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Internal friction related to the mobility of domain walls in sol-gel derived PZT ceramics

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Internal friction Q^{-1} and Young's modulus E were measured as functions of temperature for undoped $Pb(Zr_{0.65}Ti_{0.35})O_3$ ceramics obtained by the sol-gel technique. Experiments were performed with a RAK-3 resonant mechanical spectrometer. The $E(T)$ curves show two anomalies associated with two peaks, P_R and P_F, in the $Q^{-1}(T)$ dependence. Moreover, $Q^{-1}(T)$ curves recorded for two different frequencies show that the P_R peak has a relaxation character. It was found that its activation energy and relaxation time should be attributed to the interaction of domains with point defects.

Key words: *sol-gel method; ferroelectric ceramics; PZT; internal friction; domain structure*

1. Introduction

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ ceramics (PZT) are one of the most common industrial piezoelectric materials: they are used as transducers between electrical and mechanical energy in phonograph pickups, air transducers, underwater sound and ultrasonic generators, delay-line transducers, wave filters, etc. [1–3]. Generally, all such applications require a high piezoelectric constant as well as low electrical and mechanical loss. Variations of internal friction and the elastic modulus as functions of temperature and excitation frequency can provide direct information on energy dissipation in the material. For example, Postnikov et al. [4] have shown that the internal friction in PZT is not only associated with domain walls, but also with point defects.

The chemical composition and structure of piezoceramics, which can essentially influence the stability of their parameters, play an important role in the application of piezoceramics. Changes in their real structure, texture, and properties are possible, for

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example, by inserting point structural defects. These defects can be the result of mechanical treatment of the ceramics, irradiation with molecules or photons with high energy, or annealing in vacuum.

With their many applications and controlling factors, PZT materials have been subject to continuous research over the past few decades. In the present study, the temperature dependencies of the internal friction Q^{-1} and dynamic Young's modulus E of PZT 65/35 ceramics obtained by the sol-gel method were measured.

2. Experimental

The technological process of fabricating PZT ceramics consists of two basic stages. The first is the preparation of amorphous nanopowders of the solid solution $Pb(Zr_{0.65}Ti_{0.35})O_3$ by the sol-gel method, and the other is the consolidation of these nanopowders and preparing fine-grained PZT ceramics by conventional ceramic sintering (CCS). The powder was obtained by introducing lead in the form of trihydrate lead acetate into the environment of the chemical reaction during the sol-gel process. Titanium and zirconium were introduced in the form of aloxides, namely $Ti(OCH_2CH_2CH_3)_4$-titanium(IV) propoxide, and $Zr(OCH_2CH_2CH_3)_4$-zirconium(IV) propoxide. To dissolve all compounds and form a solution, *n*-propanol was used. Synthesis was carried out in an argon atmosphere by heating the solution for 2 hours below the solvent boiling point, forming alkoxide complexes. The by-product obtained (propyl acetate ester) was removed from the solution by distillation. After cooling the reaction mixture to room temperature, *n*-propanol and acetyloacetone were added. The mixture was then hydrolysed (to activate the hydrolysis reaction, distilled water was used) and a colloid solution was formed. After a few minutes, the sol-gel system was formed. The sol-gel derived powder obtained in this way was ground in a mortar with the addition of a softening agent, and annealed at 573 K for 2 hours. The powder obtained after disintegrating the annealed pallets was mixed with liquid paraffin and finally used for preparing the ceramic samples [5, 6]. Ceramic bodies were fabricated by conventional ceramics sintering (CCS) [7], after which samples in rectangular bars (80×10×1) mm^3 were received. The samples were annealed at T = 873 K for t = 4 h and then ground and polished. Electrodes were deposited on their surface by the silver paste burning method.

The temperature dependencies of $Q^{-1}(T)$ and $E(T)$ were determined while heating at a constant rate of 3 K/min. Additionally, the temperature dependencies $Q^{-1}(T)$ and $E(T)$ were determined at two different frequencies: 524 Hz and 555 Hz (at a constant heating rate of 3 K/min.).

