

THE INFLUENCE OF PB VACANCIES ON THE PROPERTIES OF PZT-TYPE CERAMIC TRANSDUCERS

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This article is dedicated to prof. J. Ranachowski

The result of investigations of the influence of lead vacancies on the crystalline structure of PZT-type ceramic piezoelectric materials is presented. The solid solution of $\text{PbTiO}_3 - \text{PbZrO}_3 - \sum_{n=1}^3 \text{Pb}(\text{B}'_{1-\alpha}\text{B}''_{\alpha})\text{O}_3$, characterized by the perovskite-type structure (ABO_3), is the basis of those materials. The lead vacancies (V^{Pb}) was originated by a thermal treatment. Investigations of the influence of the lead deficiency on the crystalline structure of PZT-type ceramics have been performed for solid solutions characterized by compositions corresponding to the tetragonal or rhombohedral boundary of the morphotropic region (PCR-1, PCR-8: *Piezoelectric Ceramics of Rostov*) and to tetragonal phase region compositions (ceramics of $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$). It has been found that the deficiency in lead causes a reconstruction of the perovskite phase crystalline structure or a change of the elementary cell parameters of that phase. The solid solutions on the basis of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ resolve themselves into PbTiO_3 , ZrO_2 and PbO when the lead deficiency caused by thermal treatment increases.

Keywords: piezoelectrics ceramic, PZT-type solid solution, lead vacancies, structure, electroacoustic properties, transducers.

1. Introduction

The PZT-type ceramic material is a solid solution of PbTiO_3 and PbZrO_3 , the general molecular formula of which is $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$. The phase diagram of the non-modified

PZT ceramic material (Fig. 1) indicates that when Ti^{4+} ions are substituted by the Zr^{4+} ions the tetragonal deformation of PbTiO_3 decreases. Next (for $\text{Zr}:\text{Ti} = 55:45$), the so-called morphotropic boundary (MB) appears at room temperature. A further increase in the Zr^{4+} concentration involves the creation of a new rhombohedral ferroelectric phase (R3m). The boundary between the tetragonal and rhombohedral phase (morphotropic boundary) depends on the temperature. If the concentration of Zr^{4+} is greater than 95 mol.%, there is an antiferroelectric orthorhombic phase (typical for PbZrO_3) in the PZT solid solution. A narrow region of the stable antiferroelectric tetragonal phase occurs close to the Curie point in this case.

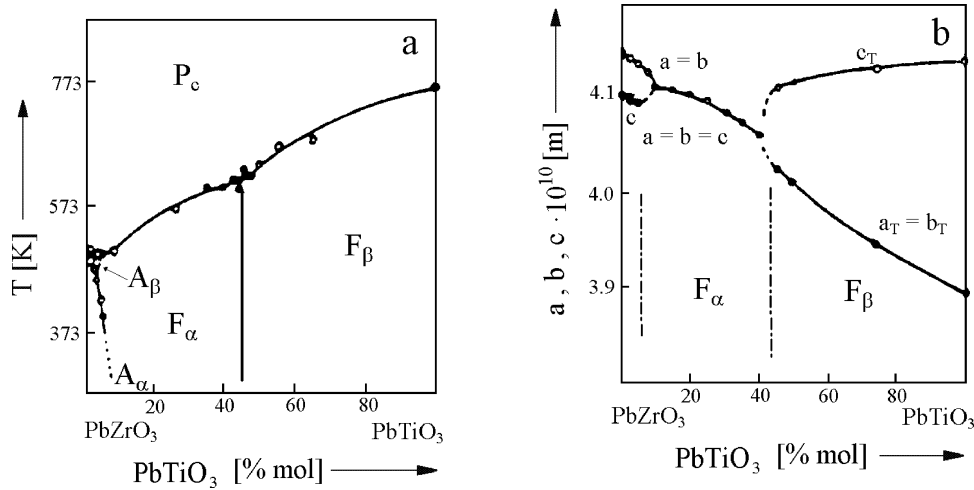
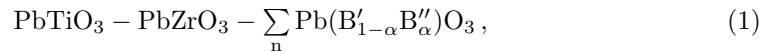


Fig. 1. The phase diagram of the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid solution [1–2]. F_β — ferroelectric tetragonal phase; F_α — ferroelectric rhombohedral phase; A_α , A_β — antiferroelectric phases; P_c — cubic phase; F_α/F_β — morphotropic boundary.

PZT materials characterized by constitutions, which are close to the morphotropic phase boundary show distinct piezoelectric properties. One can optimize these properties according to the requirements of the applications by modifying the basic constitution or by doping, e.g. in accordance to the following molecular formula:



where $\alpha = 1/2; 1/3; 1/4$ (depending on valence number of the B' and B'' cations); $\text{B}' = \text{Nb}^{5+}, \text{Sb}^{5+}, \text{Ta}^{5+}, \text{W}^{6+}$; $\text{B}'' = \text{Li}^{1+}, \text{Mg}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}, \text{Cd}^{2+}, \text{Fe}^{2+}, \text{Bi}^{3+}, \text{Sb}^{3+}$.

The addition of some modifiers amounting to (1–3) mol.%, causes, among other things, a broadening of the range of coexistence of the rhombohedral and tetragonal phases. In this case, the morphotropic region (MR) appears in the phase diagram in the range of (40–43.5) mol.% of Ti^{4+} (Fig. 2) instead of the morphotropic boundary MB (line). Materials prepared on the basis of the $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ solid solution are called PZT-type materials for short. Depending on the chemical constitution, different patent

symbols have been given to them (e.g. Polish: PP-4, PP6-CM, PP-N; Russian: CTS-836, PCR-1, PCR-8; Brush-Clevite firm: PZT-4; Mullard firm: PXE5).

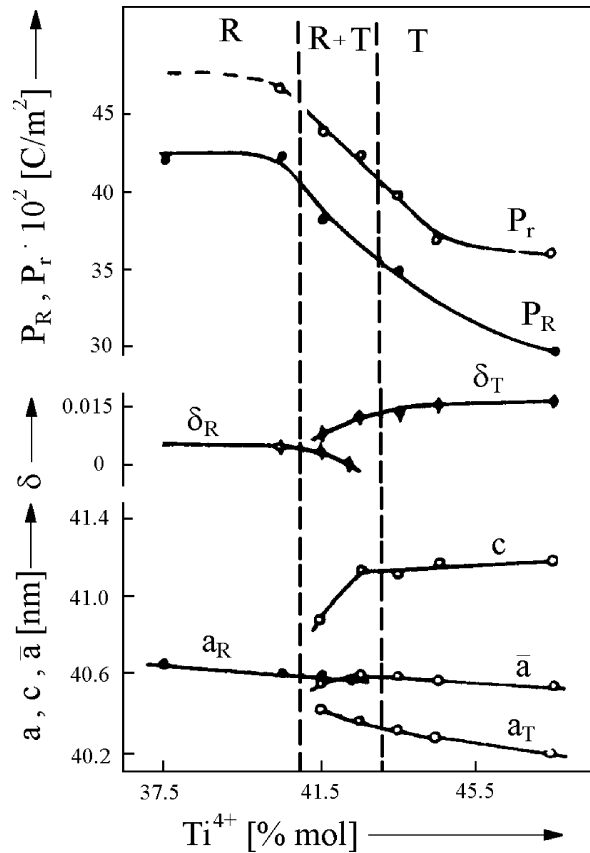


Fig. 2. Changes of the parameters (a_R , a_T , c_T , \bar{a}), the spontaneous deformation (δ_R , δ_T) of the elementary cell, orientational polarization (P_r) and residual polarization (P_R) during the transition from the rhombohedral (R) phase through the morphotropic region (R+T) to the tetragonal (T) phase for PZT-type ceramics at 293 K.

