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TECHNOLOGY AND ELECTROPHYSICAL PROPERTIES OF MULTIFERROIC PZT-PFT CERAMICS

TECHNOLOGIA I WŁAŚCIWOŚCI ELEKTROFIZYCZNE MULTIFERROIKOWEJ CERAMIKI TYPU PZT-PFT

We present the results of obtaining and investigating ceramic samples of solid solution (1-x)($PbZr_{0.53}Ti_{0.47}O_3$)-x($PbFe_{0.5}Ta_{0.5}O_3$) [i.e. (1-x)PZT-xPFT] with x =0.25, 0.35 and 0.45 obtained using conventional ceramic technology. These materials belong to class of materials known as multiferroics. Solid solutions PZT-PFT are the lowest-loss room-temperature multiferroics known, and as a result there are very interesting for magnetoelectric devices.

Paper presents the results of termogravimetric investigations, EDS, XRD and main dielectric measurements. It has been stated that with increasing content of PFT decreases the mean diameter of grains and more wide distribution of grain diameters is observed. For x =0.25 sharp phase transition from ferroelectric phase to paraelectric one is observed and high values of dielectric permittivity. Composition PZT-PFT with x =0.45 has the lowest values of dielectric permittivity, and the transition is more diffused. The increase of x leads also to the shift of the temperature of maximum of dielectric permittivity towards lower temperatures. Samples with x =0.25 and x =0.35 exhibit very low values of dielectric losses up to about 100°C. Dielectric losses for samples with x =0.45 are higher.

For obtained PZT-PFT samples we have investigated P–E hysteresis loops at room temperature for frequency 1 Hz. For composition x =0.25 it after application the field about 2.5 kV/mm polarization is equal approximately 28 μC/cm^2, while for x =0.35, and x =0.45 after application the field about 2.0 kV/mm the polarizations are equal about 25 μC/cm^2 and 20 μC/cm^2 respectively.

Very low values of losses and high values of polarization lead to the conclusion that interesting material PZT-PFT for applications should be composition with x =0.25.

Keywords: dielectric losses, ferroelectromagnetics, multiferroics, PZT-PFT solid solution

Prezentujemy wyniki otrzymywania i badania próbek ceramicznych roztworu stałego (1-x)($PbZr_{0,53}Ti_{0,47}O_3$)-x($PbFe_{0,5}Ta_{0,5}O_3$) [tj. (1-x)PZT-xPFT)], gdzie x =0,25; 0,35 i 0,45. Próbki zostały otrzymane przy użyciu konwencjonalnej technologii ceramicznej. Materiały te należą do klasy materiałów, znanych jako multiferroiki. Roztwory stałe PZT-PFT są obecnie multiferroikami o najniższych stratach dielektrycznych w temperaturze pokojowej i w efekcie są bardzo interesujące dla urządzeń magnetoelektrycznych.

Artykuł przedstawia wyniki badań termograwimetrycznych, EDS, XRD i podstawowych pomiarów dielektrycznych. Stwierdzono, że wraz ze wzrostem zawartości PFT zmniejsza się średnia średnica ziaren i obserwuje się bardziej szeroki rozkład średnic ziaren. Dla wartości x =0,25 obserwujemy ostre przejście z fazy ferroelektrycznej do fazy paraelektrycznej, przy czym wartość przenikalności elektrycznej w maksimum jest wysoka. Skład PZT-PFT x =0,45 ma najniższą wartość przenikalności elektrycznej w maksimum i przejście jest bardziej rozmyte. Wzrost x prowadzi również do obniżenia temperatury, w której występuje maksymalna wartość przenikalności elektrycznej. Próbki z x =0,25 i x =0,35 wykazują bardzo niskie wartości strat dielektrycznych do około 100°C. Straty dielektryczne dla próbek z x =0,45 są wyższe.

Dla otrzymanych próbek PZT-PFT zostały wykonane również badania pętli histerezy P–E w temperaturze pokojowej z użyciem pola o częstotliwości 1 Hz. Do składu x =0,25 w polu elektrycznym o wartości 2,5 kV/mm polaryzacja jest równa około 28 μC/cm^2, a dla x =0,35 i x =0,45 w polu o wartości 2,0 kV/mm polaryzacja jest równa około 25 μC/cm^2 i 20 μC/cm^2 odpowiednio.

