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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THE PROPERTIES OF PBZTS CERAMICS NEAR ORTHORHOMBIC-RHOMBOHEDRAL MORPHOTROPIC PHASE BOUNDARY

WŁAŚCIWOŚCI CERAMIKI PBZTS W POBLIŻU GRANICY MORFOTROPOWEJ POMIĘDZY FAZĄ ORTOROMBOWĄ I ROMBOEDRYCZNĄ

We present the results of obtaining and investigations of $(Pb_{1-x}Ba_x)((Zr_{1-y}Ti_y)_{1-z}Sn_z)O_3$ (PBZTS) ceramics with x=const=0.2, y=const=0.08, z=0, 0.02, 0.04, 0.06 and 0.08. Ceramic samples have been obtained by conventional ceramic technology from oxides PbO, ZrO_2, TiO_2, SnO_2 and barium carbonate $BaCO_3$. The calcination of powders was performed at T_{calc}=850°C/t_{calc}=3h and next calcinated powders were pressed into discs and were sintered at T_s=1250°C/t_s=4h using free sintering (FS) method.

For such obtained samples the following investigations have been done: EDS, XRD, microstructure of fractured samples, dielectric measurements, $P-E$ hysteresis loops investigations at various temperatures and electromechanical measurements at the room temperature using optical displacement meter.

Investigated compositions are close to rhombohedral-orthorhombic morphotropic phase boundary. The results of dielectric and electromechanical properties are typical for ferroelectric materials.

Keywords: PBZT and PBZTS ceramics, phase transitions, dielectric properties

Przedstawiono wyniki badań ceramiki $(Pb_{1-x}Ba_x)((Zr_{1-y}Ti_y)_{1-z}Sn_z)O_3$ (PBZTS) dla stałych wartości parametrów x=0.2 i y=0.08 oraz dla różnych wartości z=0, 0.02, 0.04, 0.06, 0.08 Badana ceramika PBZTS została otrzymana z prostych tlenków PbO, ZrO_2, TiO_2, SnO_2 i węglanu baru $BaCO_3$. Syntezę proszków przeprowadzono metodą kalcynacji w warunkach T_{calc}=850°C/t_{calc}=3h, a następnie uformowano wypraski w formie dysków zagęszczono metodą swobodnego spiekania (FS) w warunkach T_s=1250°C/t_s=4h.

Dla otrzymanych próbek PBZT/PBZTS przeprowadzono badania EDS, XRD, badania mikrostruktury przełamów, badania przenikalności elektrycznej i tangensa kąta strat dielektrycznych, badania pętli histerezy w różnych temperaturach oraz badania elektromechaniczne w temperaturze pokojowej przy użyciu optycznego miernika przesunięcia.

Wybrane składy PBZTS znajdują się w pobliżu granicy fazowej między fazami o romboedrycznej i ortorombowej deformacji komórek elementarnych. Z badań dielektrycznych i elektromechanicznych wynika, iż jest to materiał ferroelektryczny.

1. Introduction

Lead containing perovskite-type oxides are very important for practical applications. Very good electromechanical properties of such materials are connected with the big amplitude of vibrations of the heaviest Pb-ion. [1-2]. The properties of such ceramics depend on technology of obtaining. (i.e. the methods of synthesis, purity of starting components, the degree of granulation, densification e.t.c.) [3-4]. First systematic investigations of $Pb_{1-x}Ba_x(Zr_{1-y}Ti_y)O_3$ solid solution (PBZT) were described in [5]. The phase diagram and another properties of PBZT were presented in works [5-8]. Below we describe a solid solution of $(Pb_{0,8}Ba_{0,2})(Zr_{0,92}Ti_{0,08})O_3$ with $PbSnO_3$. This composition is close to orthorhombic-rhombohedral phase boundary. There are relatively a few literature data on such solutions.

