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The influence of microstructure on the magnetoelectric effect in ceramic composites

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Abstract

In the multiferroic composite material, the ferroelectric and ferromagnetic properties are closely correlated through the coupling interaction between the electric and magnetic orders. We attempted to receive the magnetoelectric composite materials and to determine the values of magnetoelectric coupling coefficient. The microstructure of obtained ferroelectric-ferromagnetic composite materials were also studied. The main component of the ferroelectric-ferromagnetic composite was PZT type powder (with ferroelectric properties) which was synthesized using the sintering of a mixture of simple oxides in a solid phase. The second element of the ferroelectric-ferromagnetic composite was the ferrite powder with ferromagnetic properties. The ferrite powder was synthesized using calcination. Next, the mixed components were compacted by pressing, consequently pressureless sintered and characterized. Based on the theoretical model of coupling between ferroelectric and ferromagnetic properties in multiferroic composites, values of the magnetoelectric coupling coefficients were specified.

Keywords: Magnetoelectric composite, Magnetoelectric coupling coefficient, Microstructure, Multiferroics

WPŁYW MIKROSTRUKTURY NA EFEKT MAGNETOELEKTRYCZNY W KOMPOZYTACH CERAMICZNYCH

Ferroelektryczność i ferromagnetyzm w multiferroikowym materiale kompozytowym są ze sobą ściśle związane poprzez oddziaływanie sprzężenia pomiędzy uporządkowaniem elektrycznym i magnetycznym. Podjęto próbę otrzymania magnetoelektrycznego materiału kompozytowego i określono wartości współczynnika sprzężenia magnetoelektrycznego. Zbadano także mikrostrukturę otrzymanego materiału kompozytowego. Głównym składnikiem kompozytu ferroelektryczno-ferromagnetycznego był proszek typu PZT o ferroelektrycznych właściwościach, który zsyntezowano z mieszaniny prostych tlenków w fazie stałej. Drugim składnikiem kompozytu ferroelektryczno-ferromagnetycznego był proszek ferrytowy o właściwościach ferromagnetycznych. Proszek ferrytowy zsyntezowano metodą kalcynacji. Następnie mieszanina składników została zagęszczona poprzez prasowanie i poddana swobodnemu spiekaniu. Wartości współczynnika sprzężenia magnetoelektrycznego zostały określone na podstawie teoretycznego modelu sprzężenia pomiędzy właściwościami ferroelektrycznymi i ferromagnetycznymi w kompozycie multiferroikowym.

Słowa kluczowe: kompozyt magnetoelektryczny, współczynnik sprzężenia magnetoelektrycznego, mikrostruktura finalna, multiferroiki

1. Introduction

Multiferroic magnetoelectric materials simultaneously exhibit ferroelectricity and ferromagnetism. These materials have recently stimulated a sharply increasing number of research activities for their scientific interest and a significant technological promise [1-4].

There are the different origins of ferroelectricity and magnetism in solids, ferromagnetism arises through the quantum mechanical phenomenon of exchange, while electric polarization is manifested in the form of cooperative atomic displacements.

There are technical difficulties in combination of ferroelectric and magnetic behaviour in one material. In conventional ferroelectrics such as $BaTiO_3$, the transition ions (Ti in $BaTiO_3$) have empty *d*-shells [5]. The hybridization effects between these empty *d* states and the filled oxygen *p* states, drives the off-centring of a cation towards the neighbouring anion, inducing electric polarization. On the other hand, magnetism requires a partly filled *d* shell. Thus the usual atomic-level mechanisms driving ferromagnetism and ferroelectricity are mutually exclusive, and multiferroics, in general, require a different mechanism of electric polarization than in prototypical ferroelectrics. Magnetoelectric multiferroics are insulating materials, containing transition metal atoms. Consequently, various approaches of mixing both phases in the single material were tried: heterostructures with the epoxy-layer bonding [6], a magnetic film on a piezoelectric slab [7] and particulate composites of various ferroelectric and magnetic components [8].

