

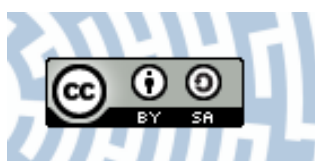


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**Title:** Multicomponent ceramic materials on the basis of PZT for the production of piezoelectric resonators

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## MULTICOMPONENT CERAMIC MATERIALS ON THE BASIS OF PZT FOR THE PRODUCTION OF PIEZOELECTRIC RESONATORS

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Investigations on the influence of the  $\text{PbTiO}_3$  content on the crystalline and domain structure of PZT-based four-component solid solutions have been performed. It has been shown that there is a close relation between the structure and temperature stability of the resonance frequency ( $f_r$ ) of the fabricated piezoceramic transducers. Better and more stable results have been obtained by doping and modifying the basic chemical composition obtaining  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ .

The compositions with minimal  $\Delta f_r/f_r$ , within the temperature range  $T = 213\text{--}358\text{ K}$  (in relation to room temperature  $T_r = 293\text{ K}$ ), exhibited (i) the smallest internal friction ( $Q_m^{-1}$ ), (ii) the highest mechanical quality ( $Q_m$ ), (iii) high values of spontaneous deformation of the elementary cell ( $\delta_T$  and  $\delta_{\text{Re}}$ ), (iv) the complex *a-c*-domain structure in the tetragonal phase (T) and the simple domain structure in the rhombohedral phase (Re).

The practical result of the present work was the fabrication of piezoceramic electric band filters exhibiting  $\Delta f_r/f_r < 0.2\%$  and a high mechanical quality factor ( $Q_m = 3225$ ).

**Key words:** PZT, piezoelectric transducers, resonance frequency, thermal stability.

### 1. Introduction

Piezoceramic transducers exhibiting high thermal stability of the resonance frequency are necessary in many fields of electro-acoustics. The stability of  $f_r$  is of special importance in the case of band filters and other selective piezoelectronic systems. Apart from the high stability of  $f_r$ , the following parameters of piezoelectric materials are

very important: the electromechanical coupling coefficient  $k_p$ , which determines the pass band width as well as the mechanical quality factor  $Q_m$  and the sharpness of the amplitude-frequency characteristics within the pass band.

The basic material used in the construction of piezoceramic band filters is the  $(x)\text{PbTiO}_3-(1-x)\text{PbZrO}_3$  solid solution known as PZT. Attempts have been made to increase the thermal stability of  $f_r$ ,  $k_p$ , and  $Q_m$  of piezoceramic transducers by different methods. Among other methods, one can mention irradiation, thermocycling, quenching, annealing, and selection of poling conditions [1–3]. The basic disadvantage of the above mentioned methods is their inefficiency and the instability of the changes produced.

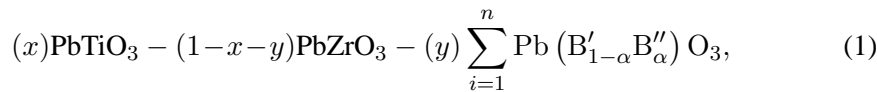
Better and more stable results have been obtained by doping and modifying the basic chemical composition obtaining  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ , e.g. [4–9]. It has been stated that the stability of  $f_r$  increases, among other things, with increasing the doping of PZT by rare earth elements,  $\text{PbNbO}_2$ , and  $\text{MgF}_2$ . It also increases as a result of (i) the partial isovalent substitution of  $\text{Pb}^{2+}$  by  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , or  $\text{Ba}^{2+}$  cations, (ii) the introduction of the pyrochlore phase peroxide and  $\text{MnO}_2$  into the PZT perovskite phase, and (iii) sintering under oxygen atmosphere. It is worthy of noting, however, that too little attention has been paid so far to the physical mechanisms which condition the obtained increase in the thermal stability of the operation of piezoceramic resonators.

A detailed analysis of the literature as well as the results of the research work carried by the authors [10–12] leads to the general conclusion that thermal stability of  $f_r$ ,  $k_p$ , and  $Q_m$  increases with increasing stability of the domain structure of the poled piezoceramics.

The goal of the present paper was to obtain PZT-based piezoceramic resonators having high values of the parameters  $k_p$ , and  $Q_m$  and, at the same time, exhibiting high thermal stability of the resonance frequency  $f_r$ . With this end in view the mutual relations between thermal stability of the domain structure on the one hand, and the chemical composition, crystalline structure and microstructure of the piezoceramics on the other hand, have been determined.

## 2. Experimental

A comprehensive research on the thermal stability of the resonance frequency  $f_r$  of piezoceramic transducers has been carried out on the basis of four-component PZT-type solid solutions with the general chemical composition:



where:

$\text{B}'$  –  $\text{Nb}^{5+}$ ,  $\text{Sb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$ ;

$\text{B}''$  –  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Sb}^{3+}$  and other cations;

- $n - 1, 2$ ;  
 $x$  –  $\text{PbTiO}_3$  content (mole fraction);  
 $y$  – content of dope  $\text{Pb}(\text{B}'_{1-\alpha}\text{B}''_{\alpha})\text{O}_3 + \text{Pb}(\text{B}'''_{1-\beta}\text{B}''''_{\beta})\text{O}_3$ ;  $y = 0.01\text{--}0.05$   
 mole fraction.

Ceramic powders of the suitable chemical composition (Eq. (1)) have been synthesized by the conventional mixed oxide method (solid phase reaction) or by the sol-gel method, e.g., [13]. The derived powders underwent consolidation and sintering to fabricate PZT-type ceramics. The hot pressing method was used (UGP-20 type hot pressing system) and the following technological parameters were applied: uniaxial pressing, constant pressure during sintering  $p_s = 20$  MPa, time of sintering  $t_s = 40$  min, air atmosphere, temperature of sintering  $T_s = 1273\text{--}1473$  K (depending on chemical composition of the solid solution and the method of the ceramic powder synthesis).

To evoke piezoelectric activity in the fabricated ceramic samples, electrodes were first deposited on them and then the samples underwent a low-temperature poling under a constant external electric field ( $E_{\text{pol}} = 35\text{--}45$  kV/cm;  $T_{\text{pol}} = 413\text{--}433$  K). After  $t_{\text{pol}} = 20$  min the samples were cooled down to  $T = 363\text{--}353$  K during  $t = 25\text{--}30$  min under the electric field; finally the electric field was turned off and the samples were left to cool to room temperature without further control.

Piezoelectric parameters (i.e. the electromechanical coupling coefficient for radial oscillations in disk-shaped samples  $k_p$ , mechanical quality factor  $Q_m$ , internal friction  $Q_m^{-1}$ ) of the samples were measured by the dynamical resonance-antiresonance method. The bridge technique at the frequency of  $\nu = 1$  kHz was employed to quantify the dielectric parameters (i.e. the specific dielectric permittivity of poled samples  $\varepsilon_{33}^{\sigma}/\varepsilon_o$ , where  $\varepsilon_{33}^{\sigma}$  is the absolute dielectric permittivity of the unclamped ( $\sigma = 0$ ) poled sample and  $\varepsilon_o$  is the dielectric permittivity of vacuum, and the dielectric loss tangent  $\tan \delta$ ) of the ceramic samples. The remanent polarization ( $P_r$ ) as well as the domain-orientational polarization ( $P_R$ ) were measured by the Sawyer–Tower method. The domain structure was investigated by TEM (carbon-platinum replica method, TESLA B-613 electron microscope).

The Curie temperature ( $T_c$ ) was determined on the basis of the dependence of the specific dielectric permittivity  $\varepsilon$  of the non-poled samples on temperature  $T$  at  $T = T_m = T_c$ , where  $T_m$  – temperature at which the function  $\varepsilon(T)$  reaches its maximum.

The relative change in the resonance frequency ( $\Delta f_r/f_r$ ) within the temperature range  $T = 213\text{--}358$  K was measured in relation to room temperature  $T_r = 293$  K.

