A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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FABRICATION OF Mn DOPED PZT FOR CERAMIC-POLYMER COMPOSITES

OTRZYMYWANIE PZT DOMIESZKOWANEGO Mn DO KOMPOZYTÓW CERAMICZNO-POLIMEROWYCH

Lead zirconate titanate (PZT) ceramics, with general chemical formula $Pb(Zr_{1-x}Ti_x)O_3$ are used in numerous piezo- and pyroelectric applications. In practice, PZT is rarely used in a chemical pure form. The dielectric, piezoelectric and pyroelectric properties of PZT can be modified by adding dopants to the ABO_3-type PZT perovskite structure.

Ceramics powders of manganese-doped lead zirconate titanate with composition $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ (PMZT) were prepared by the sol-gel method using: lead(II)acetate trihydrate, zirconium(IV)propoxide, titanium(IV)propoxide and manganese(II)acetate tetrahydrate as precursors. The PMZT-PVC composites were fabricated from PMZT and polymer powders by hot-pressing method.

Keywords: ceramic-polymer composites, PZT+Mn, sol-gel

Ceramiczne roztwory stałe cyrkonianu tytanianu ołowiu (PZT) o wzorze ogólnym $Pb(Zr_{1-x}Ti_x)O_3$ znajdują szerokie zastosowanie jako piezo- i piroelektryki. W praktyce czysty PZT jest rzadko używany. Właściwości piezoelektryczne i piroelektryczne PZT modyfikuje się poprzez dodawanie domieszek do struktury typu perowskitu ABO_3.

Ceramiczne proszki cyrkonianu tytanianu ołowiu domieszkowanego manganem o składzie $Pb(Zr_{0,3}Ti_{0,7})_{0,97}Mn_{0,03}O_3$ (PMZT) otrzymano metodą zolowo-żelową. Jako prekursorów użyto: octanu ołowiu, propanolanu cyrkonu, propanolanu tytanu i octanu manganu.

Kompozyty ceramiczno-polimerowe PMZT-PVC otrzymano z proszku PMZT i proszku polimeru PVC metodą prasowania na gorąco.

1. Introduction

Lead zirconate titanate (in short PZT) is one of the most frequently studied ferroelectric materials, due to its extremely wide field of application as a pyroelectric material. Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ is a solid solution of ferroelectric $PbTiO_3$ (T_c=490°C) and antiferroelectric $PbZrO_3$ (T_c=230°C). PZT properties depend on the ratio of Zr/Ti. In the room temperature T_r = 20°C PZT is a ferroelectric, so it possesses also piezo and pyroelectric properties for: $0.042 < x < 0.380$ (rhombohedral *R*3*c*), $0.380 < x < 0.470$ (rhombohedral *R*3*m*) as well as $0.480 < x < 1.000$ (tetragonal *P4mm*). Solid solutions from the area of $0.47 < x < 0.48$ in $T > 227$°C constitute a mixture of tetragonal and rhombohedral phase, in T_r = 20°C they indicate monoclinic system symmetry (it is so called morphotropic phase boundary region).

Physical properties of the PZT ceramics depend on technology, especially on temperature and time of densification because during the densification process evaporation of lead can be observed, which causes disturbance in the initial chemical composition. In practice, PZT is rarely used in a pure chemical form. The dielectric, piezoelectric and pyroelectric properties of PZT can be modified by adding dopants [1]. Appropriate choice of a type and a quantity of dopant ions is important.

There are reports about obtaining Mn-doped $Pb(Zr_{0.3}Ti_{0.7})O_3$ ceramics (by conventional ceramic method) [2, 3] and thin films [4, 5] for pyroelectric applications. Doping manganese into PZT led to a significant increase of the pyroelectric effect and decrease of the dielectric permittivity ε' and dielectric losses coefficient tgδ [6]. In this work powders preparation of manganese-doped lead zirconate titanate with composition of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ (PMZT) is presented. The powders were obtained by sol-gel method. The obtained powders were then used for preparing ceramic-polymer composites for pyroelectric applications. Ceramic-polymer composites have lots of advan-

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tages in comparison with monolithic ceramics and thin films. They can be prepared at low cost in any sizes and shapes required for specific uses.