The goal of this study was to investigate the magnetoelectric (ME) effect in multiferroic particulate composites with the PZT type matrix and nickel-zinc ferrite inclusions. Two types of the PZT matrix with composition close to the morphotropic phase boundary and with barium or strontium doping were chosen as well as two types of sintering additives (Cr_2O_3 and Nb_2O_5) were tried in order to compare the effect of microscopic features on the ME outcome.

2. Experiment

The materials of investigations were two ferroelectric-ferromagnetic composites that were obtained from two types of the PZT type powder with ferroelectric properties and ferrite powder with ferromagnetic properties. The first PZT type ceramic powder comprised $Pb_{0.90}Ba_{0.10}(Zr_{0.53}Ti_{0.47})O_3$ + 2 at.% Nb_2O_5 (PBZTN), the second one, $Pb_{0.94}Sr_{0.06}(Zr_{0.46}Ti_{0.54})O_3$+0.25 at.% Cr_2O_3 (PSZTC). The ferrite powder had a composition of $Ni_{0.64}Zn_{0.36}Fe_2O_4$ (NiZn). The initial constituents for obtaining PZT type powder were commercially available oxides: PbO (POCH 99.5% purity), ZrO_2 (MERCK, 99.0% purity), TiO_2 (MERCK 99.0% purity), Nb_2O_5 (SIGMA 99.9% purity), Cr_2O_3 (MERCK 99.0% purity), as well as barium carbonate $BaCO_3$ (POCH 99.0% purity) and strontium carbonate $SrCO_3$ (CHEMPUR 99.0% purity). In order to keep a designed lead content in the powder, an excess of 5 wt.% PbO was introduced into the stoichiometric mixture of the relevant oxides. The main component of the composite namely PZT type powder was synthesized using soaking of a mixture of simple oxides in solid phase at temperature T_{synth} = 850°C for time t_{synth} = 2 h. The second element of the composite that is ferrite powder ($Ni_{0.64}Zn_{0.36}Fe_2O_4$) was synthesized using calcination at temperature 1100°C for 4 h. The designed magnetoelectric composite should comprise 90 wt.% of the synthesized PZT powder and 10 wt.% of the ferrite powder. The resultant powders of both components were mixed and milled in an agate mortar. The milled powders were then pressed by a hydraulic press under a pressure of 75 MPa to give the discs with a diameter of 10 mm and a thickness of 1 mm. Final densification of the synthesized composite powder was carried out using the free sintering method under the following conditions: temperature T_s = 1250°C and time t_s = 2 h. The obtained material exhibits ferroelectric and ferromagnetic properties shown elsewhere [9].

Microstructures of the fractured multiferroic materials were observed using a scanning electron microscope Hitachi S-4700, the X-ray tests were performed at room temperature using Philips X'pert diffractometer (with a Cu lamp and a graphite monochromator) in the range of 2θ changing from 12° to 62° (step 0.02° and measurement time 4 s/step) and the magnetoelectric coupling was investigated based on the theoretical model of internal interactions.

Additional microscopic studies were performed on the specimen's polished surface utilizing the scanning electron microscopy (SEM) method in secondary electrons (SE) and backscattered electron detector (BSE) modes (Hitachi S-3400N device). The analysis of the chemical composition in microareas was performed by the standard less method, using an energy dispersive X-ray spectrometer (EDS) Thermo Noran (System Six). The SEM/EDS studies were performed by the accelerating voltage 25 keV, low vacuum and without the Au sputtering.

3. Results and discussion

Microscopic studies showed a significant difference in the microstructure of both investigated ceramic samples. The results of microstructure study for the composite ceramics PBZTN-NiZn are presented in Fig. 1. The SEM images of microstructure of this ferroelectric-ferromagnetic composite show two type of grains, namely larger and smaller ones.

The larger grains reveal irregular grain boundaries while the small grains seem to have a more regular shape. The boundary layer between grains is imprecisely determined.