Investigations of the ceramic structure were carried out with the DRON-2.0-type X-ray diffractometer ( $\text{CuK}_{\alpha}$  radiation) equipped with a high-temperature attachment. The investigations included: (i) the phase analysis, (ii) determination of the elementary cell parameters, (iii) determination of the spontaneous tetragonal ( $\delta_T$ ) or rhombohedral ( $\delta_{Re}$ ) deformation parameters (at  $T < T_c$ ) of the cubic elementary cell (at  $T > T_c$ ), and (iv) determination of  $\eta$ , i.e. the degree of reorientations of domains during the poling process other than  $180^\circ$  and the polarization switching. It should be noted that in the last case an attachment was used, which made it possible to apply an external electric field to the sample like in the X-ray investigations.

### 3. Results and discussion

#### 3.1. Selection of the composition of the base solid solution

By means of selection of the  $\text{PbTiO}_3$  content ( $x$ ) in the PZT-type solid solutions (Fig. 1), the ferroelectric ceramic materials exhibiting a rhombohedral (Re) structure ( $0.20 < x < (0.43 - 0.46)$ ) or a tetragonal (T) one ( $x > (0.46 - 0.48)$ ) have been fabricated. However, for  $x$  ranging from 0.43 to 0.48, the ceramic material obtained is a two-phase system (Re+T). The composition for which two phases are present is considered to be the morphotropic region MR.

It is known that the  $\text{PbTiO}_3$  content has a strong influence on the Curie point of ceramics (e.g. for  $x = 32.5$  mole%  $T_c = 563$  K, while for  $x = 51.0$  mole%  $T_c = 616$  K) as well as on the values of its basic electrophysical parameters.

**The mole fraction range:  $0.25 \leq x \leq 0.6$ .** According to the aim of the present research, first of all investigations of the dependence of the thermal stability of the resonance frequency on the  $\text{PbTiO}_3$  content ( $x$ ) for the all obtained four-component PZT-based ceramic solid solutions were carried out. It was found that irrespective of the modifiers  $\left(\sum_{i=1}^2 \text{Pb}(B'_{1-\alpha}B''_{\alpha})\text{O}_3\right)$  introduced into the basic composition  $(\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3)$ , the relative change of the resonance frequency  $(\Delta f_r/f_r)$  reached its minimum for compositions of both tetragonal and rhombohedral phases situated closely to the morphotropic region. However, compositions of MR always exhibited the smallest thermal stability of  $f_r$ , i.e. they showed a maximum of  $\Delta f_r/f_r = f(x)$ .

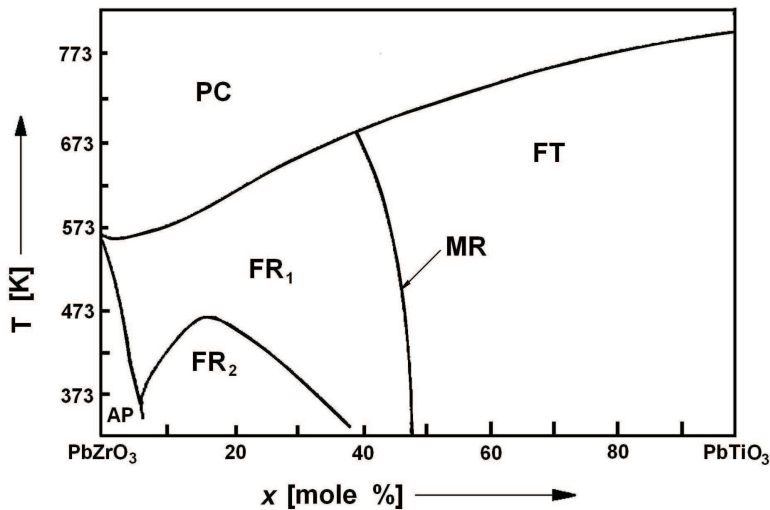


Fig. 1. Phase diagram of the solid solution  $(x)\text{PbTiO}_3 - (1-x)\text{PbZrO}_3$ : PC – paraelectric cubic phase ( $Pm3m$ ); FT – ferroelectric tetragonal phase ( $P4mm$ );  $\text{FR}_1$  – first (high temperature) ferroelectric rhombohedral phase ( $R3m$ );  $\text{FR}_2$  – second (low temperature) ferroelectric rhombohedral phase ( $R3c$ ); MR – morphotropic boundary ( $R3m+P4mm$ ); AP – antiferroelectric orthorhombic phase ( $Pba2$ ).

To explain the physical mechanism of the observed dependence of  $\Delta f_r/f_r = f(x)$ , investigations were conducted. They were aimed at ascertaining the relations between the content ( $x$ ) of  $\text{PbTiO}_3$ , the structural parameters ( $\delta_T, \delta_{\text{Re}}, \eta$ ), the electro-physical parameters ( $Q_m, Q_m^{-1}$ ) and the domain structure. The results of those investigation (especially changes of the internal friction  $Q_m^{-1} = f(x)$ ) indicate that the thermal stability of  $f_r$  is conditioned first of all by the properties of the domain structure, i.e. by the type, number and mobility of the domain walls different from  $180^\circ$ .

An experimental confirmation of this statement is given in Fig. 2, where the relationships between the thermal stability of the resonance frequency ( $f_r$ ), the internal friction ( $Q_m^{-1}$ , where  $Q_m$  – mechanical quality factor) and structural parameters ( $\eta, \delta_T, \delta_{\text{Re}}$ ) are shown.

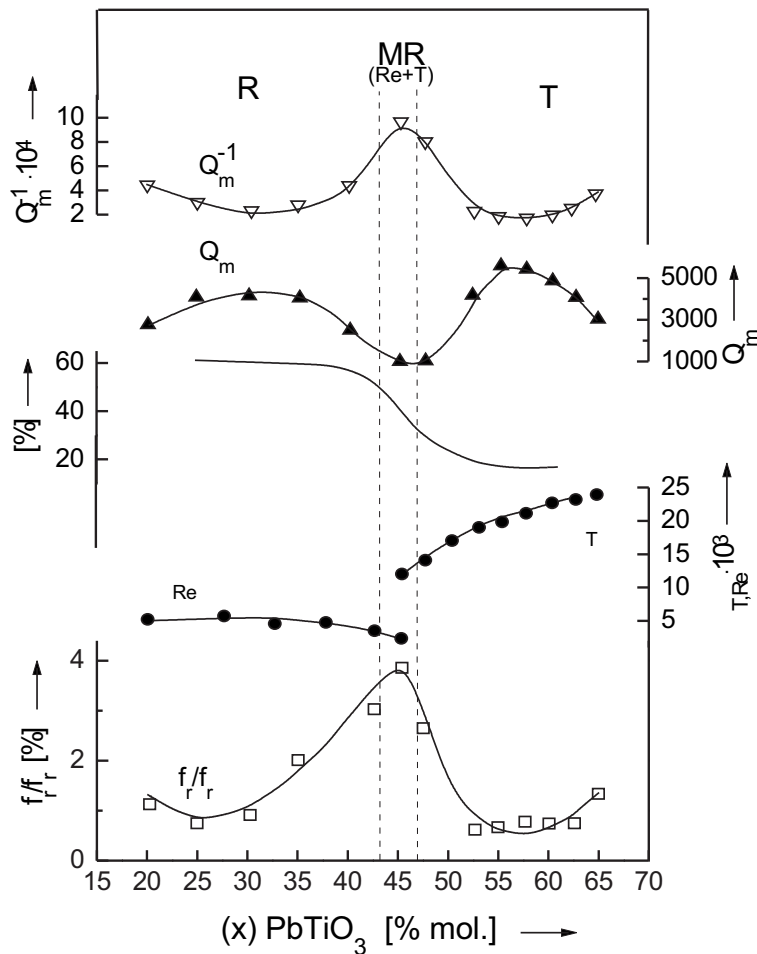


Fig. 2. Piezoelectric ( $Q_m, Q_m^{-1}, \Delta f_r/f_r$ ) and structural ( $\delta_{T, \text{Re}}, \eta$ ) parameters of the four-component piezoceramic solid solutions  $(x)\text{PbTiO}_3 - (1-x-y)\text{PbZrO}_3 - (y)[\text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbW}_{1/2}\text{Mg}_{1/2}\text{O}_3]$  as a function of  $(x)\text{PbTiO}_3$  concentration.

