THE INFLUENCE OF THE La³⁺ CONTENT ON THE MECHANICAL PROPERTIES OF ELECTROOPTIC TRANSDUCERS BASED ON PLZT TYPE CERAMICS

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Modification of the PZT system by the addition La³⁺ ions has marked beneficial effect on several the basic parameters, such as squerness of the hysteresis loop, decreased coercive filed, increased dielectric constant, maximum coupling coefficients, increased mechanical compliance, decreased T_c temperature, and enhanced optical transparency.

The mechanical and electrical properties in lanthanum modified lead zirconate-titanate ceramics of 5/50/50 and 10/50/50 were studied by internal friction Q^{-1}, dynamic Young modulus E, electric permittivity ε and tangent of dielectric loss of angle $\tan\delta$ measurements. The temperature dependences of $Q^{-1} = f(T)$ and $E = f(T)$ were determinated in temperature range from 300 K to 600 K. The temperature dependences of $\varepsilon = f(T)$ and $\tan\delta = f(T)$ were determinated in temperature range from 300 K to 730 K. The values of T_C obtained during ε and $\tan\delta$ measurements were respectively: 560 K for 5/50/50 and 419 K for 10/50/50.

Keywords: internal friction, electrooptic transducers, PLZT ceramics.

1. Introduction

Pb(Zr, Ti)O₃ (PZT) crystallizes with the ABO₃ type structure in which the A-site is occupied by Pb²⁺ ions; Zr⁴⁺ and Ti⁴⁺ are accommodated on the B-site. The influence of various substitutions in the A and B-site of PZT unit cell has been studied by numerous investigators. The PLZT formula $(\mathrm{Pb}_{1-x}\mathrm{La}_x(\mathrm{Zr}_y\mathrm{Ti}_{1-y})_{1-x/4}\mathrm{O}_3)$ assumes that La³⁺ substitutes for Pb²⁺ in the A-site and the B-site vacancies are created for electrical balance. The composition of PLZT is routinely represented by the notation $x/(1-y)/y$, which denotes the amount of La/Zr/Ti, given in mole fractions or mole per cent. The PLZT type ceramics may be used as a materials for device applications such as nonvolatile memories, transducers, modulators, etc. [1–4].

2. Experiment

The material tested were solid solution of the PLZT type from ferroelectric phase with constant ratio Zr/Ti = 50/50 and variable concentration of La^{3+} ions: **$Pb_{0.95}La_{0.05}(Zr_{50}Ti_{50})_{0.9875}O_3$ – PLZT 5/50/50** and **$Pb_{0.95}La_{0.10}(Zr_{50}Ti_{50})_{0.975}O_3$ – PLZT 10/50/50**.

Ceramic samples were obtained as a reaction in solid state from simple oxides: PbO, ZrO_2, TiO_2, La_2O_3 by conventional ceramic sintering (CCS) method. Ceramic powders were mixed and milled through 20 h and next formed in cylindrical tablets of diameter 10 mm. After this tablets were synthesized at the temperature $T_S = 1123$ K through $t_s = 6$ h. Then polycrystalline samples were crumbled and mixed to obtained more homogenous structure. The range of sintering temperatures (1223–1523 K) and sintering times (6–12 h) were dependable from chemical composition. The electrodes were deposited on the surface of PLZT samples by the silver paste burning method. The obtained samples were subjected to polarization using the low temperature method ($T_p = 423$ K, $E_p = 30$ kV/cm, $t_p = 30$ min). The measurement of dielectric permittivity ε and tangent of dielectric loss of angle $\tan\delta$ were obtained by the capacity bridge BM 507/538 Tesla type with frequency 1 kHz and temperature range between 300 K and 730 K. Temperatures dependences $Q^{-1}(T)$ and $E(T)$ were performed by automatic resonance spectrometer RAK-3 type controlled by computer.

3. Results and disscusion

In Fig. 1 temperature dependences of $Q^{-1}(T)$ and $E(T)$ are presented. For the composition 5/50/50 the measurements were made during two cycle of heating with different resonance frequency (f_r) of sample vibration. At the temperature $T_r = 393$ K the values of f_r were respectively: 838 Hz for 1st cycle of heating and 800 Hz for 2nd cycle.

