Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 7635–7640

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The PZT system ($PbTi_xZr_{1-x}O_3$, $0\leq x\leq 1.0$): The dependences of electrophysical properties of solid solutions on the electric field strength and component concentration (Part 5)

I.N. Andryushina*, L.A. Reznichenko, L.A. Shilkina, K.P. Andryushin, Yu. I. Yurasov, S.I. Dudkina

Research Institute of Physics, Southern Federal University, Stachki Avenue 194, 344090 Rostov-on-Don, Russia

Received in revised form 8 February 2013; accepted 25 February 2013

Abstract

The physical properties of PZT ($PbTi_xZr_{1-x}O_3$, $0.0\leq x\leq 1.0$) ceramics were studied in broad ranges of constant and alternating electric field strengths (0 kV/cm≤E≤30 kV/cm). Dielectric, piezoelectric and elastic parameters of the solid solutions at room temperature were investigated. The results can be helpful to develop of PZT based materials for use in various high-voltage devices and bend components such as varactors, phase shifters, etc.

Keywords: D. PZT; Electrophysical properties; Electric field

1. Introduction

The binary solid solutions (SSs) of the composition (1−x) $PbZrO_{3-x}$–$x$$PbTiO_3$ (PZT) have hitherto retained their uniqueness and practical value. Multicomponent systems with their participation became the basis for most of the industrially produced ferropiezoelectric materials (FPM). At the same time the technical needs pose material science problems, which require the knowledge of the laws of formation of electrophysical properties of such materials in wide ranges of component concentrations and external actions including the electric field strengths. The latter is important for the prediction of potential application of the PZT based FPM in high-voltage devices: varactors, phase shifters, etc.

The aim of the present work was to study the formation of piezoelectric properties of SS of the PZT system in broad ranges of the electric bias field strengths and component concentrations.

2. Objects under study, their synthesis and study methods

The objects under study were the ceramics of SS of the $PbTi_xZr_{1-x}O_3$ system with $0.0\leq x\leq 1.0$. Their synthesis methods are described in detail in [1]. The measurements of the deformative (the reciprocal piezoelectric coefficients $d_{33}^{rec}(E)$ and strains ξ_3 induced by the applied electric field E_3) and reverse properties (the relative dielectric constant, which was measured using weak alternating electric field in the presence of cyclically changing strong biasing electric field) were conducted employing previously polarized piezoelectric elements using home-made test benches. The polarization properties were studied using the oscillographic method (according to the Sawyer–Tower scheme).

Dielectric, piezoelectric and elastic parameters of the SSs at room temperature were measured by the resonance–antiresonance method [2]. In doing this, we determined the relative dielectric permittivities of poled ($\varepsilon_{33}^T/\varepsilon_0$) and unpoled ($\varepsilon/\varepsilon_0$) samples, the dielectric losses at a low electric field (loss tangent, tg δ), the piezoelectric modulus (d_{31}), the electromechanical coupling factor of a planar mode of vibration (K_p), the mechanical quality factor (Q_M), Young's modulus (Y_{11}^E) and the sound speed (V_1^E). The relative errors in determining these parameters were as follows: $\leq\pm1.5\%$ for $\varepsilon_{33}{}^T/\varepsilon_0$, $\leq\pm2.0\%$ for K_p, $\leq\pm4.0\%$ for $|d_{31}|$, $\leq\pm12\%$ for Q_M, and $\leq\pm1.0\%$ for Y_{11}^E.

