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The internal friction background in PZT ceramics obtained by the sol-gel method

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The results of internal friction background examined in fine-grained lead zirconate titanate PZT ceramics are presented. The aim of the study was to describe the influence of change in concentration of the lead titanate on the internal friction background. The internal friction examinations were performed using modern automatic frequency relaxator of the RAK-3 type at 293 K. PZT ceramics of the chemical composition $PbZrO_3$-$PbTiO_3$ with $PbTiO_3$ concentration ranging from 25% to 75% were the examined material. The nanopowders were prepared by the sol-gel method. PZT ceramics were obtained by the conventional sintering method. The influence of the changes in the structure of ceramic materials on the internal friction background was reported. SEM images of the domain structure were used to describe the obtained results.

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

1. Introduction

In order to extend the applicability of ceramic materials it is necessary to learn about their physical, chemical and mechanical properties, their real structure and relaxation properties. Detailed studies of the dependences between the chemical composition, crystalline structure, elctrophysical properties and the domain structure will allow us to obtain ceramics with better properties, needed for the modern technology. Rapid development of modern investigation methods, and especially non-destructive methods, has been observed in the research on ceramic materials. Methods of mechanical spectroscopy, and the internal friction method in particular, have been used more and more frequently. A great interest in the method based on the measurement of internal friction in investigations of real structure of the ceramic material is caused by the fact that by observing macroscopic vibrations of a specimen, information about the behaviour of the material on atomic level can be obtained. This method is character-

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ized by high sensitivity to changes in the concentration of point defects, to interaction between the defects, and changes in the real structure of materials [1–4].

Apart from the development of modern methods of investigation, a development of technologies of ceramics production can also observed. The PZT ceramics were obtained from PbO, ZrO_2, TiO_2 by the baking method at the temperature of 970–1200 K which caused significant deviations from stoichiometry as a result of loss of PbO. For that reason, conventional methods of synthesis of ceramic materials based on the reaction in the solid phase have been used less frequently in favour of chemical methods (reactions in the liquid phase) enabling us to obtain powders of high homogeneity of chemical composition and having grain size of the order of nanometers. The sol-gel method is one of the most widespread chemical methods. The method guarantees high purity of the materials obtained and enables one to conduct syntheses at a relatively low temperature, thus reducing the vaporization of components and favouring preservation of the stoichiometric composition. The possibility to conduct the synthesis at a lower temperature is of great importance, particularly in ceramics containing lead oxide. Ceramic grains of the size of 0.3–3 μm are made of crystallites of the size of 20–75 nm [5, 6]. The ceramics obtained from powders synthesized by this method have a high density, close to the theoretical value, which has a significant influence on its dielectric, piezoelectric, and mechanical parameters, allowing us to use it as piezoelectric and electro-acoustic transducers, pick-ups (vibration, pressure), servo-motors, filters, piezoelectric transformers, engines, parametric amplifiers, and ferroelectric memories [2, 6–8].

The aim of this paper was to examine the influence of changes in the lead titanate content on the phenomena of internal friction in the fine-grained PZT type ceramics obtained by the method of free sintering of powders synthesized by the sol-gel method.

2. Test material and test methods

The $Pb(Zr, Ti)O_3$ ceramics with various lead titanate contents from 25 mol % to 75 mol % was the test material. In order to obtain ceramic powders, a chemical synthesis method – the sol-gel method was used. Lead in the form of the lead acetate (II) – $Pb(COOCH_3)_2$, titanium and zirconium in the form of alcoholates: *n*-titanium propanolate $Ti(CH_3CH_2CH_2O)_4$ and *n*-zirconium propanolate $Zr(CH_3CH_2CH_2O)_4$ were added to the reaction medium. The synthesis reaction was carried out in argon atmosphere. The reaction product obtained was subject to distillation to remove propyl acetate. After cooling the solution to room temperature the solvent was added to obtain the solution of the concentration 0.8–1 mol/dm^3. In order to stabilize the alcoholate solution, acetylacetone was added and the solution was subjected to hydrolysis. Sol was obtained as a result of a series of hydrolysis reactions, and the sol, after transofrming into gel, underwent the drying process at the temperature of 573 K. Then the obtained product was calcinated at 873 K for 4 h to remove organic residues.

The powder obtained was comminuted (grinding 2 h), and then after adding plasticizer (liquid paraffin) moldings were formed in a plate-like shape of the following dimensions: length – 40 mm, width – 10 mm, thickness – 3 mm. They were sintered by the free sintering method at the temperature of 1523 K for 5 h. The specimens obtained were ground, polished, and then they were coated with silver paste electrodes by the baking method.

The internal friction for all specimens in question was determined by an automatic relaxator of acoustic frequencies RAK-3, controlled by a computer [9]. This relaxator allowed us to determine internal friction (IF) by the measurement of damping of the specimen free vibrations.

3. Results and discussion

Dependences of the internal friction background on the lead titanate content in the tested specimens determined at 293 K are presented in Fig. 1.