All measurements were done with a RAK-3 resonance mechanical spectrometer controlled by a computer [8]. In order to quantify internal friction, a logarithmic decrement of suppression was used:

$$\delta = \frac{1}{N} \ln \frac{A_0}{A_N} \tag{1}$$

where: A_0 – the initial amplitude of deformation, A_N – the amplitude after N vibrations.

Young's moduli E were calculated from the resonance frequency f vibration of the sample, measured simultaneously with the internal friction measurements, from the dependence: f

$$E = 94,68 \left(\frac{l_r}{h} \right)^3 \frac{m_d}{b} f^2 \tag{2}$$

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

3. Results and discussion

The crystal structure of PZT 65/35 samples was investigated by XRD using a Philips PW 3710 diffractometer. Diffraction data (Table 1) were collected for 2Θ between 20° and 65° and CuK_α radiation was used. Figure 1 shows the XRD pattern recorded for a PZT 65/35 sample. PZT 65/35 piezoceramics shows an XRD pattern typical of the perovskite-type structure. No pyrochlore-type phase was observed. In general, the activation energy of nucleation for perovskite PZT decreases with increasing Ti content [9]. Therefore, the crystalline structure depends strongly on the composition ratio of Zr/Ti. The structure was identified as a rhombohedral *R*3*m* phase (space group number 160), with the following parameters of the elementary cell: a_h = 0.5756 nm, c_h = 0.7058 nm. It can be seen that PZT materials with the perovskite structure were formed (a good correspondence with the PZT phase diagram was found).

Figure 2 presents $Q^{-1}(T)$ and $E(T)$ curves obtained for PZT 65/35 ceramics for five heating cycles, with a temperature ramp of 3 K/min in vacuum. The $E(T)$ curves show two anomalies, called M_R and M_F. The minimum M_R is located at 385, 391, 395, 383, and 379 K for the 1st, 2nd, 3rd, 5th, and 8th heating cycle, respectively. It is correlated to a sharp internal friction peak called P_R. The M_F anomaly in Young's modulus E and the P_F peak are due to the phase transition from the rhombohedral to the cubic (ferroelectric to paraelectric) phase.

In the $Q^{-1}(T)$ curve shown in Fig. 2, it is possible to divide the temperature range according to the level of internal friction. From 293 K to 355 K, Q^{-1} remains constant. Above 355 K, Q^{-1} increases and the P_R peak is formed. Above 450 K, Q^{-1} increases strongly up to a maximum at the P_F peak (at the Curie temperature). In the paraelectric region, the drastic decrease in Q^{-1} reminds us that the mechanisms of energy dissipation in the ferroelectric state are obviously linked to the motion of domain walls.

The same shapes of the $Q^{-1}(T)$ and $E(T)$ curves are obtained for all five heating processes.

Table. 1. The Miller indices, positions of diffraction peaks, and interplanar distances for PZT 65/35 sol-gel ceramics

Indices *hkl*	2Θ [deg]	d_{hkl} [Å]
101	21.810	4.07176
012	31.023	2.88032
110	31.049	2.87802
003	38.223	2.35271
021	38.265	2.35271
202	44.464	2.03588
113	50.034	1.82153
211	50.068	1.82037
104	55.173	1.66340
122	55.221	1.66207
300	55.237	1.66163
024	66.670	1.44016
220	64.728	1.43901

