

Determination of the lead titanate zirconate phase diagram by the measurements of the internal friction and Young's modulus

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The paper presents investigations of the phase transitions for undoped PZT ceramics obtained by the conventional ceramic sintering from amorphous nanopowders prepared by the sol-gel method, with various compositions and Zr/Ti ratios. The phase transitions are also studied by electric conductivity (σ) measurements as a function of the temperature. The values of σ , till the point of phase transition (T_C), are low and are in the range of 10^{-7} – $10^{-3} \Omega^{-1} \cdot \text{m}^{-1}$. In the paraelectric phase (above T_C) the values of σ as a function of the Zr/Ti ratio are in the range of 5×10^{-3} – $3 \times 10^{-1} \Omega^{-1} \cdot \text{m}^{-1}$. Phase transitions, identified by Young's modulus anomalies and internal friction peaks are in accordance with those found by electric conductivity studies and correspond to the transition point between cubic paraelectric phase and tetragonal or rhombohedral ferroelectric phase. The values of Young's modulus at room temperature are in the range of 80–140 GPa, and their rapid growth in the phase transition point is observed.

Key words: *sol-gel method; Young's modulus; internal friction; PZT phase diagram; electric conductivity*

1. Introduction

Lead titanate zirconate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) ceramics are among the most common piezoelectric materials in industry: they are used as transducers between electrical and mechanical energy, such as phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay-line transducers, wave filters, piezoelectric micromotors, microrobots, actuators, etc. [1, 2]. All those applications need rather high piezoelectric constants and low dielectric and mechanical losses in the ceramics. The study of temperature dependences of internal friction Q^{-1} , and elastic moduli E of the materials can provide extensive information about the physics of the processes occurring within the materials, for example about the energy dissipation and phase

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transitions. The investigations conducted for many years have shown that mechanical losses Q^{-1} and changes of Young's modulus E in the PZT are not only associated with domain walls motion but also with interaction of point defects with the domain walls [3–5]. The ratio Zr/Ti in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, the method of the obtaining the materials, the sintering temperature and atmosphere are the controlling factors to obtain good PZT ceramics for the application. Therefore, variety of controlling factors and wide applications of the PZT materials are the base to continuous research of these materials.

This paper presents the investigations of the phase transitions in undoped PZT ceramics with various compositions, prepared by conventional ceramics sintering (CCS) with the following Zr/Ti ratio: $\text{Pb}(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (ferroelectric rhombohedral phase), $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.46}\text{Ti}_{0.54})\text{O}_3$ (morphotropic area), $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ (ferroelectric tetragonal phase). The preparation procedure, measurements of Young's modulus E , mechanical losses Q^{-1} and electric conductivity σ , till the point of phase transition (T_C) will be presented as well.

2. Experimental

The technological process of the production of PZT ceramics consists of two basic stages. In the first stage, amorphous nanopowders of solid solution $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ are prepared by the sol-gel method, whereas the second one consists in consolidation of nanopowders and preparation of fine-grained PZT ceramics by the conventional ceramic sintering (CCS). The preparation procedure of amorphous nanopowders is described in our previous publication [6]. The powder obtained after disintegrating the annealed pallets was mixed with liquid paraffin and it was finally used for preparation of the ceramic samples [3]. Ceramic bodies were produced by conventional ceramics sintering (CCS) [7]. After that, samples in rectangular bars ($80 \times 10 \times 1 \text{ mm}^3$) were obtained. The average grain size for obtained samples was about $3.0 \text{ }\mu\text{m}$. The samples were annealed at $T = 1523 \text{ K}$ for $t = 4 \text{ h}$ and next were polished. Electrodes on their surface were deposited by the silver paste burning method.

