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Phenomena responsible for energy dissipation in fine-grained PZT-type ceramics

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Description of the mechanisms responsible for the dissipation of energy in materials is possible thanks to the internal friction (IF) method – a non-destructive method thought to be one of the most sensitive ones [1–3]. The method is based on measurements of mechanical losses at various temperatures or various frequencies. The study of the IF of ferroelectrics can provide extensive information about the physics of processes within these materials, and about their domain structures and their interactions with various structural defects. The aim of the present study was to describe the mechanisms responsible for energy dissipation in PZT ceramics obtained by the sol-gel method and sintered by conventional ceramics sintering (CCS). This work presents results of investigations of the influence of $PbTiO_3$ concentration in PZT ceramics on these processes.

Key words: *PZT; sol-gel method; internal friction*

1. Introduction

PZT ceramics, solid solutions of titanate and lead zirconates, have been widely investigated due to its electromechanical properties allowing them to be used in a lot of devices of a practical character such as electromechanical transducers, vibration pick-ups, filters, ultrasonic generators, resonators, transformers, stabilizers, modulators, parametric amplifiers, frequency multipliers, and ferroelectric memories [4–6].

Since it is necessary for the materials to have specific properties for given applications, it is essential to find out the correlation between the structure, chemical composition, and the ceramics properties. For this reason, non-destructive investigation methods have been developed for some years and the internal friction method belongs to this type. The method is very sensitive to changes in the structure of the materials under the influence of external factors such as e.g. temperature. Its use to examine

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phenomena responsible for energy dissipation enables us to get information about processes taking place in the material under the influence of temperature, including both relaxation processes (migration of defects, mutual interaction of the domain walls), and occurring phase changes [3, 7].

The objective of this work was to determine the phenomena responsible for energy dissipation in the fine-grained PZT- type ceramics.

2. Materials

Fine-grained PZT-type ceramic with the concentration of 25, 35, 52, 53, 54, 65, 75 mol % of $PbTiO_3$ was used for the tests. The synthesis of powders was carried out using the sol-gel method. Lead acetate, zirconium(IV) propoxide, and titanium(IV) propoxide were used as precursors. The synthesis leading to the formation of the complex of alcoholates lasted 2 hs. The reaction by-product (ester – propyl acetate) was removed in the distillation process. After cooling the solution to room temperature, acetylacetone was added to stabilize the complex of alcoholates. The hydrolysis process, resulting in a change of sol into gel, was initiated by adding H_2O. The gel obtained was calcinated at 573 K for 2h in order to remove organic residues. The powders made in this way were compressed and condensed by two methods: free sintering (1523 K/5 h) and uniaxial (1473 K/2 h). The specimens prepared by this method were ground and polished. Conductive electrodes were made with the silver paste by the burning method at the temperature of 1123 K for 15 min.

3. Results of measurements and their discussion

The dependence of the internal friction on the temperature obtained for the ceramics in question (PZT 25/75, PZT 35/65, PZT 46/54, PZT 47/53, PZT 48/52, PZT 65/35, PZT 75/25) during heating at the rate of 3 K/min and at the frequency of 850 Hz by a resonance mechanical spectrometer RAK-3 [1] are presented in Fig. 1. The presence of two peaks of the internal friction P_{R1} and *PF* was observed on all dependences. On the $Q^{-1}(T)$ plot, obtained for the PZT 75/25 ceramics, a third peak P_p, between the P_{R1} and P_F peaks, was also observed. The maximum of the P_F peak moved toward higher temperatures with an increase of $PbTiO_3$ concentration (Fig. 1, Table 1). In order to determine the mechanism responsible for the formation of this maximum, measurements of the internal friction dependence on temperature at different frequencies were conducted. On changing the measurement frequency, there occured a change in the temperature position of the maxima of IF peaks of relaxation character, originating from, e.g., mutual interaction of domain walls, and the interaction of defects and domain walls. However, in the case of peaks originating from phase changes, their temperature should be independent of the frequency [8–10]. Thus, the presence of the P_F peak at a stable temperature during the measurements conducted at different frequencies (Fig. 2, Table 1) points to the origin of the P_F peak from the phase change.