2. Samples and experiment

Obtained and investigated in this paper compositions of $(Pb_{1-x}Ba_x)((Zr_{1-y}Ti_y)_{1-z}Sn_z)O_3$ (PBZTS), brief indication PBZT 100x/100(1-y)(1-z)/100z = Ba/Zr/Sn were:

$(Pb_{0,8}Ba_{0,2})(Zr_{0,92}Ti_{0,08})O_3$ abbreviation PBZTS 20/92/0,

$(Pb_{0,8}Ba_{0,2})[(Zr_{0,92}Ti_{0,08})_{0,98}\ Sn_{0,02}]O_3$ abbreviation PBZTS 20/90/2,

$(Pb_{0,8}Ba_{0,2})[(Zr_{0,92}Ti_{0,08})_{0,96}\ Sn_{0,04}]O_3$ abbreviation PBZTS 20/88/4,

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$(Pb_{0,8}Ba_{0,2})[(Zr_{0,92}Ti_{0,08})_{0,94}\ Sn_{0,06}]O_3$ abbreviation PBZTS 20/86/6,

$(Pb_{0,8}Ba_{0,2})[(Zr_{0,92}Ti_{0,08})_{0,92}\ Sn_{0,08}]O_3$ abbreviation PBZTS 20/84/8.

Ceramic samples have been obtained by conventional ceramic technology from oxides and carbonides i.e. PbO, ZrO_2, TiO_2, SnO_2 and $BaCO_3$. Mixed and milled powders have been calcinated at T_{calc}=850°C/t_{calc}=3h and next were pressed into discs and were pressureless sintered at T_s=1250°C/ t_s=4h (free sintering – FS method).

EDS spectra have been obtained using NORAN VANTAGE. XRD measurements were performed using a Philips diffractometer and CuK_α filtered radiation with a 0.02 deg step. Microstructure of fractured samples was investigated using HITACHI S-4700SEM scanning microscope. For dielectric measurements on both surfaces of samples the silver electrodes have been put. Dielectric permittivity v.s. temperature (during heating) has been measured using QuadTech 1920 LCR-meter. $P-E$ hysteresis loops have been investigated using virtual Sawyer-Tower's bridge with HEOPS-5B6 high voltage amplifier. Electromechanical measurements were carried out using Philtec Inc. D63 optical displacement meter and above mentioned high voltage amplifier. Data were stored on a computer disc using an A/D transducer card.

3. Results and discussion

Results of EDS investigations are presented in Fig.1. EDS measurements confirmed rather good agreement between assumed and real compositions. However the deficit of Pb and the excess of Zr is observed (several percent in both cases).

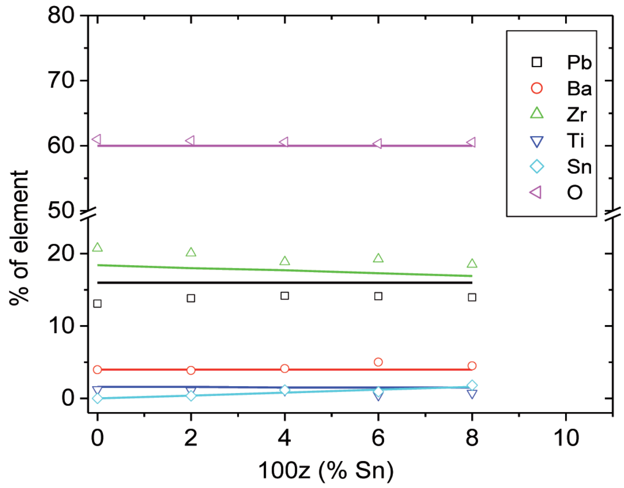

Fig. 1. Chemical composition of investigated PBZTS samples (lines – assumption, points – experimental EDS results)

Results of SEM are presented in Fig. 2. It is seen from SEM that the best shaped grains are observed in ceramics with the highest content of Sn. For PBZTS 20/86/6 we can see fracturing through the grains. It can be a result of lower strength of this material.

