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INFLUENCE OF THE Nb AND Ba DOPANDS ON THE PROPERTIES OF THE PZT TYPE CERAMICS

WPŁYW DOMIESZEK Nb i Ba NA WŁAŚCIWOŚCI CERAMIKI TYPU PZT

Investigations of an influence of an admixture of ions Ba^{2+} and Nb^{5+} on dielectric and piezoelectric properties of the $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) ceramics were conducted. The PZT type ceramics was synthesized by a conventional method, and compacted by a free sintering method. The PZT type specimens were poling by a low and high temperature method. It was found that there was a positive influence of adding 10mol%Ba and ~2mol%Nb simultaneously on a set of dielectric and piezoelectric parameters, which are important for practical applications of this PZT type ceramics.

Keywords: poling, piezoelectric and dielectric properties, PZT type ceramics

W pracy przeprowadzono badania wpływu domieszki baru Ba^{2+} i niobu Nb^{5+} na dielektryczne i piezoelektryczne właściwości ceramiki $Pb(Zr_{0.53}Ti_{0.47})O_3$(PZT). Ceramika typu PZT była syntetyzowana metodą konwencjonalną, a zagęszczana metodą swobodnego spiekania. Próbki typu PZT polaryzowano metodą niskotemperaturową i wyskotemperaturową. Wykazano, że domieszkowanie ceramiki PZT domieszką Ba w ilości 10mol%Ba oraz domieszka niobu w ilości ok. 2mol% Nb wpływa pozytywnie na jej dielektryczne i piezoelektryczne właściwości, co jest niezwykle istotne dla jej praktycznych zastosowań.

1. Introduction

The PZT type ceramics constitutes a numerous family of binary ternary quaternary and pentnary solid solutions of which the $(1\text{-}x)PbZrO_3\text{-}(x)PbTiO_3$ binary solid solution is the base. Wide isomorphism of this solution enables to substitute appropriate cations in the place of Pb, Zr and Ti [1-2]. An appropriate selection of the composition and conditions of a manufacturing technology allows obtaining the ceramics, which can be used widely in different types of piezoelectric transducers.

PZT of the $Pb(Zr_{0.53}Ti_{0.47})O_3$ composition in the phase near the morphotropy boundary (OM) in the phase diagram (Fig.1a) constitutes the base for that type of materials [3-4]. This composition is diphase structurally (the tetragonal phase (P4*mm*) and the rhombohedral phase (R3*m*)). With an increase in the $PbTiO_3$ concentration the structural phase transition R3*m* in P4*mm* (morphotropic phase transition) takes place in this solid solution. In PZT from this area in the phase diagram the domain structure is susceptible to an influence of an electric field what facilitates a poling process of the ceramics. The PZT ceramics polarized shows the maximum values of piezoelectric parameters [5]. The first phase diagram of the $(Pb_xBa_{1-x})(Zr_yTi_{1-y})O_3$ solid solution (Fig.1b) was proposed in 1959 by Ikeda [6], however in 1994 modified form of the diagram was presented [7].

The wide isomorphism of the PZT-based perovskite like ceramic materials enables to introduce dopants of the different valence into both positions A and positions B of the compound. PZT doping provides an opportunity to control electro-physical parameters of the ceramics and owing to it we can obtain materials of increased or decreased ferroelectric-hardness [8-9].

Ferroelectric and piezoelectric parameters of PZT type ceramics disappear at the Curie temperature, whereas depolarization processes commence at lower temperature ($T_{dep} < T_C$). The chemical composition (the Zr/Ti concentration ratio and admixtures), a technological process to produce the ceramics and a way of the poling process have an influence on stability of a poling state, thus on stability of equipment operating parameters, using the ceramics [5].

