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COMPOSITES THEORY AND PRACTICE

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MECHANICAL LOSSES AND DIELECTRIC PROPERTIES IN FERROELECTRIC-FERROMAGNETIC COMPOSITES

The work presents the technology and investigation results of ferroelectric-ferromagnetic composites based on ferroelectric powders of the PZT type and ferrite. The ferroelectric powder comprised two PZT type compositions: $Pb_{0.84}Ba_{0.16}(Zr_{0.54}Ti_{0.46})O_3$ + 1.0%at. Nb_2O_5 (PBZTN) and $Pb(Zr_{0.51}Ti_{0.49})O_3$ + 0.2%at. Bi_2O_3 + 0.03%at. Nb_2O_5 + 0.06%at. MnO_2 (PZTBNM). The initial constituents for obtaining the PZT type powders included oxides: PbO, ZrO_2, TiO_2, Nb_2O_5, Cr_2O_3 as well as carbonates: barium $BaCO_3$ and strontium $SrCO_3$. In the PZT-ferrite composites, the synthesized ferroelectric powder constituted 90%, whereas the ferrite powder ($Ni_{0.64}Zn_{0.36}Fe_2O_4$) was 10%.

Temperature examinations of the internal friction (IF) of the PZT-ferrite type composites, which belong to non-destructive methods of material examination in mechanical spectrometry, and also measurements of the dielectric properties were performed. The IF method enabled the authors to determine mechanical properties such as mechanical losses or value of Young's modulus in a broad range of temperatures. For both the investigated composites, an increase in mechanical losses Q^{-1} and decrease in Young's modulus Y with an increase in temperature were observed. At the phase transition point connected with an electric sub-system change while changing from the ferroelectric to paraelectric state, a rapid increase in Young's modulus Y was observed. It was confirmed in further investigations of dielectric properties $\varepsilon(T)$ i $\tan\delta(T)$.

Keywords: mechanical losses, internal friction, Young's modulus, ferroelectric-ferromagnetic composites, PZT-type ceramics, ferrites, multiferroics

STRATY MECHANICZNE I WŁAŚCIWOŚCI DIELEKTRYCZNE W KOMPOZYTACH FERROELEKTRYCZNO-FERROMAGNETYCZNYCH

Praca przedstawia technologię i rezultaty badań dwóch ferroelektryczno-ferromagnetycznych kompozytów, otrzymanych na bazie ferroelektrycznych proszków typu PZT i ferrytu. Proszek ferroelektryczny stanowiły dwa składy typu PZT: $Pb_{0.84}Ba_{0.16}(Zr_{0.54}Ti_{0.46})O_3$ + 1.0%at. Nb_2O_5 (PBZTN) i $Pb(Zr_{0.51}Ti_{0.49})O_3$ + 0.2%at. $Bi_2O_3$0.03%at. Nb_2O_5 + 0.06%at. MnO_2 (PZTBNM). Składnikami wyjściowymi do otrzymywania proszków typu PZT były tlenki: PbO, ZrO_2, TiO_2, Nb_2O_5, Cr_2O_3 oraz węglany: baru $BaCO_3$ i strontu $SrCO_3$. W kompozytach typu PZT-ferryt zsyntetyzowany proszek ferroelektryczny stanowił 90%, natomiast proszek ferrytowy ($Ni_{0.64}Zn_{0.36}Fe_2O_4$) stanowił 10%.

Przeprowadzono temperaturowe badania tarcia wewnętrznego (TW) kompozytów typu PZT-ferryt, które należą do nieniszczących metod badań materiałów w spektroskopii mechanicznej, a także pomiary właściwości dielektrycznych (temperaturowe zależności przenikalności elektrycznej i tangensa kąta strat dielektrycznych). Metoda TW pozwoliła określić właściwości mechaniczne, takie jak straty mechaniczne czy wartość modułu Younga, w szerokim zakresie temperatur. Dla obu badanych kompozytów zaobserwowano wzrost wartości strat mechanicznych Q^{-1} wraz ze wzrostem temperatury oraz spadek modułu Younga Y. W punkcie przemiany fazowej, związanej z przemianą podukładu elektrycznego przy przejściu ze stanu ferroelektrycznego w paraelektryczny, obserwowano gwałtowny spadek wartości modułu Younga Y. Przemiana ta została potwierdzona w kolejnych badaniach właściwości dielektrycznych $\varepsilon(T)$ i $\tan\delta(T)$.