PZT-type materials are commonly used in engineering (among other things as electro-mechanical transducers). The increasing application possibilities of these materials are connected with both the selection of the chemical constitution and the improvement of the structure and microstructure (decreasing porosity, increasing density, decreasing grain dimensions) by means of a choice of suitable technological conditions. The PZT-type ceramic materials are obtained by both the classical method, which is worldwide used on an industrial scale [3, 4], and the sintering under pressure one (so-called hot-pressing method) (e.g. [5]). So far, the latter becomes more widespread in the technology of special purpose ceramics, however only in a laboratory or semiindustrial scale. By means of sintering under pressure as well as the fine-grained ((1–4) μm in diameter), the medium sized ((5–9) μm in diameter) and coarse-grained ((9–12) μm in diameter)

ceramic materials are obtained. After a mechanical treatment (cutting, grinding, polishing) one can obtain thin ceramic plates of $d_f > 8 \mu\text{m}$ thickness and a perfectly smooth surface ($\nabla 14$). This is impossible in the case of the same PZT materials obtained by the classical method (small density, large porosity and small mechanical strength).

A very important question in the technology of ceramic ferroelectric materials is to provide consistence in the stoichiometry between the product obtained and the chemical constitution described by a molecular formula of the compound or the solid solution. It is of great importance in the case of ceramic ferroelectrics containing lead. The temperature of sintering (synthesis) of those compounds is higher than the lead sublimation temperature. This is why the real ceramic ferroelectrics of that type are characterized by a disturbance in the stoichiometry. This disturbance is connected with the creation of lead vacancies (V^{Pb}) in the PZT crystalline structure. It influences strongly the electrical properties (first of all the electrical transport phenomena) and the structure parameters of those materials in the ferroelectric state.

Three methods of controlled creation of lead vacancies in the PZT-type solid solutions are generally applied, namely:

- 1) the roasting at $T_s = (1073 - 1323) \text{K}$ within $t_s = (1 - 3)$ hours under oxygen [1];
- 2) the obtaining of the PZT-type solid solution from a mixture of suitable powdered oxides deficient in PbO [6];
- 3) modification of the PZT-type ceramics by soft doping [7].

One can sometimes use a combination of those three methods to form lead vacancies V^{Pb} [8].

There are few published works on the influence of the vacancies on the crystalline structure of the solid solutions of the PZT basis. However, there are experimental data about the influence of V^{Pb} on the physical properties (mechanical, dielectric, semiconductive, piezoelectric) of such solid solutions [7, 8]. It is relevant to PZT modified by soft admixtures [9].

In the present paper, the results of investigations on the influence of lead vacancies (V^{Pb}) on the crystalline structure of the PZT-type piezoceramics are described.

2. Results and discussion

2.1. Basic dielectric, piezoelectric and mechanical properties of the electro-acoustic transducers obtained

On the phase diagram of every of the PZT-type solid solutions, there are some regions of the chemical constitutions which provide an optimal set of values of the electromechanical parameters of the materials obtained on the basis of these solutions. This is shown in Fig. 3 and Table 1. High effective piezoceramic materials have been obtained by choosing a proper chemical constitution and technological conditions. The materials are characterized by parameters, which are optimal for the application, e.g. in acousto-electronics. All the new piezoelectric materials obtained can be divided into the seven following groups:

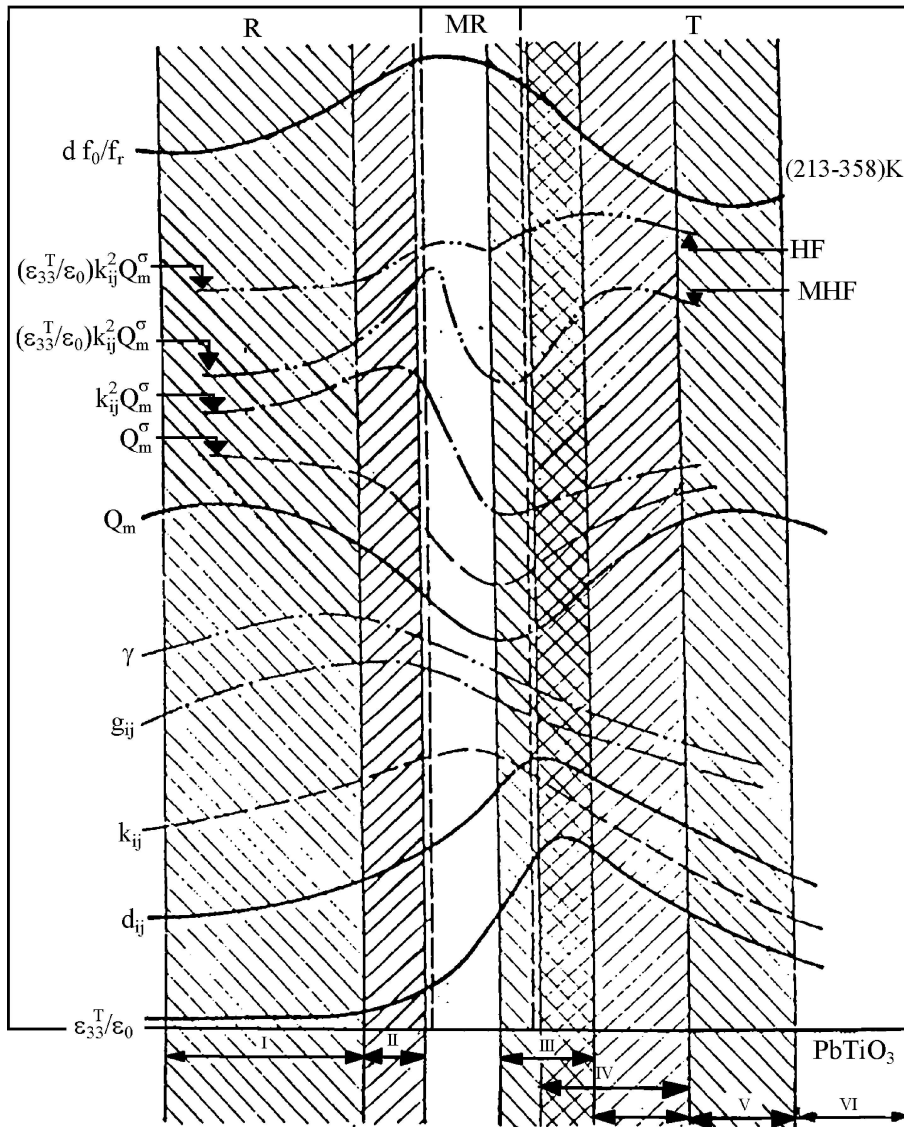


Fig. 3. Influence of the concentration of $PbTiO_3$ on the values of the electrophysical parameters of the multicomponent solid solutions on the basis of PZT in the vicinity of the morphotropic region.