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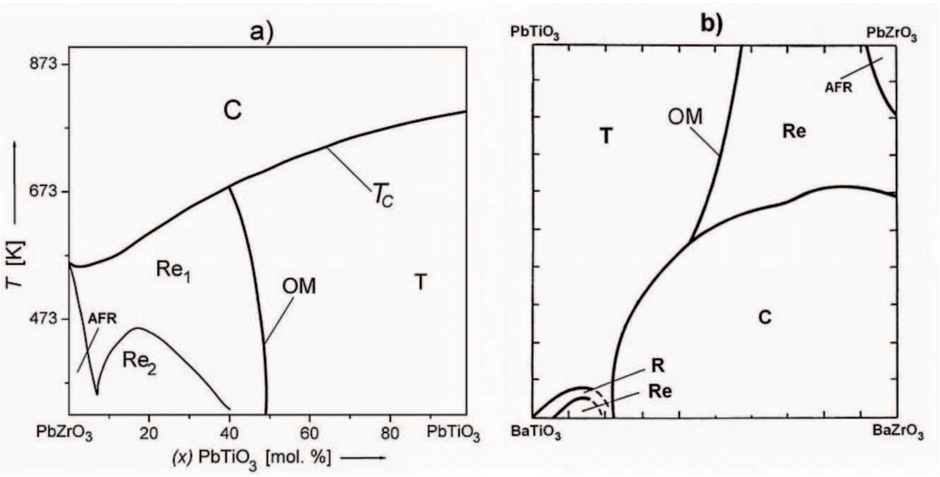

Fig. 1. A phase diagrams of the $PbTiO_3$ – $PbZrO_3$ [3] (a) and $PbTiO_3$ – $PbZrO_3$ – $BaTiO_3$ – $BaZrO_3$ [6] (b) solid solution at room temperature; where: T - tetragonal ferroelectric phase, R – rhombic ferroelectric phase, Re – rhombohedral ferroelectric phase, AFR – rhombic antiferroelectric phase, C – regular paraelectric phase

An aim of this work was to investigate an influence of admixtures of ions Ba^{2+} and ions Nb^{5+} introduced into the $Pb(Zr_{0.53}Ti_{0.47})O_3$ solid solution on values of dielectric parameters, enabling to use this ceramics in acoustic engineering.

2. Experiment

In the work four compositions of the PZT type ceramic specimens were obtained: (I) $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT), (II) $(Pb_{0.9}Ba_{0.1})(Zr_{0.53}Ti_{0.47})O_3$ (PBZT), (III) $Pb(Zr_{0.53}Ti_{0.47})_{0.98}Nb_{0.02}O_3$ (PZTN) and (IV) $(Pb_{0.9}Ba_{0.1})(Zr_{0.53}Ti_{0.47})_{0.98}Nb_{0.02}O_3$(PBZTN). The initial components to obtain particular compositions of the PZT type were simple oxides: PbO, ZrO_2, TiO_2, Nb_2O_5 and the $BaCO_3$ barium carbonate. The PbO lead oxide was added in excess. The powders underwent mixing, and then they were synthesized in the following conditions: T_{pol}=850°C for $t_{synt.}$=2h. After the synthesis the powders were mixed once more, and next they were pressed into compacts and sintered by the free sintering method in the conditions: T_s=1200°C/t_{s1}=3h.

For electric tests silver electrodes were spread on the polished surfaces of the ceramic specimens by a paste burning method.

The SEM microstructure and EDS examinations were made by a SEM scanning microscope with field emission, HITACHI S-4700, and with EDS Noran Vantage system, dielectric measurements were performed on a capacity bridge of a BR2817 type, with a heating rate of 0.5°/min, for a cycle of cooling at frequency of the measurement field ν=1kHz. The PZT type specimens were poled by applying a dc electric field E_{pol}=40kV/cm for t_{pol}=40min at temperature T_{pol}=140°C in the silicon oil (the low temperature method), and in conditions E_{pol}=9kV/cm/t_{pol}=30min/T_{pol}=400°C (the high temperature method) using a Matsusada Precision Inc. HEOPS-5B6 high voltage supply. Measurements of dielectric and piezoelectric parameters were conducted after 15 days from poling for the aging process to be completed. The piezoelectric parameters (k_p, d_{31}, Q_m,S_{11}^E, v_R) were determined by a resonance/antiresonance method [10].