The temperature dependences of the $Q^{-1}(T)$, $f_r(T)$ and $\sigma(T)$ were determined upon heating at the constant rate of $3 \text{ K}\cdot\text{min}^{-1}$. The values of Young's modulus E were calculated from the measurements of resonance vibration frequency f_r of the sample, conducted simultaneously with the mechanical losses (internal friction Q^{-1}) measurements, using the dependence:

$$E = 94.68 \left(\frac{l_r}{h} \right)^3 \frac{m_d}{b} f_r^2 \quad (1)$$

where: l_r , h , b and m_d are: the length, thickness, width and mass of vibratile part of the sample, respectively.

3. Results and discussion

Figure 1 shows the variations of mechanical losses Q^{-1} and Young's modulus E as a function of the temperature for the PZT75/25 and PZT65/35 samples. Young's modulus shows three anomalies M_R , M_{RR} and M_F . The anomaly M_R corresponds to the peaks P_R on the mechanical losses (internal friction) curves, both for the ceramics with Zr/Ti 75/25 and 65/35. Based on investigations conducted so far, it is known that the P_R peak has a relaxation nature and it is connected with influence of the domain walls and point defects (oxygen vacancies) located in the ceramic structure [8, 9]. Minimum M_F on the $E(T)$ dependences correlates with P_F maximum on the $Q^{-1}(T)$ curves. In the case of the PZT 75/25 ceramics, the temperature of the M_F and P_F occurrence is $T_F = 590$ K, whereas for the composition PZT65/35 can be as high as $T_F = 609$ K. With reference to PZT phase diagram (Fig. 7) it appears that the T_F temperature determined for both chemical compositions is consistent with the temperature of the phase transition from ferroelectric rhomboedral phase to paraelectric regular phase [10–12]. Additionally, for the ceramics with the Zr/Ti = 75/25 composition, appearance of the M_{RR} minimum on the $E(T)$ dependence, correlating with P_{RR} maximum on the $Q^{-1}(T)$ curve was observed. Based on the analysis of the phase diagram it was shown that the M_{RR} minimum is connected with the phase transition from ferroelectric low temperature rhomboedral phase $F_{R(LT)}$ to ferroelectric high temperature rhomboedral $F_{R(HT)}$ phase.

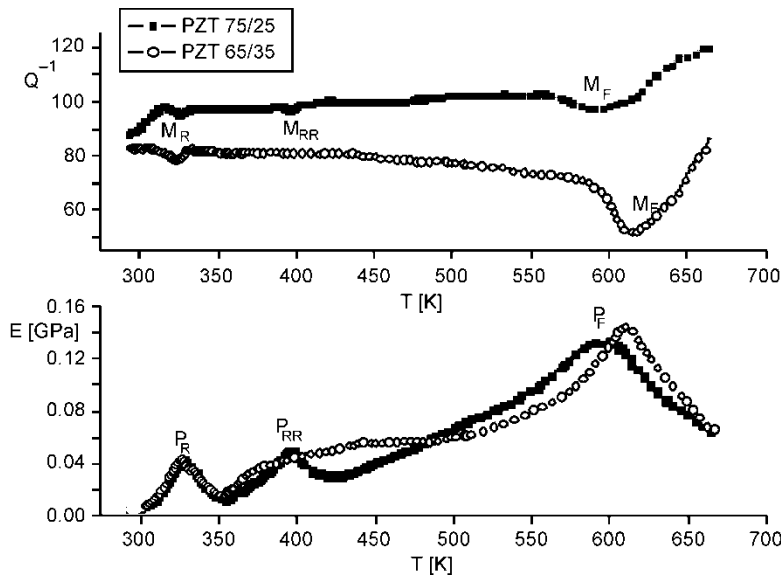


Fig. 1. Temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ obtained for PZT ceramic samples from ferroelectric rhombohedral phase

In order to confirm the determined values of the temperatures of phase transition T_F for the examined samples, temperature dependences of electric conductivity σ in

ferroelectric and paraelectric phases ($\ln\sigma = f(1/T)$) have been determined (Fig. 2). The changes of slope of rectilinear parts on the dependences were observed. This phenomena took place near the point of ferroelectric to paraelectric (T_F) phase transition, as well as for both phases for the investigated samples. For the PZT75/25 ceramics $T_F = 592$ K, whereas for samples PZT65/35 $T_F = 610$ K have been determined. It is evident that the values of temperatures determined correlate with the results obtained on the basis of the measurements of internal friction Q^{-1} and Young's modulus E .