Bardzo niskie wartości strat i wysokie wartości polaryzacji prowadzą do wniosku, że ciekawym materiałem dla aplikacji jest skład x =0,25.

1. Introduction

The aim of this paper is to obtain and to examine ceramic samples of multiferroic solid solution (1-x)($PbZr_{0.53}Ti_{0.47}O_3$)-x($PbFe_{0.5}Ta_{0.5}O_3$) (abbreviation PZT-PFT). Multiferroics are in general an attractive class of compounds because of the opportunity to understand the basics of physical phenomena of interaction, as well as their potential practical applications [1-3] and structural changes [4-5]. In the case of practical applications of multiferroics

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specially important is the magnetoelectric effect. However the main problem at the present time is that only few room temperature magnetoelectrics are known. The another problem is high dielectric loss of known multiferroics and high electric conductivity [6]. At work [7] Sanchez et. al. described solid solution PZT-PFT which is the lowest-loss room-temperature multiferroic known, what is very interesting for magnetoelectric devices.

$Pb(Fe_{0.5}Ta_{0.5})O_3$ (PFT) belongs to multiferroic materials and possess monoclinic structure (T <-53°C) tetragonal structure (-53°C <T <-3°C) and cubic structure (at T >-3°C) [8-9] related with changes in electric properties and in addition antiferromagnetic transitions in the range -140°C – -92°C [10] and the other at 264°C [11-12].

Authors of [7] reported the results of temperature dependent X-ray scattering, Raman, dielectric, magnetization and polarization studies of PZT-PFT ceramics solid solutions. It was stated that the sequence of phase transitions for the x =0.4 is rhombohedral/monoclinic (T<-23°C); orthorhombic (-23°C <T<187°C); tetragonal (187 <T <1027°C). Authors of [13] discovered in PZT-PFT significant room temperature coupling by monitoring changes in ferroelectric domain patterns induced by magnetic fields.

In presented work using conventional ceramic technology we obtained and next investigated ceramic samples of $(1\text{-}x)(PbZr_{0.53}Ti_{0.47}O_3)\text{-}x(PbFe_{0.5}Ta_{0.5}O_3)$. For obtained samples it were made basic investigations of structure, microstructure and dielectric properties at different temperatures and frequencies.

2. Samples and experiment

To obtain powders of $(1\text{-}x)(PbZr_{0.53}Ti_{0.47}O_3)\text{-}x(PbFe_{0.5}Ta_{0.5}O_3)$ with x =0.25, 0.35 and 0.45 we used simple oxides: PbO, ZrO_2, TiO_2, Fe_2O_3 and Ta_2O_5. Weighed in stoichiometric proportions powders were next milled using planetary mill FRITSH Pulwerisette 6, in ethanol, by 12 h. Basing on the results of derivatographic analysis for each compositions (Fig. 1) made using Q-1500D derivatograph (F. Paulik, J. Paulik, L. Erdey system – heating rate =10°/min, reference material Al_2O_3), the following conditions of synthesis were selected: T_{synth} =850°C, t_{synth} =10 h. The loss of mass of investigated samples is rather small. On the DTA curves at higher temperatures (759°C – 763°C) we can observe characteristic peaks associated with the formation of the main phase of the compound. In next step the powder was mixed manually by t =2 h. Such obtained resulting powder of PZT-PFT were pressed at the room temperature into pellets with diameter 10 mm and a thickness about 1 mm using hydraulic press (250 MPa). Next samples were sintered without pressure in conditions T_s =1250°C, t_s =5 h (in the environment Al_2O_3 powder). The final steps of technology were grinding, polishing, removing mechanical stresses (by heating at temperature 700°C) and putting silver paste electrodes onto both surfaces of the samples.