3. Results and discussion

The SEM micro-structural images of fractures of the PZT ceramic specimens are presented in Fig.2. The $Pb(Zr_{0.53}Ti_{0.47})O_3$ non-doped ceramics has a strongly compacted microstructure, with the fracture through the grains, without clearly visible intergranular boundaries. Doping PZT with the barium and the niobium (PBZT, PZTN and PBZTN) improves the ceramic microstructure. The barium added to PZT increases the grain size (the fracture takes place mainly through the grain), while doping with the niobium decreases the average size of the ceramic grains (the fracture takes place mainly along the grain boundary). Simultaneous doping PZT with the barium and the niobium yields intermediate sizes of the ceramic grains (Fig.2d).

Composition homogeneity tests by the EDS point and surface method (Fig.3) confirmed the assumed qualitative and composition of the specimens made and presence of the initial components of the ceramic specimens. The EDS examination results are comparable to proportions of the initial components resulting from stoichiometry (the values in the brackets – Table 1).

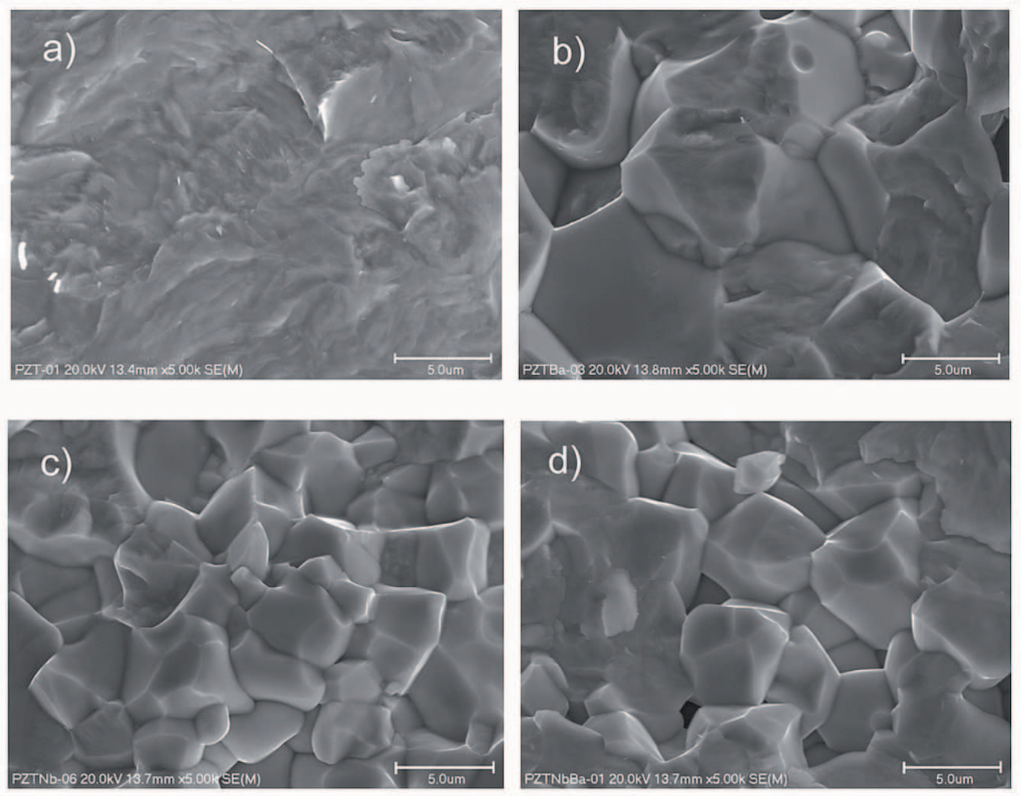

Fig. 2. An influence of dopants on the PZT type ceramics microstructure: a) PZT, b) PBZT, c) PZTN, d PBZTN

