INVESTIGATION OF TEMPERATURE DEPENDENCES OF ELECTROMECHANICAL PROPERTIES OF PLZT CERAMICS

M. CZERWIEC, R. ZACHARIASZ and J. ILCZUK

Department of Material Science, Faculty of Computer Science and Material Science, University of Silesia, 3 Zeromskiego St., 41-200 Sosnowiec, POLAND

rzachari@us.edu.pl

The mechanical and electrical properties in lanthanum modified lead zirconate-titanate ceramics of 5/50/50 and 10/50/50 were studied by mechanical loss Q-1, Young's modulus E, electric permittivity ε and tangent of dielectric loss of angle tgδ measurements. The internal friction Q-1 and Young modulus E measured from 290 K to 600 K shows that Curie temperature TC is located at 574 K and 435 K (1st cycle of heating) respectively for ceramic samples 5/50/50 and 10/50/50. The movement of TC in second cycle of heating to lower temperature (561 K for 5/50/50 and 420 K for 10/50/50) has been observed. Together with Q-1 and E measurements, temperature dependences of ε=f(T) and tgδ=f(T) were determinated in temperature range from 300 K to 730 K. The values of TC obtained during ε and tgδ measurements were respectively: 560 K for 5/50/50 and 419 K for 10/50/50. These temperatures are almost as high as the temperatures obtained by internal friction Q-1 measurements in second cycle of heating. In ceramic sample 10/50/50 the additional maximum on internal friction Q-1 curve at the temperature 316 K was observed.

1. INTRODUCTION

Pb(Zr, Ti)O_3 (PZT) crystallizes with the ABO_3 type structure in which the A-site is occupied by Pb^{2+} ions; Zr^{4+} and Ti^{4+} 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 scientists in order to modify the properties of the materials for device applications such as non-volatile memories, transducers, modulators, etc. Modification of the PZT system by the addition La^{3+} ions has marked beneficial effect on several basic parameters, such as rectangularity of the hysteresis loop, decreased coercive field, increased dielectric constant,

maximum coupling coefficients, increased mechanical compliance, and enhanced optical transparency [1-4].

2. EXPERIMENT

The material tested were solid solution of the PLZT from ferroelectric phase with the 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 for 20h and next formed in cylindrical tablets of diameter 10 mm. Then, tablets were synthesized at the temperature T_S = 1123K for t_s = 6h. Then polycrystalline samples were crumbled and mixed to obtain more homogenous structure. The range of sintering temperatures (1223K ÷ 1523K) and sintering times (6h÷12h) were depended on the chemical composition. The silver paste electrodes were deposited on the surface of PLZT samples by the burning method. The obtained samples were subjected to polarization using the low temperature method (T_p = 423K, E_p = 30kV/cm, t_p = 30min). The measurements of dielectric permittivity ε and tangent of dielectric loss of angle tgδ were obtained by the capacity bridge BM 507/538 Tesla type with frequency 1 kHz and temperature range between 300K and 730K. Temperatures dependences $Q^{-1}(T)$ and E(T) were performed by an automatic resonance spectrometer of RAK-3 type controlled by computer.

In order to maintain the same polymer in contact with the air, this additional lamellar domain must be inserted below the upper layer and gives rise to an edge dislocation line. The aim of this paper is to study both theoretically and experimentally the behaviour of the domains and the distortion to the smectic ordering induced by the associated dislocations. The aim of this paper is to study both theoretically and experimentally the behaviour of the domains and the distortion to the smectic ordering induced by the associated dislocations. The aim of this paper is to study both theoretically and experimentally the behaviour of the domains and the distortion to the smectic ordering induced by the associated dislocations.

3. RESULTS AND DISCUSSION

In the figure 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 room temperature the values of f_r were respectively: 838Hz for 1st cycle of heating and 800Hz for 2nd cycle. Similarly for 10/50/50 composition, f_r frequencies were 900Hz and 866Hz. All measurements were conducted with 3K/min ratio of heating. Both for samples 5/50/50 and 10/50/50 after 1st cycle of heating,

clear maxima P_F i P'_F on the curves $Q^{-1}(T)$ were observed. The maxima correlated with minima M_F i M'_F observed on E(T) curves. Those changes were observed at temperatures: T_F = 574K and T_F = 435K. After a detailed analysis of phase diagram of PLZT system it was proved that the temperatures were responsible for phase transition ferroelectric ↔ paraelectric (Curie temperature T_C) [2].