Group I: piezoceramics characterized by small values of the permittivity ($\epsilon_{33}^\sigma/\epsilon_0$).

Possible applications:

1. High frequency electroacoustic transducers:

- a) volume waves: — large $k_{15} = 0.75$,
- small $\epsilon_{33}^\sigma/\epsilon_0 < 500$,
- not required large $Q_m = 200 - 1000$;

Table 1. Chemical constitution-structure-physical properties-application of the multicomponent solid solutions: $\text{PbTiO}_3 - \text{PbZrO}_3 - \sum_n \text{Pb}(\text{B}'_{1-\alpha}\text{B}''_{\alpha})\text{O}_3$.

Region, phase	Ferroelectric (HF, MHF, SF)	M [mol% PbTiO_3]	External parameters-large	External parameters-small	Application (examples)
I(R)	MHF, SF	-(3 - 25)	γ	$\frac{T}{\varepsilon_{33}^T/\varepsilon_0}$ Q_m, k_{ij}	High frequency piezoelectric transducers. Pyroelectric detectors.
II(R)	HF, MHF	-(1 - 3)	$g_{ij},$ $k_{ij}^2 \cdot Q_m^\sigma$	Q_m	Defectosopes, accelerometers, high voltage piezoelectric transformers.
III (MR, T)	SF	+(0.5 - 2)	k_{ij}, d_{ij} $\varepsilon_{33}^\sigma/\varepsilon_0,$ $d_{ij}/(\varepsilon_{33}^\sigma/\varepsilon_0)$	Q_m	Low frequency transducers, microphones, hydrophones.
IV (T)	HF	+(1 - 4)	$k_{ij}^2 \cdot Q_m^\sigma \cdot (\varepsilon_{33}^T/\varepsilon_0)$ $(d_{ij} Y_{ij}^E)^2$	$\tan \delta$	Low voltage piezoelectric transformers; piezoelectric engines. Ultrasonic piezoelectric transducers.
	MHF, SF	+(2 - 4)	$k_{ij}^2/\tan \delta$		
V (T)	HF, MHF	+(4 - 10)	Q_m	$\delta f_\Theta/f_r$	Filters.
VI (T)	HF, MHF, SF	+(5 - 25)	T_c	-	High temperature transducers.

- b) surface waves: — very small $\varepsilon_{33}^\sigma/\varepsilon_0 < 290$,
 — large $Q_m = 4000$,
 — large $k_p > 0.50$;

2. High stability ultrasonic delay lines:
 — very small $\varepsilon_{33}^\sigma/\varepsilon_0 < 290$,
 — large $k_p > 0.50$,
 — large $Q_m = 2000 - 4000$;

3. Pyroelectric sensors:
 — large $\gamma > 5 \times 10^{-4} \text{ C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$,
 — small $\varepsilon_{33}^\sigma/\varepsilon_0 < 500$.

Group II: piezosensitive ceramics characterized by large $g_{ij}, k_p, k_t, k_{15}, k_{ij}^2 Q_m^\sigma$ and small Q_m (high piezoelectric sensitivity to mechanical influences).

Possible applications:

- 1) accelerometers,
- 2) defectoscopes,
- 3) devices for medical diagnostic,
- 4) ferroelectric memory elements,
- 5) high voltage step-up piezoelectric transformers.

Group III: piezoceramics characterized by large k_{ij} , d_{ij} , $\varepsilon_{33}^\sigma/\varepsilon_0$ and small Q_m (low frequency transducers).

Possible applications:

1. Direct piezoelectric effect: microphones, hydrophones, sound reproducers.
2. Converse piezoelectric effect: devices for robotics, deflectors in optical system.

Group IV (a): ferroelectrically hard (HF) piezoceramics characterized by large values of $k_{ij}^2 \cdot Q_m^\sigma \cdot \varepsilon_{33}^\sigma/\varepsilon_0$, $(d_{ij}Y_{ij})^2$, $k_{ij}^2/\tan\delta$ and a small $\tan\delta$ (piezoelectric materials which are slightly tractable to external influences).

Possible applications:

1. Piezoelectric step-down transformers (large $k_{ij}^2 \cdot Q_m^\sigma \cdot \varepsilon_{33}^\sigma/\varepsilon_0$).
2. Piezoelectric servo-motors (large $d_{31}^2 \cdot Q_m \cdot Y_{11}^E$).

Group IV (b): ferroelectrically soft (SF) piezoceramics highly tractable to external influence.

Possible applications:

1. High power ultrasonic generators (large $k_{33}^2/\tan\delta$ and $(d_{31}Y_{11}^E)^2$).

Group V: piezoceramics with high temperature and time stability of the resonance frequency (small $\Delta f_r/f_r$; large k_p provides a wide pass band of the filters; sharpness of the amplitude-frequency characteristics within the pass band of the filters depend on Q_m).

Possible applications:

1. Filters with high temperature and time stability.

Group VI: high temperature piezoelectric ceramics (materials with large $T_c > 700$ K, small $\varepsilon_{33}^\sigma/\varepsilon_0$ and relatively good piezoelectric parameters).

Possible application:

1. Electroacoustic devices operating at high temperatures and high frequencies (nuclear engineering, space technology, metallurgy).

In this work the following piezoceramic materials were investigated: PCR-1 (Group II), PCR-8 (Group IV) and $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ (Group V).

The basic physical parameters of this piezoceramics are shown in Table 2, where:

$\varepsilon_{33}^\sigma/\varepsilon_0$	free dielectric constant ($\sigma = 0$ or $\sigma = \text{const.}$);
ε_{33}^σ	permittivity ($\sigma = 0$ or $\sigma = \text{const.}$);
ε_0	permittivity of free space ($\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m);
k_p, k_{31}, k_{33}	electromechanical coupling factors;
d_{31}, g_{33}	piezoelectric constants ($g_{nj} = \sum_{-1}^{\sigma} \beta_{nm}^\sigma d_{mj}$, $g_{nj} = \sum \frac{d_{nj}}{\varepsilon_{nm}^\sigma}$);
β_{nm}^σ	dielectric impermeabilities (ε_{nm}^{-1});

Table 2. Basic physical parameters of the piezoceramics obtained.