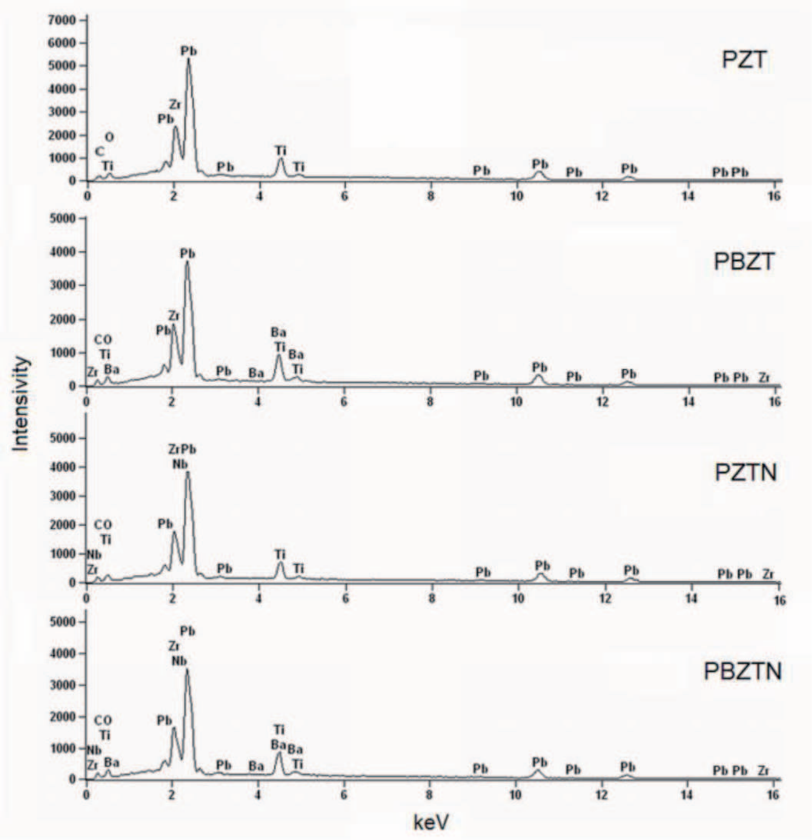

Fig. 3. EDS of the PZT type ceramics

TABLE 1
Specification of the percentage amounts of the initial components of particular compounds of the PZT type obtained from the EDS examinations

	PZT	PBZT	PZTN	PBZTN
PbO [weight %]	68.32 (68.45)	62.48 (62.96)	67.90 (68.14)	62.17 (62.66)
BaO [weight %]	–	4.59 (4.81)	–	4.84 (4.78)
TiO_2[weight %]	12.05 (11.52)	12.19 (11.76)	11.62 (10.90)	11.67 (11.15)
ZrO_2[weight %]	19.63 (20.03)	20.74 (20.47)	18.51 (18.96)	19.32 (19.38)
Nb_2O_5[weight %]	–	–	1.97 (2.00)	2.00 (2.03)

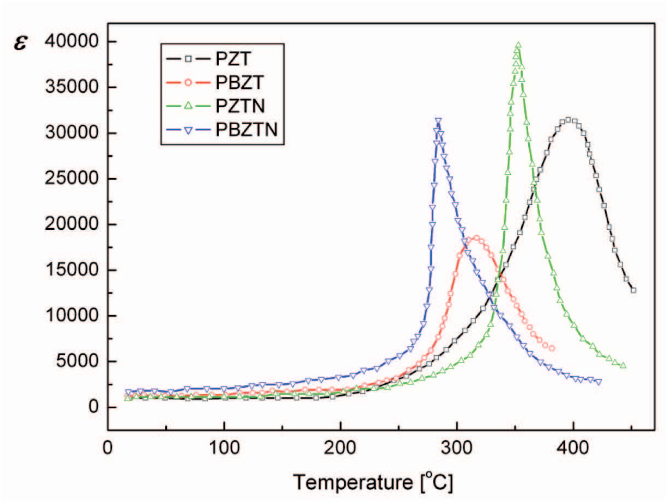

Fig. 4. Temperature relationships of electric permittivity for the PZT type ceramics (a heating cycle)