---

[*] Corresponding author. Tel.: +7 8632434066.
E-mail address: futur6@mail.ru (I.N. Andryushina).

http://dx.doi.org/10.1016/j.ceramint.2013.02.100

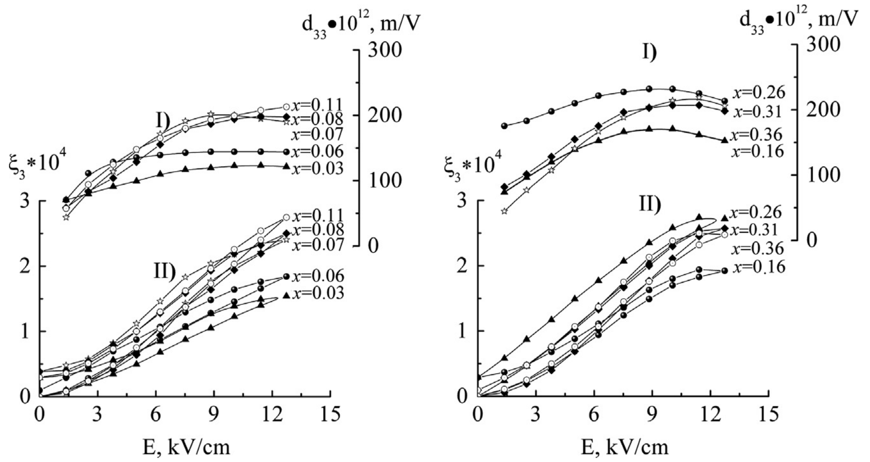

Fig. 1. The dependences of the reciprocal piezoelectric coefficient d_{33} (I) and of the half-cycles of the dielectric hysteresis loops (II) on the electric field strength for SS of the PZT system ($0.0 \leq x \leq 0.36$).

3. Experimental results and discussion

Fig. 1 shows the half-cycles of the electromechanical hysteresis loops of SS and the calculated effective reciprocal piezoelectric coefficients d_{33}. The uniform dependences of $\xi_3(E)$ in the ascending and descending half-cycle branches of the electromechanical hysteresis are typical for all SS. However, the $d_{33}(E)$ dependences are different for SSs with different concentrations. In the concentration interval $0.00 \leq x \leq 0.03$ the piezoelectric coefficient was not detected due to the antiferroelectric nature of $PbZrO_3$ and SS close to it. In the concentration range $0.03 < x \leq 0.36$ a linear increase of d_{33} is found in weak fields (d_{33} increases by 10–15%), which gives place to a plateau-like region at $E = 7.0/10.0$ kV/cm (piezoelectric coefficient either weakly decreases or remains constant). Such d_{33} dependence is typical for hard ferroelectric materials.

Fig. 2 shows the evolution of the reverse dielectric constant. One can distinguish three different regions of changes in the reverse dielectric constant. The first region belongs to intervals $0.0 < x \leq 0.05$ and $0.50 < x \leq 1.0$, in which the maximum of $(\varepsilon_{33}^T/\varepsilon_0)_{\max}$ forms only for positive values of E, whereas the dependence $(\varepsilon_{33}^T/\varepsilon_0)(E)$ becomes almost linear and without hysteresis. The second region is from $x = 0.06$ to $x = 0.465$ and is characterized by symmetrical butterfly-like loops with $(\varepsilon_{33}^T/\varepsilon_0)_{\max} = 200$–$600$, which are practically independent of x. The third region, is located at $0.465 \leq x \leq 0.50$ and characterized by asymmetrical loops with high values of $(\varepsilon_{33}^T/\varepsilon_0)_{\max}$ at increasing positive E values and by the extreme dependence of this peak value of the reverse dielectric constant on the concentration of components (Fig. 2). At the same time the maximum value of $(\varepsilon_{33}^T/\varepsilon_0)_{\max}$ corresponds to the region of positive E, whereas the extremum of $(\varepsilon_{33}^T/\varepsilon_0)_{\max}(x)$ is located at the center of the morphotropic region (MR; $x = 0.48$). It was pointed out in Refs. [3,4] that the increase of E can, on the one hand, result in the increase of the reverse dielectric constant due to the disappearance of the 180° domain walls and, as a result, cause "release" of domains after clipping. It can also result in various phase transitions, which promote increased mobility of the interphase boundaries and of the interphases of nonpolar and polar microregions and increase the number of the latter. On the other hand, the decrease of $\varepsilon_{33}^T/\varepsilon_0$ can be related to the increase of E due to the coarsening of domains and the regions of different compositions, which promotes the decrease of the number of domains and interphase walls and, as a consequence, the decrease of the contribution of their oscillations to the reverse dielectric constant. The decrease of $\varepsilon_{33}^T/\varepsilon_0$ can also be related to the 90° switching due to the existing anisotropy $\varepsilon_c \ll \varepsilon_a$, as well as to the twinning and untwining processes, which are reflected in the displacements of 90° wedges and which multiply linear defects and anchor the domain walls.