Similarly for 10/50/50 composition, f_r were 900 Hz and 866 Hz. All measurements were conducted with 3 K/min ratio of heating. Both for samples 5/50/50 and 10/50/50 after 1st cycle of heating, clearly maxima P_F and P'_F on the curves $Q^{-1}(T)$ were observed. The maxima correlated with minima M_F and M'_F observed on $E(T)$ curves. Those changes were observed in temperatures: $T_F = 574$ K and $T_F = 435$ K. After deep analysis of phase diagram of PLZT system was proved that the temperatures are responsible for phase transition ferroelectric $\leftrightarrow$ paraelectric (Curie temperature T_C) [2]. In the 2nd cycle of heating was observed clearly increase of height of peaks P_F and P'_F and their little movement to lower temperatures: $T_F = 561$ K for PLZT 5/50/50 and $T_F = 420$ K for PLZT 10/50/50. In the references of the earlier works authors proved that behavior like this of the maxim $Q^{-1}(T)$ in the areas of phase transitions is mainly connected with phenomena described by the Delorme and Gobin model [5, 6]. Additionally for composition PLZT 10/50/50 at curve $Q^{-1}(T)$ maximum P'_R was observed in temperatures 316 K and 322 K respectively for 1st and 2nd cycle of heating. The way
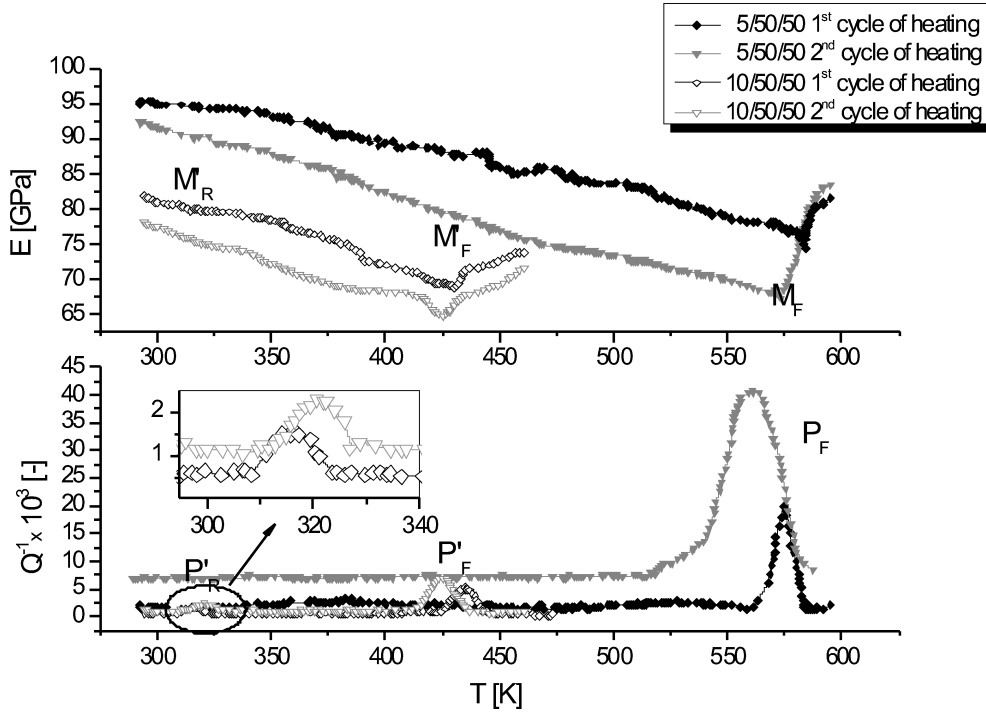
Fig. 1. The temperature dependences of $Q^{-1}(T)$ and $E(T)$ for PLZT tested samples.

of behavior of this maximum and parameters calculated by the Arrhenius' law: energy of activation $H = 2.33$ eV and preexponential $\tau_0 = 5 \cdot 10^{-29}$ s^{-1} proved that origin of the maximum is connected with more complicated processes and it will be subject of future researches.

The measurements of the temperature dependences of $\varepsilon(T)$ and $\tan\delta(T)$ were obtained as a aim of detailed analysis of the changes in the area of phase transition. The results of investigation are shown in Fig. 2. The nature of the temperature dependences of $\tan\delta(T)$ in the range of temperatures below phase transition is connected with dissipation of energy to polarization of the domains. But above the phase transition temperature (T_C) losses of energy are related with electric conductivity. For both chemical composition of PLZT type ceramics the temperature dependences of $\varepsilon(T)$ has a relaxor character with diffuse phase transition between ferroelectric and paraelectric phase. The linear and quadratic Curie–Weiss laws were used to analysis of the dependences of $1/\varepsilon(T)$.