Materials	Parameters	PCR-1	PCR-8	Pb(Zr _{0.39} Ti _{0.59} W _{0.01} Cd _{0.01})O ₃
	Phase	rhombohedral (near the MR)	tetragonal (near the MR)	tetragonal (far the MR)
	$\varepsilon_{33}^{\sigma}/\varepsilon_0$	650	1400	1300
	k_p	0.62	0.58	0.47
	k_{31}	0.70	0.34	0.32
	k_{33}	0.73	0.66	0.42
	$d_{31} \cdot 10^{12}$ [C/N]	95	130	105
	$g_{33} \cdot 10^3$ [V·m/N]	38	23.5	16
$\tan \delta \cdot 10^2$	$E_r^0 = 5$ kV/m	2	0.35	0.35
	$E_r^0 = 100$ kV/m	3.5	0.70	0.90
	Q_m	90	2000	1750
	Q_m^{σ} ($\sigma = 12$ MPa)	70	700	750
	$k_{31}^2 \cdot Q_m^{\sigma}$	34	81	74.5
	$\frac{\varepsilon_{33}^{\sigma}}{\varepsilon_0} k_{31}^2 Q_m^{\sigma} \cdot 10^{-3}$	22	114	96
	$\frac{k_{33}^2}{(E_r^0 = 100 \text{ kV/m})} \tan \delta$	26.65	62	19.6
	σ_{dyn} [MPa]	90	40	70
	T_c [K]	628	598	513
	$Y_{11}^E \cdot 10^{-11}$ [N/m ²]	0.85	0.80	0.73
	$(d_{31} \cdot Y_{11}^E)$ [C/m ²] ²	65	109	59

$\tan \delta$ dielectric loss angle tangent;

Q_m mechanical quality factor;

Q_m^{σ} mechanical quality factor (in this work $\sigma = 12$ MPa);

σ mechanical stress;

σ_{dyn} dynamic strength;

Y_{11}^E Young's modulus ($E = 0$);

E electric field intensity;

T_c Curie-temperature (Curie point);

$k_{31}^2 Q_m^{\sigma}$ piezoelectric quality factor which determines of the piezotransformer voltage ratio:

$$K_{U_0} = \frac{4k_{31}^2 Q_m^{\sigma}}{\pi^2(1 - k_{31}^2)}, \quad (2)$$

and the efficiency of the piezotransformer:

$$\eta_{\text{pt}} = \frac{1}{1 + \frac{\pi^2}{2Q_m^{\sigma} \cdot k_{33}^2}}; \quad (3)$$

$\frac{\varepsilon_{33}^{\sigma}}{\varepsilon_0} k_{31}^2 Q_m^{\sigma}$ product which determines the unit power of the piezotransformer:

$$N = \frac{2b}{\pi a} U^2 v_s \cdot \frac{\varepsilon_{33}^{\sigma}}{\varepsilon_0} k_{31}^2 Q_m^{\sigma}, \quad (4)$$

where U — supply voltage; v_s — speed of sound in the piezoelectric transducers; a , b — thickness and width of the piezoelectric ceramics;

$(d_{31} \cdot Y_{11}^E)^2$ product which determines of the unit shaft power of the piezoelectric engine:

$$N = \frac{2b}{\pi a} U^2 v_s \cdot Q_m^{\sigma} (d_{31} Y_{11}^E)^2; \quad (5)$$

$\Delta f_r / f_r$	relative change of the resonance frequency f_r ;
γ	pyroelectric coefficient;
HF	hard ferroelectrics;
MHF	moderately hard ferroelectrics;
SF	soft ferroelectrics.

2.2. The PZT-type ceramics with chemical constitutions corresponding to the R- or T-boundary of the morphotropic region

As been mentioned, there are only few data on the influence of the lead vacancies on the structure of the solid solutions prepared on the basis of PZT. PZT-type solid solutions with chemical constitutions within the morphotropic region (MR) was most often chosen as objects for the investigation. It is known (e.g. [2, 6]) that solid solutions with chemical constitutions which correspond to the diphasic system: (rhombohedral phase (RP) + tetragonal phase (TP)) are characterized by a high sensitivity to external effects and internal changes. Therefore, one could expected considerable changes of the structure with changing stoichiometry.

Investigations of the influence of V^{Pb} vacancies on the structure of PZT-type solid solutions have been performed either on the PCR-1 ceramics [10], the chemical constitution of which corresponded to the rhombohedral boundary of the morphotropic region (R-boundary of MR) or on the PCR-8 ceramics [11, 12] the chemical constitution of which corresponded to the tetragonal boundary of the morphotropic region (T-boundary of MR). The samples for the investigations have been prepared first by the classical ceramic technology and then they were roasted under oxygen (to avoid the creation of oxygen vacancies V^{O}). X-ray investigations were performed by the X-ray diffractometer DRON-3M (CuK_{α}). To separate the partially overlapped X-ray reflections, the method of approximation of the diffraction maxima was applied [13, 14]. Results of the investigations are shown in Figs. 4, 5 and 6.

It results from the analysis of Fig. 4 that a thermal treatment of the PCR-1 samples at temperatures $T < 1123$ K does not involve any considerable change of the X-ray reflection profiles registered at room temperature. After treatment at $T_s = 1123$ K, beside the 200 reflection of the R-phase, there appear in the X-ray patterns weak reflections typical of the tetragonal cell of the perovskite-type structure. After roasting at that temperature the weak reflections relevant to ZrO_2 and PbO also appear.

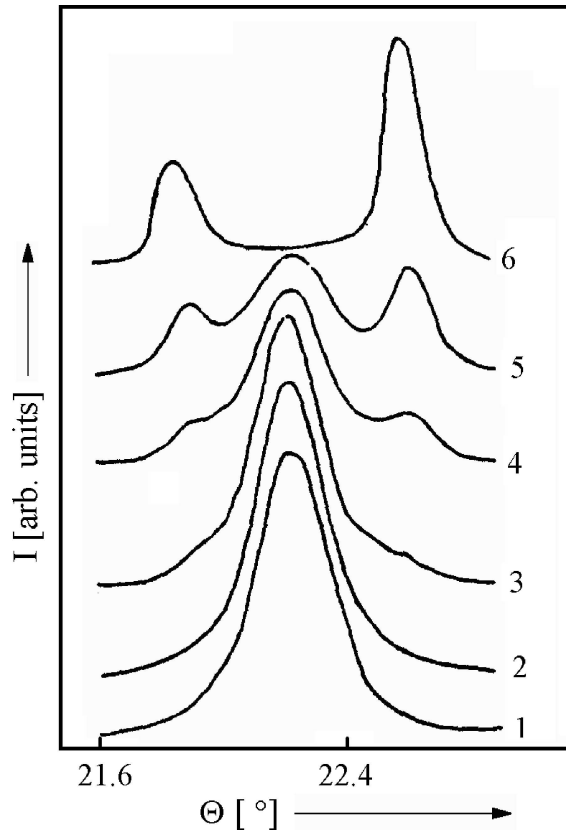


Fig. 4. Profiles of the X-ray reflections of the 200-type obtained at room temperature for the PCR-1 ceramics after roasting at different temperatures: 1 — 873 K; 2 — 1073 K; 3 — 1123 K; 4 — 1173 K; 5 — 1223 K; 6 — 1273 K.