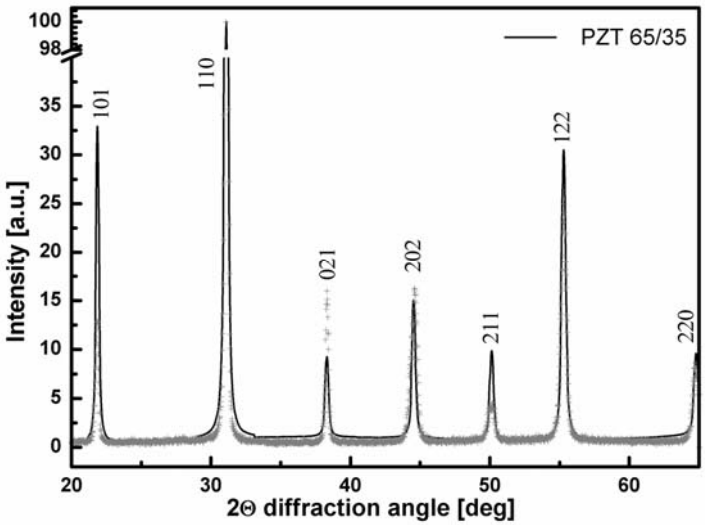

Fig. 1. X-ray diffraction pattern of PZT 65/35

Around the P_R peak, a decrease in the background value of internal friction Q^{-1} and a displacement of the temperature of the P_R peak towards higher temperatures were observed for the 1st, 2nd, and 3rd cycles of heating. In the 5th and 8th heating cycles, the P_R peak moved towards lower temperatures.

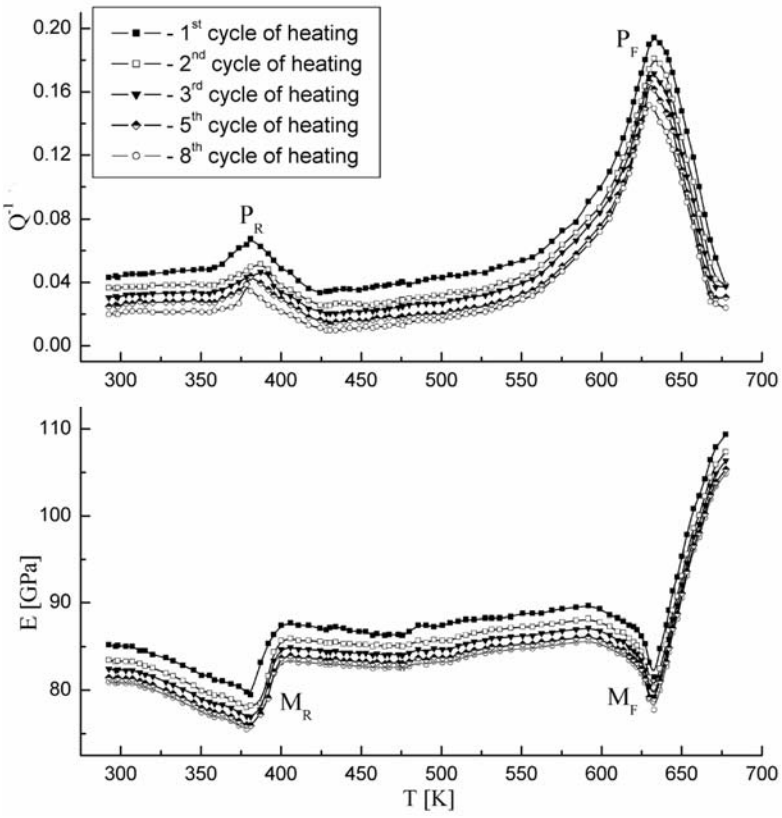

Fig. 2. Temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ obtained during five heating cycles, with a temperature ramp rate of 3 K/min in vacuum

From the above results concerning the peak temperature, the activation energy H and relaxation time τ_0 of the P_R peak are determined and shown in Table 2. According to the Arrhenius equation, the relaxation time can be written as [10]:

$$\tau = \tau_0 \exp\left(\frac{H}{kT}\right) \tag{3}$$

where: τ_0 – the inverse of the frequency factor, H – the activation energy, k – the Boltzmann constant, T – absolute temperature.

The activation energy was obtained on the basis of the half width of the $Q^{-1}(T)$ curve:

$$H = \frac{2.63kT_1T_2}{T_2 - T_1} \tag{4}$$

where T_1 and T_2 are the temperatures for $(1/2)Q_{\max}^{-1}$, respectively.