At the paraelectric phase above temperature T_1 (PLZT 5/50/50) and T_1' (PLZT 10/50/50), the linear Curie–Weiss law was used [7]:

$$\varepsilon = \frac{C_{CW}^+}{T - T_m},\tag{1}$$

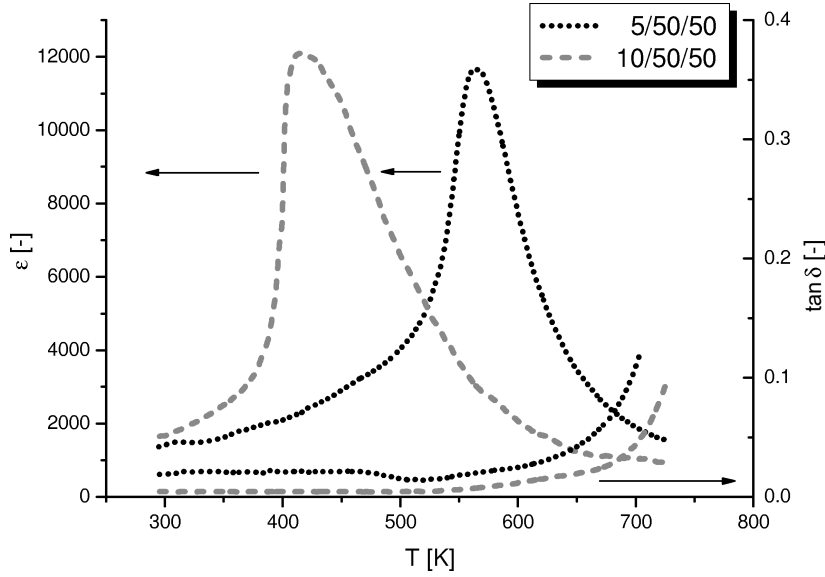where C_{CW}^+ – Curie–Weiss constant.

Fig. 2. The temperature dependences of $\varepsilon(T)$ and $\tan\delta(T)$ for PLZT tested samples.

In the ferroelectric phase Curie–Weiss law:

$$\varepsilon = \frac{C_{CW}^-}{T_m - T},\qquad(2)$$

where C_{CW}^- – Curie–Weiss constant.

The values of the Curie–Weiss constants as well for paraelectric and ferroelectric phase are presented in Table 1. The range of temperatures $T_1 - T_2$ is responsible for relaxor diffuse phase transition. In the range of temperatures between T_m and T_1 experimental curves of dependences $\varepsilon(T)$ are described by quadratic Curie–Weiss law [8]:

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = K(T - T_m)^\gamma,\qquad(3)$$

where ε_m electric permittivity at the temperature of phase transition T_m.

Table 1. The values of the Curie–Weiss constants.

PLZT	T_m [K]	$C_{CW}^- \times 10^{-5}$ [K^{-2}]	$C_{CW}^+ \times 10^{-5}$ [K^{-2}]	$K^+ \times 10^{-6}$ [K^{-2}]	$T_1 - T_2$ [K]	γ [–]
5/50/50	566	4.23 ± 0.02	2.09 ± 0.02	8.26 ± 0.01	122	1.67
10/50/50	417	2.54 ± 0.02	2.08 ± 0.02	69.2 ± 0.01	172	1.92