Słowa kluczowe: straty mechaniczne, tarcie wewnętrzne, moduł Younga, kompozyty ferroelektryczno-ferromagnetyczne, ceramika PZT, ferryty, multiferroiki

INTRODUCTION

In view of unique ferroelectric, electromechanical and piezoelectric properties, PZT type solid solutions are the base for improving their application parameters [1-3]. PZT belongs to the family of multi-component solid solutions of the $(1-x)PbZrO_3 - xPbTiO_3$ ($0< x<1$) type, in which Ti^{4+} ions in $PbTiO_3$ are substituted partly by Zr^{4+} ions in the x mol ratio. PZT has a perovskite type structure (ABO_3), in which Ti^{4+} and Zr^{4+} cations occupy positions B in a random way, whereas Pb^{2+} cations occupy positions A [4]. Modified PZT is the simplest and most effective way to control the physical properties of PZT ceramics regarding the needs of modern electronics [5]. The modified $Pb(Zr_{1-x}Ti_x)O_3$ solid solution is one of a few materials which can be the base to construct various devices having different functions and operating parameters [1-3]. Spinel ferrites (the Fe_2O_3 iron oxide compounds with metal oxides) have a structure of the $MgAl_2O_4$ mineral spinel (with MeO general formula, where Me: Zn, Cd, Fe, Ni, Cu, Co or Mg). Their magnetic properties depend on the chemical composition and distribution of the cations in the inter-oxide tetrahedral and octahedral positions, which are formed at the synthesis stage in the technological process. As far as the magnetic properties are concerned, magnetically soft and hard ferrites can be differentiated [6]. They can be used in radio engineering, high frequency engineering and ultrasonic engineering and as coil cores for chokers, transformers, magnetic aerials, etc. [7]. Nickel-zinc ferrite ($Ni_{0.64}Zn_{0.36}Fe_2O_4$), which belongs to so-called soft ferrites of a high value of magnetic permeability and resistance (operating frequency in the range 50÷1000 MHz) [8], is used, among others, for signal processing (telecommunication filters, distance sensors, delay lines), in EMI filters and broad-band transformers. The aim of this work was to obtain ferroelectric-ferromagnetic composites based on PZT type ferroelectric powders and nickel-zinc ferrite, and then to investigate their mechanical properties (mechanical losses) and compare with the dielectric parameters.

The internal friction method (IF), which belongs to non-destructive examination methods in mechanical spectroscopy, was used in the investigations of the obtained composites. Internal friction is caused by irreversible energy losses, taking place in solid bodies as a result of many processes, in which they take part, among others, crystal lattice defects. It is characterized by inelastic behavior of the bodies when external stresses act upon them, and it is manifested by losses of some energy of mechanical vibrations (some mechanical energy changes into thermal energy) [9, 10]. The great interest in the internal friction method in the examination of the real structure of materials is caused by the fact that by observing macroscopic vibrations of a specimen, one can obtain information about material behavior at the atomic level. This method is characterized by high sensitivity to changes in the real structure of materials [11, 12]. Analysis in the IF method can be made by either temperature measurements (at a constant measurement frequency) or frequency measurements (at a stable temperature) [13]. Other temperature measurements e.g. electric permittivity and the tangent of the dielectric loss angle must be made to determine the mechanisms of the processes taking place in the material [11, 14-20].

EXPERIMENT

Ferroelectric-ferromagnetic composites were obtained by joining ferroelectric powder of the PZT type and zinc-nickel ferrite powder ($Ni_{0.64}Zn_{0.36}Fe_2O_4$) of ferromagnetic properties. The ferroelectric powder consisted of two compositions of the PZT type: $Pb_{0.84}Ba_{0.16}(Zr_{0.54}Ti_{0.46})O_3$ + 1.0%at. Nb_2O_5 (PBZTN) and $Pb(Zr_{0.51}Ti_{0.49})O_3$ + 0.2%at.Bi_2O_3 + 0.03%at. Nb_2O_5 + 0.06%at. MnO_2 (PZTBNM).

The initial components to obtain the powders of the PZT type were: PbO, ZrO_2, TiO_2, Nb_2O_5, Bi_2O_3, MnO_2 oxides and barium carbonate $BaCO_3$. The main component of the composite - ferroelectric powder of the PZT type was synthesized by sintering a mixture of simple oxides in the solid phase (by a compacting method) in the conditions: T_{synth} = 850°C, t_{synth} = 2 h. The second component of the composite with the ferromagnetic properties (ferrite powder $Ni_{0.64}Zn_{0.36}Fe_2O_4$) was synthesized by the powder calcination method in the conditions: 1000°C/4 h. In the PZT-ferrite type composites, the synthesized ceramic powder was 90%, whereas the ferrite powder 10%. The powders of the initial components were mixed wet in a FRITSH Pulverisette 6 planetary ball mill (in ethyl alcohol) for 8 h. Synthesizing of the composite powders was done by the calcination method in the conditions: T_{synth} = 950°C and t_{synth} = 2 h, and their compacting (sintering) by free sintering of the compacts in the conditions: T_s = 1250°C/t_s = 2 h. Complex research of ceramic composites is presented in [21].