Fig. 3 shows the typical dielectric hysteresis loops of SS of the PZT system. One can distinguish six characteristic concentration regions.

The first one is located between $x = 0.00$ and $x = 0.05$. Neither nonpoled nor poled samples from this region show dielectric hysteresis loops, which are obvious due to the antiferroelectric character of SS compositionally close to $PbZrO_3$.

The second region ($0.06 \leq x \leq 0.13$) is characterized by the presence of quasistatic loops at $t = 10$ s. The increase of the measurement time to 30 s results in the loop broadening (in height and width), whereas its form is retained. After 120 s the loop takes a saturated quasistatic form. The poled samples of the same compositions show similar behavior.

In the third region with $0.14 \leq x \leq 0.19$ for measurement times of 10 s one observes loops with waists, which disappear after 20 s. The loops take quasistatic form after 120 s. The poled samples behave analogously to the SS from the second region.

In the fourth region with $0.19 < x \leq 0.40$ pronounced loops with waists are observed at 10 s, which remain after 20 s measurement time. After 120 s the loop improves and takes quasistatic form. The poled samples from the $0.19 < x < 0.37$ range possess quasistatic loops similar to those from the second region. Only above the concentration of $x = 0.37$ the

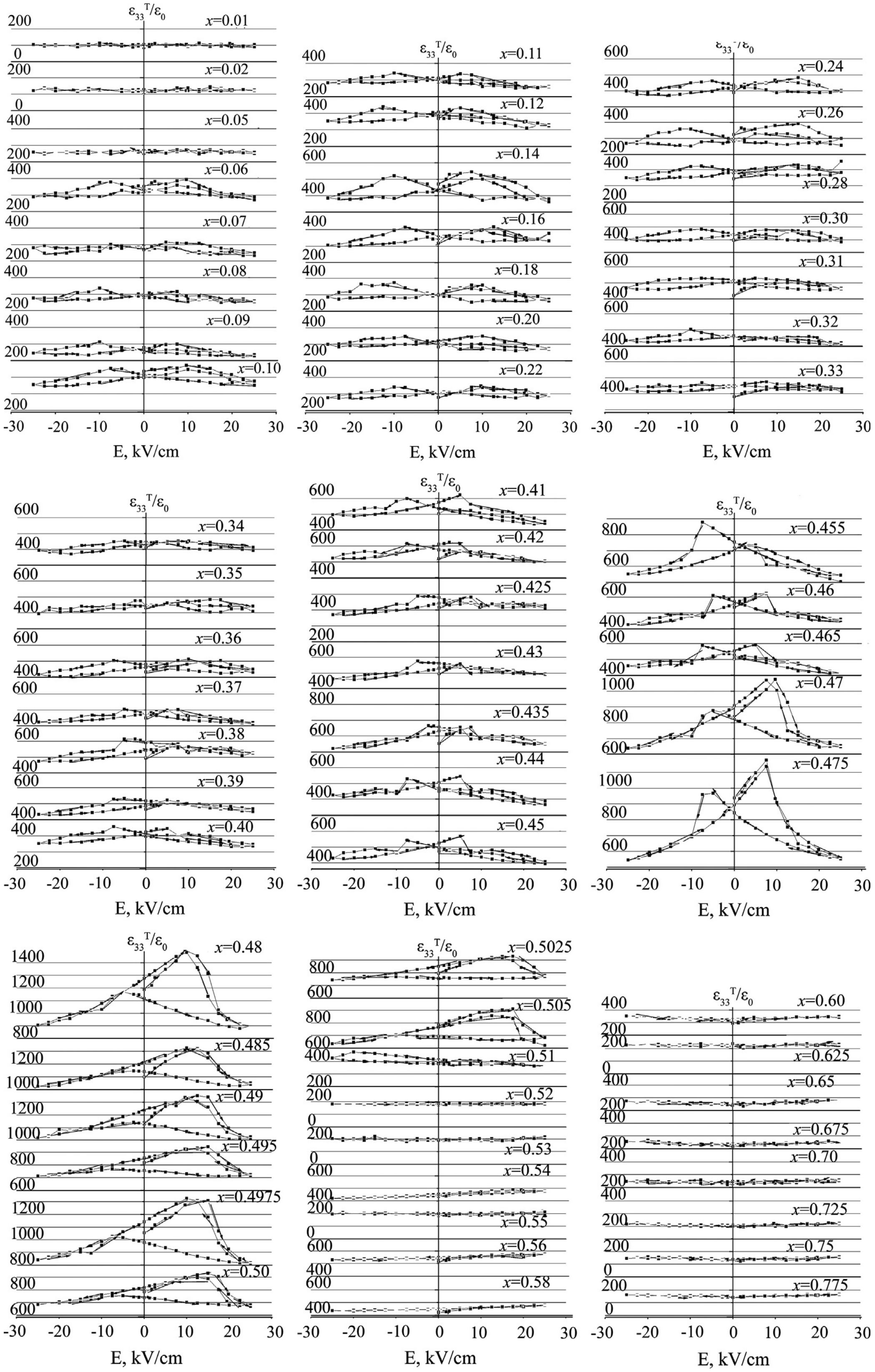

Fig. 2. The dependence of the reverse dielectric constant $\varepsilon_{33}^{T}/\varepsilon_0$ of the poled samples of $(1-x)$PbZrO$_{3-x}$ PbTiO$_3$ ($0.00 \leq x \leq 1.00$) SS on the electric field strength. The curves are denoted by the values of x and the symmetry of SS: R—rhombic, Rh—rhombohedral, and T—tetragonal.