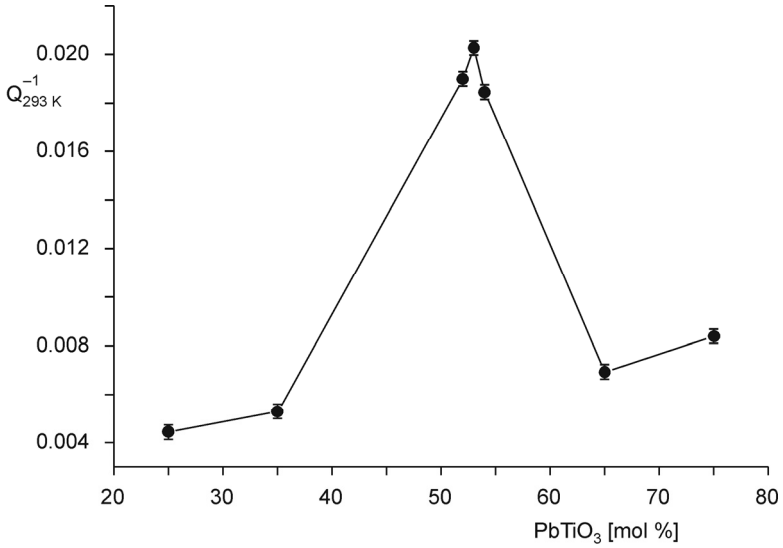

Fig. 1. Dependences of the internal friction background on the $PbTiO_3$ concentration in PZT ceramics obtained via the synthesis by the sol-gel method

The level of internal friction in the PZT ceramics depends, among others, on the type and number of domain walls and their mobility. However, the character of crystal fragmentation into ferroelectric domains depends on the presence of structural defects deformation, on electric conductivity and conditions involving a transformation into the ferroelectric phase, and the thermal and electric history of a material [3, 10].

The value of internal friction (*TW*) decreases with a decrease of the mobility of domain walls and a decrease in the number of domain walls. It is generally known that with a

change in the lead titanate concentration in the PZT ceramics there is a change in the material structure from the antiferritic orthorhombic phase for low concentrations of the lead titanate via the rhombohedral phase (25 and 35 mol % $PbTiO_3$), to the tetragonal phase concentrations (65 and 75 mol % $PbTiO_3$). The morphotropic phase boundary represented in the diagram by a line corresponds to the apparent equilibrium of the tetragonal (T) and rhombohedral phases (R) [11]. However, real phase diagrams reveal most frequently an area of coexistence of the phases and not the lines. In the range of the PZT compositions from the dual phase morphotropic area, a great number of domain walls with high mobility (Fig. 2) can be observed. Both 180° domain walls and 90°, 71°, 109° domain walls were present [3, 4, 10].

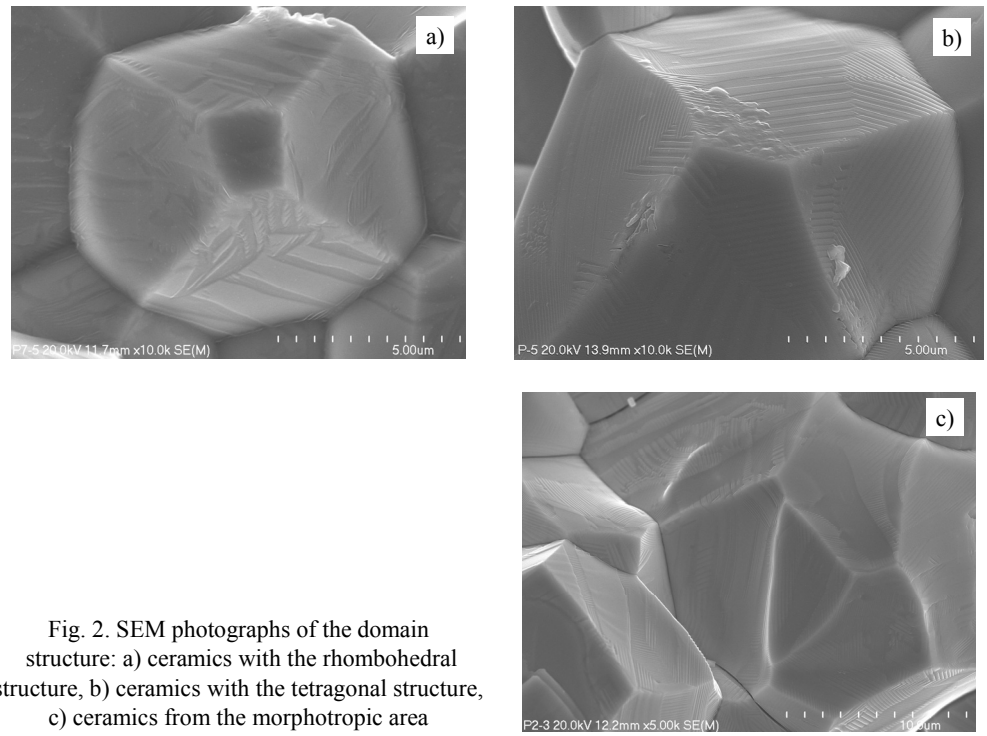

Fig. 2. SEM photographs of the domain structure: a) ceramics with the rhombohedral structure, b) ceramics with the tetragonal structure, c) ceramics from the morphotropic area