With increasing temperature of the thermal treatment the intensity of reflections typical of the T-phase increases, whereas the R-phase reflections are gradually broadened and weakened. After roasting at $T_s = 1273$ K one can observe strong reflections which are typical of the T-phase and weak reflections due to ZrO_2 and PbO . The presence of those free oxides in the samples makes one suppose that the main reason of observed reconstruction of the crystalline structure in the ferroelectric phases of the PZT-type ceramics is a partial decay of the solid solution caused by the thermal treatment.

As a result of the decay of the solid solution, the T-phase is characterized by smaller, volume of the elementary cell in comparison with the R-phase and a greater spontaneous deformation δ_T in comparison with δ_R (where: $\delta_T = \frac{2}{3} \left(\frac{c_T}{c_a} - 1 \right)$; $\delta_R \approx \cos \alpha_R$, [15]). The transition of the R-phase into the T-phase is accompanied by a decrease of the a_R parameter (R-phase) and increase of the spontaneous deformation δ_T (see Fig. 5).

Similar results were obtained from the investigations of the influence of a high temperature thermal treatment on the structural characteristics of PCR-8 ceramic ferroelectrics

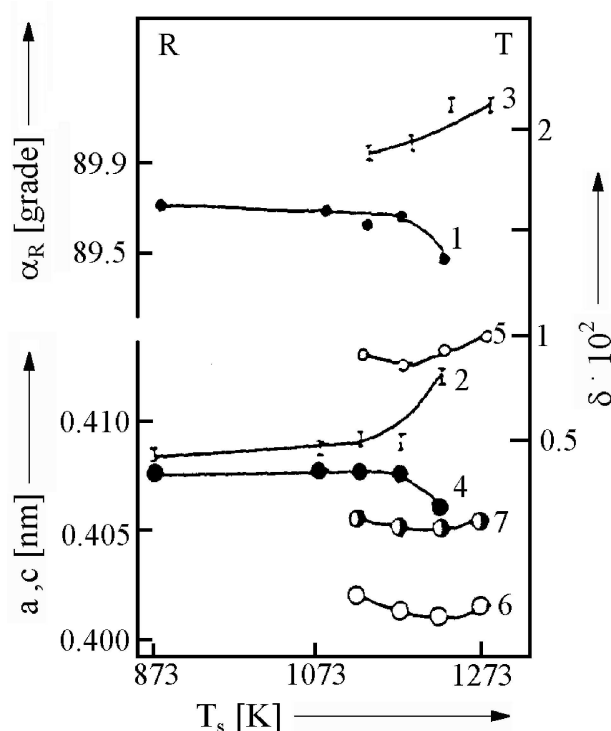


Fig. 5. Dependence of the elementary cell parameters of the rhombohedral (R) and tetragonal (T) phases determined for the PCR-1 ceramics after roasting at different temperatures (873–1273 K): 1 — α_R ; 2 — δ_R ; 3 — δ_T ; 4 — a_R ; 5 — c_T ; 6 — a_T ; 7 — $\bar{a}_T = \sqrt{a_T^2 c_T}$.

(Fig. 6). With a roasting temperature increasing from $T_s = 1123$ K one can observe additional diffraction reflections on the X-ray patterns recorded at room temperature. Some of those reflections came from the oxides: ZrO_2 and PbO . Moreover, a change of the diffraction profiles of the perovskite-type multiplets took place. The character of that change proves that the second T-phase appears and that the concentration of the new phase increases as well as the primary T-phase. That additional T-phase is characterized by a smaller a_T parameter, a smaller volume of the elementary cell ($a_T^2 c_T$) and a greater spontaneous deformation (δ_T) in comparison to the primary T-phase.

The most probable reason of the observed changes of the crystalline structure of the piezoceramics during the thermal treatment is the evaporation of lead from some crystallites. The results of the structure investigations, carried out on PCR-8 samples obtained by a synthesis of the parent substance with a 15% deficiency in lead, seem to prove that. In the case of stoichiometric samples, which were roasted as well as in the case mentioned above a decrease in a_T parameter and increase in δ_T at the room temperature have been ascertained.

The appearance of the reflections connected with ZrO_2 and PbO on the X-ray pattern and the lack of reflections related to TiO_2 show that the disturbance of stoichiometry

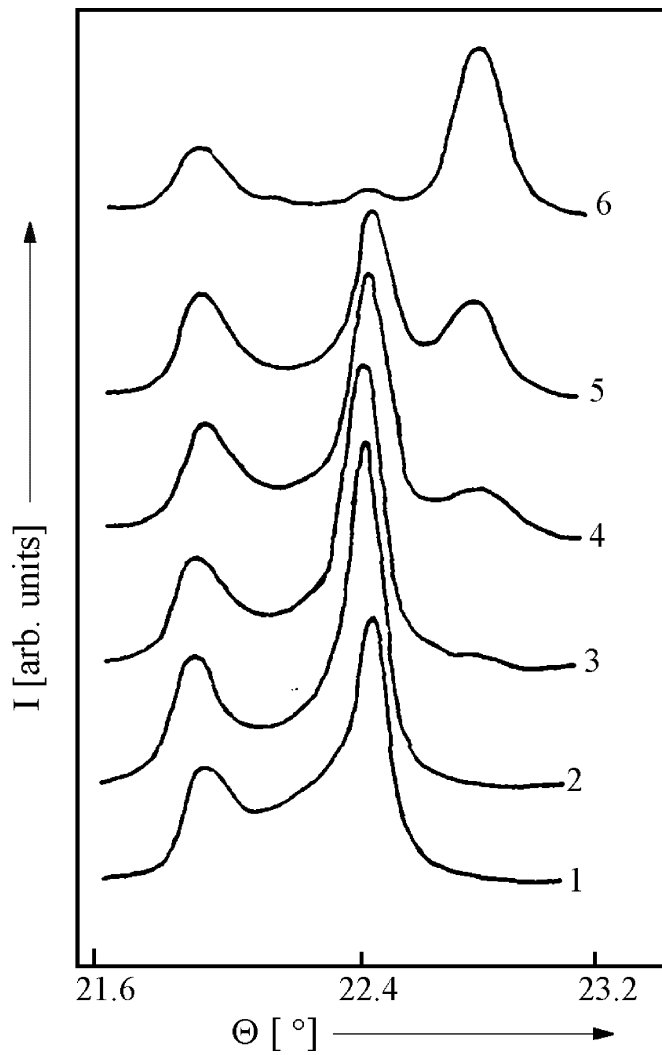


Fig. 6. Profiles of the X-ray reflections of the 200-type obtained at room temperature for the PCR-8 ceramics after roasting at different temperatures: 1 — 873 K; 2 — 1073 K; 3 — 1123 K; 4 — 1173 K; 5 — 1223 K; 6 — 1323 K.

by Pb evaporation takes place first of all as the result of breaking the Zr–Pb bonds in the crystalline lattice. Therefore, the concentration of Ti increases in the sublattice B of the ABO_3 perovskite structure (where: A–Pb; B–Zr,Ti) of the crystallites with Pb vacancies. This leads to a gradual decay of the solid solution into the new perovskite phase and the oxides ZrO_2 , PbO. At a temperature $T < T_c$, the new perovskite phase is characterized by smaller a_T and greater δ_T values in comparison with the primary T-phase because its chemical constitution becomes closer to $PbTiO_3$ for which $a_T = 0.3904$ nm, $c_T = 0.4150$ nm and $\delta_T = 0.0420$ [16].