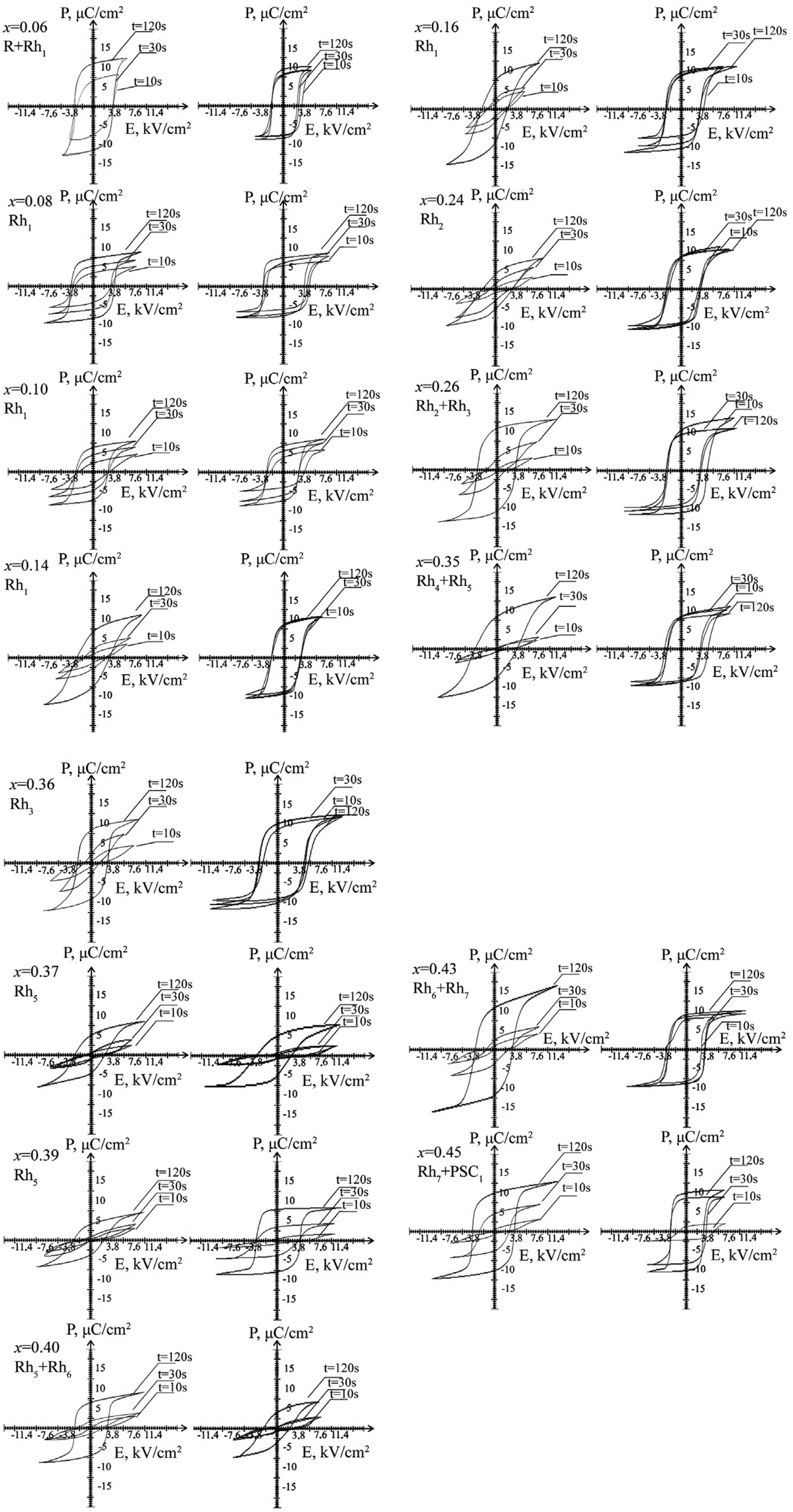

Fig. 3. Typical dielectric hysteresis loops of the nonpoled (left) and poled (right) SS of the PZT system ($0.06 \leq x \leq 0.47$).

SS behave analogously to the nonpoled samples of this group and shows loops with waists both after 10 and 30 s measurement times.

The fifth region with concentrations $0.41 \leq x \leq 0.48$ is characterized by the loops with waists at $t = 10$ s, whereas already after 20 s the loops take the quasistatic form. After 120 s the loops stretch and saturate. The behavior of the poled SS is analogous to that of the SS from the second region.

In the sixth concentration region $0.48 \leq x \leq 1.00$ the dielectric hysteresis loops could not be registered either for nonpoled or for poled samples due to their high conductivity.

The appearance of loops with waists is not the consequence of the ageing of the samples. The effect recurred for naturally "old" and newly-synthesized ceramics independent of the experiment conduction time (we repeated the studies systematically during half a year). It is possible that this form of the loops is related to different phase contents of the samples close to and inside the MR. This assumption is favored by the more pronounced loops of SS in the vicinity of the MR.

Fig. 4 shows the concentration dependence of electrophysical properties of $PbTi_xZr_{1-x}O_3$ SS. As can be seen, the "absolutely" extreme values of parameters are achieved at the transition from one phase to another. The maximum values of the main characteristics $\varepsilon/\varepsilon_0$, $\varepsilon_{33}^T/\varepsilon_0$, K_p, and d_{31} correspond to the MR (Rh→T). At the transition from one phase state to another the electrophysical parameters experience minor changes (local extrema). All these determine the strong irregularity of the concentration dependences of electrophysical characteristics and their extreme values in the MR can probably be attributed to several causes including:

(1) the rotation of the spontaneous polarization vector between the directions of the tetragonal [001] and rhombohedral [111] phases [5];
(2) the greater mobility of small (nano-) domains, which form in the vicinity of the morphotropic phase transitions [6];
(3) the crystal-chemical peculiar properties of the A and B cations and of the structure-forming oxygen octahedra [7].