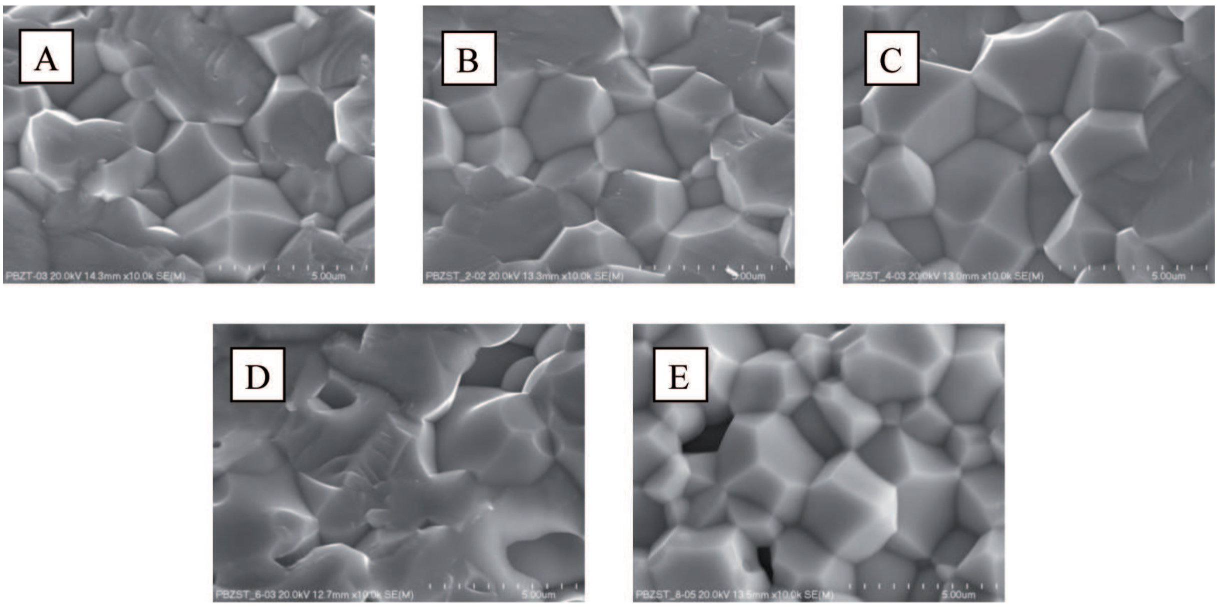

Fig. 2. Microphotograps of fractured PBZTS samples: A) PBZTS 20/92/0, B) PBZTS 20/90/2, C) PBZTS 20/88/4, D) PBZTS 20/86/6, E) PBZTS 20/84/8. All samples sintered at 1250°C/4h

