fig. 10 shows the variation of the imaginary $Z''$ parts of impedance as a function of frequency at temperatures from 150 to 350 °C for the BFN ceramics (Fig. 9a) and for the BFN–ferrite composite (Fig. 9b). Inset: this figure shows magnification of $Z''$ at high frequency range. The real $Z'$ parts of impedance decrease with an increase in frequency and temperature.

For both compositions, values of $Z''$ decrease with increasing frequency and temperature. For the BFN ceramics (inset of Fig. 10a) at 235 °C, a distinct peak appeared in $Z''$, at frequency slightly before $10^3$ Hz, while in case of the BFN–ferrite composite (inset of Fig. 10b) peaks appear before $10^3$ Hz, however of weaker intensity and at a lower temperature (200 °C). Decreasing values of imaginary $Z''$ with increasing temperature indicate the increasing loss in the samples (increase of conductivity). It is shown that this $Z''$ peak became weaker in intensity, and shifts towards the high frequency side with increasing temperature. This behavior indicates that the relaxation in these materials is a thermally activated process. Connection of all the curves at high frequency indicates the depletion of space charges at those frequencies [21].

The occurrence of relaxation peaks in the imaginary part of the complex impedance in this frequency range (inset of Fig. 9a) might be due to the existence of the space-charge layer in the BFN–ferrite composite sample. Space-charge polarization mechanism prevails in heterogeneous structures, where a material is assumed to be composed of different areas (grain and grain boundaries). These areas (phases) have different electrical conductivities and thus the accumulation of charges will be occurred at the phase boundary [22]. These point charges result in an additional space charge polarization (i.e. Maxwell–Wagner relaxation type), and it can by assumed that the maximum is originating from the Maxwell–Wagner polarization between the BFN phase with higher resistivity and the ferrite phase with much lower resistivity [22].

The relaxation time $\tau$ of the composite BFN–ferrite sample decreases with an increasing temperature according to the equation $\tau = 2\pi f_{\text{max}} \tau' = 1$ (Fig. 11). At higher temperatures, more electrons are thermally excited, and therefore the
relaxation time of the carrier becomes shorter and/or the dissipated thermal energy assists formed dipoles to follow the motion of the alternating field [23]. This analysis confirms the presence of temperature dependent electrical relaxation phenomena in the BFN–ferrite composite. This variation of $\tau$ can be described by the known Arrhenius equation [1].

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$$

(1)

where:

$\tau_0$ characteristic relaxation time at infinite temperature,
$\Delta E$ activation energy of the relaxation process,
$k_B$ Boltzmann constant.

The plot of $\ln \tau$ v. $1000/T$ for the composite BFN–ferrite is shown in the inset of Fig. 11. The values of $\Delta E$ and $\tau_0$ were calculated from the slope of the linear fit and are summarized in Table 1.

The temperature relationship of magnetization $M(T)$, in the external 0.1 T magnetic field, of the BFN–ferrite composite is presented in Fig. 12a. The $M(T)$ curves comprise two components. The first one is ferro/ferrimagnetic with Curie temperature of nearly 450 °C, while the second one is para/superparamagnetic, clearly visible at a temperature under −173 °C. Above the temperature 460 °C, the BFN–ferrite composite is a paramagnetic.

The magnetic hysteresis loops $M(H)$ of the ceramic BFN–ferrite composite obtained in the temperatures of −271 °C, 173 °C and 27 °C are characteristic for soft ferromagnetic materials (Fig. 12b). These materials ought to have high magnetic permeability (which allows achieving high values of magnetic induction with the use of weak magnetizing current), the lowest possible losses — the field embraced by a hysteresis loop (which allows a high–performance energy conversion), high saturation induction (allowing to achieve the highest mechanical power — proportional to the induction squared) and high resistivity (in order to reduce power loss caused by eddy currents). The ceramic BFN–ferrite composite has properties and parameter characteristics for a soft ferromagnetic material.

