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Features of the structural and magnetic properties of $Pb(Ti_xZr_{1-x}O_3)$-$NiFe_{1.98}Co_{0.02}O_4$ in the polarized state

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Abstract. Composites with a $90\%Pb(Ti_xZr_{1-x}O_3)$-$10\%NiFe_{1.98}Co_{0.02}O_4$ composition have been synthesized. It has been established that the polarization of samples resulting from exposure to an electric field for 1 hour of 4 kV/mm in strength at a temperature of 400 K leads to crystal structure deformation. The compression of elementary crystal cells in some areas during polarization of the sample creates conditions suitable for the enhancement of magnetic exchange interactions. It has been found that the polarization process of such compositions leads to increases in specific magnetization and magnetic susceptibility. The analysis of Mössbauer spectra has shown that the polarization of the $90\%Pb(Ti_xZr_{1-x}O_3)$-$10\%NiFe_{1.98}Co_{0.02}O_4$ composite leads to significant changes in the effective magnetic fields of iron subspectra in various positions.

Keywords: Mössbauer effect • X-ray diffraction • lead zirconate titanate (PZT) • unpolarized and polarized states • specific magnetization • magnetic susceptibility • effective magnetic fields

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Introduction

The synthesis of ceramic composite structures whose properties, including the piezoelectric effect, can be changed by exposure to external magnetic fields is a current problem. In the case of polycrystalline composite structures, magnetoelectric properties are observed by the transfer of mechanical strain from the magnetostrictive phase, deformed by the external magnetic field, to the piezostrictive one. Unlike single-crystal piezoelectrics, where the magnitude of the piezoelectric properties is determined by the crystal lattice type and depends on the orientations of crystal axes, the structure of the powder does not exhibit piezostrictive properties. Since each of the domains of the individual grains that exhibit piezoelectric properties in ceramics occupies the most energetically favourable state, the piezoelectric effect of the total structure is usually zero. For observation of the piezoelectric properties of the composite structures, powders are heated in an external electric field at a temperature higher than that of the ferroelectric phase transition. This creates conditions suitable for changes in the orientation of the domains in the grains of ceramics to occur and the appearance of an internal electric field to reduce an external electric field. Cooling the composite in an electric field allows the direction of polarization to be maintained and fixes the acquired piezoelectric properties.

The aim of the present work was to study the crystal structure and peculiarities of the magnetic properties of composites containing 90% of piezoelectric lead zirconate titanate (PZT), i.e. the $Pb(Ti_xZr_{1-x}O_3)$ [1–4] compound, and 10% of $NiFe_{1.98}Co_{0.02}O_4$ ferrite [5, 6] in unpolarized and polarized states.

Experimental details

The synthesis of the composites was carried out following the solid-state reaction method at a temperature of ca. 1460 K for two hours, using the required ratios of the final fractions of the piezoelectric compound and ferrite. Polarization of the samples was carried out in an electric field of ~4 kV/mm in strength at 400 K for one hour. The samples were cooled at a rate of three degrees per minute. During cooling, the magnitude of the electric field was increased up to 4.5–5 kV/mm. X-ray diffraction studies were performed at room temperature using CuK_α radiation at angles between $3° \leq 2\theta \leq 100°$. Information at each angle was recorded at $\Delta\tau = 3$ s at the scan step angle $\Delta 2\theta = 0.03$ angular degrees. Specific magnetization and magnetic susceptibility were measured using the ponderomotive method at room temperature in a magnetic field with induction $B = 0.86$ T.

The local configurations of the iron atoms in the studied composites were investigated by ^{57}Fe Mössbauer spectroscopy at a temperature of 3.7 K and at room temperature (RT). Spectra were fitted assuming the Gaussian distribution of the hyperfine magnetic fields (H_{hf}) and quadrupole splittings (Δ) within iron nuclei [7] apply. The spectrometer was calibrated to pure α-Fe by collecting the spectra of a standard α-Fe foil at RT.