The characteristic behaviour of the $\varepsilon(T)$ courses, typical for the ferroelectrics, is observed on the temperature relationships of electric permittivity of the PZT type ceramic compositions obtained. For the non-doped PZT and PBZT compositions the phase transition from the ferroelectric to paraelectric phase takes place in a wide range of temperatures (the diffused phase transition). The PZTN and PBZTN are characterized by a sharp phase transition. The non-doped PZT ceramics has the highest temperature of the phase transition, and adding the Ba and Nb dopants results in a considerable displacement of the Curie temperature towards lower temperatures (Table 2). The barium dopant added to PZT decreases the maximum value of electric permittivity (ε_m) at T_m, whereas the niobium dopant gives an increase in ε_m. Simultaneous doping PZT with the niobium and barium dopant lowers the phase transition temperature, and the values of the electric permittivity are intermediate. As for the PZT composition doped with the niobium (PZTN), the ferroelectric phase transition in PBZTN has a sharp character. In the work [11], the analysis of influence the Nb and Sr admixture on the properties on the $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics was presented. This material shows equally high values ε_m and high temperature of the phase transition T_m, in comparison with PZT ceramics with Nb and Ba admixture.

The temperature relationships of the tangent of the angle of dielectric losses tan$\delta(T)$ for the PZT type ceramics for the measurement field frequency ν=1.0kHz are presented in Fig.5. The typical behaviour of the ferroelectrics in the tan$\delta(T)$ diagrams is presence of the characteristic maximum of the tanδ value just before the phase transition. It is clearly visible for the doped compositions of the PZT type ceramics. Doping PZT with the barium and the niobium lowers dielectric losses. The best effects to minimize the dielectric losses are given by simultaneous doping PZT with the niobium and the barium in the optimum amounts (Table 2).

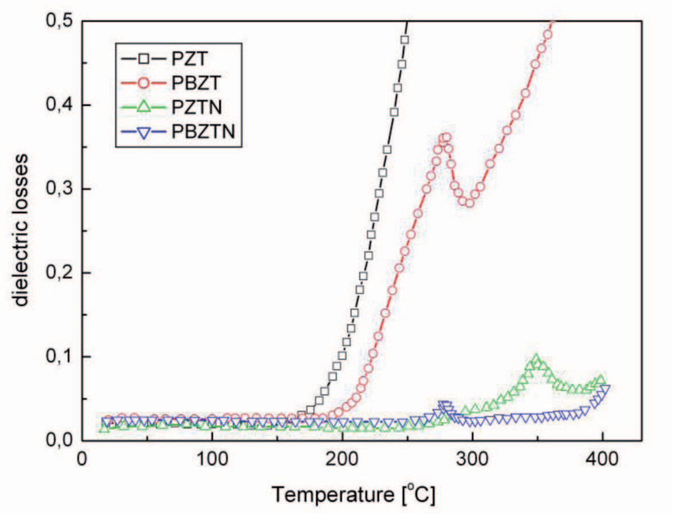

Fig. 5. Temperature relationships of the tangent of the dielectric loss angle for the PZT type ceramics (a heating cycle)

The 10mol%Ba^{2+} dopant makes the PZT ceramics harder dielectrically (lower ε and tanδ values, a bigger coercion field E_C and greater mechanical quality factor and a slight increase in the piezoelectric parameter values). This ceramics is less susceptible to depolarization than the non-doped PZT ceramics, what increases stability of working parameters of such a piezo-element. The barium ion (R_{Ba}=0.144nm) occupies the lead position (R_{Pb}=0.126nm) in PZT. As an iso-valence ion, Ba^{2+} does not make a change of through electric conductivity, but only slight changes of other parameters. The conducted tests showed that 10mol% dopants of the barium added to PZT are the optimum amount.

TABLE 2

Influence of Ba^{2+} and Nb^{5+} admixtures on values of the piezoelectric and dielectric parameters of the PZT type ceramics

Ceramics	PZT	PBZT	PZTN	PBZTN
$\rho \times 10^3$[g/cm^3]	7.53	7.58	7.56	7.58
T_m [°C]	397	316	351	285
ε at T_m	31370	18420	39440	31370
tanδ [%] at T_r	0.85	0.71	1.69	2.19
$\rho_v \times 10^{-12}$[Ωm]	0.32	0.33	0.29	0.39
$\varepsilon_{33}^{\sigma}/\varepsilon_0$ at T_r	1263	1180	1420	1380
P_r [C/m^2]	0.27	0.25	0.30	0.50
E_C [kV/cm]	1.40	1.48	1.20	1.32
k_p	0.41	0.35	0.50	0.58
k_{31}	0.31	0.30	0.29	0.28
$d_{31}\times10^{-12}$ [C/N]	-68	-62	-132	-135
$d_{33}\times10^{-12}$ [C/N]	~ 218	~ 213	~ 340	~ 380
Q_m	700	~ 800	~ 500	~ 185
V_R [m/s]	2534	~ 2610	~ 2530	2820
S_{11}^{E} x10^{12}[m^2/N]	10.5	10.8	11.2	9.74