The multi-ferroic composites were designated in the following way: PBZTN-ferrite and PZTBNM-ferrite. After sintering the specimens were ground, polished and electrodes were laid by the silver paste burning method. The temperature dependencies of $Q^{-1}(T)$ and $Y(T)$ were determined while heating at the constant rate of 3°C/min. Measurements were made by an automatic relaxator of acoustic frequencies of the RAK-3 type. Dielectric measurements were performed on a capacity bridge of a QuadTech 1920 Precision LCR Meter for a cycle of heating (for ν = 1 kHz).

RESULTS

In Figures 1 and 2, the temperature relationships of mechanical losses $Q^{-1}(T)$ and Young's modulus $Y(T)$ were shown for the PBZTN-ferrite (Fig. 1) and PZTBNM-ferrite (Fig. 2) composites, respectively in the range of low temperatures from about –130°C to about 20°C. By analyzing the $Q^{-1}(T)$ courses, a slow increase in the mechanical losses can be seen in the whole temperature range. Such behavior is connected mainly with an increase in domain wall mobility in the composite structure, hence, increasing the possibility of their mutual influence with a temperature increase (the thermal energy increase). A gradual decrease in Young's modulus Y, caused mainly by a stress decrease in the structure of the specimens and their surface is observed simultaneously on the $Y(T)$ curves [14].

In Figures 3 and 4, relationships $Q^{-1}(T)$ and $Y(T)$ are presented for the composites in question made in the positive temperature range (from about 20 to about 450°C).

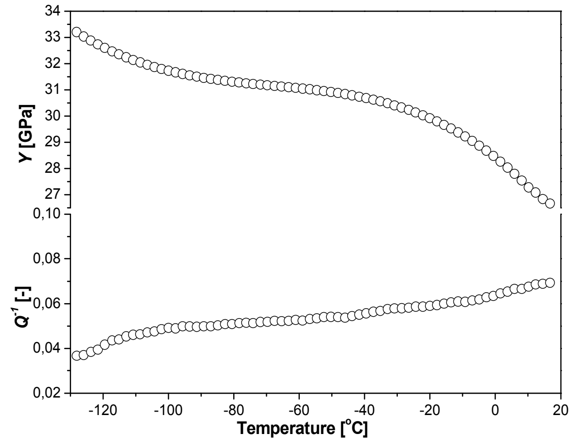

Fig. 1. Temperature relationships of mechanical losses $Q^{-1}(T)$ and Young's modulus $Y(T)$ for composite PBZTN-ferrite in –130 to 20°C range

Rys. 1. Temperaturowe zależności strat mechanicznych $Q^{-1}(T)$ i modułu Younga $Y(T)$ dla kompozytu PBZTN-ferryt w zakresie od –130 do 20°C

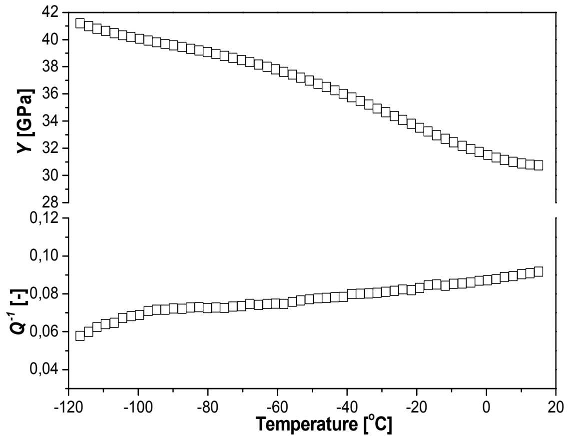

Fig. 2. Temperature relationships of mechanical losses $Q^{-1}(T)$ and Young's modulus $Y(T)$ for composite PZTBNM-ferrite in –120°C to 20°C range

Rys. 2. Temperaturowe zależności strat mechanicznych $Q^{-1}(T)$ i modułu Younga $Y(T)$ dla kompozytu PZTBNM-ferryt w zakresie od –120°C do 20°C