2. Experimental procedure

To obtain $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders a sol-gel method was used. Using this method ensures preserving stoichiometry of the chemical composition. The chemical composition of pure and admixed PZT powders is similar to assumed, which is difficult to achieve while obtaining PZT by conventional ceramics method. While preparing PZT powders by conventional method, by solid-state reaction synthesis of: PbO, ZrO_2 and TiO_2, unequal vaporization of components is observed, lead evaporates faster. Despite performing various technological operations, such as lead excess in the green ceramics, or using a protective atmosphere of sintering to prevent the evaporation of lead, it is difficult to obtain powders with required chemical composition. As synthesis reaction of pure and doped PZT occurs at temperature below 100°C, the chemical composition of powders obtained by the sol-gel method is similar to the assumed. The second, equally important reason for choosing the sol-gel method was possibility of obtaining nano-sized and homogenous powders. It has a practical value while obtaining ceramic-polymer composites 0-3. Homogenous ceramic powders regularly distribute in the polymer matrix of the composite.

A flow chart for the preparation of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders is described in Fig. 1. Lead(II)acetate trihydrate $Pb(CH_3COO)_2{\cdot}3H_2O$ and manganese(II)acetate tetrahydrate $Mn(CH_3CO_2)_2{\cdot}4H_2O$ were dissolved in a heated acetic acid CH_3COOH. The solution was stirred at 50°C for 1 hour. Zirconium(IV)propoxide $Zr(CH_3CH_2CH_2O)_4$ and titanium(IV) propoxide $Ti(CH_3CH_2CH_2O)_4$ were dissolved in n-propoxide $CH_3(CH_2)OH$. The solution was stirred at room temperature for 1 hour. Both solutions were mixed and stirred further at 50°C for 1 hour. Next, acetylacetone $C_5H_8O_2$ was added as a stabilizer. After water hydrolysis a yellow sol was obtained. The process of gelation, transforms a liquid sol into a gel. The obtained gel was dried in the air. In order to burn out the organic part, the obtained powder was calcinated at 650°C for 4 hours. The powder obtained by sol-gel method is amorphous and it has to be transformed into crystal state to gain piezo- and pyroelectric properties. This is achieved during burning out of the organic parts.

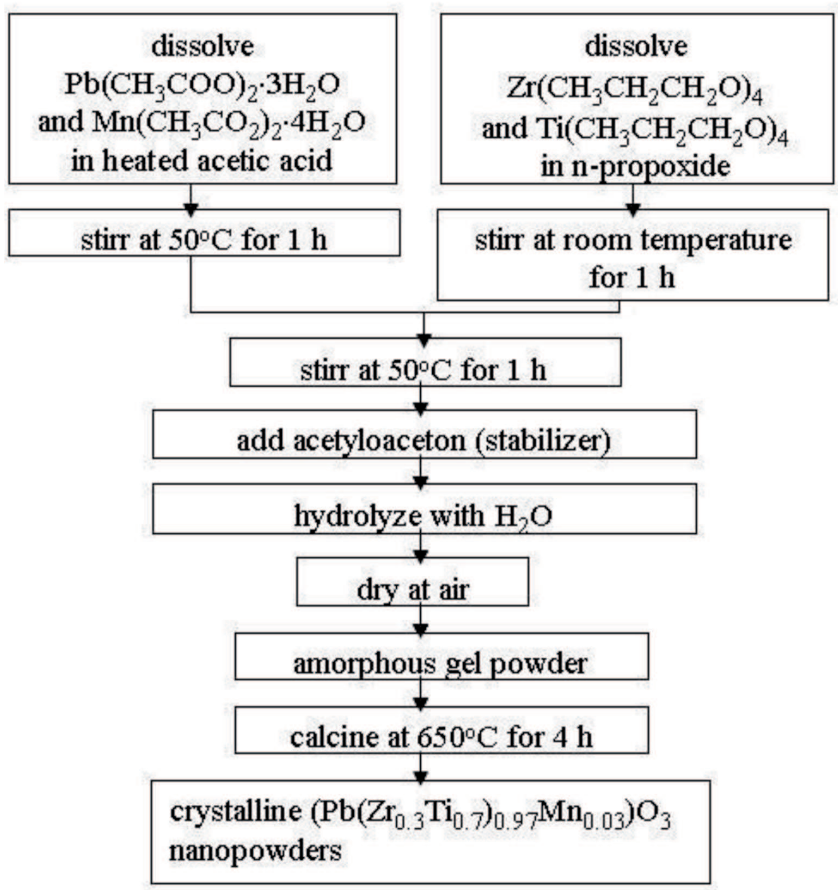

Fig. 1. A flow chart for the preparation of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders

3. Results and discussion

Qualitative and quantitative tests of chemical composition (EDS) of powders were carried out using a scanning electron microscopy HITACHI S-4700 with NORAN Vantage microanalysis system. The EDS measurements confirmed the qualitative and quantitative chemical composition of powders (Fig. 2).