Results and discussion

The X-ray diffraction patterns of the 90% PZT-10% $NiFe_{1.98}Co_{0.02}O_4$ composite in the unpolarized (a) and

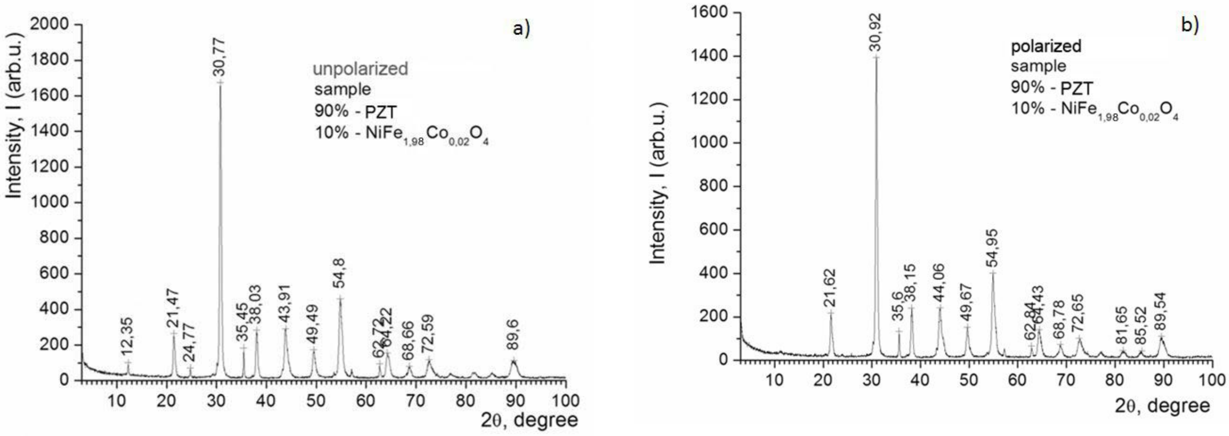

Fig. 1. X-ray diffraction patterns of 90% PZT-10% $NiFe_{1.98}Co_{0.02}O_4$ composites in unpolarized (a) and polarized (b) states.

Table 1. Specific magnetization and reversible magnetic susceptibility of the $Pb(Ti_xZr_{1-x}O_3)$-$NiFe_{1.98}Co_{0.02}O_4$ composite in unpolarized and polarized states. The measurements were performed for samples no. 1–5 which were synthetized in the same way

Unpolarized state

No.	Specific magnetization, σ [$A \cdot m^2 \cdot kg^{-1}$ ($Gauss \cdot cm^3 \cdot g^{-1}$)]	Reversible magnetic susceptibility $10^{-2}/\chi$ [kg/m^{-3}]
1	3.875	20.663
2	3.882	20.923
3	3.876	20.703
4	3.875	20.663
5	3.882	20.623
Average	3.878	20.715

Polarized state

No.	Specific magnetization, σ [$A \cdot m^2 \cdot kg^{-1}$ ($Gauss \cdot cm^3 \cdot g^{-1}$)]	Reversible magnetic susceptibility $10^{-2}/\chi$ [kg/m^{-3}]
1	3.951	20.265
2	3.959	20.224
3	3.967	20.183
4	3.959	20.224
5	3.959	20.224
Average	3.959	20.224

polarized (b) states are shown in Fig. 1. The analysis of the X-ray patterns of the studied composites revealed that during the polarization of the composite, the crystal structure changes such that the intensity of several reflexes is reduced (some almost to zero). It was found that most modifications were made to the crystal structure of the main phase of the composite, i.e. to piezoelectric Pb($Ti_xZr_{1-x}O_3$). Changes in the crystal structure of the ferrite $NiFe_{1.98}Co_{0.02}O_4$ phase were observed to a lesser extent. In the unpolarized sample, the elementary crystal cells of ferrite were initially, i.e. during the synthesis and formation of the solid $NiFe_{1.98}Co_{0.02}O_4$ solution when the substitution of iron cations by 2% of Co occurs, highly deformed and extended in the crystallographic direction (311). The main (311) reflex of the cubic *Fd*3*m* (227) space group structure of ferrite $NiFe_2O_4$ is shifted towards smaller angles from $2\theta \approx 35.69$ up to $2\theta \approx 35.45$ degrees. During polarization of the samples in the electric field, compression of not only the unit cell of the ferrite but also the main matrix of the piezoelectric PZT containing it is observed.

The results of the specific magnetization and magnetic susceptibility measurements at a temperature of ~300 K for the unpolarized and polarized samples are presented in Table 1.