The inverse of the mechanical quality factor  $Q_m^{-1}$  or, in other words, the internal friction (mechanical losses) describes the ability of piezoceramics to dissipate energy of mechanical oscillations irreversibly. In the case of ferroelectrics the internal friction is conditioned to a large degree by the domain reorientation process. A component of internal friction connected with the inelastic movement of the domain walls is the parameter most sensitive to changes of the domain structure.

One can also relate the dependence of the mechanical quality factor  $Q_m$  on the  $\text{PbTiO}_3$  content ( $x$ ) to the change of the domain structure. The mechanical quality factor  $Q_m$  increases with the decrease in the domain wall movement or, in other words, with the increase in  $\delta$  and with the decrease in the domain wall number or increase in  $\eta$ .

The structural parameters  $\delta$  and  $\eta$  are commonly accepted characteristics of the domain structure. The spontaneous deformation parameter ( $\delta$ ) may be connected with mobility of the domain walls, whereas the degree of reorientation other than  $180^\circ$  of the domains during poling or polarization switching ( $\eta$ ) may be connected with the number of the domain walls.

The smaller the mobility and the number of the domain walls, the smaller the change of the position of the domain boundaries, caused by influence of temperature, leading to a change of the resonance frequency ( $f_r$ ). These two factors (i.e. the mobility and number of the domain walls) can explain the dependence of  $\Delta f_r/f_r$  on the  $\text{PbTiO}_3$  content observed in the solid solution under investigation (Fig. 2).

As we move away on the phase diagram from MR towards compositions with the tetragonal structure, the mobility of the domain walls decreases due to the increasing  $\delta$ . Such a stable domain structure determines ferroelectric hardness of piezoceramics, which, among other things, manifests itself in the increasing  $Q_m$  and decreasing  $\Delta f_r/f_r$  and thus in the increasing stability of  $f_r$  (Fig. 2).

An increase in the number of the domain walls (indicated by the decreasing parameter  $\eta$ ) has a much smaller effect on the stability of  $f_r$  and  $Q_m$  of PZT-based piezoceramics than an increase in the  $\delta$  parameter.

Decreasing of the  $\text{PbTiO}_3$  content ( $x$ ) below the value of the morphotropic region causes the appearance of another ferroelectric phase of rhombohedral symmetry (Re). An increase in the stability of the resonance frequency  $f_r$  (i.e. a decrease in  $\Delta f_r/f_r$ ) and an increase in the mechanical quality factor  $Q_m$  (i.e. a decrease in the internal friction  $Q_m^{-1}$ ) is connected with such a phase transition. The changes are conditioned by the decreasing number of the domain walls (i.e. an increase in the  $\eta$  parameter), however; they are smaller in comparison with the changes caused by the transition from MR to the tetragonal symmetry phase.

Within the range of PZT compositions from the two-phase (Re+T) morphotropic region the value of  $\Delta f_r/f_r$  reaches its maximum (the smallest stability of  $f_r$ ), however,  $Q_m$  reaches its minimum. Parameters  $\delta$  and  $\eta$  also exhibit values halfway between the values they possess in the T and Re phase. Such a state is characterized by a large number of domain walls (i.e. small  $\eta$ ) and a high mobility of the domain walls (i.e. small  $\delta$ ). Moreover, a movement of the Re/T interfacial boundaries, caused by a temper-



ature change, can make a certain contribution to the thermal instability of the resonance frequency within the two-phase morphotropic region.

The results mentioned above show indirectly that there is a close relation between the properties of PZT-based piezoceramics and the domain structure. The direct investigations of the domain structure confirm such a correlation experimentally. The samples under investigation exhibited a rhombohedral phase (Fig. 3), a tetragonal phase (Fig. 4), as well as a two-phase mixture (Re+T), which is typical of the morphotropic region (Fig. 5) before (a) and after (b) poling in an external electric field. Investigations of the surfaces of samples exhibiting tetragonal or rhombohedral symmetry and of a decreasing  $\text{PbTiO}_3$  content ( $x$ ) show the influence of the  $\text{PbTiO}_3$  content on the domain structure of the poled PZT-type ceramic samples. It has been found that the samples which possess a tetragonal symmetry exhibit a complex domain structure with a large

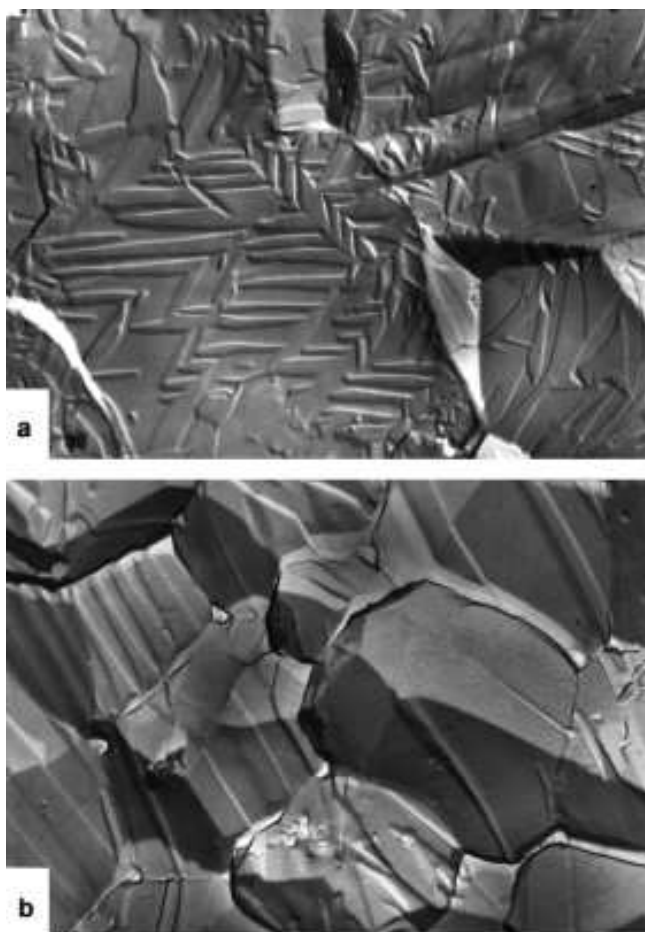


Fig. 3. The domain-twinning structure of the PZT-type ceramics at the rhombohedral phase (Re) revealed by chemical etching of the surface fracture: a) non-poled sample; b) poled sample; mag. 10000 $\times$ ; C/Pt replicas.



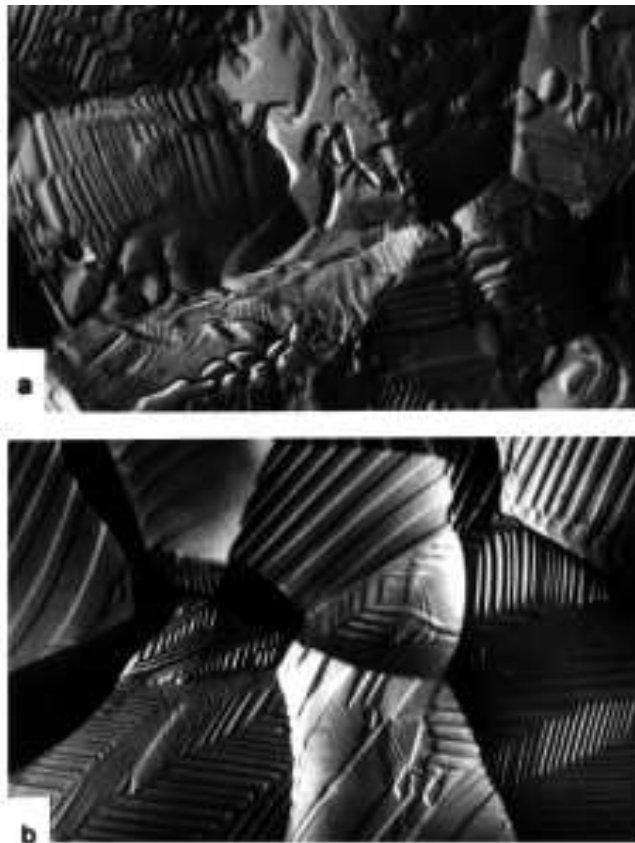


Fig. 4. The domain-twinning structure of the PZT-type ceramics exhibiting a tetragonal phase (T) revealed by chemical etching of the surface fracture: a) non-poled sample; b) poled sample; mag. 10000 $\times$ ; C/Pt replicas.

number of domain walls. This complex domain structure becomes simplified and is getting more ordered as the  $\text{PbTiO}_3$  content ( $x$ ) decreases and approaches the morphotropic region. When the rhombohedral symmetry is reached, the image of the domain structure is changed markedly. The number of the domain walls decreases and some of the crystallites approach the single-domain state.