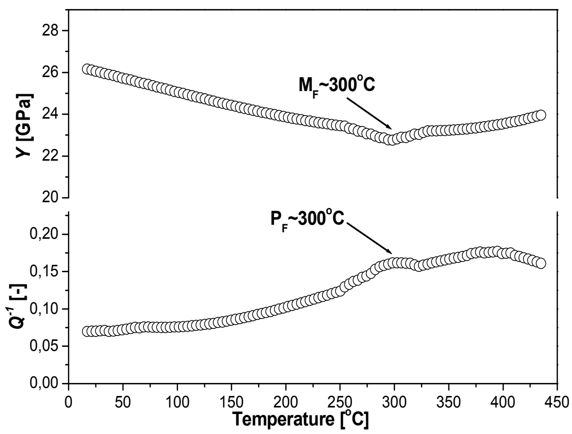

Fig. 3. Temperature relationships of $Q^{-1}(T)$ mechanical losses and $Y(T)$ Young's modulus for PBZTN-ferrite composite in 20 to 450°C range

Rys. 3. Temperaturowe zależności strat mechanicznych $Q^{-1}(T)$ i modułu Younga $Y(T)$ dla kompozytu PBZTN-ferryt w zakresie od 20°C do 450°C

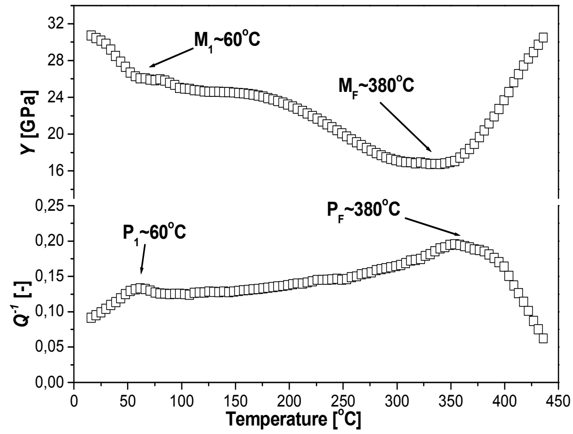

Fig. 4. Temperature relationships of $Q^{-1}(T)$ mechanical losses and $Y(T)$ Young's modulus for PZTBNM-ferrite composite in 20 to 450°C range

Rys. 4. Temperaturowe zależności strat mechanicznych $Q^{-1}(T)$ i modułu Younga $Y(T)$ dla kompozytu PZTBNM-ferryt w zakresie od 20 do 450°C

In the case of the PBZTN-ferrite composite (Fig. 3), with a temperature increase there is a visible increase in the mechanical losses with the diffused P_F maximum at about 300°C. The characteristic M_F minimum, correlating with the P_F maximum, is observed simultaneously on the $Y(T)$ temperature relationship of Young's modulus. Such behavior of both the $Q^{-1}(T)$ and $Y(T)$ relationships shows that there are phase changes in the temperature range. It is shown by a significant increase in the Q^{-1} mechanical losses at a simultaneous decrease in Young's modulus Y value. This change is connected with an electric sub-system change while changing from the ferroelectric to paraelectric state. It was confirmed in further investigations of the dielectric properties. Similar behavior of temperature relationships of $Q^{-1}(T)$ and $Y(T)$ is observed for the second composite in question, that is PZTBNM-ferrite. With a temperature increase there is an increase in the mechanical losses and the Young's modulus value decreases. Additionally, at about 60°C the P_1 maximum of internal friction and M_1 correlating with it are observed. Those anomalies are connected with the presence of two phases in the composite compositions, that is, a tetragonal and rhombohedral phase, coming from the morphotropic area of the ferroelectric component of the PZT type. The P_1 maximum observed at low temperatures (T = 60°C) is connected with the appearance of a second phase, that is besides a tetragonal phase there is a rhombohedral phase as well, which confirms that the composition of the PZT ceramics is within the morphotropic area (a mixture of tetragonal and rhombohedral phase).

At about 380°C, on the $Q^{-1}(T)$ there is the characteristic P_F maximum correlating with the M_F minimum on the $Y(T)$ curve connected with the ferroelectric-paraelectric phase change. A rapid increase in Young's modulus Y connected with a change in the crystal structure to a regular system is observed above this temperature.

Examinations of the temperature relationships of electric permittivity $\varepsilon(T)$ (Fig. 5) and the tangent of dielectric loss angle $\tan\delta(T)$ (Fig. 6) were made for both composites obtained on the base of ferroelectric powders of the PZT type and the NiZnFe ferrite powder.