A mixed nature of fracture occurs in this material, that is the fractures occur along boundaries as well as through grains (the occurrence of intergranular or interphase boundaries in this material). The experimental density of this material was determined and it is equal to 7310 kg·m^{-3}.

The results of microstructure study for the PSZTC-NiZn composite ceramics are presented in Fig. 2. Microstructure study of this composite reveals clear grains boundaries after fracturing. The fracture along the grain boundaries is becoming dominating in this ceramic composite. The experi-

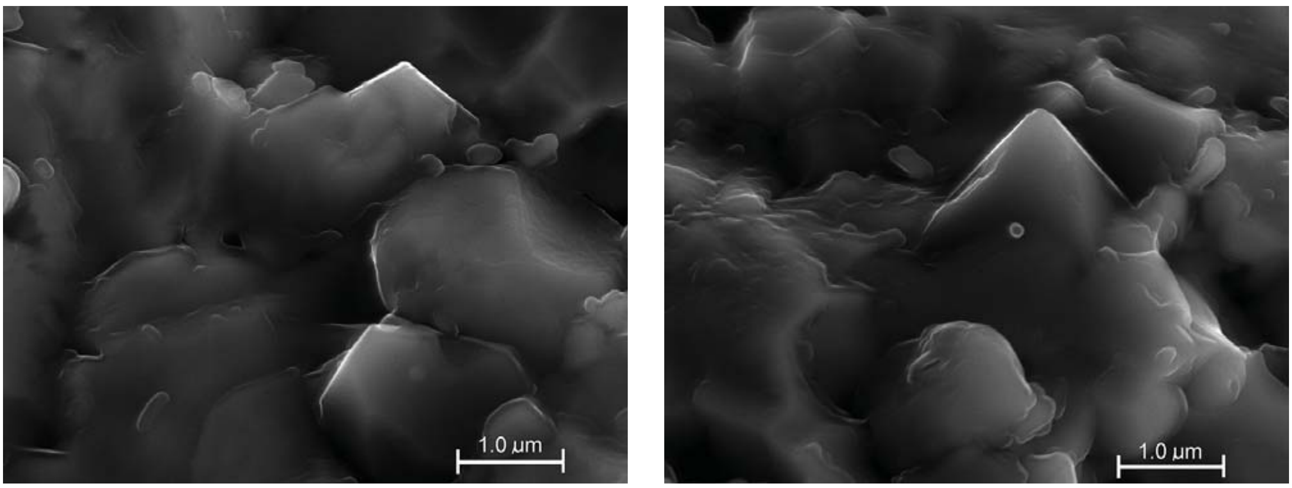


Fig. 1. SEM images of the fracture microstructure of magnetoelectric composite PBZTN-NiZn.
Rys. 1. Obrazy SEM mikrostruktury przełamu magnetoelektrycznego kompozytu PBZTN-NiZn.