The domain structure of the samples before poling (Fig. 3a, 4a, 5a) differs markedly from that of the samples after poling (Fig. 3b, 4b, 5b). The poling process has a strongest influence on the domain structure in the case of the samples from the morphotropic region (Fig. 5), whereas in the case of the samples exhibiting the tetragonal symmetry (Fig. 3) the influence of poling is weak.

A good correlation between the increase in the parameter  $\eta$ , the decrease in the number of domain walls, and the increase of thermal stability of the resonance frequency is observed for samples exhibiting rhombohedral symmetry. It has been found, however, that the thermal stability of  $f_r$  for PZT samples with compositions exhibiting

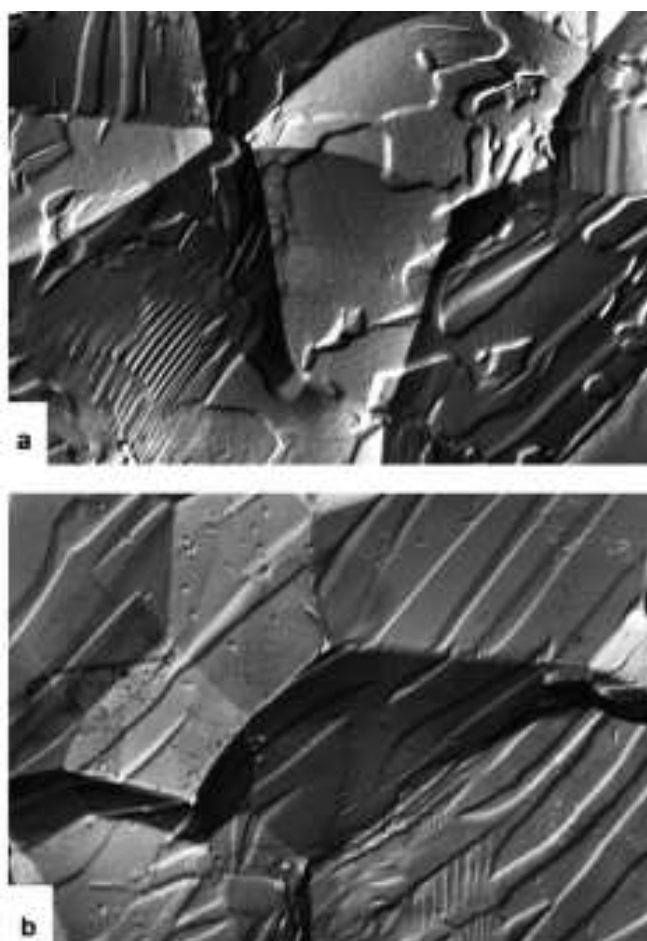


Fig. 5. Domain-twinning structure of PZT-type ceramics of compositions ranging from the morphotropic region (MR) (Re-phase with small amount of the T-phase) revealed by chemical etching of the surface fracture: a) non-poled sample; b) poled sample; mag. 10000 $\times$ ; C/Pt replicas.

the tetragonal structure is smaller in comparison with those exhibiting the rhombohedral one (the range of minimum of  $\Delta f_r/f_r$  is considered). On the other hand, the mechanical quality factor is somewhat larger in the rhombohedral phase compared with the tetragonal one (the range of maximum of  $Q_m$  is considered).

It should be noted that the thermal instability of the resonance frequency might be connected also with changes of the elastic constants of PZT-based piezoceramics with temperature and  $\text{PbTiO}_3$  content. However, the results obtained in the present work support the thesis, that the elastic constants of the multicomponent PZT-based system change insignificantly within the range of its compositions. In the case of piezoceramics the changes of  $\Delta f_r/f_r$  caused by a transition from the morphotropic region to the tetragonal phase greater are by an order of magnitude than the changes of the inverse

(elastic) compliance  $1/S_{11}^E$  or coefficient of stiffness  $c_{11}^E$ . This means that the domain-orientation processes condition mainly the thermal stability of  $f_r$  for radial oscillations of the piezoceramic samples.

**Range of mole fraction  $x < 0.25$  or  $x > 0.60$ .** It results from Fig. 2, that at a large  $\text{PbTiO}_3$  content ( $x > 0.6$  mole fraction) or a large amount of  $\text{PbZrO}_3$  ( $x < 0.25$  mole fraction), the thermal stability of  $f_r$  decreases (an increase in  $\Delta f_r/f_r$ ). The appearance of such an effect at large  $\text{Ti}(\text{Zr})$  contents suggests that a certain disturbance of isomorphism, typical of perovskites, takes place. In consequence the solubility of the two other components of the four-component system Eq. (1) in  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  decreases. Our investigations and analysis have experimentally confirmed the above statement. A brief report will be given below.

It is well known that the  $\text{ABO}_3$  structure permits large variations in the composition by the substitution of radius-compatible ions on the A or B sites. Let's consider restrictions imposed on the radius-compatibility rule between the substituant ions and substituted ions in the case of the PZT-based systems, when the formation of a series of solid solutions  $(\text{Pb,A})(\text{Zr,Ti,B}',\text{B}'',\dots)\text{O}_3$  exhibiting perovskite structure takes place. A measure of the departure from the rule of radius-compatibility is  $\Delta r/r_{\min}$ , or the relative difference of the ion radii between the substituant ions (A, B) and the substituted ions (Pb, Zr, and Ti). Basing on results of investigations of the  $\text{Pb}(\text{B}'_{1-\alpha}\text{B}''_{\alpha})\text{O}_3$ -type complex oxides, one can show that the discrepancy between the  $\text{Zr-B}'$  ion radii and the  $\text{Ti-B}''$  ion radii may exceed the constraints given in literature e.g. [2] if the  $\text{B}'$  and  $\text{B}''$  ion radii do not exceed a value of  $r_j$  for an averaged cation  $\text{Zr}_{1/2}\text{Ti}_{1/2}$  (Table 1). Similar criteria may be determined for another mole fraction  $x$  of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  solid solution.

It follows that one may substitute  $\text{Zr}^{4+}$  cations in the crystalline lattice of  $\text{PbZrO}_3$ -based systems for large  $\text{B}''$  cations, and that  $\text{Ti}^{4+}$  cations may be substituted in  $\text{PbTiO}_3$ -based systems for small  $\text{B}'$  cations. However, in the case of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ -based systems there is a possibility to substitute both  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  cations for ions exhibiting a radius  $r(\text{B}',\text{B}'') \leq \bar{r}_j$  (for an averaged  $(\text{Zr}_{1-x}\text{Ti}_x)^{4+}$  cation). It should be noted, however, that at high concentrations of  $\text{Zr}^{4+}$  or  $\text{Ti}^{4+}$  the difference between the averaged radius  $\bar{r}_j$  for  $(\text{Zr}_{1-x}\text{Ti}_x)^{4+}$  and the radius of the substituant ion  $r(\text{B}',\text{B}'')$  increases decreasing in this way the solubility of complex oxides. As a result of that, the technological and physical properties of thus modified PZT-type solid solutions worsen. Such a situation takes place in the case of piezoceramic materials under investigation. The materials exhibited compositions from outside the regions of minimum of  $\Delta f_r/f_r$  situated on both sides of MR in the Re and T phases.