In the case of the PBZTN-ferrite composite, the characteristic maximum of electric permittivity is observed in the phase change temperature of the electric sub-system (about 298°C). Considerable diffusion of the phase change is seen simultaneously (phase change from ordered - ferroelectric phase to disordered - paraelectric phase takes place in a wide range of temperatures). The phase change diffusion can be connected with a random distribution of ions in positions B of the perovskite lattice, which leads to the formation of microscopic areas with different Curie temperatures.

In the case of the PZTBNM-ferrite composite, the electric permittivity maximum in the phase temperature of the electric sub-system occurs at a much higher temperature (about 378°C). At the same time, the phase change from the ferroelectric to paraelectric phase takes place in a narrower temperature range. The character of the phase change diffusion shows a degree of ordering of the crystal structure. When the ordering is higher, the phase change, taking place in a narrow temperature range, is observed [22, 23]. It has a positive influence on the set of electro-physical parameters of the material.

The phase change temperatures for both composites, visible on the $\varepsilon(T)$ temperature relationships (Fig. 5), agree rather well with the anomaly places, which occur on the $Q^{-1}(T)$ and $Y(T)$ temperature relationships - Figures 3 and 4. In spite of the lower values of the maximum permittivity (at temp. T_C) from room temperature to about 300°C, the PBZTN-ferrite composite shows higher values of electric permittivity comparing to the PZTBNM-ferrite composite.

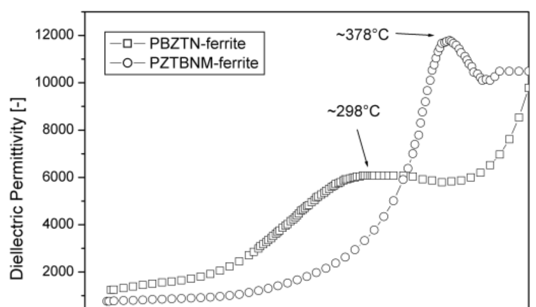

Fig. 5. $\varepsilon(T)$ temperature relationships of electric permittivity for PBZTN-ferrite and PZTBNM-ferrite composite (ν = 1 kHz)

Rys. 5. Temperaturowe zależności przenikalności elektrycznej $\varepsilon(T)$ dla kompozytów PBZTN-ferryt i PZTBNM-ferryt (ν = 1 kHz)

At lower temperatures, the dielectric losses of the PZT-ferrite composites are low and show similar values (Fig. 6). Above 100°C the values of the dielectric losses in the composite increase significantly, which is connected with a rapid increase in electrical conductivity at high temperatures. In the case of the PBZTN-ferrite composite, the dielectric losses do not exceed 0.2 at about 250°C.

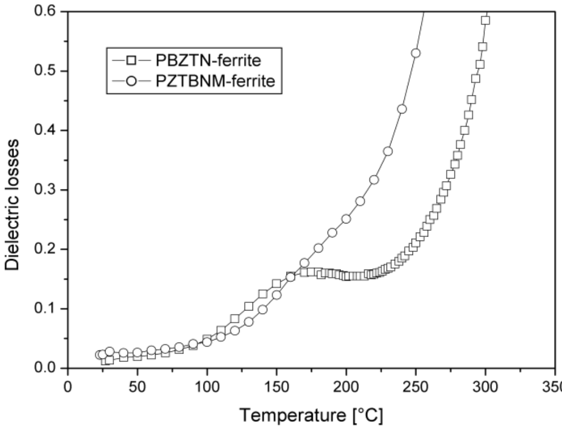

Fig. 6. Temperature relationships of tangent of dielectric loss angle $\tan\delta$ for PBZTN-ferrite and PZTBNM-ferrite composite (ν = 1 kHz)

Rys. 6. Temperaturowe zależności tangensa kąta strat dielektrycznych $\tan\delta$ dla kompozytów PBZTN-ferryt i PZTBNM-ferryt (ν = 1 kHz)

SUMMARY

Selection of the technology of obtaining composites enables one to control their final parameters, such as the mechanical or dielectric properties. The results of investigations of two ferroelectric-ferromagnetic composites are presented in the work.

In the case of the PBZTN-ferrite in which the Ba admixture was used, we observe lower values of mechanical and dielectric losses at room temperature, lower values of Young's modulus *Y*, a decrease in the electric permittivity value, as well as displacement of the phase change temperature from the ferroelectric to paraelectric state towards lower temperatures.

By analyzing the results of the investigations of the PZTBNM composite, in which among others, a hard Mn admixture was used, one can see Young's modulus *Y* value increase, higher mechanical and dielectric losses. In this composite, displacement of the phase change temperature towards higher temperatures is observed and there is a simultaneous increase in the maximum value of electric permittivity.

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