Powders were examined by XRD using D-Max Rapid II X-ray diffractometer, Ag radiation was used. The results calculated into CuK_α radiation are shown in Fig. 3. Crystalline, single-phase powders with tetragonal structure were obtained. To asses sizes of the single particles of the powder, scanning electron microscopy HITACHI S-4700 was used. Fig. 4 shows single particles smaller than 500 nm. This is the best size for the particles. The powders cannot be too fine because below the critical size r_{cr} their ferro-, pyro- and piezoelectric properties disappear [7, 8].

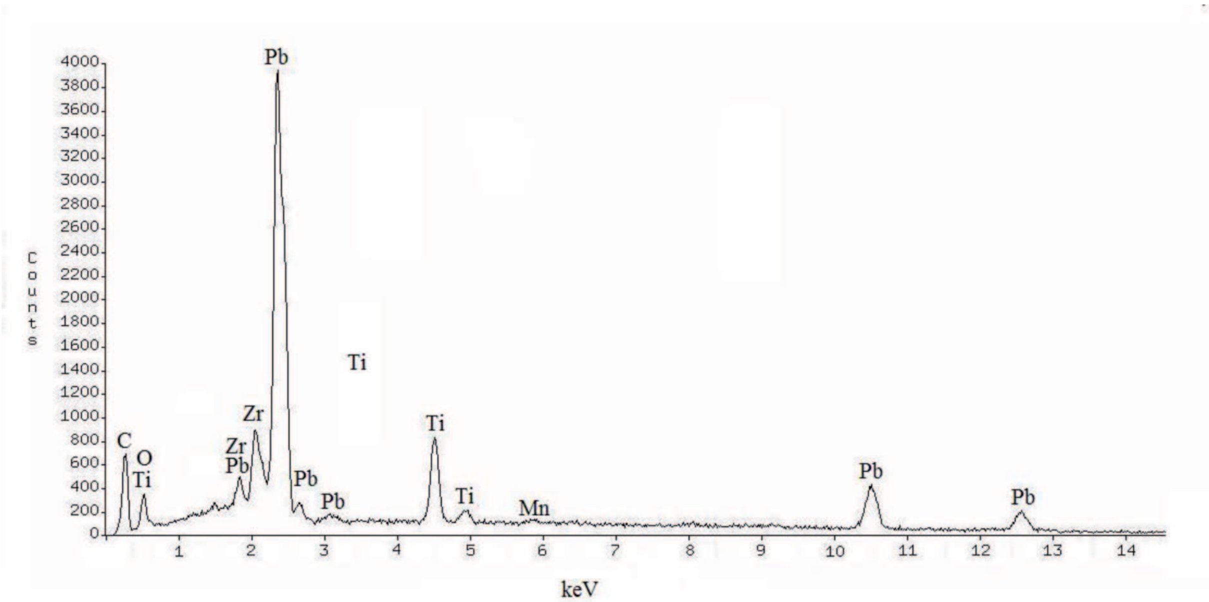

Fig. 2. EDS spectrum of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders

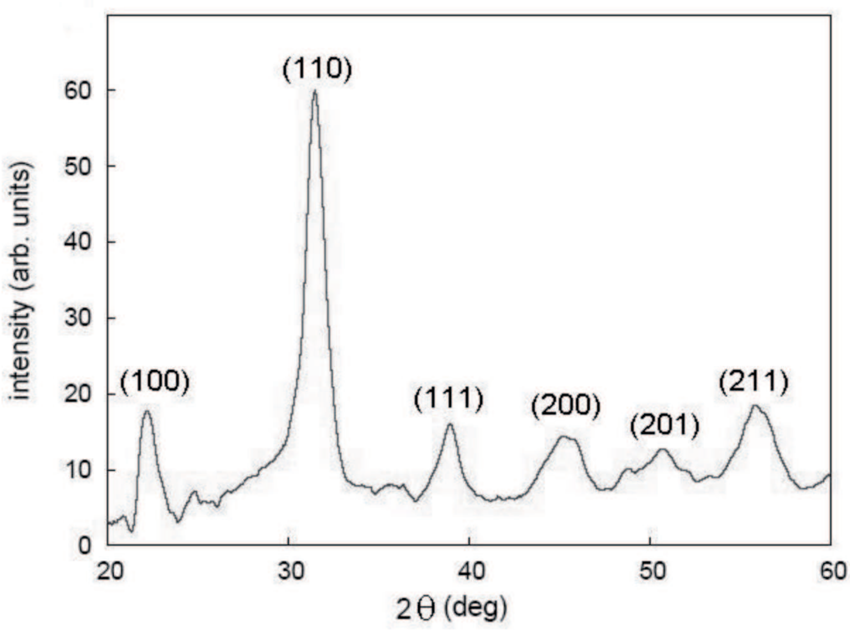

Fig. 3. X-ray diffraction pattern of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders