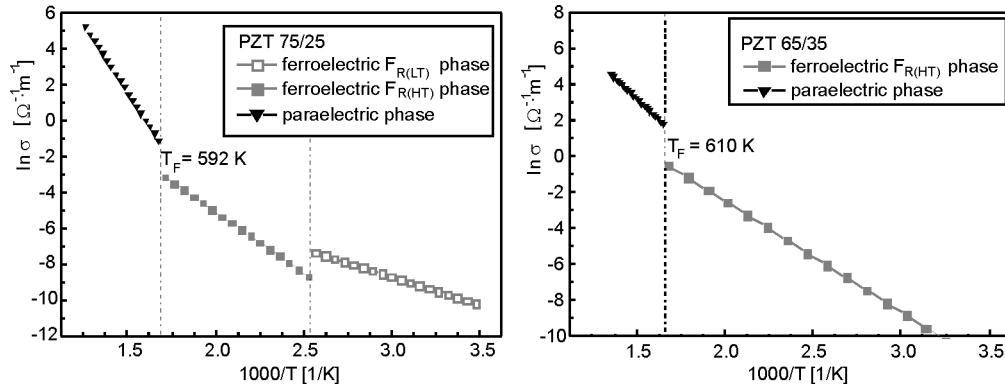


Fig. 2. Temperature dependences $\ln\sigma = f(1/T)$ obtained for the PZT ceramic samples from the ferroelectric rhombohedral phase

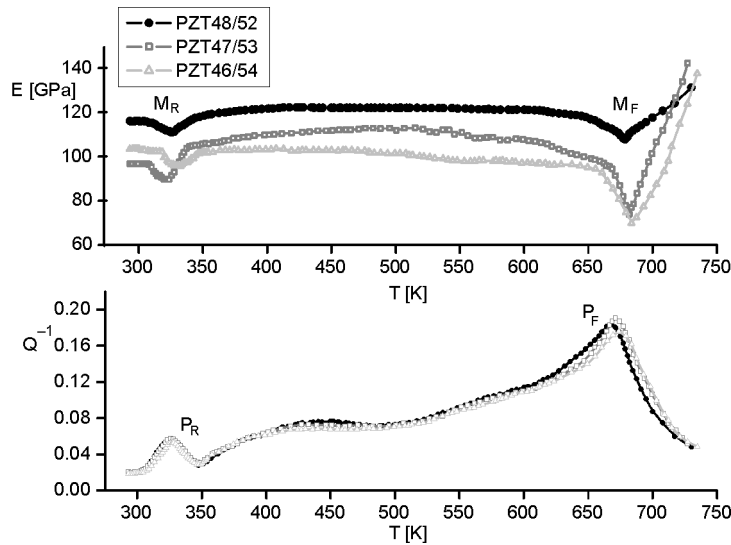


Fig. 3. Temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ obtained for the PZT ceramic samples from the morphotropic area

Then internal friction, Young's modulus and electric conductivity at various temperatures were measured for the ceramic samples from the morphotropic area (Fig. 7), i.e.: $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$, $\text{Pb}(\text{Zr}_{0.46}\text{Ti}_{0.54})\text{O}_3$. The analysis of the dependences obtained was made (Figs. 3, 4). The occurrence of the relaxation maximum P_R on the $Q^{-1}(T)$ dependences correlating with the M_R minimum on the $E(T)$ curves, was proved again. The temperatures of the phase transitions determined on the basis of the analysis of the $E(T)$ and $Q^{-1}(T)$ dependences were: for the PZT48/52 samples – $T_F = 668$ K, for the PZT47/53 ceramics – $T_F = 671$ K and for the PZT46/54 – $T_F = 673$ K. The values of these temperatures correspond to the temperatures determined from the analysis of $\ln\sigma = f(1/T)$ dependences (fig. 4) and they amount to: 668 K for $\text{Zr}/\text{Ti} = 48/52$, 670 K for $\text{Zr}/\text{Ti} = 47/53$ and 673 K for $\text{Zr}/\text{Ti} = 46/54$.