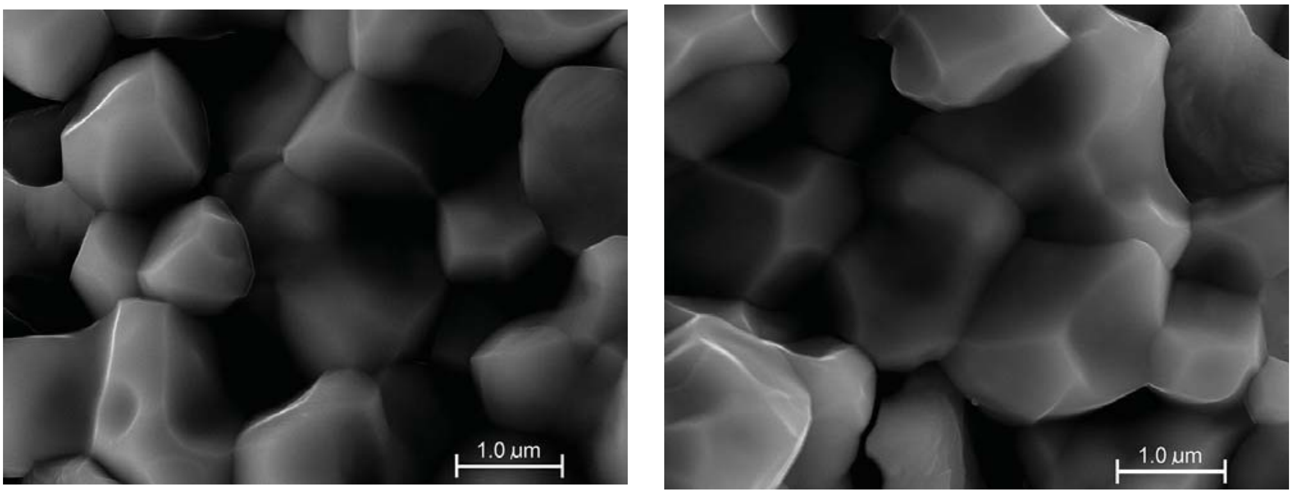
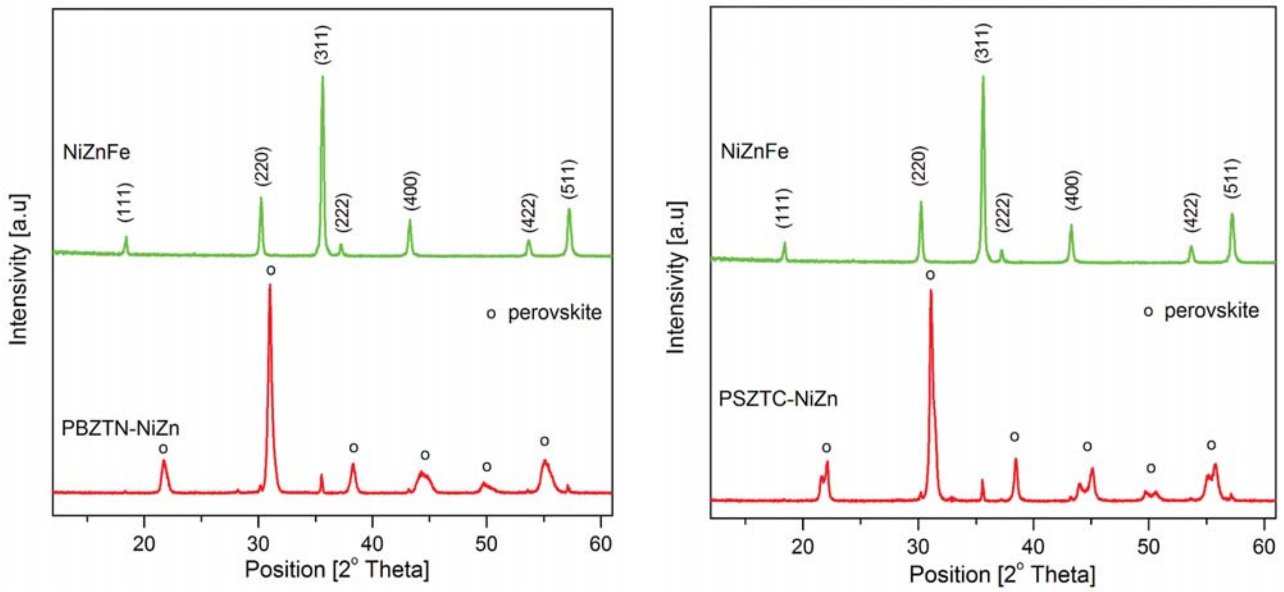


Fig. 2. SEM images of the fracture microstructure of magnetoelectric composite PSZTC-NiZn.
Rys. 2. Obrazy SEM mikrostruktury przełamu magnetoelektrycznego kompozytu PSZTC-NiZn.



a) b)

Fig. 3. X-ray spectra of PBZTN-NiZn (a) and PSZTC-NiZn (b) composites with the reference NiZn-ferrite pattern (upper part).
Rys. 3. Widma rentgenowskie dla kompozytów PBZTN-NiZn (a) i PSZTC-NiZn (b) oraz wzorcowe widmo dla ferrytu NiZn (górna część).

mental density of this material was determined and it is equal 7220 to kg·m^{-3}.