The unusual behavior of K_p and d_{31} with two peaks, one of which coincides with the maximum of $\varepsilon_{33}^T/\varepsilon_0$, can be explained as follows. Based on the fact that the piezoelectric parameters K (the electromechanical coupling coefficient) and d (the piezoelectric constant) depend primarily on two variables, namely on the residual polarization and the dielectric constant, one can write the following expressions for ceramics: $d \sim \varepsilon^T P_r$ and $K \sim (\varepsilon^T)^{1/2} P_r$, where P_r is the residual reorientational polarization [8]. Thus, K and d are influenced by two parameters (ε^T and P_r). At relatively low values of P_r the piezoelectric parameters apparently behave similar to $\varepsilon^T(x)$, whereas at low values of ε^T they are determined by the changes of $P_r(x)$. In the case of high values of both P_r and ε^T, both of them have significant influence on K and d, forming two peaks of these parameters. The minima of Q_M and Y_{11}^E in MR are associated with the increased defectiveness of SS due to the motion of the interphase and domain boundaries.

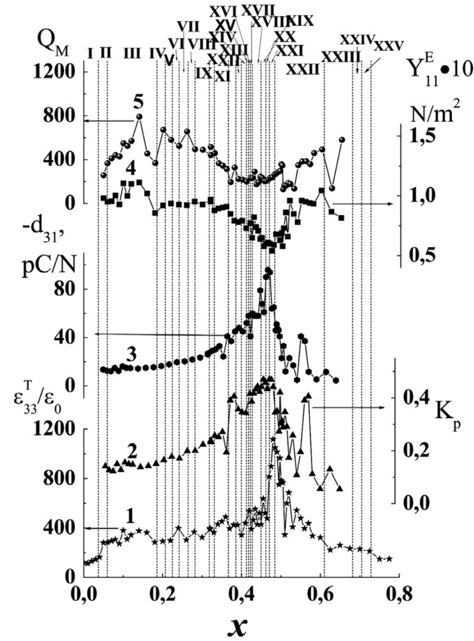

Fig. 4. The dependence of electrophysical properties on concentration of $PbTi_xZr_{1-x}O_3$ SS: $\varepsilon_{33}^T/\varepsilon_0$ (1), K_p (2), d_{31} (3), Y_{11}^E (4), and Q_M (5). The notation of the phases and phase states is given in Table 1 (where R—rhombic, Rh—rhombohedral, T—tetragonal, and PsC—pseudocubic).

Table 1
Localization of phases, phase states and their coexistence regions of the PZT system for the concentration interval $0.0 \leq x \leq 1.0$.

Region	Phase composition	Concentration interval	Region	Symmetry	Concentration interval
I	R	$0 \leq x \leq 0.04$	XV	Rh_7	$0.44 < x \leq 0.445$
II	$R+Rh_1$	$0.04 < x \leq 0.065$	XVI	Rh_7+Psc_1	$0.445 < x \leq 0.45$
III	Rh_1	$0.065 < x \leq 0.20$	XVII	$Rh_7+PsC_1+PsC_2$	$0.45 < x \leq 0.455$
IV	Rh_1+Rh_2	$0.20 < x \leq 0.22$	XVIII	$Rh_7+PsC_1+PsC_2+T_1$	$0.455 < x \leq 0.48$
V	Rh_2	$0.22 < x \leq 0.24$	XIX	PsC_2+T_1	$0.48 < x \leq 0.49$
VI	Rh_2+Rh_3	$0.24 < x \leq 0.26$	XX	T_1	$0.49 < x \leq 0.50$
VII	Rh_3	$0.26 < x \leq 0.28$	XXI	T_1+T_2	$0.50 < x \leq 0.515$
VIII	Rh_3+Rh_4	$0.28 < x \leq 0.30$	XXII	T_2	$0.515 < x \leq 0.65$
IX	Rh_4	$0.30 < x \leq 0.34$	XXIII	T_2+T_3	$0.65 < x \leq 0.725$
X	Rh_4+Rh_5	$0.34 < x \leq 0.35$	XXIV	T_3	$0.725 < x \leq 0.75$
XI	Rh_5	$0.35 < x \leq 0.39$	XXV	T_3+T_4	$0.75 < x \leq 0.775$
XII	Rh_5+Rh_6	$0.39 < x \leq 0.41$	XXVI	T_4	$0.775 < x \leq 0.925$
XIII	Rh_6	$0.41 < x \leq 0.425$	XXVII	T_4+T_5	$0.925 < x \leq 0.95$
XIV	Rh_6+Rh_7	$0.425 < x \leq 0.44$	XXVIII	T_5	$0.95 < x \leq 1.0$