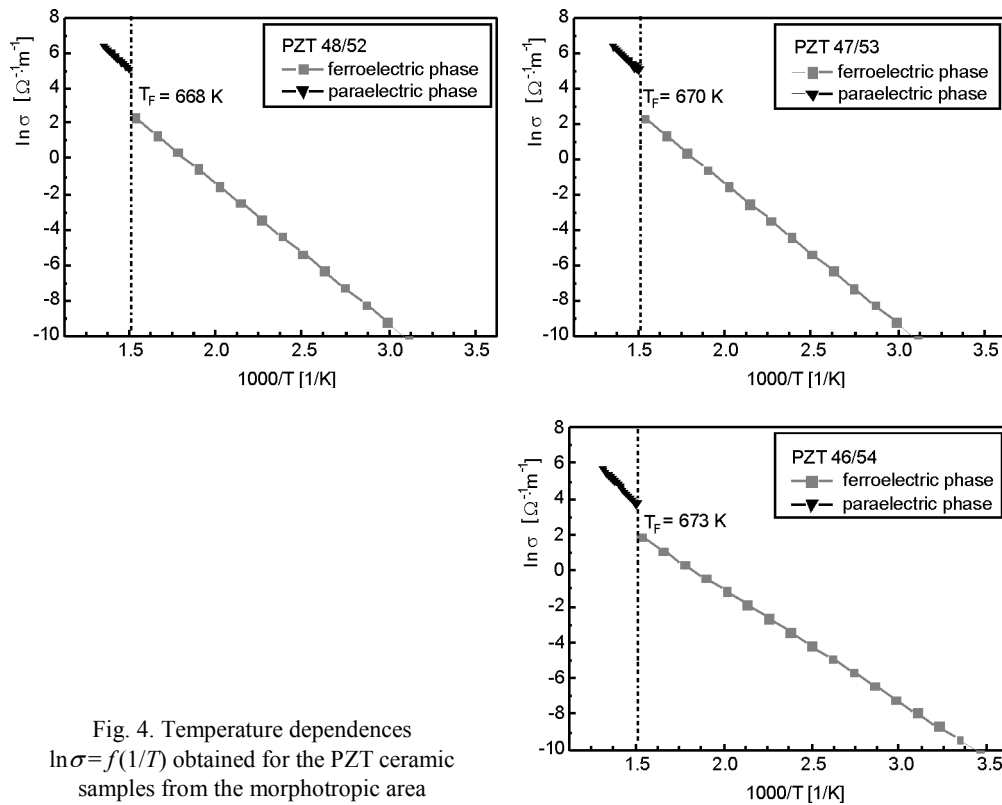


Fig. 4. Temperature dependences $\ln\sigma = f(1/T)$ obtained for the PZT ceramic samples from the morphotropic area

In the next stage of the investigations, the characteristics of the PZT35/65 and PZT25/75 ceramic samples with the ferroelectric tetragonal phase have been made. The temperature dependences $Q^{-1}(T)$ and $E(T)$ for the samples are presented in Fig. 5. As in the previous measurements, presence of two characteristic minima on the $E(T)$ curves was confirmed: M_R correlating with the P_R maximum, corresponds to relaxation phenomena, taking place in the structure of the ceramics examined and minimum M_F correlating with the P_F maximum, corresponds to the transition between ferroelec-

tric and paraelectric phases. The determined temperatures T_F for both compositions are shown in the PZT phase diagram (Fig. 7). Their values confirm the origin of the P_F maximum from phase transition (PZT35/65 – $T_F = 681$ K, PZT25/75 – $T_F = 695$ K). The $\ln\sigma = f(1/T)$ dependences (Fig. 6) and thence the temperatures T_F point out clearly to the phase transition (682 K for Zr/Ti = 35/65, 696 K for Zr/Ti = 25/75).