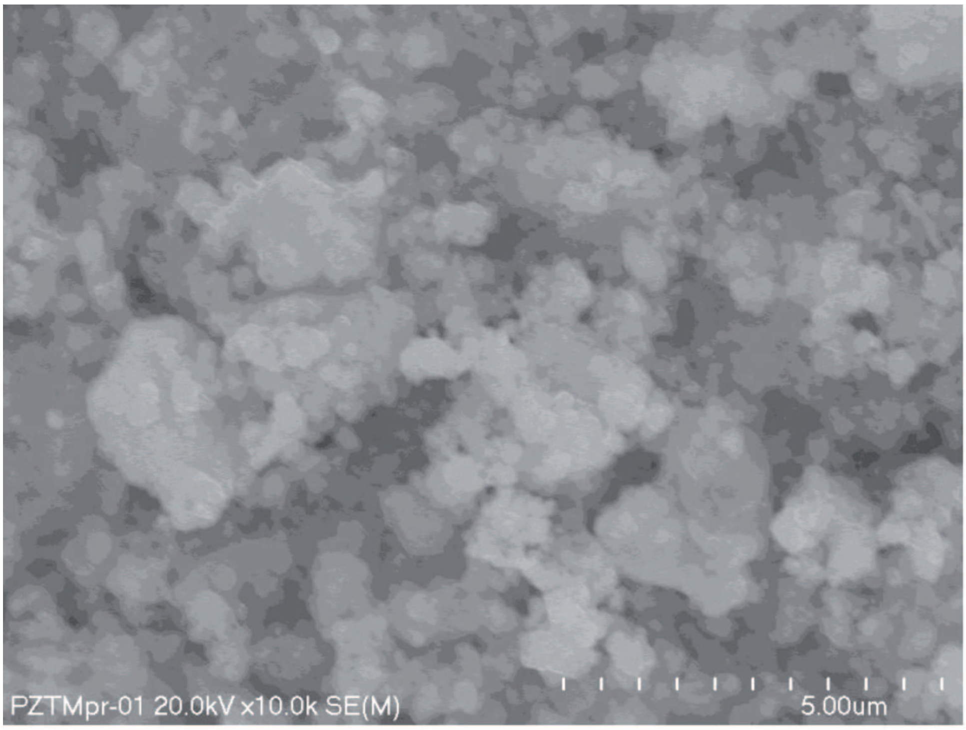

Fig. 4. SEM micrograph of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ powders

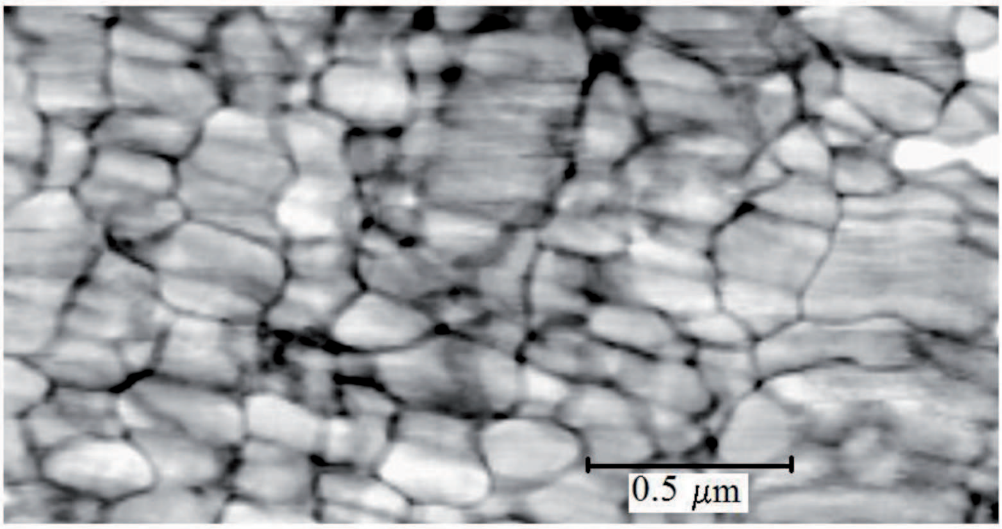

Fig. 5. Surface of $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$-PVC (PMZT-PVC) composite