4. Conclusions

The changes in the physical properties of the SS are determined in the broad ranges of component concentrations and electric field amplitudes. Three types of the reverse dielectric constant dependences are established resulting from the different degrees of ferroelectric hardness of SS and their different positions in the phase diagram.

It is found that the appearance of the $P(E)$ loops with waists is not related to the ageing of the samples, but rather to their different phase contents.

The degree of the ferroelectric hardness of the SS, which increases with increasing lead titanate concentration, substantially influences the formation of their deformative, polarization and reverse properties.

The analysis of Fig. 4 and Table 1 shows that the SS from the neighborhood of MR (XVIII–XX), which have the highest piezoelectric responses ($\varepsilon_{33}^T/\varepsilon_0 \sim 820$, $K_P \sim 0.50$, $|d_{31}| \sim 100$; $Y_{11}^E \sim 0.60$, $Q_M \sim 240$), can be the most suitable for the subsequent creation of materials.

The results can be helpful during the development of PZT based materials for use in various high-voltage devices and bend components such as varactors, phase shifters, etc.

Acknowledgments

We appreciate the help of Nikita Ter-Oganessian in the preparation of the manuscript. This work was financially supported by the Ministry of Education and Science of the Russian Federation, State Contract no. 16.740.11.0587.

References

[1] I.N. Andryushina, L.A. Reznichenko, V.A. Alyoshin, L.A. Shilkina, et al., The PZT system ($PbZr_{1-x}Ti_xO_3$, 0.0≤x≤1.0): specific features of recrystallization sintering and microstructures of solid solutions (part 1), Ceramics International 39 (1) (January 2013) 753–761.

[2] OST 11 0444- 87. Materiali piezokeramicheskie. Tehnicheskie usloviya. Vveden 01.01.88. Gruppa E10. 1988. 141p. (in Russian).

[3] G.A. Smolenskii, V.A. Bokov, V.A. Isupov, et al., Fizika segnetoelektricheskih yavlenii, Nauka, Leningrad, 1985 in Russian.

[4] A.V. Turik, E.N. Sidorenko, V.F. Zhestkov, V.D. Komarov, Reversivnye svoistva segnetokeramiki tipa $BaTiO_3$ na SVCh, Izv. AN SSSR. Ser. fiz. 34 (12) (1970) 2590–2593 In Russian.

[5] B. Noheda, J.A. Gonzalo, L.E. Cross, R. Guo, S.E. Park, D.E. Cox, G. Shirane, Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: the structure of $PbZr_{0.52}Ti_{0.48}O_3$, Physical Review B 61 (13) (2000) 8687–8695.

[6] K.A. Schönau, L.A. Schmitt, M. Knapp, H. Fuess, R.-A. Eichel, H. Kungl, M.J. Hoffmann, Nanodomain structure of $Pb[Zr_{1-x}Ti_x]O_3$ at its morphotropic phase boundary: investigations from local to average structure, Physical Review B 75 (18) (2007) 184117.

[7] J. Frantti, S. Ivanov, S. Eriksson, H. Rundlöf, V. Lantto, J. Lappalainen, M. Kakihana, Phase transitions of $Pb(Zr_xTi_{1-x})O_3$ ceramics, Physical Review B 66 (6) (2002) 641081–6410815.

[8] E.G. Fesenko, A.Ya. Dantsiger, O.N. Razumovskaya, Novie piezokeramicheskie materiali Rostov-na-Donu, Izd-vo RGU, 1983. (in Russian).