The results of the specific magnetization and magnetic susceptibility measurements using the ponderomotive method (see Table 1) show that the unpolarized sample produces a smaller specific magnetization value than the polarized one. Obviously, this fact is a consequence of the compression of the crystal unit cell and the reduction of unit cell parameters of both phases of the composite components. Reduction of the distance between the magnetically active atoms in the crystal unit cell leads to an increase in exchange magnetic interactions. As a result, an increase in the specific magnetization, magnetic susceptibility and effective magnetic moment of the substance is observed.

The correlation between the differences in the macroscopic magnetic parameters of the unpolarized and polarized states of the investigated composite is identical to the parameters of hyperfine interactions, which are determined for this complex composite by Mössbauer spectroscopy. Figure 2 shows Mössbauer spectra of the 90%Pb($Ti_xZr_{1-x}O_3$)-10%$NiFe_{1.98}Co_{0.02}O_4$ composite at RT and at 3.7 K in the unpolarized (S_1) and polarized states (S_2). Clear differences may be observed not only in the magnetic fields of the Zeeman splitting of the hyperfine structure, but also in the intensity of the paramagnetic components. The values of the parameters obtained from the fitting of the Mössbauer spectra of the ferrite $NiFe_{1.98}Co_{0.02}O_4$ at RT and at 3.7 K are shown in Table 2.

The Mössbauer spectra were fitted by two sextets corresponding to Fe^{3+} ions occupying tetrahedral sites (A sites) and octahedral sites (B sites) within the spinel structure of the ferrite $NiFe_{1.98}Co_{0.02}O_4$ and by one doublet associated with Fe^{3+} ions in a non-magnetic/superparamagnetic state. As can be seen, the fitting parameters of Mössbauer spectra recorded at RT of the S_1 and S_2 samples first of all differ in terms of the contribution of the magnetic/non-magnetic phase: the content of the non-magnetic phase is greater for S_2 (20.5%) compared to for S_1 (11.3%). On the other hand, the Mössbauer spectra recorded at 3.7 K demonstrate a decrease in the contribution of the non-magnetic phase to 7.8%

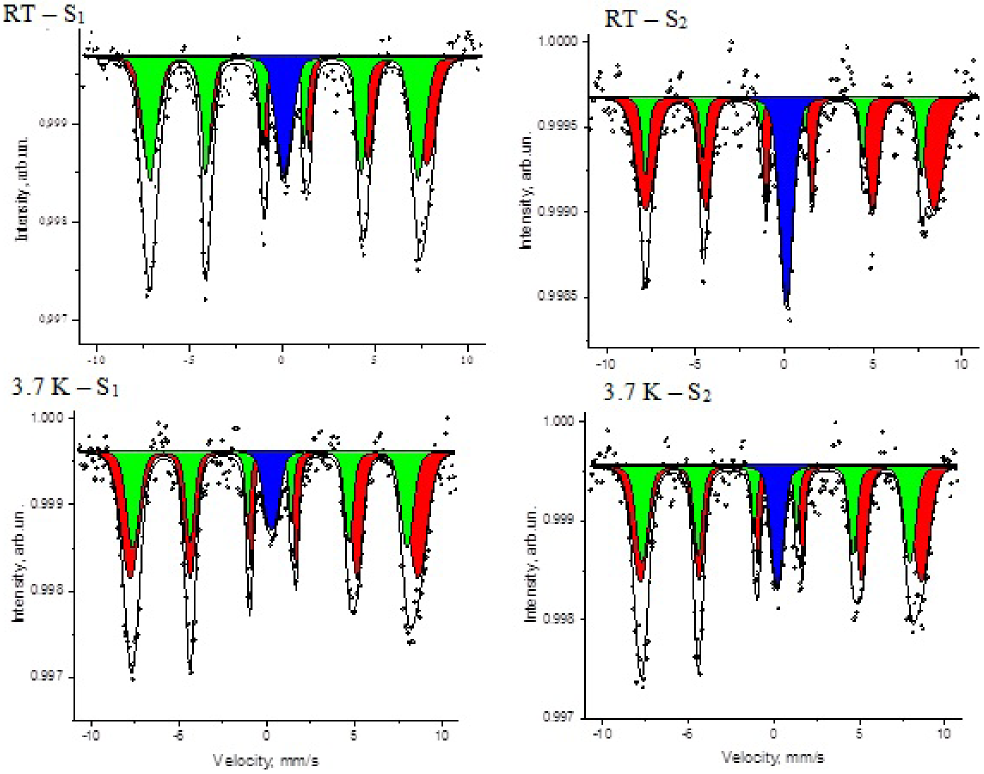

Fig. 2. Mössbauer spectra at room temperature and at 3.7 K in the unpolarized (S_1) and polarized states (S_2) of the 90% Pb($Ti_xZr_{1-x}O_3$)-10% $NiFe_{1.98}Co_{0.02}O_4$ composite.