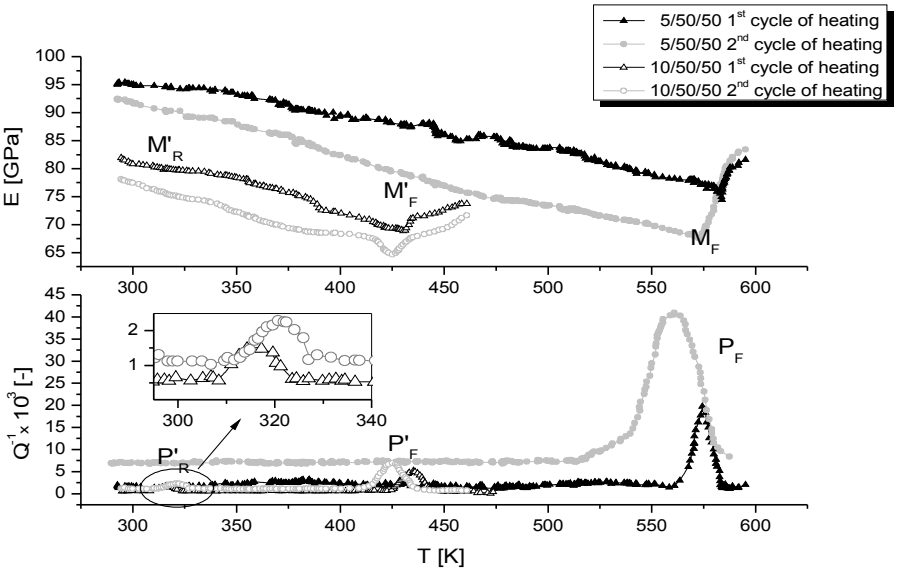


Fig. 1**.** The temperature dependences of $Q^{-1}(T)$ and E(T) for PLZT tested samples.

In the 2nd cycle of heating, a clear increase of height of peaks P_F i P'_F and their slight movement towards lower temperatures: T_F = 561K for PLZT 5/50/50 and T_F = 420K for PLZT 10/50/50 were observed. Referring to the earlier works authors proved that such of the maxim $Q^{-1}(T)$ in the areas of phase transitions was mainly connected with phenomena described by the Delorme and Gobin model [5]. The relative changes of the volume undergoing to phase transition are shown in this model. These changes are the function of the heating and cooling processes. Thus the following formula was derived:

$$Q^{-1} = \frac{KG}{\omega} \cdot \frac{\partial m}{\partial T} \cdot \frac{\partial T}{\partial t}, \tag{1}$$

where: K – material constant, G – shear modulus, ω - periodicity of the sample, $\omega = 2\pi f_r$ (f_r – resonance frequency), $\frac{\partial m}{\partial T}$ - the volume of substance undergoing the phase transition in unit temperature change, $\frac{\partial T}{\partial t}$ - the rate of the temperature changes (during heating or cooling processes).

Height of the internal friction peaks P_F i P'_F, connected with the phase transition is directly proportional to rate of the temperature changes and inversely proportional to

resonance frequency changes, what was introduced in the formula 1. Additionally for composition PLZT 10/50/50 at curve $Q^{-1}(T)$ maximum P'_R was observed at temperatures 316K and 322K respectively for 1st and 2nd cycle of heating. The way of behavior of this maximum and parameters calculated by the Arrhenius' law: energy of activation H = 2,33eV and pre-exponential factor $\tau_0 = 5 \cdot 10^{-29} s^{-1}$ proved that origin of the maximum is connected with more complicated processes and it will be subject of future researche.