To confirm the correctness of the assumed physical mechanism of the increase in  $\Delta f_r/f_r$  at large concentrations of  $\text{Zr}^{4+}$  or  $\text{Ti}^{4+}$  cations, the differences of the ion radii  $\Delta r/r_{\min}$  of the equivalent cations  $(\text{Zr}_{1-x}\text{Ti}_x)$  and  $\sum_{i=1}^2 \text{B}'_{1-\alpha}\text{B}''_{\alpha}$  were calculated for different mole fractions  $x$  and set against the  $\Delta f_r/f_r$  dependence. Figure 6 shows the results for the four-component ceramic solid solutions exhibiting compositions consistent with Eq. (1) for the following substituant ions:  $\text{B}' = \text{B}''' - \text{W}, \text{Nb}; \text{B}'' = \text{Mn}; \text{B}'''' = \text{Mg}, \text{Ni}, \text{Zn}$ .

**Table 1.** Ion radii ( $r_i$ ) of then B-type cations with different valency ( $n$ ) creating the solid solution  $(x)\text{PbTiO}_3 - (1-x-y)\text{PbZrO}_3 - (y)[\text{PbB}'\text{O}_3 - \text{PbB}''\text{O}_3]$

Cations B''			Cations B', Ti, Zr		
$n$	Symbol	$r_j$ [nm]	$n$	Symbol	$r_j$ [nm]
2	$\text{Mg}^{2+}$	0.074	4	$\text{Ti}^{4+}$	0.064
2	$\text{Ni}^{2+}$	0.074	4	$\text{Zr}^{4+}$	0.082
2	$\text{Co}^{2+}$	0.078	5	$\text{Ta}^{5+}$	0.060
2	$\text{Zn}^{2+}$	0.083	5	$\text{Sb}^{5+}$	0.062
2	$\text{Mn}^{2+}$	0.091	5	$\text{Nb}^{5+}$	0.066
2	$\text{Cd}^{2+}$	0.099	6	$\text{W}^{6+}$	0.065

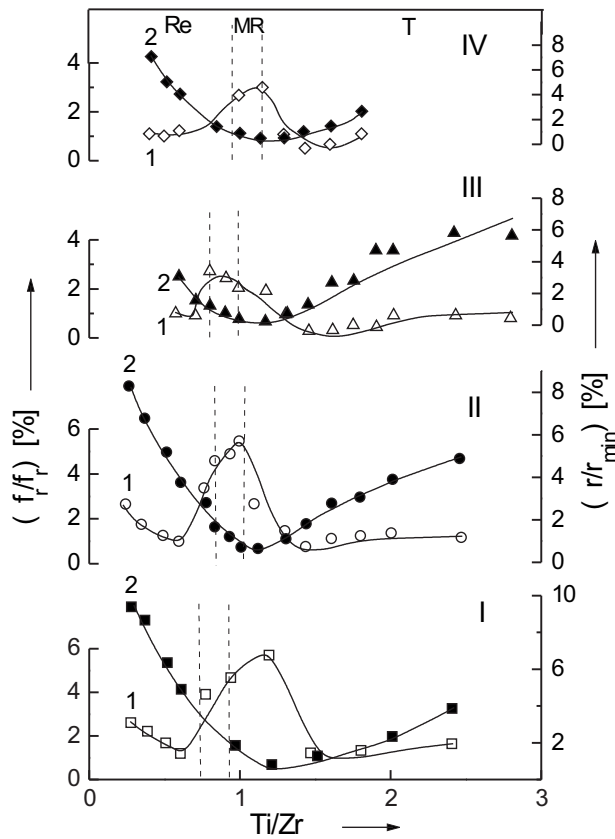


Fig. 6. Dependence of the relative change of the resonance frequency  $\Delta f_r/f_r$  within the temperature range 213–358 K (1) and difference of the ionic radii  $\Delta r/r_{\min}$  (2) of cations (Ti, Zr) and  $\sum_{i=1}^2 B'_{1-\alpha} B''_{\alpha}$ , taking into consideration their concentration on Ti/Zr ratio for four-component solid solutions on the base of PZT:

- I  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbW}_{1/2}\text{Mn}_{1/2}\text{O}_3 - \text{PbW}_{1/2}\text{Mg}_{1/2}\text{O}_3$ ;
- II  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbW}_{1/2}\text{Mn}_{1/2}\text{O}_3 - \text{PbW}_{1/2}\text{Ni}_{1/2}\text{O}_3$ ;
- III  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbW}_{1/2}\text{Mg}_{1/2}\text{O}_3$ ;
- IV  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$ .

The temperature range of the frequency measurements was  $T = 213\text{--}358$  K. One can see that  $\Delta r/r_{\min}$  reaches its minimum near the MR-T phase boundary and increases for both the tetragonal and rhombohedral compositions. This means that the solubility of the solid solutions under investigation is getting worse in the regions of large contents of the  $\text{PbZrO}_3$  or  $\text{PbTiO}_3$  components. These are the regions where an increase in  $\Delta f_r/f_r$  is observed. Inhomogeneity of the granular structure of the ceramic samples also shows small solubility and sinterability of the solid solutions of such compositions.

On the basis of the X-ray investigations (Fig. 7) carried out for the solid solutions:



one can conclude that the solubility deteriorate in the regions of large concentrations of the  $\text{PbTiO}_3$  or  $\text{PbZrO}_3$  components.

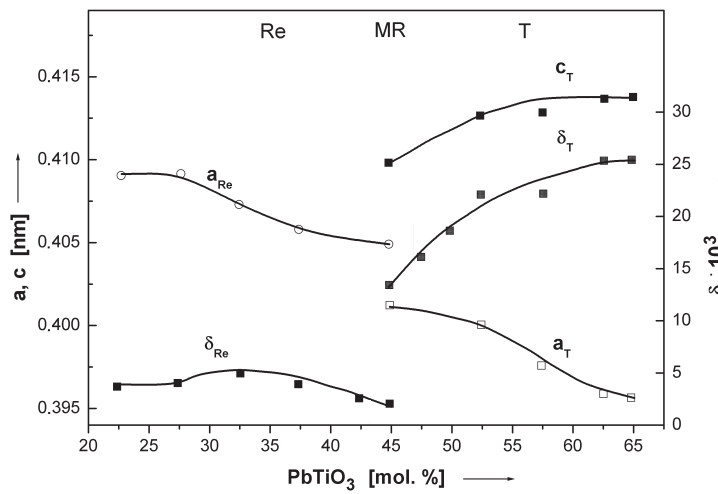


Fig. 7. Dependence of the tetragonal elementary cell parameters ( $a_T$ ,  $c_T$ ) and the rhombohedral ones ( $a_{Re}$ ) as well as the spontaneous tetragonal deformation ( $\delta_T$ ) and rhombohedral one ( $\delta_{Re}$ ) on the  $\text{PbTiO}_3$  content in four-component solid solution:  $(x)\text{PbTiO}_3 - (1-x-y)\text{PbZrO}_3 - (y)[\text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbW}_{1/2}\text{Mg}_{1/2}\text{O}_3]$ .

It results from the dependence of the elementary cell parameters on the  $\text{PbTiO}_3$  content ( $x$ ) for the above mentioned solid solution, that if the mole fraction of  $\text{PbTiO}_3$   $x > 0.6$  (tetragonal phase), the lattice constants  $a_T$ ,  $c_T$  and the  $\delta_T$  parameter  $\delta$  do not depend on the chemical composition (Fig. 7). The similar behavior of the lattice constant  $a_{Re}$  and parameter  $\delta_{Re}$  of the rhombohedral symmetry is observed for the  $\text{PbTiO}_3$  content  $x < 0.275$ . In other words, in the case of  $0.275 \geq (x)\text{PbTiO}_3 \geq 0.6$  the solubility of  $\text{PbTiO}_3$  ( $\text{PbZrO}_3$ ) in the solid solution is limited.

It results from the investigations reported above, that the piezoceramic resonators built on the base of the PZT solid solution with a  $\text{PbTiO}_3$  content  $x \approx 57.5$  mole percent will exhibit high thermal stability of the resonance frequency  $f_r$ . One can achieve

a further increase in the  $f_r$  stability by means of doping of  $\text{Pb}(\text{Zr}_{1-0.575-y}\text{Ti}_{0.575})\text{O}_3$  according to Eq. (1).