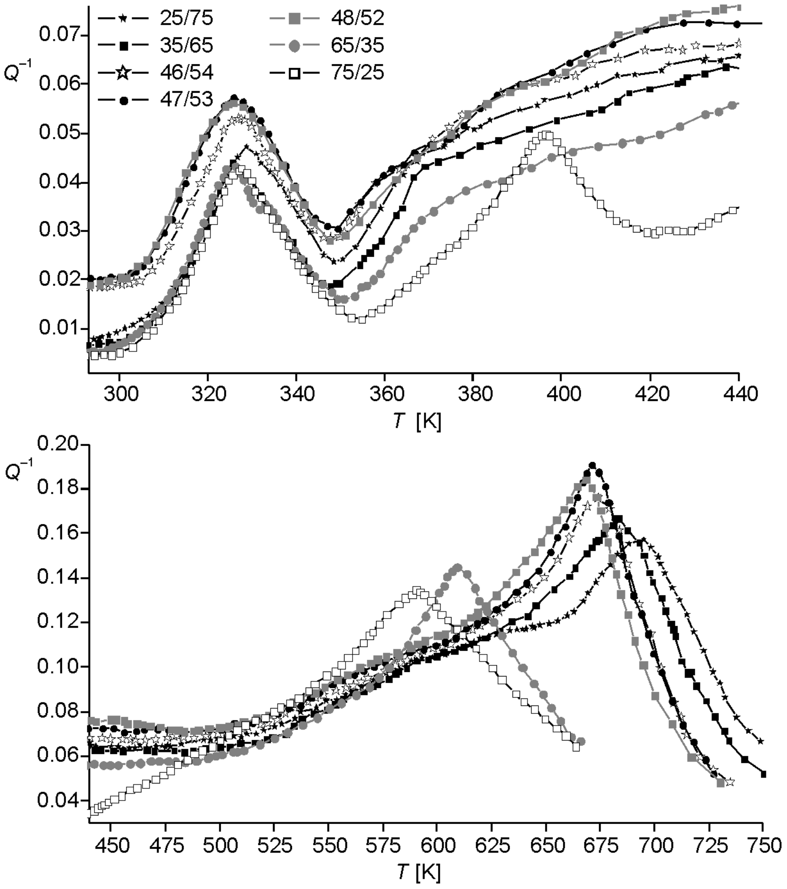

Fig. 1. Dependences of the internal friction on the temperature obtained for the PZT ceramics during heating at the rate of 3 K/min at the frequency of 850 Hz

An increase in the Curie temperature with the increase in the lead titanate concentration in the solid solution is a generally known property of PZT ceramics. For this reason, the dependence of electric permittivity on temperature determined from the Curie temperature values (Table 1) confirm the origin of the P_F peak from a phase transition from the ferroelectric phase to the paraelectric one. The observed decrease in the *IF* value after the P_F maximum is connected with the disappearance of the domain structure as the result of the transition to the paraelectric state.

With an increase of $PbTiO_3$ concentration, the increase in the height of P_F was also observed until 53 mol %, and then a decrease in the peak height occurred. It is generally known that with a change of $PbTiO_3$ concentration in the PZT ceramics there is a change in the maximum permittivity value at the Curie temperature. For the nonpolarized PZT ceramics the highest values are observed for the compositions near the morphotrophic boundary and there is a decrease in its value as it moves away from the morphotropic boundary toward compositions with the rhombohedral and tetragonal structure [11]. Changes in the P_F peak height are similar to changes in the electrical permittivity values.

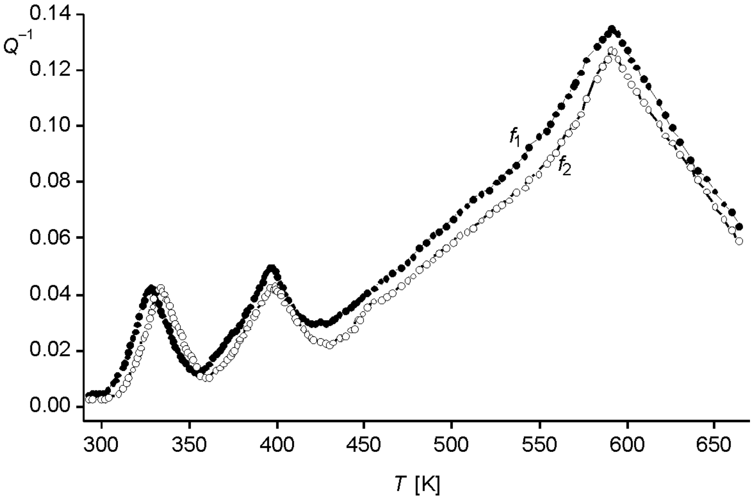

Fig. 2. Temperature dependences of the internal friction obtained for PZT 75/25 at various measurements frequencies; f_1 = 850 Hz, f_2 = 960 Hz