2.3. PZT-type piezoceramics with chemical constitution of the T-phase region

The solid solution of $\text{PbTiO}_3 - \text{PbZrO}_3 - \text{Pb}(\text{W}_{1/2}\text{Cd}_{1/2})\text{O}_3$ with a little amount of the third component was chosen to find how the lead deficiency influences the PZT-type piezoceramic materials with the constitutions from the T-phase region. The samples $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ have been synthesized with x varying stepwise by 0.025 in the from 0 to 0.1 and next by 0.1 from 0.1 to 0.5. The synthesis took place by a solid state reaction in the mixture of lead oxide, titanium oxide, zirconium oxide, cadmium oxide and tungsten oxide (all the oxides were analytically pure). Cadmium and tungsten oxides were introduced into the $\text{PbTiO}_3 - \text{PbZrO}_3$ system to accelerate the synthesis during the sintering process.

The ceramic material was obtained by the classical technology [3, 4]. The mixture of the oxides was obtained in the water medium by a vibration mixer. The disk compacts of 20 mm in diameter and 1 mm thickness (pressing pressure 5 MPa) were prepared from that mixture.

To determine each stage of the phase formation, the compacts were sintered four times in the temperature range 1173–1473 K. Each time the temperature was increased by 100 K. After the particular sintering, the samples were powdered and the compacts made again. The time of sintering was 10 hours (excluding the time of heating and cooling).

The investigations of the crystalline structure have been performed by the X-ray diffraction method (DRON-3; CuK_α , β -filtr).

There are fragments of the X-ray patterns of the samples characterized by $x = 0$, $x = 0.075$ and $x = 0.400$ in Figs. 7–9, respectively.

From analysis of those X-ray patterns it result that after roasting at 1173 K the perovskite-type structure was formed in all the cases. The reflections 001, 100, 011, 110 etc. confirm it. The reflections from ZrO_2 were also registered in the case of $x = 0$ (Fig. 7).

In the case of low x values ($x < 0.2$) the perovskite type structure was not a “monotetragonal” one. This is indicated by the profiles of the 011 and 110 reflections and their location in relation to 2θ seen in Figs. 7 and 8, when the roasting temperature increases both the profiles of the above mentioned reflections and their location versus 2θ changed.

For samples which are characterized by large x values ($x > 0.3$), the “monotetragonal” structure appears just after the first sintering at $T_s = 1173$ K and the elementary cell parameters are: $a_T = 0.3920$ nm and $c_T = 0.4145$ nm. These parameters are close to those of pure PbTiO_3 ($a_T = 0.3904$ nm; $c_T = 0.4150$ nm [16]). The similarity of the structure of pure PbTiO_3 to that of the PZT-type piezoceramic having $x = 0.4$, is shown most clearly by a comparison of the suitable X-ray patterns (see Figs. 9 and 10). One can see that not only the locations of the suitable reflections are close to each other but also the ratios of their total intersites are nearly the same.

When the roasting temperature increases, the degree of the structural perfection of the obtained piezoceramics increases (see Figs. 7, 8 and 9).

The parameters of the perovskite-type structure tetragonal cells of piezoceramics with different x , determined after sintering at 1473 K for 10 hours, are shown in Table 3. It results from the analysis of the data given in that table and after a comparison

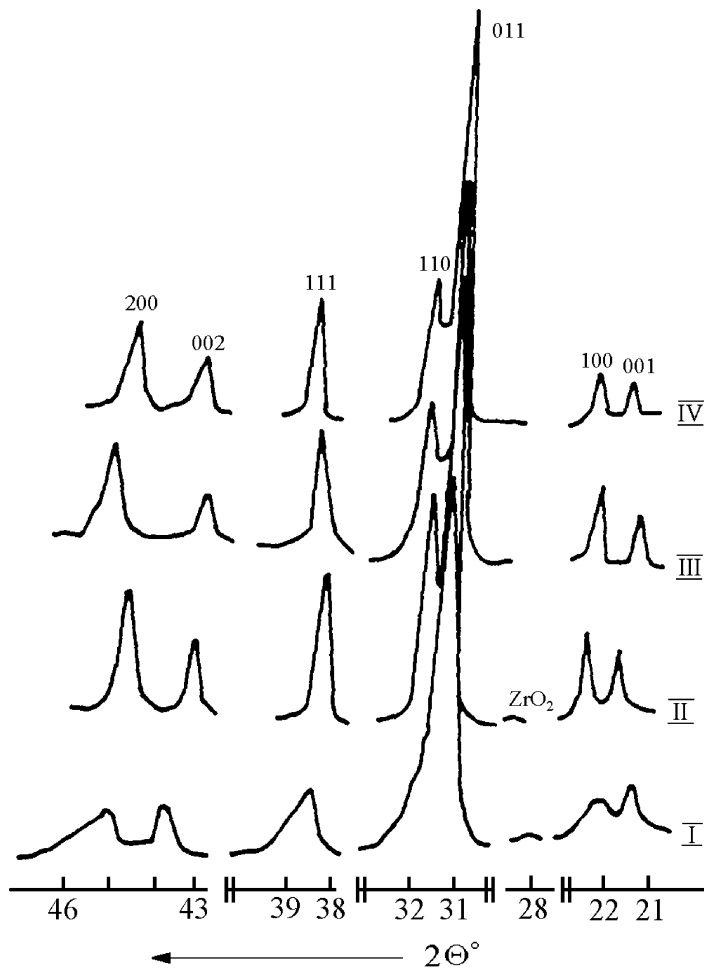


Fig. 7. Fragments of the X-ray patterns obtained at room temperature for the $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ piezoceramics in the case of $x = 0$ after sintering at the following temperatures: I — 1173 K; II — 1273 K; III — 1373 K; IV — 1473 K (sintering time $t_s = 10$ h).

with the PbTiO_3 elementary cell parameters ($a_T = 0.3904$ nm; $c_T = 0.4150$ nm) and with those of the PbZrO_3 elementary cell ($a_T = 0.4159$ nm; $c_T = 0.4109$ nm; pseudotetragonal system) and with the $\text{PbTiO}_3 - \text{PbZrO}_3$ solid solution elementary cell parameters [1], that when the lead deficiency increases, the perovskite-type phase of $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ becomes similar to PbTiO_3 as regards the chemical constitution and the parameters of the elementary cell. That result is consistent with the kinetic data of the synthesis in the $\text{PbO} - \text{TiO}_2 - \text{ZrO}_2$ system. According to ref. [1], the synthesis at low temperatures ($T_s < 973$ K) begins from the creation of PbTiO_3 . The latter reacts with ZrO_2 only at higher temperatures ($T_s > 973$ K) and forms $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with the oxides PbO and TiO_2 remaining free.