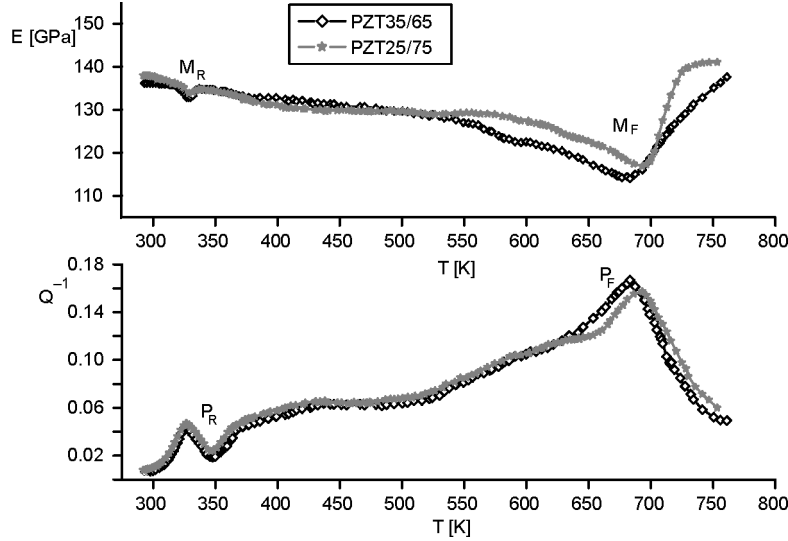


Fig. 5. Temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ obtained for the PZT ceramic samples from the ferroelectric tetragonal phase

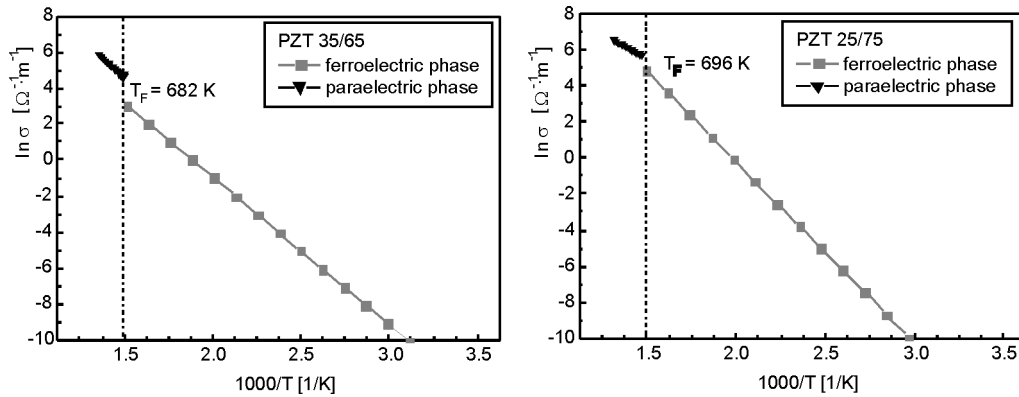


Fig. 6. Temperature dependences $\ln\sigma = f(1/T)$ obtained for the PZT ceramic samples from the ferroelectric tetragonal phase

Analysis of the temperature dependences of the Young's modulus $E(T)$ performed for all examined samples, confirm that the room-temperature values of the Young modulus increase with increasing PbTiO_3 concentration. This is caused mainly by the

growth of ferroelectric hardness and size of the grains along with the growth of the PbTiO_3 concentration.