Table 1. Temperatures of the P_F peak occurrence and the Curie temperatures for the PZT ceramics ($f_1 < f_2$)

Type of specimen	T_F [K] at f_1 $\Delta T = \pm 1.5$ K	T_F [K] at f_2 $\Delta T = \pm 1.5$ K	T_c [K] $\Delta T = \pm 2.0$ K
PZT 25/75	695	695	694
PZT 35/65	681	681	678
PZT 46/54	673	674	671
PZT 47/53	671	671	668
PZT 48/52	668	667	665
PZT 65/35	609	609	607
PZT 75/25	590	590	589

The observed temperature changes of the P_{R1} peak position (Fig. 2) at the measurements $Q^{-1}f(T)$ for various frequencies (a movement toward higher temperatures) suggests that a relaxation process is responsible for its formation. In order to prove the above thesis, calculations of the activation energy H and the pre-exponential factor τ_0 were made based on the Arrhenius law [3]. The values of H and τ_0 (Table 2) confirm the origin of the P_{R1} peak from the relaxation process. The activation energy of about

1 eV is a typical value of interaction of point defects with domain walls [9, 12]. This phenomenon is also proved by the τ_0 value (Table 2). Oxygen vacancies are the prevailing defects in PZT ceramics, therefore the interaction of oxygen vacancies with domain walls is responsible for the P_{R1} peak formation. The τ_0 value obtained for PZT 65/35 is an exception. The value of the pre-exponential factor (2.94×10^{-17}) points out that a simple relaxation process described by a single relaxation time cannot be responsible for the P_{R1} peak formation for the PZT 65/35 ceramics.

Table 2. Values of the activation energy and pre-exponential factor

Specimen	H [eV]	τ_0 [s]
PZT 25/75	1,04±0,02	$(3{,}17\pm0{,}04)\cdot10^{-15}$
PZT 35/65	1,02±0,02	$(2{,}46\pm0{,}04)\cdot10^{-15}$
PZT 46/54	1,10±0,02	$(1{,}54\pm0{,}04)\cdot10^{-15}$
PZT 47/53	0,97±0,02	$(1{,}07\pm0{,}04)\cdot10^{-15}$
PZT 48/52	0,98±0,02	$(1{,}02\pm0{,}04)\cdot10^{-15}$
PZT 65/35	1,00±0,02	$(2{,}94\pm0{,}04)\cdot10^{-17}$
PZT 75/25	1,05±0,02	$(2{,}01\pm0{,}04)\cdot10^{-15}$

No changes in the temperature position of the P_{R1} peak were observed for the examined ceramics with an increase in $PbTiO_3$ concentration (Fig. 1). Small fluctuations of the H activation energy values (Table 2) point to small differences in the concentration of defects in the examined ceramics, introduced during the technological process [13]. Thus the position and height of the peak originating from the interaction of point defects and domain walls do no depend on changes in $PbTiO_3$ concentration, but only on the concentration of defects in the examined ceramics. Regarding the P_{R1} peak in PZT 65/35 ceramics as as resulting from an overlapping of several processes, an attempt was made to find the mechanisms responsible for its formation. The analysis of the shape of the P_{R1} peak obtained for different measurement frequencies for PZT 65/35 ceramics shows that it can be deconvoluted into two peaks (Fig. 3): P'_{R1}, for which the temperature position undergoes a change with the change in the measurement frequency and the P_p peak for which the temperature position does not undergo a change with the change in the measurement frequency.

During the measurement of the internal friction in the temperature range of the P_{R1} peak at lower frequency, a movement of the P'_{R1} peak toward lower temperatures is observed which proves its relaxational character. The calculated values of the activation energy $H = 0.97$ eV and the pre-exponential factor $\tau_0 = 1.8\times10^{-15}$ s show that it comes from the interaction of the point defects with the domain walls. In the phase diagram (Fig. 4) for the solid solution of lead titanate and zirconate, a phase change from the rhombohedral phase II (R3c) to the rhombohedral phase I (R3m) can be observed in the range of $PbTiO_3$ concentrations from 4.2 mol % to about 38 mol %.