The X-ray spectra of the resultant PBZTN-NiZn and PSZTC-NiZn ceramic composites and the NiZn-ferrite reference XRD pattern are presented in Figs. 3a and 3b, respectively.

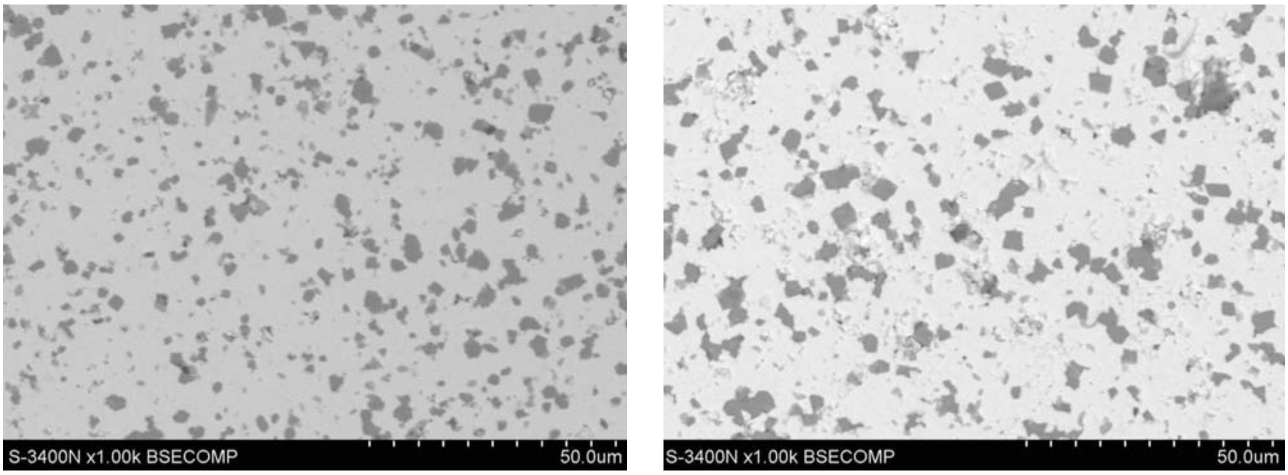
The X-ray analysis of ferroelectric-ferromagnetic ceramic composites confirmed the occurrence of the strong diffraction peaks from specific PZT type material as well as weak reflexes from the ferrite component (Fig. 3.).

The back scattered electron mode was applied for observation of the specimen's surface morphology and elements distribution in both PBZTN-NiZn and PSZTC-NiZn composites (Fig. 4a and Fig. 4b, respectively). The BSE image of the composite surface shows the existence of PZT matrix and ferrite inclusions (dark grains with lower average atomic mass).

An EDS analysis of the tested composite samples qualitatively confirmed the assumed share of the specific components and the occurrence of the ferrite component and ferroelectric PZT type matrix in the composite structure (Figs. 5 and 6).