In the range of weak magnetic fields and these, for which the magnetization curve changing its shape (curves), an increase of the sample’s magnetization is caused by a growth of domains of a privileged direction of magnetization, at the cost of adjacent domains. It is related to the mechanism of domain’s boundary shifting (boundaries between the areas of spontaneous magnetization), which is a reversible process up to the point where the magnetic energy of the wall is comparable with the energy of magnetic interaction. In stronger magnetic fields,
the phenomena related to momentum rotations of particular areas of spontaneous magnetization which approach to position themselves in parallel to the direction of magnetic field (the sample's magnetization changes are irreversible), show predominance. Saturation is achieved in a proper $H_s$ field. The foregoing phenomena overlap in ferromagnetic materials, and their character is strongly related to the structural properties of the ferromagnetic material. For the ceramic BFN–ferrite composite, with the increase of temperature the magnetic saturation of hysteresis loop and the value of spontaneous magnetization $M_s$ decreases (Fig. 12b). The steepest parts of the $M(H)$ diagram curves correspond to the process of rotation in the spontaneous magnetization areas. The BFN–ferrite composite values of $H_C$ coercive field are very low and with the increase of temperature they decrease insignificantly ($\mu_0H_C = 0.016\ T$ for $-271^\circ\ C$, $\mu_0H_C = 0.012\ T$ for $-171^\circ\ C$ and $\mu_0H_C = 0.007\ T$ for $27^\circ\ C$). With the increase of temperature, spontaneous polarization also decreases ($M_s = 9.88\ emu/g$ for $-271^\circ\ C$, $M_s = 9.16\ emu/g$ for $-171^\circ\ C$ and $M_s = 7.22\ emu/g$ for $27^\circ\ C$). For the BFN ceramics, the magnetic hysteresis loop is of a different shape [14].

Mössbauer investigations of the composite BFN–ferrite performed at room temperature in the transmission geometry (Fig. 13 and Table 2) indicate the presence of three absorption cross-sections originating from the ferrite, BFN phase and some additional components due to the minor impurity phase. Magnetically split spectral component is generated by the Fe$^{3+}$ high spin ion. This ion is located in the ferrite and it has high crystallographic local symmetry, as the electric quadrupole interaction is negligible.

A dominance spectral doublet originates from the paramagnetic BFN phase with lower symmetry around iron generating quadrupole splitting. The ionic state of iron is Fe$^{3+}$ with high spin on this site. Prior to annealing, the mixture of BFN phase and ferrite (90 wt.% of BaFe$_{0.5}$Nb$_{0.5}$O$_3$ and 10 wt.% of Ni$_{0.63}$Zn$_{0.37}$Fe$_2$O$_4$) contained 67 at.% of iron in BFN and 33 at.% of iron in ferrite. Mössbauer result indicates that after annealing the iron distribution is as follows: 65 at.% in BFN (Fe$^{3+}$), 33 at.% in ferrite and 2 at.% in impurity phase. Hence, the iron isn’t transferred from ferrite to BFN phase during annealing.

4. Conclusion

The ferroelectromagnetic BaFe$_{0.5}$Nb$_{0.5}$O$_3$ ceramics are an alternative material for PbFe$_{0.5}$Nb$_{0.5}$O$_3$ ceramics, which exhibits ferroelectric and magnetic properties. BFN also exhibits
ferroelectric properties connected with the occurrence of characteristic frequency dispersion with high values of electric permittivity.

The multiferroic ceramic BFN-ferrite composite possesses good magnetic parameters: high values of magnetization, narrow magnetic hysteresis loop of low losses and of high saturation induction. The aforementioned properties are characteristic of the soft ferromagnetic material. The X-ray analysis confirmed the presence of phases from the ferroelectromagnetic (BFN) and magnetic (ferrite) components (no foreign phases present). Detailed Mössbauer analysis showed, however, trace amounts of another phase (containing iron) in an amount of 2.0%.

The microstructural research revealed the presence of small ferrite grains surrounded by much larger ferroelectromagnetic component grains in the fracture.

In comparison with BaFe0.5Nb0.5O3, dielectric loss in the two-phase ceramic BFN-ferrite composite decreases yet is still too high. In order to reduce them, doping of ions of elements of small ionic radius (e.g. lithium or chromium) to the basic component of the composite (BFN) appears to be necessary. The optimization of the two-phase BFN-ferrite composition and research in this direction will be continued (also in order to increase the competitiveness of the ceramic BFN-ferrite composite in magnetoelectric transducers).

Table 2 - The values of hyperfine parameters (IS, QS, B_hf) and A for BFN-ferrite composite, where: A — contribution of the respective sub-profile (phase/site) to the total absorption profile; IS — isomeric shift; QS — quadrupole splitting; B_hf — hyperfine magnetic field. Errors for all values are of the order of unity for the last digit shown.

<table>
<thead>
<tr>
<th>Component</th>
<th>A [%]</th>
<th>IS [mm/s]</th>
<th>QS [mm/s]</th>
<th>B_hf [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>33</td>
<td>0.29</td>
<td>–</td>
<td>46.8</td>
</tr>
<tr>
<td>BFN</td>
<td>65</td>
<td>0.43</td>
<td>0.55</td>
<td>–</td>
</tr>
<tr>
<td>Impurity phase</td>
<td>2</td>
<td>0.30</td>
<td>2.35</td>
<td>–</td>
</tr>
</tbody>
</table>

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