The XRD tests were carried out at room temperature using Phillips diffractometer (with a Cu K_α source and a graphite monochromator, step 0.02° and measurement time 4 s/step). The microstructure of fractured samples were examined using Hitachi S-4700 SEM field emission scanning electron microscope with a Noran Vantage EDS system. The investigations of dielectric properties were performed using QuadTech1920 LCR meter during the heating cycle (heating rate of about 3°/min and measurement field frequencies from ν =0.1 kHz to 1000 kHz). Hysteresis loops (P-E) at various electric field frequencies were investigated with a Sawyer-Tower circuit and a Matsusada Inc. HEOPS-5B6 precision high voltage amplifier. Data were stored on a computer disc using an A/D, D/A transducer card.

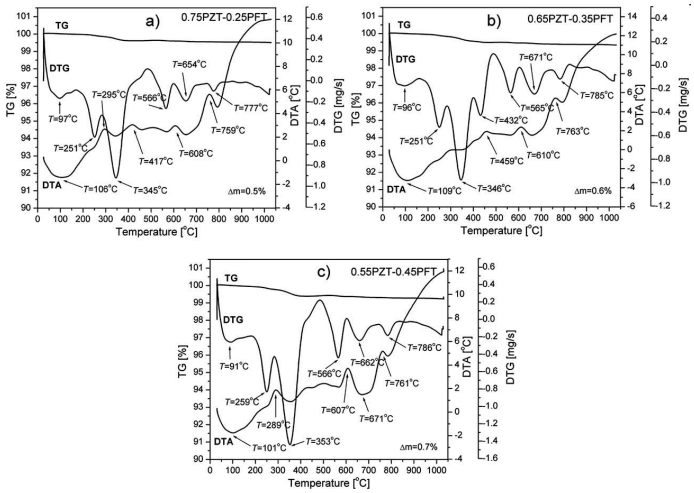

Fig. 1. DTA, TG and DTG curves of the PZT-PFT powders

3. Results

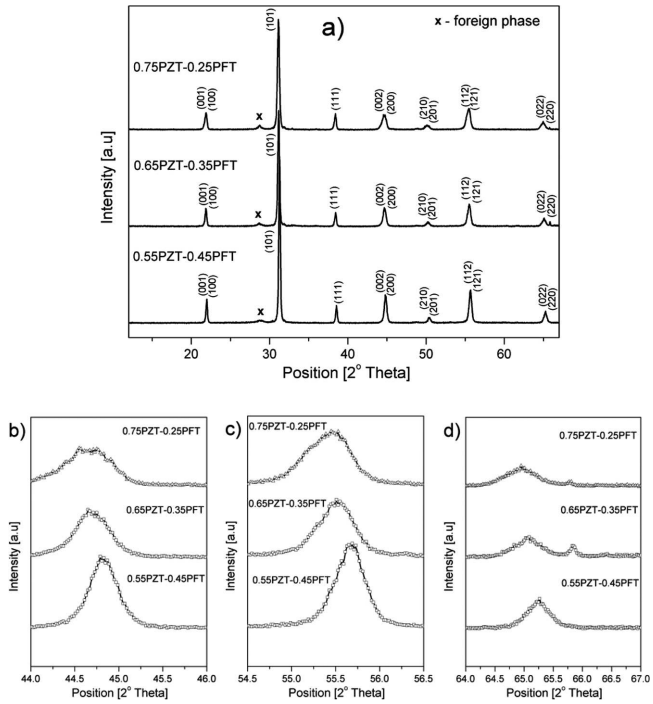

Fig. 2. XRD patterns for synthetized PZT-PFT type powders

XRD data obtained at room temperature are presented in Fig. 2a and the selected fragments in Fig. 2b-d. It is seen that in Fig. 2a at the room temperature obtained material is

perovskite-type, with a small amount of the foreign phase. Obtained by us results are similar to obtained in [7] at room temperature however in this paper XRD investigations at higher temperatures have been also done. In our paper the small peak (220) is visible at room temperature in the XRD pattern about 65° (Fig. 2d). In work [7] peak (220) is more pronounced at higher temperatures.