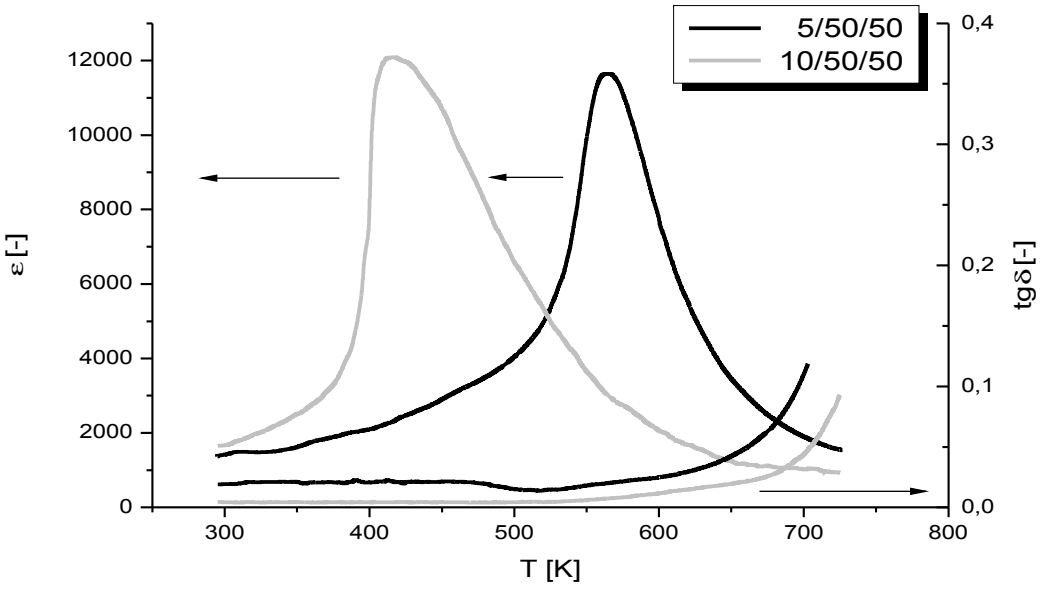


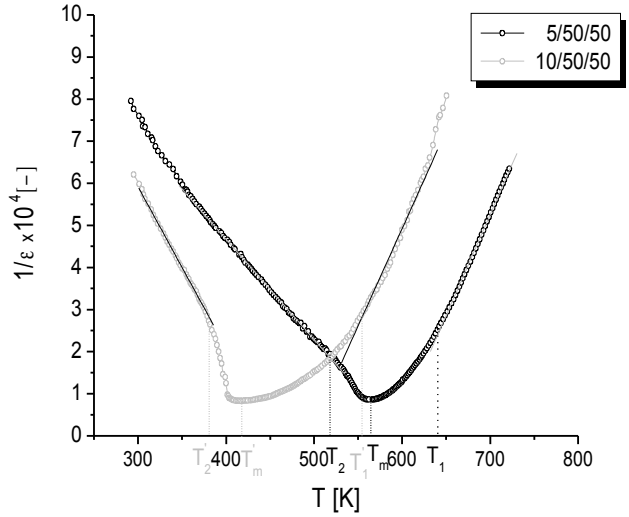
Fig. 2. The temperature dependences of ε(T) and tgδ(T) for PLZT tested samples.

The measurements of the temperature dependences of ε(T) and tgδ(T) were obtained as an aim of detailed analysis of the changes in the area of phase transition. The results of investigation are shown in figure 2. The nature of the temperature dependences of tgδ(T) in the range of temperatures below phase transition is connected with dissipation of energy to polarization of the domains. However, 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 ε(T) has a relaxor character with diffuse phase transition between ferroelectric and paraelectric phase. The linear and quadratic Curie-Weiss laws were used to analyze the dependences of 1/ε (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 [6]:

$$\varepsilon = \frac{C^{+}_{CW}}{T - T_m} \tag{2}$$

where: C^{+}_{CW} – Curie-Weiss constant.

a)



b)