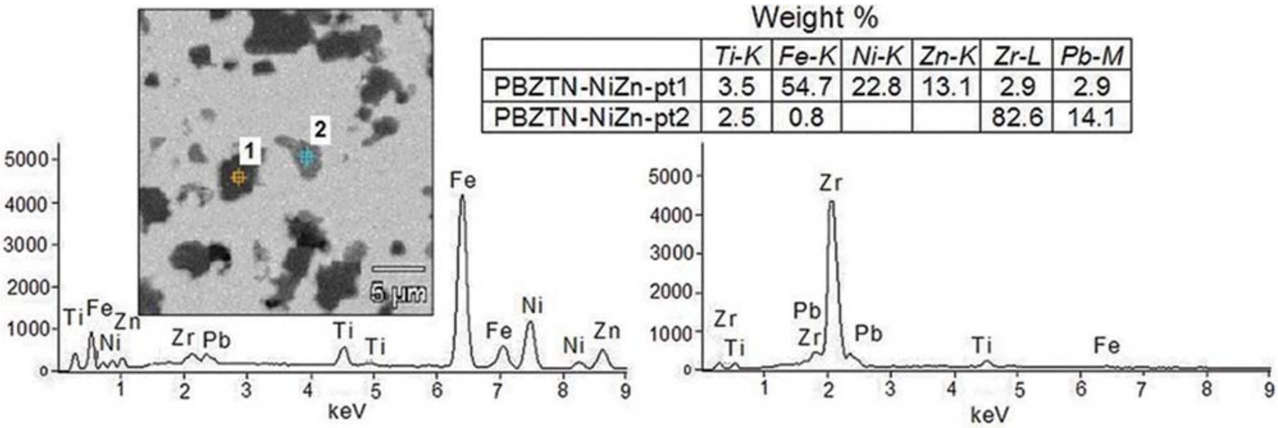
The EDS analysis of studied composite materials PBZT-N-NiZn and PSZTC-NiZn was performed at several points on the specimen surface but only 2 points of analysis are marked in the interior of Figs. 5 and 6.

The analysis of the elements distribution showed some differences in the chemical composition of the matrix and ferrite inclusions if both materials are compared. In the PSZTC-NiZn composite, the matrix itself showed quite stable chemical composition since the atomic fraction of the main elements (Ti, Zr and Pb) was close to 0.94-0.96 of the initial value. However, some zirconia inclusions were found in the barium modified PZT matrix (PBZTN) and consequently, a slightly lower Zr content in the matrix was observed (Fig. 5b). On the other hand, sintering additives demonstrated different behaviour in both materials since chromium was found only in ferrite precipitates while niobium was detected in both phases: the matrix and ferrite inclusions.



a) b)

Fig. 4. BSE images of the microstructure of magnetoelectric composites PBZTN- NiZn (a) and PSZTC-NiZn (b).
Rys. 4. Obrazy BSE mikrostruktury magnetoelektrycznego kompozytu PBZTN-NiZn (a) oraz PSZTC-NiZn (b).

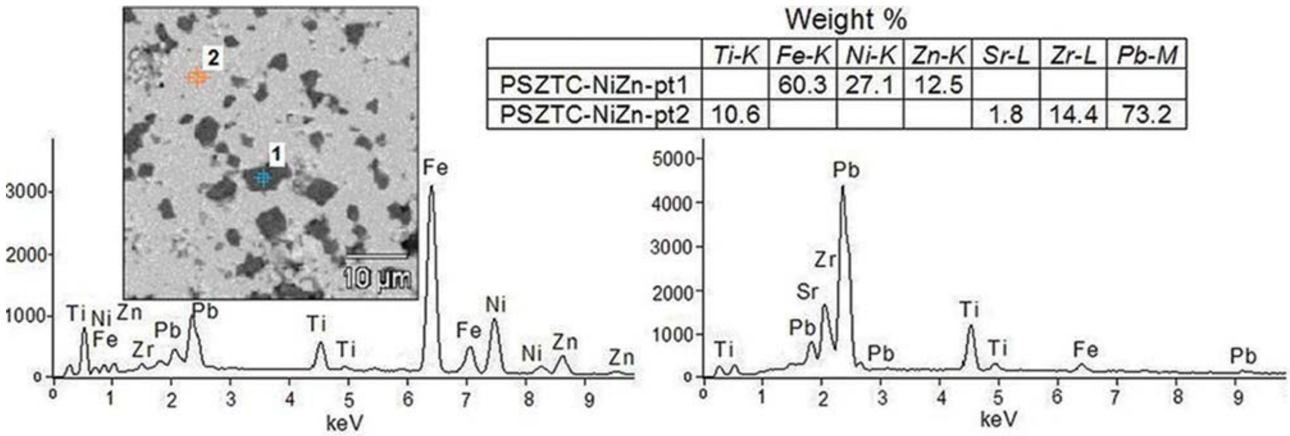


Weight %

	Ti-K	Fe-K	Ni-K	Zn-K	Zr-L	Pb-M
PBZTN-NiZn-pt1	3.5	54.7	22.8	13.1	2.9	2.9
PBZTN-NiZn-pt2	2.5	0.8			82.6	14.1

a) b)