Table 2. Results of the approximation of Mössbauer spectra as the superposition of subspectra at RT and at 3.7 K

Sample	Phase state of Fe	IS [mm/s]	Δ*E* [±0.01 mm/s]	B_{hf} [T]	Contribution *A* [%]
S_1 RT	Fe^{3+} (B site)	0.28 ± 0.03	0.02	46.6 ± 0.3	47 ± 3
	Fe^{3+} (A site)	0.07 ± 0.03	0.02	44.9 ± 0.3	42 ± 8
	non-magnetic	0.09 ± 0.03	0.01	–	11.3 ± 0.7
S_2 RT	Fe^{3+} (B site)	0.28 ± 0.03	0.02	50.5 ± 0.3	62 ± 5
	Fe^{3+} (A site)	–0.08 ± 0.03	0.02	48.3 ± 0.2	18 ± 4
	non-magnetic	0.10 ± 0.03	0.06	–	20.5 ± 1.4
S_1 3.7 K	Fe^{3+} (B site)	0.39 ± 0.03	0.02	50.9 ± 0.3	60 ± 9
	Fe^{3+} (A site)	0.16 ± 0.03	0.02	48.5 ± 0.2	32 ± 8
	non-magnetic	0.26 ± 0.06	0.49 ± 0.16	–	7.8 ± 0.9
S_2 3.7 K	Fe^{3+} (B site)	0.39 ± 0.02	0.02	50.9 ± 0.3	55 ± 7
	Fe^{3+} (A site)	0.11 ± 0.03	0.02	48.6 ± 0.2	34 ± 7
	non-magnetic	0.19 ± 0.04	0.39 ± 0.13	–	10.9 ± 1.0

for S_1 and to 10.9% for S_2. This means that some of the Fe atoms of the non-magnetic phase detected at RT should be assigned to the ferrite $NiFe_{1.98}Co_{0.02}O_4$ in the superparamagnetic state. Another difference in the Mössbauer spectra between the S_1 and S_2 samples at room temperature are the B_{hf} values of magnetic components that appear to be greater for S_2 (50.5 T and 48.3 T) compared to S_1 (46.6 T and 44.9 T) for sextets corresponding to Fe^{3+} ions at the A and B sites of the spinel structure [8]. According to the fitting results, the contents of Fe^{3+} ions at the A and B sites of the spinel structure in the unpolarized sample (S_1) are very similar, while the contents of Fe^{3+} ions at B sites are prevalent in the polarized sample (S_2). This means that sample polarization greatly affects the degree of sample inversion at room temperature. At the same time, the results of Mössbauer spectroscopy at ultra-low temperatures (3.7 K) indicate that the aforementioned differences in the parameters of magnetic sextets are negligible considering the degree of error. The difference in the IS values of spectrum approximation components observed in the Mössbauer spectra recorded at room temperature and at 3.7 K can be explained by the second order Doppler shift. At the same time, the IS value of pure α-Fe at room temperature and at 3.7 K differs by ~0.11 mm/s. Assuming the presence of an IS error, it can be claimed that the charge state of Fe nuclei does not change at 3.7 K.

Summary and conclusions

1. The complex composites according to piezoelectric $Pb(Ti_xZr_{1-x}O_3)$ and $NiFe_{1.98}Co_{0.02}O_4$ ferrite were synthesized successfully using the solid-state reaction method.
2. The X-ray diffraction results exhibit compression of unit cells of both phases of the composite by 7–8% during polarization of the samples at 400 K in an electric field of 4 kV/mm in strength.
3. It has been identified that the polarization of these composites leads to an increase in specific magnetization and effective magnetic field values of ^{57}Fe nuclei in the $NiFe_{1.98}Co_{0.02}O_4$ matrix.

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