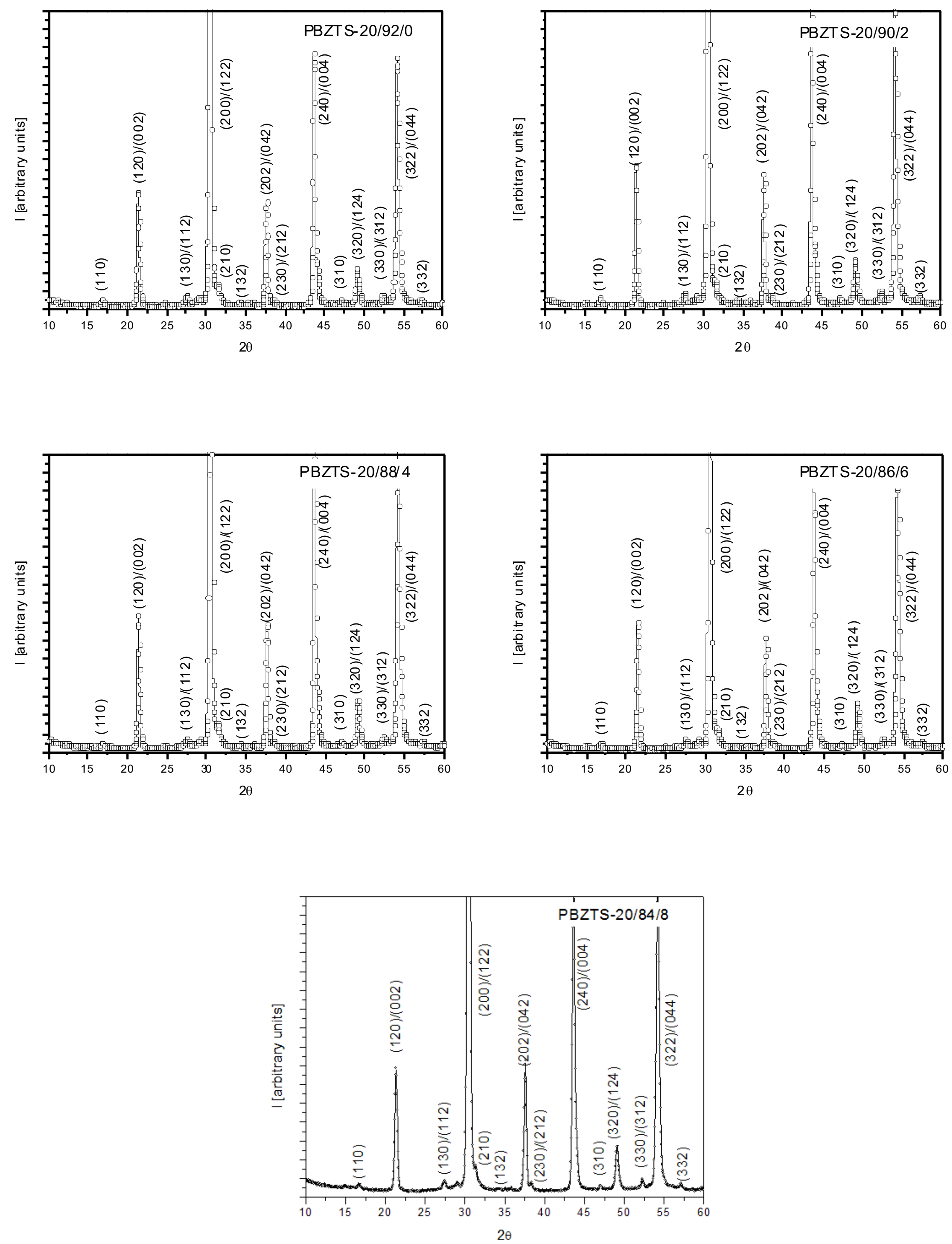

Fig. 3. XRD diffraction patterns of PBZTS ceramics powders at room temperature

Results of XRD investigations are presented in Fig.3. XRD shown the presence of the maxima related with orthorhombic phase, however this phase exists probably as a one of two or more phases.

In Fig.4 the results of measurements of dielectric permittivity are presented. In all samples the maximum of $\varepsilon(T)$ dependency is a little diffused but the dispersion of dielectric permittivity is insignificant.

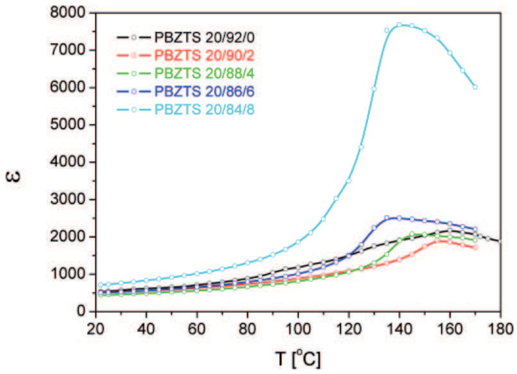

Fig. 4. Temperature dependencies of dielectric permittivity for PBZTS ceramic samples

In Fig.5 we present the dependencies $\varepsilon(T)$ and $tg\delta(T)$. It is not observed the evident decrease of the temperature of maximum of dielectric permittivity with increasing Sn-content however such tendency exists. With increasing Sn-content it is seen the decrease of dielectric losses.

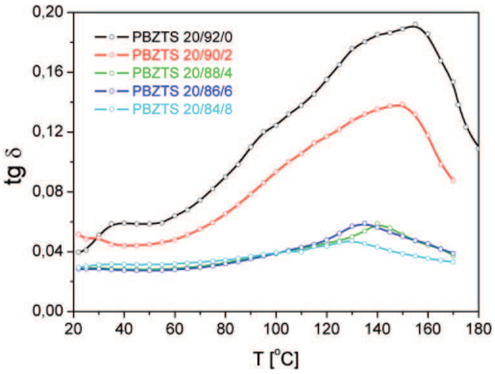

Fig. 5. Dependency $tg\delta(T)$ for investigated ceramic samples

$P-E$ hysteresis loops at various temperatures are presented in Fig.6. In spite of the fact that in XRD patterns are presented reflexes typical for orthorhombic phase the $P-E$ hysteresis loops are typical for ferroelectric materials.

$E_C(T)$ and $P_r(T)$ for PBZTS ceramics dependencies also show that with increasing Sn content the temperature of the phase transition decreases present in Fig.7.