The values of the dielectric parameters are presented in Table 2. The values of electric permittivity at room temperature are decreasing with increasing of La^{3+} content, but at the temperature of the maximum of electric permittivity situation are exactly opposite. The values of tangent of dielectric loss of angle decreasing with increasing of La^{3+} content as well as room temperature and temperature of the maximum.
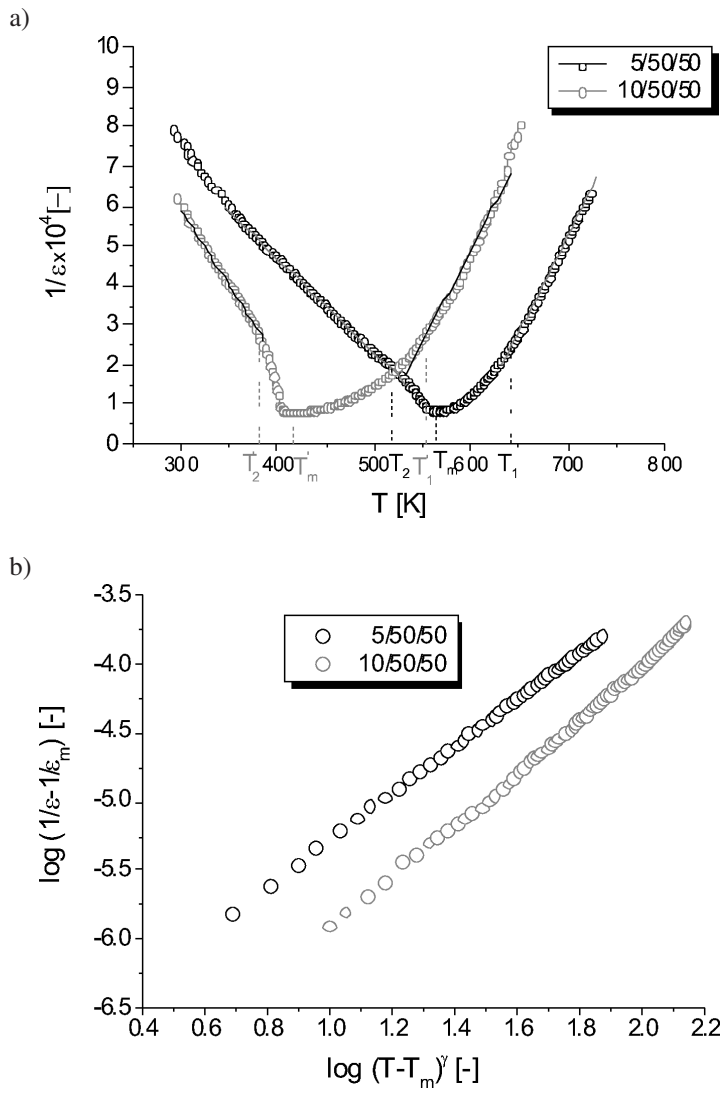
Fig. 3. The temperature dependences of $1/\varepsilon(T)$ (a) and $\log(1/\varepsilon - 1/\varepsilon_m) = f(\log(T - T_m)^\gamma)$ (b) for PLZT tested samples.

Table 2. The values of the dielectric parameters obtained for PZT* [9] and PZLT ceramics at room temperature $T_r = 293$ K and T_m.

Chemical composition	ε [–] ($f = 1$ kHz)		tanδ [–] ($f = 1$ kHz)		T_m [K]
	T_r	T_m	T_r	T_m	
PZT 50/50*	879	18151	0.0031	0.0933	635
PLZT 5/50/50	1277	12402	0.0189	0.0196	563
PLZT 10/50/50	2378	11887	0.0027	0.0028	408

4. Results and disscusion

Obtained PLZT type ceramic samples are characterized by low values of tangent of dielectric loss of angle $\tan\delta = 1$–1.5% and high values of electric permittivity $\varepsilon = 11000$–12000 (at the $T_r = 393$ K temperature). The measurement of the temperature dependences of Q^{-1} and E let to obtained the temperature of phase transition (T_C). The value of T_C is decreasing with increasing of La^{3+} content. Lanthanum has also significant influence for level of diffuse phase transition.

References

[1] HEARTLING G.H., *Ferroelectric ceramics: History and technology*, J. Am. Ceram. Soc., **82**, 4, 797 (1999).

[2] WANG K.Z., XUE Z.Q., OUYANG M., ZHANG H.X., HUANG C.H., *Electronic Memory Switching in a New Charge Transfer Complex Thin Film*, Solid State Comm., **96**, 481 (1995).

[3] BOURIM E.M., TANAKA H., GABBAY M., FANTOZZI G., CHENG B.L., *Domain wall motion effect on the anelastic behavior in lead zirconate titanate piezoelectric ceramics*, J. Appl. Phys., **91**, 6662 (2002).

[4] BRUŚ B., ZACHARIASZ R., ILCZUK J., *The influence of the point defects on the relaxation processes in a ceramics of the PZT type*, Physica Stat. Solidi (a), **201**, 798 (2004).

[5] ZHENG–CUN Z., *Internal friction observation of the $\varepsilon \rightarrow \gamma$ transformation in a Fe-Mn alloy*, Materials Science and Engineering, **A 438-440**, 336 (2006).

[6] BARTKOWSKA J.A. *et al.*, *Domain wall motion effect in piezoelectric ceramics*, J. de Phys. IV, **137**, 19 (2006).

[7] PILGRIM S., AUDREY M., SUTHERLAND E., WINZER E.R., *Diffuseness as a Useful Parameter for Relaxor Ceramics*, J. Am. Ceram. Soc., **73**, 3122 (1990).

[8] CHENG Z.-Y., KATIYAR R.S., YAO X., GUO A., *Dielectric behavior of lead magnesium niobate relaxors*, Phys. Rev., |**B 55**, 8165 (1997).

[9] GORSZA A.W., *Fizika segnetoelektriczeskoj kjeramiki*, Radiotechnika, Moskwa 1999.