Thus, the stability of the temperature position of the P_p peak with the change in the measurement frequency shows that the phase composition of the ceramic material is responsible for its formation.

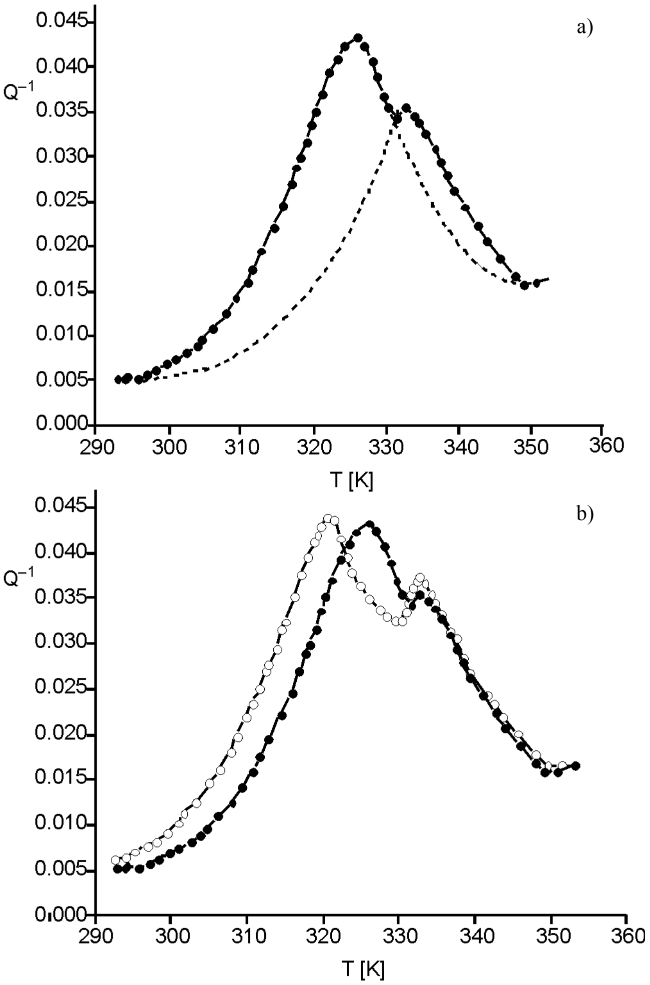

Fig. 3. Temperature dependences of the internal friction obtained in the temperature range of the P_{R1} occurrence: a) the division of the P_{R1} peak into components, b) for the frequency $f_1 = 960$ Hz, $f_2 = 850$ Hz

Changes in the height of P_F and P_p peaks also point to their dependence on the phase changes. According to the model developed by Delorme and Gobin, the dependence of $Q^{-1}(T)$ on the internal friction in the area of the phase change is described by the equation [14]:

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

where: K is a material constant, G – modulus of rigidity, ω – angular frequency of the specimen vibrations ($\omega = 2\pi f$, f – frequency), $\frac{\partial m}{\partial T}$ – quantity of the material undergoing the change at the unit temperature change, $\frac{\partial T}{\partial t}$ – rate of temperature changes (heating or cooling). Therefore, the increase in the P_F and P_p peak heights with a decrease in the measurement frequency is fully confirmed by the Delmore–Gobin model.

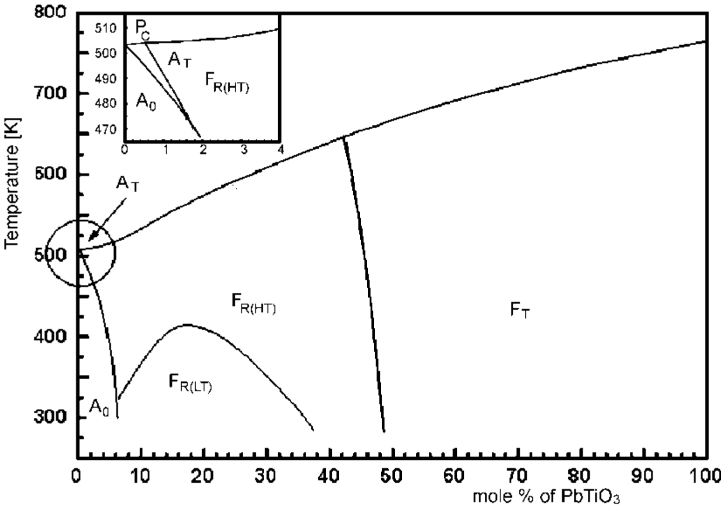

Fig. 4. Phase diagram $PbTiO_3$–$PbZrO_3$– PZT [15]