Fig. 5. The EDS analysis of element of surface for PBZTN-NiZn composite in a microarea 1 (a) and 2 (b).
Rys. 5. Analiza EDS elementu powierzchni dla kompozytu PBZTN-NiZn w mikroobszarze 1(a) i 2 (b).



Weight %

	Ti-K	Fe-K	Ni-K	Zn-K	Sr-L	Zr-L	Pb-M
PSZTC-NiZn-pt1		60.3	27.1	12.5			
PSZTC-NiZn-pt2	10.6				1.8	14.4	73.2

a) b)

Fig. 6. The EDS analysis of element of surface for PSZTC-NiZn composite in a microarea 1 (a) and 2 (b).
Rys. 6. Analiza EDS elementu powierzchni dla kompozytu PSZTC-NiZn w mikroobszarze 1(a) i 2 (b).

The chemical composition of the ferrites in both composites displayed higher deviation from the expected composition since only 83-84 at.% of Fe and 73-75 at.% of Zn in comparison to the designed composition were present in the analysed ferrite precipitates. Moreover, the highest deviation was observed for the nickel constituent since only 64 at.% of its initial content was present in ferrite precipitates in barium modified PZT composite specimen while 78 at.% was present in ferrite inclusions in strontium modified PZT-based composites. It shows that ferrite phase is not stable in the presence of the PTZ compound at the sintering temperature and it decomposes. Since no ferrite constituting elements (Ni, Zn, Fe) were found in the composite matrix, we could anticipate formation of thick grain boundaries or a reaction zone as a result of the limited dissolution of ferrites during densification. That process is more enhanced in barium doped PZT-based composites (PBZTN-NiZn) and it is in good agreement with observations of the fractured surface in both materials (Figs. 1 and 2).

It must be underlined that this composite suffered also from the deviation of the designed Ti to Zr ratio because of zirconia inclusions. The latter effect could be explained by the higher ionic radius of Ba in comparison to Sr ions and thus lower thermal stability of PZT solid solution. In contrary, strontium doped PZT matrix with combination of chromium oxide provided better circumstances for the ferrite stability and the clear composite structure was preserved after densification. The preferential presence of chromium in the ferrite inclusions could be related to Cr cations ability of entering NiZn ferrite crystal structure and thus improvement of its thermal stability.

The resultant magnetoelectric composites are multiphase materials that are composed of different phases, but neither phase supports the magnetoelectric effect. The magnetoelectric effect in composite materials is known as a product tensor property [10-11], and it is the results from the cross interaction between the two phases in the composite. The magnetoelectric coupling is a result of the product of the magnetostrictive effect in the magnetic phase and the piezoelectric effect in the piezoelectric phase. The magnetostrictive effect is a magnetic-mechanical effect and piezoelectric effect is a mechanical-electrical effect thus the carrier of magnetoelectric coupling is the strain [12].

For understanding the coupling between ferroelectric and ferromagnetic properties, we treat the multiferroic material like a magnetoelectric system. This system consists of two separated subsystems, namely the ferromagnetic and the ferroelectric subsystems. The interaction between these subsystems causes the coupling between the ferroelectric and ferromagnetic properties. Values of the magnetoelectric coupling coefficient were calculated on the basis of the theoretical model from the following relationship:

$$\varepsilon_r(T) = \varepsilon_0\left[1 + (2z_2 g\varepsilon_0)\langle S_i S_j\rangle\right] \tag{1}$$

where ε_0 is the dielectric constant in the absence of the magnetoelectric coupling, z_2 is the number of the spin-pair correlation that will directly influence a given ferroelectric particle, and g is the magnetoelectric coupling coefficient and $\langle S_iS_j \rangle$ is the average value of the spin-spin correlation. Details of the model and discussion are presented elsewhere [13].