### 3.2. Selection of doping cations ( $B'$ , $B''$ , $B'''$ , $B''''$ )

Investigations of the dependence of thermal stability of the resonance frequency of PZT-based piezoceramic resonators on the chemical composition concern (i) the influence of the  $\text{PbTiO}_3$  content ( $x$ ) in the basic composition (i.e.  $(x)\text{PbTiO}_3-(1-x-y)\text{PbZrO}_3$ ) and (ii) the influence of the doping ions (i.e.  $(y) \sum_{i=1}^2 \text{Pb}(B'_{1-\alpha}B''_{\alpha})\text{O}_3$  - term of Eq. (1)) on the value of  $\Delta f_r/f_r$  within the temperature range  $T = 213-358$  K.

A basic property of the cations, which form the PZT-based solid solutions, is their electronegativity (EN). Electronegativity of the elements exhibiting a certain oxidation state is used to evaluate the condition of chemical bonds, which together with other factors, determine the physical properties of chemical compounds and solid solutions. One can consider a bond between two monovalent atoms A and B as a superposition of the three boundary structures, namely  $A^+B^-$  and  $A^-B^+$  as well as a covalent structure A-B. If the relative contributions of the two ionic structures are equal, the A-B bond is purely covalent. This means that both the atoms possess an equal electronegativity. On the other hand, if one of the ionic structures predominates (e.g.  $A^+B^-$ ) one of the atoms is more electronegative (e.g. B).

In a specific chemical composition, the greater the difference in the electronegativity between both the constituent elements the more the ionic bond predominates the atomic bond.

The character of the chemical bonds can be described on the basis of the difference in EN between the elements constituting a solid solution. The major point is that with

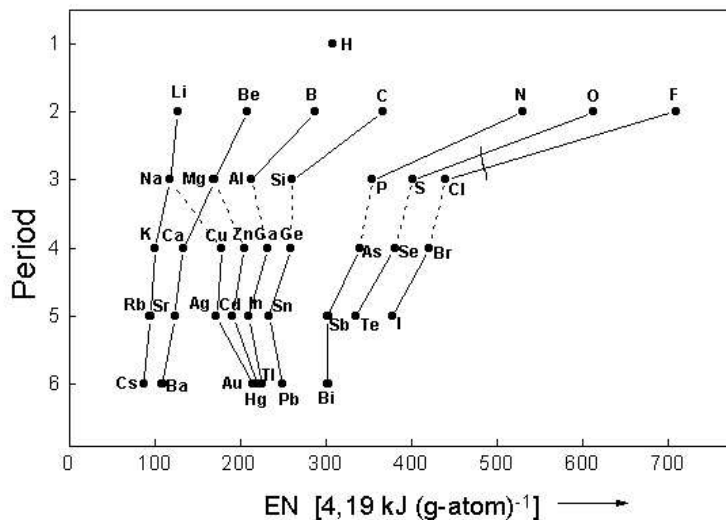
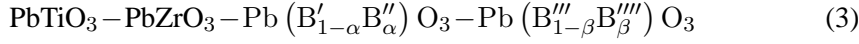


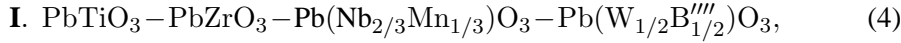
Fig. 8. Electronegativity (EN) of selected elements.

a decrease in that difference the degree of the covalency of the bond increases. It results from this rule that an increase in the electronegativity of the element B in the  $ABO_3$  system leads to an increase in the degree of covalency in the B-O bond because the EN of oxygen is greater than that of the B elements (Fig. 8). Thus, one can consider the EN of the element B as a measure of the degree of covalency of the B-O bond.

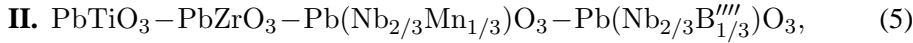
To evidence in what way the EN of B elements influence the covalence character of the B-O bond and thus the physical properties of PZT-based piezoceramics a comprehensive investigation of the system



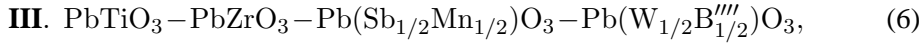
has been carried out (Fig. 9). The system included:



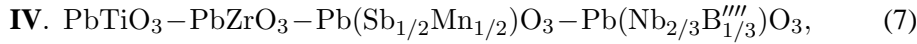
where  $B'''' - Mg, Zn, Co, Mn$ ;



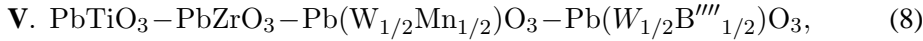
where  $B'''' - Mg, Zn, Co$ ;



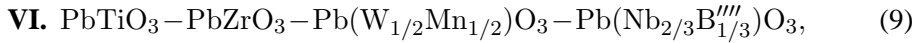
where  $B'''' - Mg, Zn, Ni, Co$ ;



where  $B'''' - Mg, Zn, Ni, Co, Mn$ ;



where  $B'''' - Mg, Zn, Ni, Co$ ;



where  $B'''' - Mg, Zn, Ni, Mn$ .

All the solid solution systems under investigation exhibited a  $PbTiO_3$  content close to the mole fraction  $x \approx 0.575$ . In other words, the composition belonged to the tetragonal region of the minimum of the  $f(x) = \Delta f_r / f_r$  curve and thus the investigated systems exhibited a maximal thermal stability of the resonance frequency  $f_r$  (Fig. 2). The samples were obtained by the hot pressing method. They were classified according to the homogeneity of the grain size. This enabled to exclude the influence of factors connected with the inhomogeneity of the microstructure and the grain size on the thermal stability of  $f_r$ .

It has been found that a decrease in  $\Delta f_r / f_r$  and thus an improvement of the thermal stability of  $f_r$  occurs in the following order of the  $B''''$  cations: group I: Mg, Zn, Co, Mn; group II: Mg, Zn, Co; group III: Mg, Ni, Zn, Co; group IV: Mg, Zn, Ni, Co, Mn; group V: Mg, Zn, Ni, Co; group VI: Mg, Zn, Ni, Mn.

Values of EN for the above mentioned  $B''''$ ,  $B'$  and  $B''$  elements exhibiting right oxidation state are given in Table 2.



**Table 2.** Electronegativity of elements in solid solution on the base of PZT.

Element	Oxidation number	Electronegativity [J · (g-at) <sup>-1</sup> ]
Mn	IV	1280
Mn	III	1080
Mn	II	710
Co	III	1080
Co	II	835
Ni	III	1140
Ni	II	920
Zn	II	870
Mg	II	730
Nb	V	1000
Sb	V	1120
Sb	III	815
W	VI	975
W	IV	855

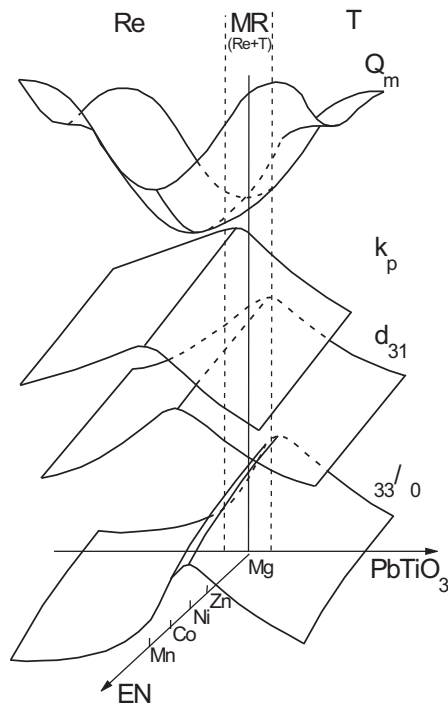
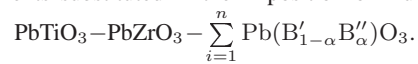


Fig. 9. Scheme of the dependence of  $\varepsilon_{33}^{\sigma}/\varepsilon_0$ ,  $d_{31}$ ,  $k_p$  and  $Q_m$  on the  $\text{PbTiO}_3$  concentration and electronegativity (EN) of elements substituted in the B position of multicomponent solid solution of:



Analyzing the properties of solid solutions one has to take into account a change in the oxidation state of the elements during the synthesis, if possible. For instance, at the synthesis of Mn-containing solid solutions compounds of Mn (II) are used. Mn (II) undergoes an oxidation to the Mn (III) state in the air atmosphere but at the presence of the lead oxide it can transform into a higher oxidation state (e.g. Mn (IV)). In systems containing Co (II) a partial oxidation to Co (III) occurs. Thus the PZT-based solid solutions, which were under investigation, contained the following B<sup>IV</sup> cations:  $Mn^{2+} + Mn^{3+} + Mn^{4+}$ ,  $Co^{2+} + Co^{3+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ .