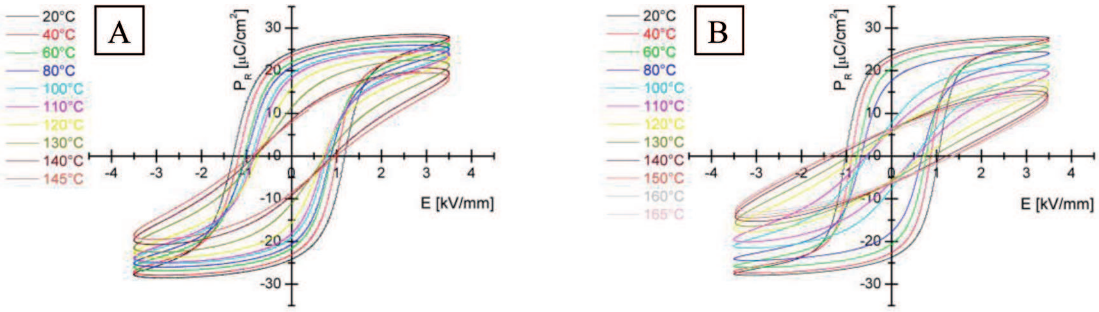

Fig. 6. $P-E$ hysteresis loops for investigated PBZTS ceramics (frequency of measurements – 1Hz), A) PBZTS 20/92/0, B) PBZTS 20/84/8

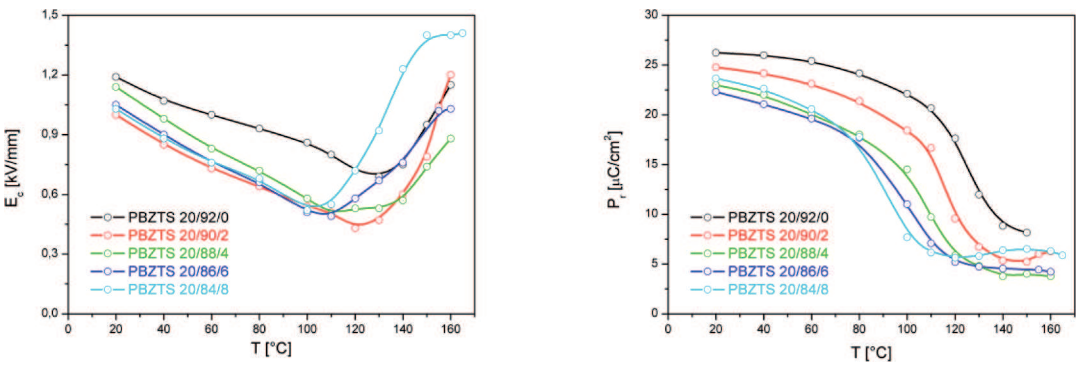

Fig. 7. Dependencies $E_c(T)$ and remanent polarization – $P_r(T)$ for PBZTS ceramics

Strain-electric field dependencies are typical for piezoelectric materials (see Fig.8.).

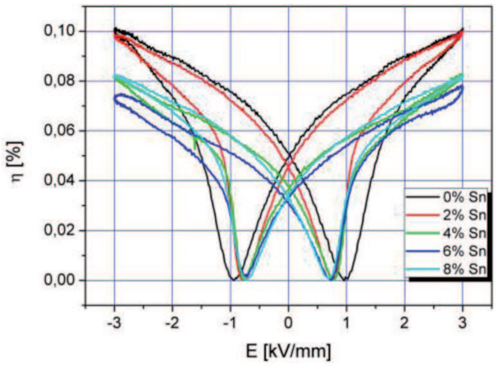

Fig. 8. Electric fields dependencies of strain for PBZTS ceramics at room temperature. Frequency of measurements – 1Hz

4. Conclusions

It is shown that it is possible to obtain PBZTS ceramics using conventional ceramic technology. Investigated samples have the composition close to the boundary between rhombohedral and orthorhombic and should be rhombohedral. However our XRD investigations shown maxima typical for orthorhombic phase. On the other hand dielectric and electromechanical properties are typical for ferroelectric materials. Is probably related to the fact, that in investigated samples the mixture of rhombohedral and orthorhmbic phases is present.

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Acknowledgements

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