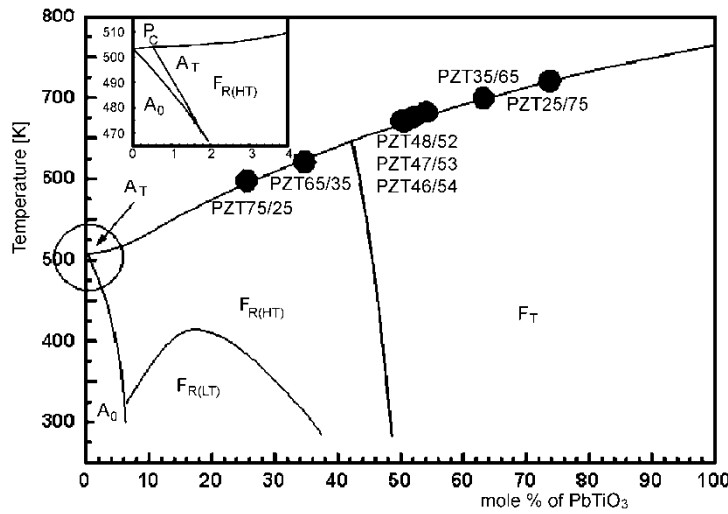


Fig. 7. PZT ceramics phase diagram: A_0 – antiferroelectric orthorhombic phase ($Pba2$), $F_{R(LT)}$ – ferroelectric rhomboedral phase ($R3c$), $F_{R(HT)}$ – ferroelectric rhomboedral phase ($R3m$), F_T – ferroelectric tetragonal phase ($P4mm$), P_C – paraelectric regular phase ($Pm3m$) [1]

It results in generating additional stresses on the boundaries of grains, their values being directly proportional to the E value (Eq. (2)). The determined values of Young's moduli at room temperature for various ratios of Zr/Ti are given in Table 1.

Table 1. The values of Young's modulus E at room temperature for various Zr/Ti ratios

Zr/Ti ratio	E [GPa]
75/25	87
65/35	85
48/52	103
47/53	100
46/54	110
35/65	135
25/75	139

A decrease in the E values until they achieve a minimum at the phase transition and then, a rapid increase to infinity is a characteristic phenomenon observed on the $E(T)$ curves (Figs. 1, 3, 5). At the point of transition, ferroelectric phase with tetragonal or rhomboedral structure undergoes a change to the paraelectric regular phase. This results in movement of deformity of lattice ($c/a - 1$) to zero, according to equation [13]:

$$3\delta = \left(\frac{c}{a} - 1\right)E \quad (2)$$

where: δ is a mechanical stress in the sample, c , a – the lattice constants, E – the value of Young's modulus.

4. Conclusions

A good compatibility was found between the results of the phase transition temperatures obtained from the measurement of internal friction, Young's modulus and electric conductivity on the PZT phase diagram, as shown in Fig. 7. The temperatures obtained of the ferroelectric \leftrightarrow paraelectric phase transition for the ceramic samples from the sol-gel powders are from 7 to 10 K higher than for the same chemical compositions obtained from oxides. The main cause of it is the size of grains in the structure of PZT materials. For the ceramics obtained from oxides the average size of grains amounts to about 10 μm , whereas for studied ceramics about 3.0 μm . In the case of larger grains, the structure is less stable, and a larger quantity of structural defects and strains appear. In such ceramic materials it is easier to cause changes of the structure by the action of external factors as for example temperature. The observed ferroelectric \leftrightarrow paraelectric phase transition is one of such changes.

The values of the electric conductivity up to the point of phase transition (T_C), are low being in the range of 10^{-7} – $10^{-3} \Omega^{-1}\cdot\text{m}^{-1}$. Such low values of σ show that dielectric losses are low, what is advantageous from the practical point of view. In the paraelectric phase (above T_C) the values of σ are in the range of 5×10^{-3} – $3 \times 10^{-1} \Omega^{-1}\cdot\text{m}^{-1}$ being a function of the Zr/Ti ratio. This is connected with mobility of domain structure and their disappearance above T_C and with high values of dielectric loss in the vicinity of the phase transition.

The ceramics obtained from the sol-gel powders may work at a higher range of temperatures, which is very advantageous from the point of view of their practical use in converters. To sum up it should be emphasized that the measurement of Young's modulus provides a suitable method to determine the phase transitions in ceramics.

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