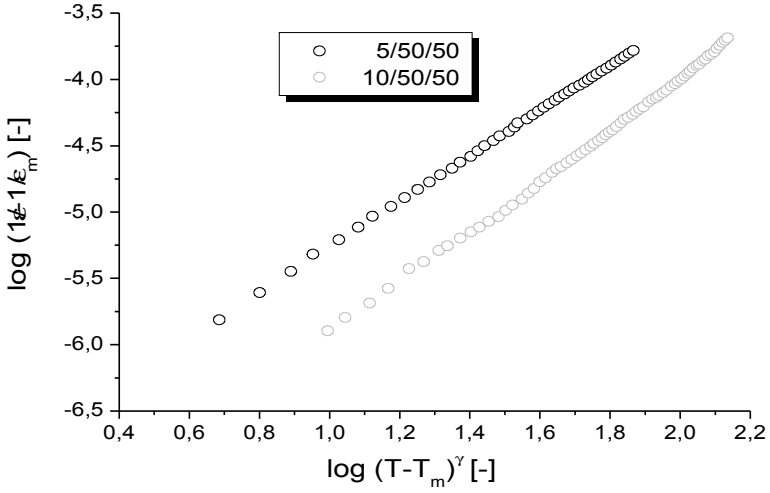


Fig. 3**.** The dependences 1/ε(T) fig. 3a, and $\log(1/\varepsilon - 1/\varepsilon_m)=f(\log (T - T_m)^{\gamma})$ fig. 3b.

In the ferroelectric phase a scope of applicability of the Curie-Weiss law can be described in the following form:

$$\varepsilon = \frac{C_{CW}^{-}}{T_m - T} \tag{3}$$

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 corresponds to relaxor diffuse phase transition. In the range of temperatures between T_m and T_1 experimental curves of dependences ε(T) are described by quadratic Curie-Weiss law [9-12]:

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = K(T - T_m)^{\gamma} \tag{4}$$

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

Table 1. The values of the parameters calculated for PLZT tested ceramics.

PLZT	T_m [K]	C^-_{CW} x 10^{-5} [K^{-2}]	C^+_{CW} x 10^{-5} [K^{-2}]	K^+ x 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 K and γ coefficients were conducted on the base of $\log(1/\varepsilon - 1/\varepsilon_m) = f(\log(T - T_m)^{\gamma})$ (figure 3) dependences and are presented in Table 1.

4. CONCLUSIONS

Obtained PLZT type ceramic samples are characterized by low values of tangent of dielectric loss of angle tgδ=1÷1,5% and high values of electric permittivity ε=11000÷12000 (at room temperature). The measurements of the temperature dependences of Q^{-1} and E allowed to obtain the temperature of phase transition (T_C). The value of T_C decreases with an increase in La content. Lanthanum has also a significant influence on the diffuse degree of the phase transition.

REFERENCES

1. T.J. Evans, R. Womack, *IEEE J. Solid State Circuits* 23**,** 1171 (1988).
2. G.H. Haertling, *J. Am. Ceram. Soc.* 82 (4), 797 (1999).
3. E.M. Bourim, H.Tanaka, M. Gabbay, G. Fantozzi, B.L. Cheng, *J.Appl. Phys.* 91, 6662 (2002).
4. C.L. Hulang, B.H. Chen, L. Wu, *Solid State Comm.* 130, 19 (2004).
5. J.F. Delorme, P.F. Gobin, *Metaux, Corr. Ind*. 573, 185 (1973).
6. S. Pilgrim, M. Audrey, E. Sutherland, E.R. Winzer, *J. Am. Ceram. Soc*. 73, 3122 (1990).
7. B. Brus, R. Zachariasz, J. Ilczuk, *Moelcular and Quantum Acoustics* 26 55-60, (2005).
8. B. Brus, A. Zarycka, M. Czerwiec, J. Ilczuk, *Molecular and Quantum Acoustics* 27, 63-70 (2006).
9. Z. Y. Cheng, R.S. Katiyar, X. Yao, A. Guo, *Phys. Rev. B* 55**,** 8165 (1997).
10. J. Skrzypek, P. Pacek, Z. Pedzich, Z. Surowiak, *Molecular and Quantum Acoustics* 25, 219-226 (2004).
11. J. Skrzypek, M. Kosec, Z. Surowiak, *Molecular and Quantum Acoustics* 26, 227-234 (2005).
12. Z. Sutowiak, *Molecular and Quantum Acoustics* 27, 265-284 (2006).