Calculated values of the magnetoelectric coupling coefficient for ferroelectric-ferromagnetic PBZTN-NiZn and PSZTC-NiZn composites are presented in Table 1.

The magnetoelectric effect is substantially stronger in the PSZTC-NiZn ceramic composite than in the PBZTN-NiZn ceramic composite. Both composites show various features of their microstructure (grain boundaries between the PZT matrix and ferrite grains), and it can has an impact on the magnetoelectric effect because the coupling between ferroelectric and ferromagnetic properties takes place through the elastic interaction at the phase boundary. That is, for the magnetoelectric effect, when magnetic field is applied to the composite the magnetic phase changes its shape causing the polarization. Therefore the magnetoelectric effect in composite is an effect of which the magnitude can be dependent on the contact surface, between ferroelectric and magnetic phases i.e. the magnetoelectric coupling is depended on the composite microstructure. Our studies confirmed this assumption because a larger magnetoelectric effect, calculated on the basis of the model, exhibits the PSZTC-NiZn composite with well shaped grains and clearer grain boundaries than PBZTN-NiZn (Figs. 1 and 2).

Depending on the potential applications, the relevant properties of the individual phases (ferroelectric and ferromagnetic) can be established in order to design such multiferroic composite which will have appropriate properties for their applications e.g. to achieve the high level of the device integration and multifunctionality [14-17]. The results of microstructure studies, which are presented elsewhere [18], indicate that the optimal microstructures that provide the largest magnetoelectric coupling are the plate-like microstructures. The plate-like microstructures provide the greatest overlap of the strain field generated by polarization and magnetization, and this overlap is responsible for the strain-induced magnetoelectric effect.

4. Summary

Two types of composites with the ferroelectric PZT-based matrix and ferromagnetic NiZn-ferrite grains were produced as a result of application of two different sintering additives: Cr_2O_3 and Nb_2O_3 apart from two various substitutes in the PZT solid solution: barium or strontium in order to obtain multiferroic ceramic materials. Application of various sintering additives changed the microstructure of the resultant composites in such a way that various contact zone/grain boundaries between the PZT-matrix and NiZn-ferrite inclusions were formed. It has been shown that significant decomposition of the ferrite grains occurred in PBZTN-NiZn specimens with some decomposition of barium-doped PZT matrix. It has been confirmed by a mixed nature of fracturing in this material that is along boundaries as well as through grains

Table 1. Calculated values of magnetoelectric coupling coefficient g for two kinds of magnetoelectric composites.
Tabela 1. Obliczone wartości współczynnika sprzężenia magnetoelektrycznego g dla dwóch rodzajów magnetoelektrycznego kompozytu.

Frequency *(f)* [kHz]	0,5	5	50	100
PBZTN-NiZn *(g)* [s/m]	606380	783042	878535	888085
PSZTC-NiZn *(g)* [s/m]	785430	1057585	1353613	1422849

(transgranular). On the other hand, a higher thermal stability of NiZn ferrite has been accomplished in PSZTC-NiZn composites as a result of chromium oxide sintering additives and possibility of entering NiFe ferrite crystal structure by Cr cations. Accordingly, both phases were better separated as confirmed by intergranular fracture of this composites.

The multiferroic ceramic composite PSZTC-NiZn with well separated grains of both phases shows a stronger magnetoelectric effect than ceramic composite PBZTN-NiZn according to the results of the studies of the values of the magnetoelectric coupling coefficient which has a higher value for ceramic composite PSZTC-NiZn. Values of magnetoelectric coupling coefficient are of the order of 10^6 s·m^{-1} namely of tens of mV·cm^{-1}·Oe^{-1}. These properties create possibilities for applying this type of composites in manufacturing magnetoelectric transducers.

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