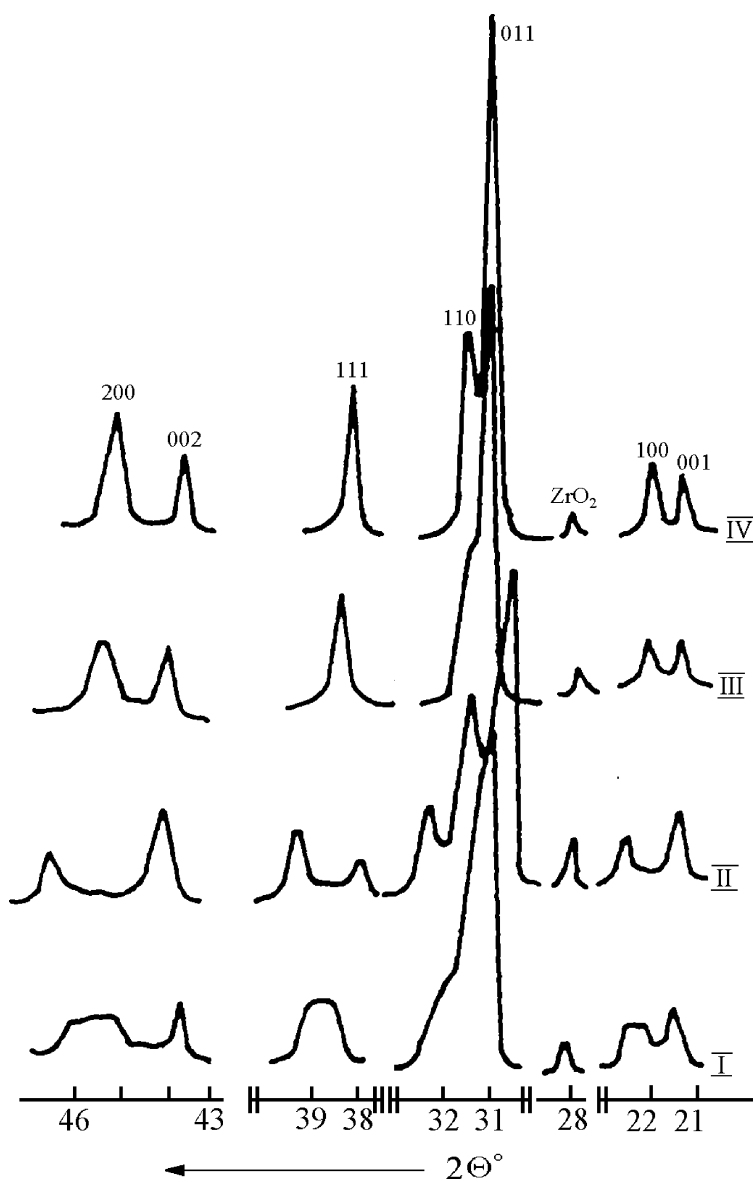


Fig. 8. Fragments of the X-ray patterns obtained at room temperature for the $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ piezoceramics in the case of $x = 0.075$ after sintering at the following temperatures: I — 1173 K; II — 1273 K; III — 1373 K; IV — 1473 K (sintering time $t_s = 10$ h).

The chemical constitution of the perovskite-type phase is shown in the column 5 of Table 3. The constitution has been calculated with the assumption that the valency balance can be satisfied even if there is no excess of ZrO_2 in the reaction.

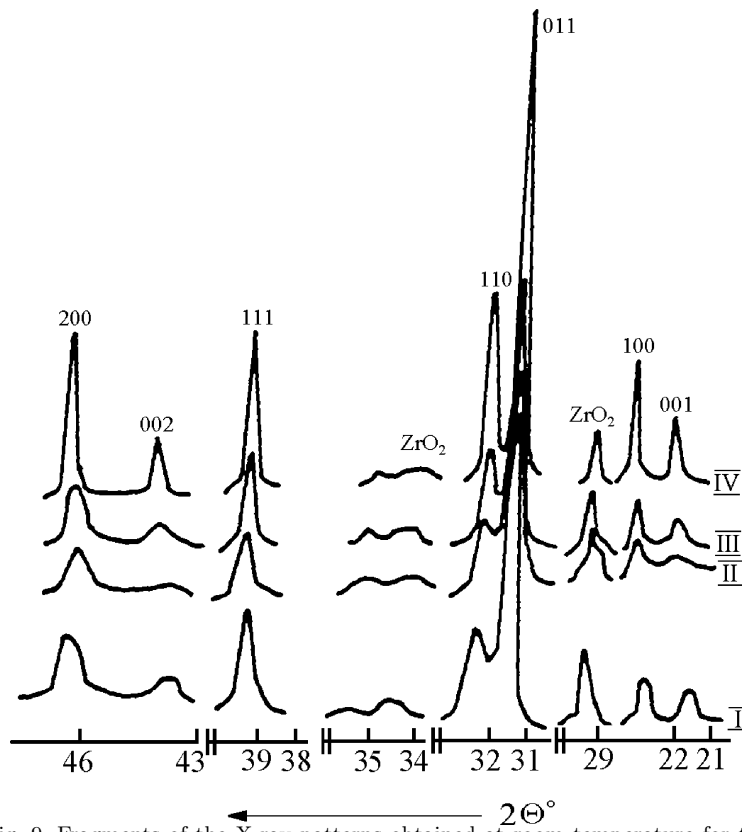


Fig. 9. Fragments of the X-ray patterns obtained at room temperature for the $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$ piezoceramics in the case of $x = 0.4$ after sintering at the following temperatures: I — 1173 K; II — 1273 K; III — 1373 K; IV — 1473 K (sintering time $t_s = 10$ h).