The presence of a great number of domain walls with high mobility is responsible for the high value of internal friction for ceramics with the concentration of 53 mol % $PbTiO_3$ belonging to the morphotropic area and slightly lower values for the ceramics with the concentration of 52% i 54 mol % $PbTiO_3$ also belonging to the morphoropic area. Moving away from the morphotropic area towards compositions with tetragonal structure, a decrease in the internal friction value can be observed (Fig. 1). In the range of higher $PbTiO_3$ concentrations corresponding to tetragonal structure (specimens with 65 mol % and 75 mol % of $PbTiO_3$) the configuration of domain structures must ensure the maximum compensation of mechanical stresses caused by an increase in the deformation of a unit cell. For this reason, there is a complex structure with a great

number of 90° domain boundaries (Fig. 2) characterized by low mobility [12] in the tetragonal phase. Such a stabilized domain structure determines the ferroelectric hardness of ceramics, which causes an increase in mechanical quality factor, and therefore a decrease in internal friction. Moving toward the compositions with lower $PbTiO_3$ concentrations (25 mol % and 35 mol % of $PbTiO_3$), corresponding to a rhombohedral phase, an increase in the mechanical quality factor is also observed, thus a decrease in the internal friction background value (Fig. 1). This phenomenon is conditioned by a strong decrease in the number of domain walls for the ceramics with the rhombohedral phase structure. In this kind of ceramics, the 180° domain structure prevails (Fig. 2).

Values of internal friction background in the tested ceramics obtained from the synthesized powders by the sol-gel method are lower than the values of the internal friction background for ceramics obtained by a synthesis in the reaction method in the solid phase and sintering by the free sintering method. The value of internal friction depends on the domain width which in turn depends on the grain size in the ceramics. The domain width in the fine-grained ceramics obtained by the sol-gel method is much lower than the domain width in the coarse-grained ceramics [13–15]. This is why the values of the internal friction background are lower in these ceramics. An application of the sol-gel method to synthesize ceramic powders allows one to obtain PZT ceramics with high density and piezoelectric and dielectric parameters comparable with the parameters of the multi-component PZT type ceramics.

4. Conclusions

The value of internal friction background depends on the ceramics structure, grain size, type of domain structure. Ceramics belonging to the morphothropic area have the highest value of internal friction background. When moving from the $PbTiO_3$ concentration corresponding to the morphotropic area, both for the phase with the rhombohedral and tetragonal structure, a decrease in the value of internal friction background is observed, as a result of the presence of 90° domain structure with low mobility (the tetragonal phase) or a decrease in the number of domain walls (the rhombohedral phase). The characteristics of the dependence of $PbTiO_3$ concentration on internal friction background in PZT ceramics (obtained by the sol-gel method) are the same for ceramic materials sintered for different methods.

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References

[1] BRUS B., ILCZUK J., Solid State Phen., 89 (2003), 309.
[2] XU H., *Ferroelectric Materials and Their Applications*, North Holland, New York, 1991.
[3] JAFFE B., COOK W.R., JAFFE H., *Piezoelectric Ceramic*s, Academic Press, London, 1971.

[4] FESENKO E.G., DANCINGER A.YA., RAZUMOVSKAYA O.N., *Novye piezokeramiczeskie materially*, RGU, Rostov-na-Donu, 1983 (in Russian).
[5] SUROWIAK Z., KUPRIYANOV M.F., CZEKAJ D., J. Eur. Cer. Soc., 21 (2001), 1377.
[6] SUROWIAK Z., CZEKAJ D., Mol. Quant. Acoust., 24 (2003), 183.
[7] WALLASCHEK J., J. Intell. Mat. Syst. Struct., 6 (1995), 71.
[8] SUN F.P., CHANDHRY Z., LIANG C., ROGERS C.A., J. Intell. Mat. Syst. Struct., 6 (1995), 134.
[9] ZACHARIASZ R., ILCZUK J., CHROBAK A., Ceramics, 66 (2001), 630.
[10] TAN Q., VIEHLAND D., J. Am. Ceram. Soc., 81 (1998), 328.
[11] ZACHARIASZ R., ZARYCKA A., ILCZUK J., Mater. Sci.-Poland, 25 (2007), 781.
[12] BOCHENEK D., DUDEK J., SUROWIAK Z., Ceramics, 80 (2003), 445.
[13] CHENG B.L., GABBAY M., FANTOZZI G., J. Mater. Sci., 31 (1996), 4141.
[14] WANG C., FANG Q.F., ZHU Z.G., J. Phys. D: Appl. Phys., 35 (2002), 1545.
[15] BOUZID A., GABBAY M., FANTOZZI G., Mater. Sci. Eng., A 370 (2004), 123.

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