The PZT 75/25 ceramics group also includes PZT ceramics for which a change from the II rhombohedral phase to the I rhombohedral phase is observed. This change takes place at a temperature higher than a change into the PZT 65/35 composition (Fig. 4). Thus, the P_p maximum observed on the temperature dependences of the internal friction (Figs. 1, 2), moving toward neither higher nor lower temperatures with a change in the measurement frequency is related to the phase change.

4. Conclusions

Variations of internal friction as a function of temperature and excitation frequency can provide direct information on energy dissipation in the materials. In the fine-grained PZT type ceramics phase changes (from the ferroelectric to paraelelectric and from the II rhombohedral phase to the I rhombohedral phase) and the relaxation process, the interaction of the point defects with the domain walls are responsible for the energy dissipation. An increase of the concentration of lead titanate causes a shift of the position of the peak connected with the ferroelectric-paraelectric phase toward higher temperatures (a Curie temperature change). A change in $PbTiO_3$ concentration does not have an influence on the height and the temperature position of the peak connected with the interaction of the oxygen vacancies with the domain walls. However, all wet, chemistry-based methods, for example the sol-gel method, have a very strong influence on the occurrence of particle agglomerates in the resulting PZT powder. In PZT powders with a high $PbTiO_3$ concentration, hard particle agglomerates will significantly reduce the stability of the powders and lead to the formation of microstructural defects in the sintered PZT ceramics, particularly during the free sintering (CCS) method.

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References

[1] ZACHARIASZ R., ILCZUK J., CHROBAK A., Ceramics, 66 (2001), 710.

[2] ZARYCKA A., ZACHARIASZ R., BRUŚ B., ILCZUK J., Mol. Quant. Acoust., 24 (2003), 255.

[3] XU Y.H., *Ferroelectric Materials and Their Applications*, New York, North Holland, 1991, pp. 72–100.

[4] SUROWIAK Z., KUPRYANOV M.F., CZEKAJ D., J. Eur. Ceram. Soc., 21 (2001), 1377.

[5] YI C.H., CHIA C. W., CHENG C.L., CAO G.Z., SHEN I.Y., Sensors Act. A, 116 (2004), 369.

[6] YAN F., CHEN X., BAO P., WANG Y., LIU J., J. Appl. Phys., 87 (2000), 1453.

[7] ZACHARIASZ R., ILCZUK J., CHROBAK A., Ceramics, 66 (2001), 630.

[8] BOUZID A., GABBAY M., FANTOZZI G., Mater. Sci. Eng, A 370 (2004), 123.

[9] WANG C., FANG Q.F., SHI Y., ZHU Z.G., Mater. Res. Bull., 36 (2001), 2657.

[10] BRUŚ B., ZACHARIASZ R., ILCZUK J., Phys. Stat. Sol. A, 201 (2004), 789.

[11] KUPRIYANOV M.F., KONSTANTINOV G.M., PANICH A.E., *Segnetoelektritcheskiye morphotropnye* perekhody, Izd. Rostovskogo Uniwiersiteta, Rostov na Donu (1992).

[12] WANG Z.Y., CHEN T.G., Phys. Stat. Sol. A, 167 (1998), R3–R4.

[13] WANG C., FANG Q.F., ZHU Z.G., J. Phys. D: Appl. Phys., 35 (2002), 1545.

[14] DELORME J.F., GOBIN P.F., Metaux, Corr. Ind., 573 (1973), 185.

[15] CZEKAJ D., *Technology*, *Properties and Applications of PZT Thin Films*, University of Silesia, Katowice, 2002.

[16] ZARYCKA A., ZACHARIASZ R., ILCZUK J., CHROBAK A., Mater. Sci.-Poland, 23, (2005), 159.

[17] GUO L., LYASHCHENKO A., DONG X., Mater. Lett. 56 (2002), 849.

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