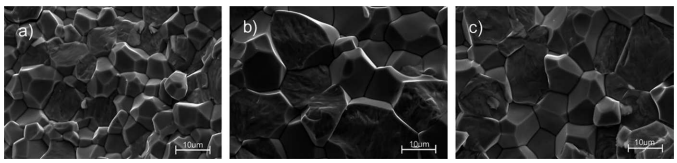

Fig. 3. SEM images of the fractured surfaces of PZT-PFT ceramics for: a) 0.75PZT-0.25PFT, b) 0.65PZT-0.35PFT and c) 0.55PZT-0.45PFT

At the SEM images (Fig. 3) it is seen that the smallest average size of grains has the composition 0.75PZT-0.25PFT with particle size uniformity in whole volume of the sample. For samples with a higher content of PFT it is observed the worsening of the uniformity of grain size, and average size of grains in these configurations is increasing. For all compositions presented in Fig. 3 we can observe coexistence of two types of cracking through grain boundaries as well as through the grains too. This indicates that obtained material has good mechanical properties with high strength in both the interior of the grains, as well as grain boundaries. Results of EDS investigations are presented in Fig. 4 and they confirm that the compositions of obtained samples are close to assumed ones.

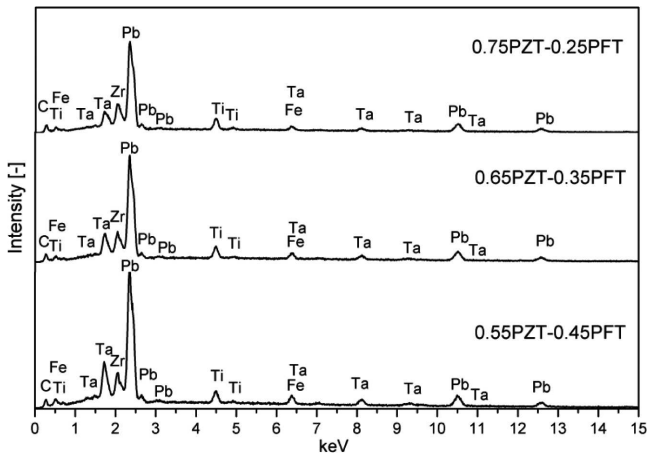

Fig. 4. Images EDS analysis of content element for the 0.75PZT-0.25PFT ceramics, 0.65PZT-0.35PFT ceramics and 0.55PZT-0.45PFT ceramics

Results of dielectric measurements are presented in Fig. 5. It is seen that for x =0.25 sharp phase transition from ferroelectric phase to paraelectric one is observed and high values of dielectric permittivity while for x =0.45 the values of dielectric permittivity are lower, and the transition take place in more wide range of temperatures. With increasing x the temperature of maximum of dielectric permittivity shifts towards lower temperatures. Samples with x =0.25 and x =0.35 exhibit low values of dielectric losses up to temperature about 100°C. Dielectric losses for sample with x =0.45 are much higher.

Electric hysteresis loops at room temperature for PZT-PFT ceramics are presented in Fig. 6. It is seen that hysteresis loops are typical for ferroelectric materials. At the field 2.0 kV/mm hysteresis loops become saturated. Due to the presence of space charge in samples, resulting in momentary increase in electrical conductivity application of larger fields than 2.5 kV/mm was not possible. For x =0.25 spontaneous polarization P_S ≈28 μC/cm^2 (at field about 2.5 kV/mm), for x =0.35 spontaneous polarization is $P_S \approx 25\,\mu$C/cm^2 (at field about 2.0 kV/mm), for x =0.45 spontaneous polarization is P_S ≈20 μC/cm^2 (at field about 2.0 kV/mm). Hysteresis loops are rather wide. Coercive fields are 0.77 kV/mm for 0.75PZT-0.25PFT, 0.74 kV/mm for 0.65PZT-0.35PFT and 0.64 kV/mm for 0.55PZT-0.45PFT.