On the basis of the experimental results and taking into account the data collected in Table 2, one can draw the following conclusions:

(i) A decrease in  $\Delta f_r/f_r$ , i.e. an increase in the thermal stability of  $f_r$ , is conditioned by an increase of EN of the B<sup>IV</sup> cations in case of solid solution of the groups I, II, IV, V and VI as well as by the presence of B<sup>IV</sup> cations exhibiting different oxidation states;

(ii) in case of solid solutions group III, a certain change in the cations order occurs (compared with other groups); it is likely conditioned by the concurrent presence of three elements exhibiting a varying valence (Sb, Mn, W);

(iii) a complex constitution of PZT-based solid solutions leads to a change in the nature of the B-O bonds for the B', B'', B<sup>IV</sup> cations; this has an impact on the value of  $\Delta f_r/f_r$  and leads to a change in order of the B<sup>IV</sup> cations, which corresponds to an increase in the thermal stability of  $f_r$  (decrease in  $\Delta f_r/f_r$ ).

The regularities concerning the influence of the electronegativity of the B<sup>IV</sup>-cations on the  $\Delta f_r/f_r$  value for four-component PZT-based solid solutions are shown in Fig. 10. One can see that an increase in EN (due to a appropriate selection of B<sup>IV</sup>-cations) in-

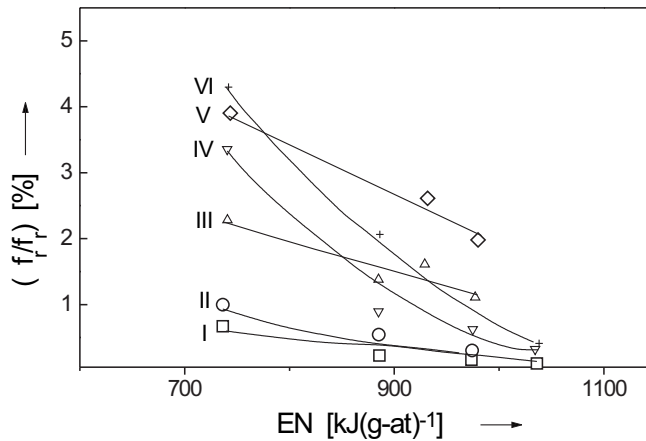


Fig. 10. Dependence of relative change of resonance frequency ( $\Delta f_r/f_r$ ) on the electronegativity (EN) of B<sup>IV</sup> cations in four-component piezoceramic materials on the base of PZT:

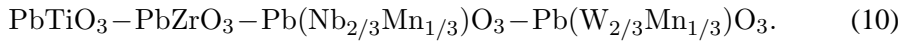
- I.  $PbTiO_3 - PbZrO_3 - PbNb_{2/3}Mn_{1/3}O_3 - PbW_{1/2}B_{1/2}^{IV}O_3$ ; B<sup>IV</sup> – Mg, Zn, Co, Mn;
- II.  $PbTiO_3 - PbZrO_3 - PbNb_{2/3}Mn_{1/3}O_3 - PbNb_{2/3}B_{1/3}^{IV}O_3$ ; B<sup>IV</sup> – Mg, Zn, Co;
- III.  $PbTiO_3 - PbZrO_3 - PbSb_{1/2}Mn_{1/2}O_3 - Pb(W_{1/2}B_{1/2}^{IV})O_3$ ; B<sup>IV</sup> – Mg, Zn, Ni, Co;
- IV.  $PbTiO_3 - PbZrO_3 - PbSb_{1/2}Mn_{1/2}O_3 - PbNb_{2/3}B_{1/3}^{IV}O_3$ ; B<sup>IV</sup> – Mg, Zn, Ni, Co, Mn;
- V.  $PbTiO_3 - PbZrO_3 - PbW_{1/2}Mn_{1/2}O_3 - PbW_{1/2}B_{1/2}^{IV}O_3$ ; B<sup>IV</sup> – Mg, Zn, Ni, Co;
- VI.  $PbTiO_3 - PbZrO_3 - PbW_{1/2}Mn_{1/2}O_3 - PbNb_{2/3}B_{1/3}^{IV}O_3 - B^{IV}$  – Mg, Zn, Ni, Mn.

creases the thermal stability of  $f_r$  ( $\Delta f_r/f_r$  decreases). The dependence of  $\Delta f_r/f_r$  on EN is sharper for solid solutions of the groups II, IV, and VI containing niobium ( $\text{Nb}^{5+}$ ) on the  $\text{B}''''$  sites than in case of groups I, III, and V containing tungsten ( $\text{W}^{5+}$ ) on the  $\text{B}''''$  sites.

The value of  $\Delta f_r/f_r$  depends also on the type of the atom situated on the  $\text{B}'$  site. Substitution of tungsten W (groups V and VI) by antimony Sb (group III and IV) and niobium Nb (groups II and I) leads to a decrease in  $\Delta f_r/f_r$ .

An increase in the thermal stability of  $f_r$  with increasing EN of the  $\text{B}''''$  cations, i.e. with an increase in covalence character of the  $\text{B}''''\text{-O}$  bonds can be explained in the following way. A spontaneous tetragonal deformation of the elementary cell in the  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3 - \sum_{i=1}^n \text{Pb}(\text{B}'_{1-\alpha}\text{B}''_{\alpha})\text{O}_3$ -type solid solutions depends in a direct proportion on the degree of the covalency of the B-O bonds [4]. Consequently, the so-called ferroelectric hardness increases (Fig. 11). It manifests itself, among other things, in a weak susceptibility of the domains to external effects (e.g. temperature, electric field, etc.). In this connection it should be pointed out that a change of  $f_r$  with temperature is caused by a change of the positions of the domain walls. It follows that an increase in the ferroelectric hardness stabilizes the resonance frequency  $f_r$  of piezoceramics [14–17].

Among the four-component PZT-based solid solutions obtained within the framework the present research, the best thermal stability of  $f_r$  exhibits the following system:



The basic properties of the above system depending on the  $\text{PbTiO}_3$  content ( $x$ ) are given in Table 3.

**Table 3.** Influence of the  $\text{PbTiO}_3$  concentration on physical properties of piezoceramics of  $(x)\text{PbTiO}_3 - \text{PbZrO}_3 - \text{Pb}(\text{Nb}_{2/3}\text{Mn}_{1/3})\text{O}_3 - \text{Pb}(\text{W}_{1/2}\text{Mn}_{1/2})\text{O}_3$ .