In case of the doped Nb^{5+} cations, because of a small ionic radius (R_{Nb}=0.069nm), they can occupy a position of Ti^{4+} (R_{Ti}=0.068nm) or Zr^{4+} (R_{Zr}=0.079nm) in the base PZT. Substitution of ions of higher valence results in lead vacancy formation (V_{Pb}) to neutralize a specimen electrically [12]. Since the electric conductivity of the pure PZT is a hole type (p-type), the surplus of electrons compensates holes and electric conductivity decreases (ρ_v- increases). As a result it lowers anchoring of the domains by free charges and it facilitates poling and re-poling process. The soft Nb^{5+} dopant causes the following changes of the PZT parameters: there is an increase in values of electric permittivity ε, tanδ, electromechanical coupling k_p, a piezoelectric modulus d_{ij}, flexibility S_{ij}, resistivity ρ_v and internal friction Q_m^{-1}, whereas values of a coercion field E_C and a mechanical quality factor Q_m decrease (PZTN in table 2). 2.0 mol.% Nb^{5+} dopant is the optimum amount resulting in lowering hardness of the $Pb(Zr_{0.53}Ti_{0.47})O_3$ ceramics. Analysis of influence of the Ba and Nb admixture on the properties of PBZT type ceramics has been presented widely in work [13].

4. Conclusions

The $Pb(Zr_{0.53}Ti_{0.47})O_3$ based ceramics was obtained in the work and it was doped with barium and niobium. It has been found that the optimum amount of the barium dopant in PZT, which makes it ferro-electrically hard, is 10.0mol% Ba^{2+}. In the case of doping PZT with niobium the optimum amount, which lowers ferroelectric hardness of the ceramics, is 2.0 mol.% Nb^{5+}.

Simultaneous doping PZT with the both Ba^{2+} and Nb^{5+} admixtures improves a set of the piezoelectric parameters of the ceramics. The PBZTN ceramics has the highest density and maintains high values of k_p, d_{31} i d_{33} at slight changes of other parameters. This ceramics can be poling easily and it ages insignificantly. The polarized PBZTN ceramics shows high stability of resonance frequency $\Delta f_r/f_r$ <0.2% in the temperature range (0÷85°C). Poling the PNZTN ceramics by the high temperature method yields better stability of its piezoelectric parameters comparing to the low temperature poling method (Fig.6).

The PZT type ceramics obtained meets the requirements for applications e.g. in bio-morphic piezoelectric transducers and medium power ignition transducers.

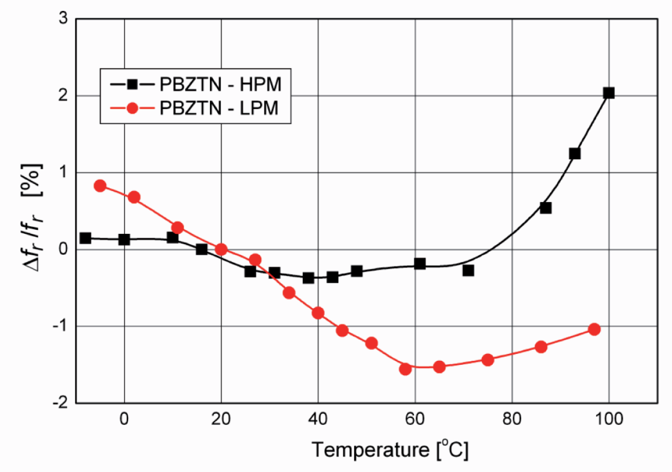

Fig. 6. An influence of the poling method on stability of the resonance frequency $\Delta f_r/f_r$ of the PBZTN ceramics. HPM – poling by the high temperature method, LPM – poling by the low temperature method

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