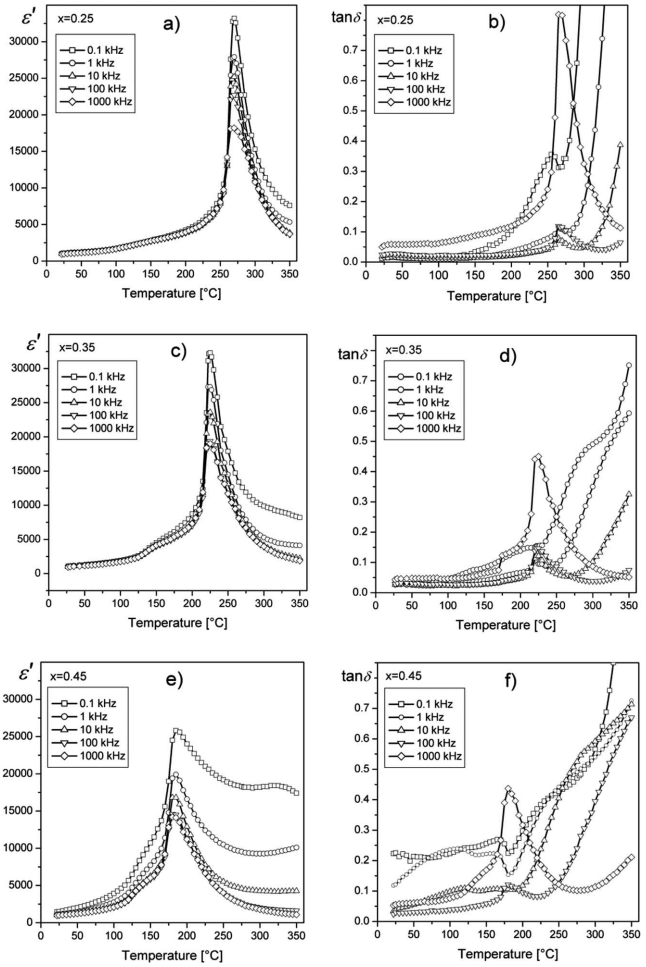

Fig. 5. Temperature dependences of dielectric permittivity ε' and dielectric loss tanδ for the PZT-PFT ceramic: a)-b) 0.75PZT-0.25PFT, c)-d) 0.65PZT-0.35PFT and e)-f) 0.55PZT-0.45PFT (heating)

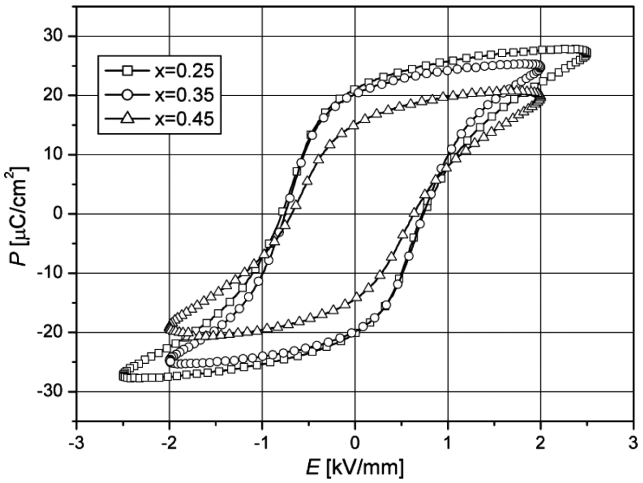

Fig. 6. Hysteresis loops for investigated PZT-PFT type ceramics at the room temperature

4. Conclusion

Main conclusions of our work are as follows. With increasing x in solid solution $(1\text{-}x)(PbZr_{0.53}Ti_{0.47}O_3)\text{-}x(PbFe_{0.5}Ta_{0.5}O_3)$ decreases mean diameter of grains and more wide distribution of grain diameters is observed. For x =0.25 sharp phase transition from ferroelectric phase to paraelectric one is observed and high values of dielectric permittivity while for x =0.45 the values of dielectric permittivity are lower, and the transition take place in more wide range of temperatures. With increasing x in PZT-PFT ceramics the temperature of maximum of dielectric permittivity shifts towards lower temperatures. Samples with x =0.25 and x =0.35 exhibit very low values of dielectric losses up to temperature about 100°C. Dielectric losses for samples with x =0.45 are much higher. Hysteresis loops for investigated ceramics are typical for ferroelectric materials with high values of spontaneous polarization P_S.

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