No.	$(x)\text{PbTiO}_3$ [mol.%]	$\varepsilon_{33}^{\sigma}/\varepsilon_0$	$k_p$	$\tan \delta \cdot 10^2$ ( $E=5$ kV/m)	$Q_m$	$Q_m^{-1} \cdot 10^3$	$T_c$ [K]	$\Delta f_r/f_r$ [%] (213–358 K)	Phase
1.	32.5	265	0.300	0.32	2632	0.38	563	0.35	Re
2.	35.0	300	0.330	0.30	2500	0.40	563	0.38	Re
3.	41.5	355	0.436	0.28	1500	0.67	593	0.47	Re
4.	44.0	390	0.52	0.34	1000	1.00	608	0.58	MR (Re+T)
5.	45.0	1100	0.50	1.70	1200	0.83	587	0.45	MR (Re+T)
6.	47.5	1030	0.49	1.40	1250	0.80	595	0.32	T
7.	49.0	800	0.48	0.74	2720	0.37	603	0.30	T
8.	49.5	750	0.47	0.62	2857	0.35	603	0.28	T
9.	50.0	830	0.46	0.78	2941	0.34	612	0.24	T
10.	50.5	780	0.41	0.63	3225	0.31	613	0.19	T
11.	51.0	740	0.41	0.72	2800	0.36	616	0.27	T

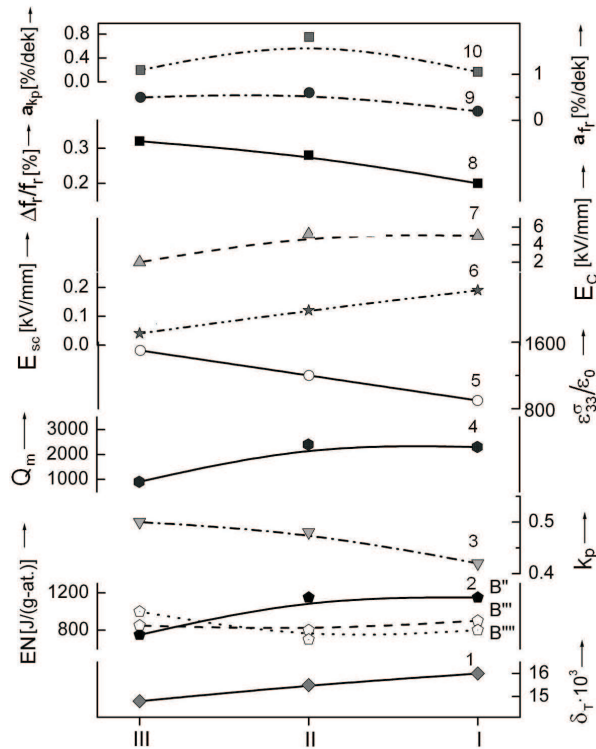


Fig. 11. Influence of the ferroelectric hardness on piezoceramic parameters of solid solution compositions: I  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbNb}_{2/3}\text{Zn}_{1/3}\text{O}_3$ ; II  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbTa}_{3/4}\text{Li}_{1/4}\text{O}_3$ ; III  $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{PbNb}_{2/3}\text{Co}_{1/3}\text{O}_3 - \text{PbNb}_{1/2}\text{Sb}_{1/2}\text{O}_3$ ; 1 -  $\delta_T$ ; 2 - EN; 3 -  $k_p$ ; 4 -  $Q_m$ ; 5 -  $\epsilon_{33}^a/\epsilon_0$ ; 6 -  $E_{sc}$ ; 7 -  $E_c$ ; 8 -  $\Delta f_r/f_r$  (in the range of 213–358 K); 9 -  $a_{fr}$ ; 10 -  $a_{kp}$ ; ferroelectric hardness of solid solution increases in the sequences: III, II and I.

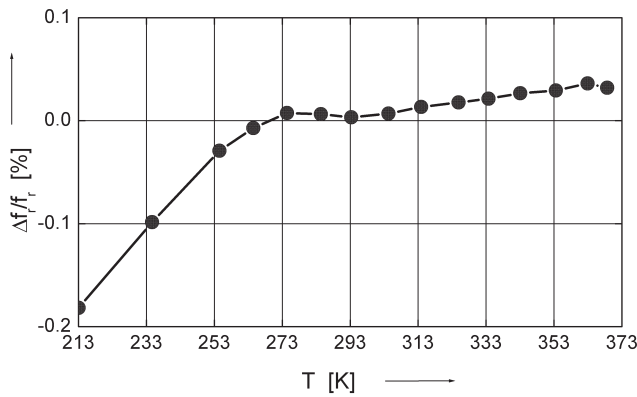


Fig. 12. Dependence of the relative change of the resonant frequency ( $\Delta f_r/f_r$ ) on temperature ( $T$ ) for the four-component piezoceramic solid solution of the PZT-type ( $0.505\text{PbTiO}_3 - 0.445\text{PbZrO}_3 - 0.05[\text{Pb}(\text{Nb}_{2/3}\text{Mn}_{1/3}\text{O}_3 - \text{PbW}_{1/2}\text{Mn}_{1/2}\text{O}_3)]$ ).

Figure 12 shows the dependence of the relative change in the resonance frequency ( $\Delta f_r/f_r$ ) on temperature ( $T$ ) within the range  $T = 213 - 373$  K for a fabricated piezoelectric resonator (chemical composition: Table 3, No 10). It follows from the figure that the relative change in frequency does not exceed 0.2%.

#### 4. Conclusions

By means of the hot pressing method the PZT-based four-component piezoceramics exhibiting different  $\text{PbTiO}_3$  contents have been obtained. The sol-gel derived ceramic powder was used and the synthesis was carried out by the conventional mixed oxide method. A strong influence of the chemical composition on the crystalline structure and the basic electro-physical parameters has been stated. Certain regularities, which determine the dependence of the thermal stability of the resonance frequency of piezoceramic transducers on their crystalline structure, domain configuration,  $\text{PbTiO}_3$  content in the basic PZT composition and the electronegativity of doping cations, have been ascertained.

The investigations have shown that the highest stability of  $f_r$  exhibit compositions of the tetragonal structure (0.50–0.56 mole fraction of  $\text{PbTiO}_3$ ) as well as those of the rhombohedral structure (c.a. 0.25 mole fraction of  $\text{PbTiO}_3$ ). These compositions are situated in the phase diagram on both sides of the morphotropic region (0.45–0.48  $\text{PbTiO}_3$ ), within which  $\Delta f_r/f_r$  reaches its maximum. Compositions corresponding to a minimum of  $\Delta f_r/f_r$  exhibit the smallest internal friction ( $Q_m^{-1}$ ), the largest mechanical quality factor ( $Q_m$ ), high values of spontaneous deformation of the elementary cell ( $\delta_T$  and  $\delta_{Re}$ ), a complex  $a - c$ -domain structure in the tetragonal symmetry phase and a simple domain structure (small number of the domain walls) in the rhombohedral symmetry phase. A close correlation has been found between the increase in the degree of reorientations other than  $180^\circ$  of domains ( $\eta$ ) in an external electric field (which is connected to a decrease in the number of domain walls) and an increase in the thermal stability of  $f_r$  and the value of  $Q_m$  for rhombohedral phase compositions. The stability of  $f_r$  for compositions exhibiting the rhombohedral phase is governed by a decrease in the number of the domain walls, which in turn is evoked by an increase in the degree of reorientations other than  $180^\circ$  of the domains ( $\eta$ ). On the other hand, in the tetragonal phase the main influence on the stability of  $f_r$  is exerted by a decrease in the domain wall mobility caused, in turn, by an increase in the spontaneous tetragonal deformation of the elementary cell ( $\delta_T$ ). The double phase morphotropic region shows medium values of  $\delta$  and  $\eta$ , which correspond to the relatively high mobility and the number of domain walls. These, in turn lead to a maximum of  $\Delta f_r/f_r$  and minimum of  $Q_m$ . The interfacial boundaries (T/Re), which move under the influence of measuring field and temperature, are conducive to this. In the case of large mole fractions of  $\text{PbTiO}_3$  or  $\text{PbZrO}_3$  their solubility in the solid solution decreases which manifests itself in the stability of the tetragonal and rhombohedral elementary cell ( $a_T$ ,  $c_T$ , and  $a_{Re}$ ) parameters as well as in the parameters of spontaneous deformation ( $\delta_T$ ,  $\delta_{Re}$ ) and consequently in an increase in  $\Delta f_r/f_r$ .

Designing multicomponent solid solutions on the basis of PZT, which exhibit high thermal stability of the resonance frequency, one has to use admixture elements B possessing the highest possible electronegativity (EN). An increase in EN causes an increase in the degree of the covalence character of the B-O bonds, and thus increases the spontaneous tetragonal deformation  $\delta_T$  of the elementary cell. Solid solutions exhibiting increased  $\delta_T$  display an enlarged ferroelectric hardness and weak susceptibility of domains to external effects including temperature changes.

The practical achievement of the present work was the obtaining of piezoceramic band electric filters exhibiting  $\Delta f_r/f_r < 0.2\%$  and a high mechanical quality factor ( $Q_m \approx 3225$ ).

### Acknowledgment

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