Composites are classified according to their connectivity. Connectivity is defined as the number of dimensions through which the material is continuous. Composite with 0-3 connectivity consists of particles connected in zero dimensions and a three dimensionally interconnected polymer matrix. In order to obtain the 0-3 composite without the interconnectivity of the ceramic powders, a low volume fraction of ceramic Φ=0.1 and Φ=0.2 was filled in a polymer matrix [9]. Mn-doped lead zirconate titanate $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ (PMZT) powders were dispersed in a poly(vinyl chloride) (PVC) matrix. Commercial PVC (Aldrich) powder was used. Ceramic and polymer powders were mixed together in a mortar. The PMZT-PVC composites samples were fabricated by hot-pressing method. The composite surface images were obtained by AFM taping mode NT-MDT Solver P47 (Fig. 5).

The dielectric response was studied in the frequency range 10 Hz – 1 MHz and the temperature range -150÷+250°C using Alpha-A High Performance Frequency Analyzer Novocontrol GmbH. The dielectric permittivity ε' of the PMZT-PVC composites is higher in comparison with that of the polymer due to the high permittivity value of PMZT. The dielectric properties of the composites were found to be a combination of properties of pure PVC polymer and PMZT ceramic.

The value of the dielectric permittivity ε' increases with increasing content of the PMZT powder (Fig. 6) [10].

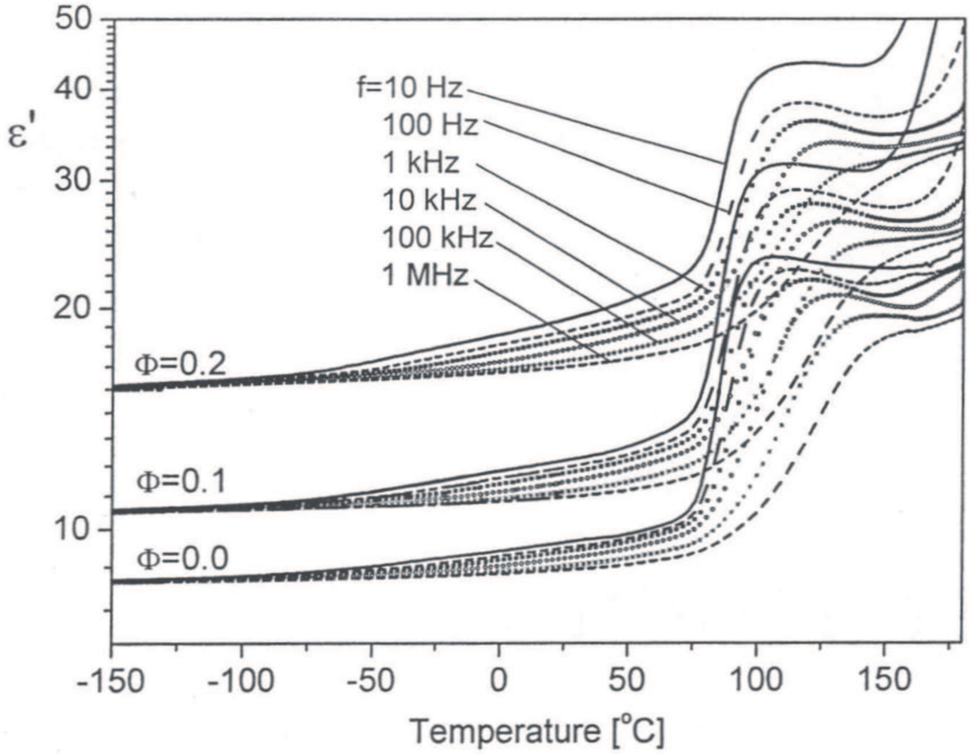

Fig. 6. Temperature dependence of dielectric permittivity ε' for different volume fraction Φ of ceramics

4. Conclusions

In this study, ceramic powders of manganese-doped lead zirconate titanate with composition $Pb(Zr_{0.3}Ti_{0.7})_{0.97}Mn_{0.03}O_3$ were successfully prepared using a sol-gel technique. Thanks to use of the sol-gel method it was possible to preserve chemical composition stoichiometry. Crystalline single-phase powders with tetragonal structure were obtained, with particles smaller than 500 nm. Powders with such properties can be successfully used to produce ceramic-polymer 0-3 composites.

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