Table 2. Activation energy and relaxation time of the P_R relaxation peak

Cycle of heating	T_{PR} [K]	H [eV]	$\tau_0 \times 10^{14}$[s]
First	385	1.05±0.03	(0.10 ± 0.06)
Second	391	0.93±0.03	(1.22 ± 0.06)
Third	395	0.90±0.03	(4.28 ± 0.06)
Fifth	383	0.85±0.03	(8.13 ± 0.06)
Eights	379	0.82±0.03	(9.94 ± 0.06)

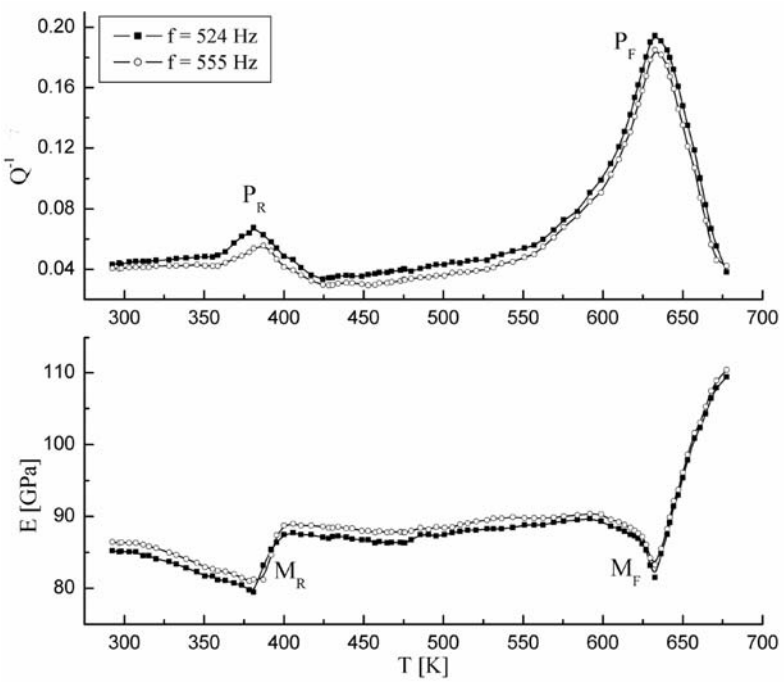

Fig. 3. Temperature dependences of the internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ obtained for two different frequencies while heating with a temperature ramp rate of 3 K/min

For the P_R peak, the magnitude of the relaxation time (τ_0 = (0.1–9.94)10^{-14} s) is coherent with a point defect relaxation and the P_R peak could be due to interaction between domain walls and oxygen vacancies, because the activation energy (H = 0.82–1.05 eV) for the diffusion of oxygen vacancies in PZT materials is about 0.9 eV. The displacement of the temperature of the P_R peak towards higher temperatures, observed for the 1st, 2nd, and 3rd cycles of heating and subsequent displacement towards lower temperatures for the 5th and 8th heating cycles is caused by the interaction of the domain walls with point defects (oxygen vacancies), anchoring them. It is confirmed that the P_R peak originates from a thermally activated relaxation process, and we think that the motion of domain walls should have a dominant role in the mechanism of the P_R peak in PZT 65/35 ceramics [11].

To attain more evidence of the dependence of the P_R peak on oxygen vacancies, internal friction Q^{-1} was measured at two frequencies: 524 Hz and 555 Hz. The results obtained with PZT 65/35 ceramic samples are shown in Fig. 3. The $E(T)$ curves show the M_R and M_F anomalies in the Young's modulus due to two peaks, P_R and P_F, in the $Q^{-1}(T)$ curves. During measurements at various frequencies, changes in the temperature position of the P_R peak were observed – a displacement of this peak from 385 K (524 Hz) to 393 K (555 Hz). Therefore, the P_R peak has a relaxation behaviour, because it is frequency-dependent and related to oxygen vacancies and domain walls [12]. The nature of the P_R peak can be explained in terms of Postnikov's model, which involves interaction between mobile point defects and stationary 90° domain walls [4].

The P_F peak originates from a ferroelectric–paraelectric phase transformation, because no change in its position was observed with changes in the measurement frequency. Only a rise in the P_F peak height with decreasing resonance frequency of the sample's vibrations were observed [13].

4. Conclusions

Two maxima of the internal friction were observed in the temperature dependences obtained for PZT 65/35 ceramics: P_F, connected with the transformation phase and the relaxation maximum in the ferroelectric phase P_R. The temperature displacement of the P_R peak's position towards higher temperatures with an increasing resonance frequency of the sample's vibrations suggest a relaxation character of the peak. The P_R peak could be attributed to the interaction of domain walls and oxygen vacancies, induced during temperature annealing in vacuum.

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