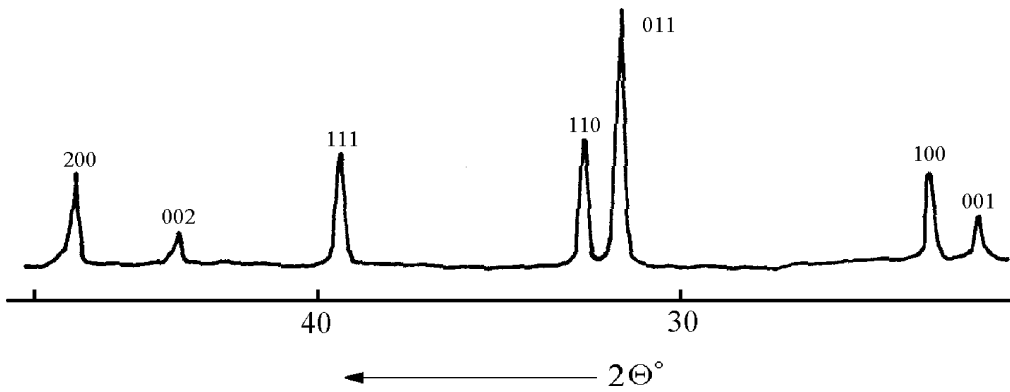


Fig. 10. X-ray pattern of the PbTiO_3 powder obtained under the same conditions as the X-ray patterns presented in Figs. 7, 8, and 9.

Table 3. Parameters of the elementary cells of the PZT-type solid solution of the chemical constitution $\text{Pb}_{1-x}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$.

No	x	a_T [nm]	c_T [nm]	Chemical constitution taking into account deficiency in lead
1	2	3	4	5
1	0.000	0.3978	0.4131	$\text{Pb}(\text{Zr}_{0.39}\text{Ti}_{0.59}\text{W}_{0.01}\text{Cd}_{0.01})\text{O}_3$
2	0.025	0.3989	0.4143	$\text{Pb}(\text{Zr}_{0.3744}\text{Ti}_{0.6050}\text{W}_{0.0103}\text{Cd}_{0.0103})\text{O}_3$
3	0.050	0.3985	0.4139	$\text{Pb}(\text{Zr}_{0.3579}\text{Ti}_{0.6211}\text{W}_{0.0105}\text{Cd}_{0.0105})\text{O}_3$
4	0.075	0.3992	0.4149	$\text{Pb}(\text{Zr}_{0.3406}\text{Ti}_{0.6378}\text{W}_{0.0108}\text{Cd}_{0.0108})\text{O}_3$
5	0.100	0.3965	0.4132	$\text{Pb}(\text{Zr}_{0.3222}\text{Ti}_{0.6556}\text{W}_{0.0111}\text{Cd}_{0.0111})\text{O}_3$
6	0.200	0.3955	0.4141	$\text{Pb}(\text{Zr}_{0.2375}\text{Ti}_{0.7375}\text{W}_{0.0125}\text{Cd}_{0.0125})\text{O}_3$
7	0.300	0.3951	0.4131	$\text{Pb}(\text{Zr}_{0.1285}\text{Ti}_{0.8429}\text{W}_{0.0143}\text{Cd}_{0.0143})\text{O}_3$
8	0.400	0.3920	0.4145	$\text{Pb}(\text{Ti}_{0.9666}\text{W}_{0.0167}\text{Cd}_{0.0167})\text{O}_3$
9	0.500	0.3921	0.4146	$\text{Pb}(\text{Ti}_{0.9600}\text{W}_{0.0200}\text{Cd}_{0.0200})\text{O}_3$

3. Conclusions

1. Creation of the lead vacancies (V^{Pb}) in the solid solutions prepared on the basis of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ causes the following changes in the physical properties:

- increase in the permittivity (ε);
- large dielectric loss ($\tan \delta$);
- increase of the elastic compliance (S_{ijkl});
- decrease in mechanical quality factor (Q_m);
- increase of the electromechanical coupling coefficient (k_p);
- decrease of the coercive field (E_c);
- increase of the squareness ratio of the dielectric hysteresis loop;
- strong increase of the specific resistance (ρ_v);
- typical weak aging process;
- non-elastic mechanical deformation compliance (deformability);
- yellow colour;
- translucency of the sample;
- darkening of the sample under the influence of light.

2. The obtaining of PZT-type piezoceramics under the conditions, which are conducive to the creation of the lead vacancies leads to the formation of structures that differ from the stoichiometric solid solution structure. The sort of those structural changes depends on the chemical constitution of the PZT-type ceramics, strictly speaking on the place the compound occupies on the solid solution phase diagram and on the concentration of the lead vacancies. Namely:

a) if the chemical constitution of the material corresponds to the rhombohedral boundary of the morphotropic region so, as the roasting temperature increases (as the deficiency in lead increases), the strong diffraction maxima corresponding to the R-phase gradually decay but the T-phase diffraction maxima increase in the X-ray patterns. Diffraction maxima corresponding to ZrO_2 and PbO appear and become distinct. Therefore the partial decay of the solid solution takes place as the result of the disturbance stoichiometry

caused by the thermal treatment. It causes the reconstruction of the perovskite-type crystalline structure from the (R+T)-phase to the T-phase;

b) if the chemical constitution of the material corresponds to the tetragonal boundary of the morphotropic region therefore, the weak diffraction maxima corresponding to the R-phase and strong maxima corresponding to the primary T-phase gradually decay, as the roasting temperature increases (i.e. as the deficiency in lead increases), whereas new T-phase maxima appear and become more distinct in the X-ray patterns. The new T-phase of the perovskite structure is characterized by a smaller a_T parameter and a larger deformation δ_T in comparison with those of the primary T-phase. The reflections corresponding to ZrO_2 and PbO also appear. Thus, in that case the partial decay of the solid solution into the perovskite-type structure phase and of the free ZrO_2 and PbO takes place as a result of the disturbance of the stoichiometry caused by the thermal treatment. The primary phase of the perovskite structure (R+T (I)) converts into the new T (II)-phase;

c) if the chemical constitution of the material corresponds to the tetragonal phase, the roasting temperature of the samples with a small deficiency in lead increases the new T-phase appearing beside the primary tetragonal phase. The new T-phase is characterized by a smaller a_T parameter and greater δ_T deformation. In case of a large deficiency in lead, only the new perovskite-type T-phase appears after roasting at 1173 K as well as free PbO and ZrO_2 . The chemical constitution and the elementary cell parameters of the perovskite-type T (II)-phase become closer to $PbTiO_3$.

3. The possibility of a disturbance in the stoichiometry resulting from the creation of lead vacancies is a serious problem of the PZT-type piezoceramic materials technology. The loss in lead takes place both during the synthesis and during the thermal treatment of this material. The knowledge of the crystalline structure changes caused by the increasing in lead deficiency makes it possible to develop methods of checking the loss of Pb atoms from the A sublattice of the perovskite-type structure (ABO_3).

4. The creation of lead vacancies in the PZT-type piezoceramic materials by introducing soft doping ions into the A sublattice makes it possible to obtain a soft ferroelectric material which is likely to be widely applied in engineering. However, the deficiency in lead in the PZT caused by the thermal treatment leads to a partial decay of the solid solution and a stepwise conversion of $Pb(Zr,Ti)O_3$ into $PbTiO_3 + ZrO_2 + PbO$. In that case the deficiency in lead is unfavorable from the point of view of the application possibilities of the obtained materials.

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