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THE INFLUENCE OF PREPARATION CONDITIONS ON THE ELECTRO-ACOUSTIC PROPERTIES OF THE PZT-TYPE PIEZOCERAMIC SENSORS

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The possibilities of the application of the microstructure analysis, X-ray powder diffraction, and Raman scattering methods for the fast and reliable control of the quality of piezoelectric ceramic sensors at every stage of preparation are shown.

1. Introduction

For the past several years an intensive research effort have been made in many laboratories around the world to prepare electrically active ceramic materials intended for electromechanical transducers and other applications. Ferroelectric ceramic materials such as $Pb(Ti_xZr_{1-x})O_3$ (PZT) solid solutions have been used extensively as both sensors and actuators due to their excellent transduction capability in elastoelectric conversion [1 – 4]. Such piezoceramics have the strongest piezoelectric charge coefficients, the largest electromechanical coupling coefficients and relative permittivities as well as the lowest dielectric losses. The large permittivities of PZT ceramic materials facilitate electrical tuning and also reduce significantly the piezoelectric voltage coefficients. The PZT ceramic materials have large mechanical quality factors (Q_m) and require the addition of a damping backing in order to reduce ringing to an acceptable level.

The composition of PZT-type with conductive parameters of widespread application belongs, as a rule, to the morphotropic phase boundary (MPB) — a region of concentrations x for which a coexistence of both the rhombohedral (R) and tetragonal (T) ferroelectric phases is observed [5 – 7]. The interval of the composition parameter x at which both these phases appear is relatively wide, it may reach 15 mol%. One of the characteristic properties of MPB is a small deviation from the temperature axis on the phase

diagram which corresponds to the large change of structural states with temperature for fixed concentration x. These peculiarities of MPB and of its vicinity are characterized by the most interesting properties of the corresponding materials: extreme values of the piezoelectric and dielectric parameters (Fig. 1). However, there are many problems in the processing of high quality ceramic materials on the basis of compounds from MPB.

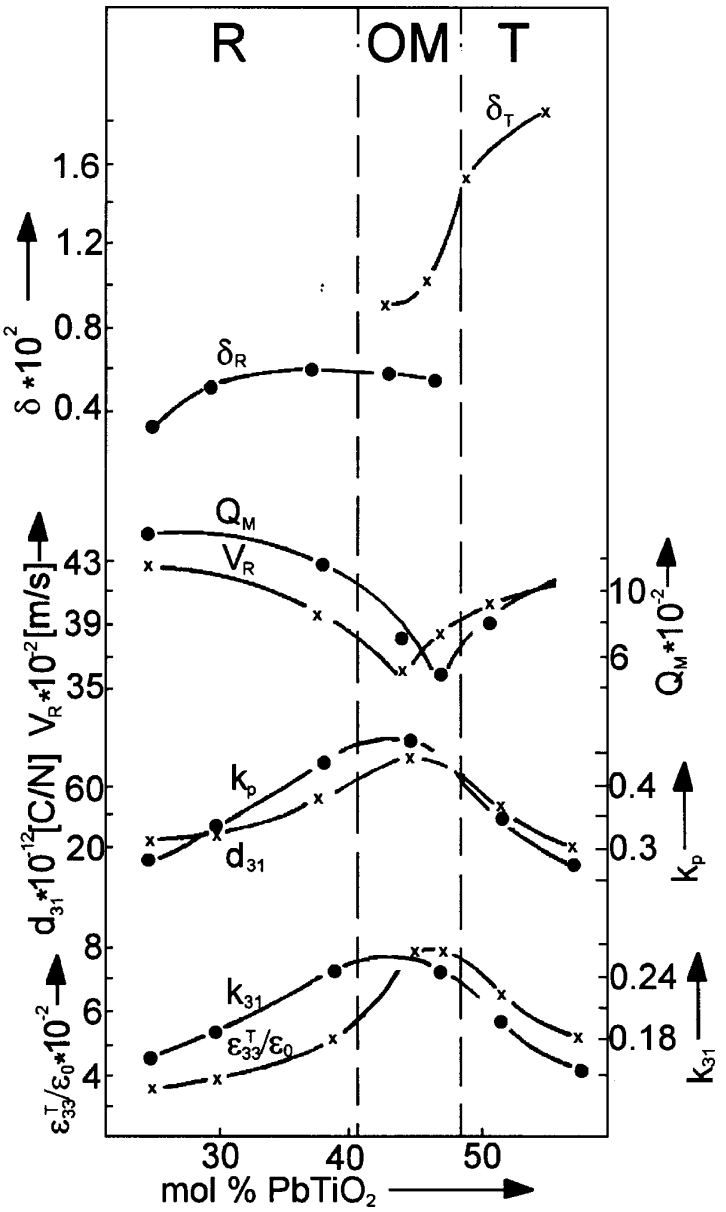

Fig. 1. The dependencies of physical parameters of the PZT-type system in the vicinity of the morphotropic phase boundary on the $PbTiO_3$ content.

It was shown (e.g [8 – 10]) that the properties of such ferroelectric ceramic materials depend strongly on the conditions of their preparation, i.e. on the synthesis, sintering, mechanical treatments, annealing and polarization processes. This is connected with the high sensitivity of these materials to the changes of the structural states of the MPB with small variations in composition, grain size, domain structure etc.

It is evident that at all stages of the production of the ceramics (synthesis, sintering, mechanical treatments, annealing and polarization) it is necessary to apply effective (fast, reliable, precise, nondestructive) control methods.

The aim of this paper is to analyse the possibilities of characterization of the PZT-type ferroelectric materials at every stage of the ceramic sample preparation by effective control methods. The best methods for this purpose are, in our opinion, X-ray diffraction (XRD), microstructure analysis and Raman spectroscopy.

2. Experimental

On the basis of the PZT-type solid solutions, the materials from MPB were prepared by the solid-phase synthesis methods. Ceramic samples were obtained under different conditions of preparation (varying times and temperatures) both by the usual sintering and by the hot-pressing method. The samples were investigated by the X-ray powder diffraction method at the stage of the preparation of the components for the synthesis, after synthesis, after sintering and after polarization. The investigations of the microstructure of the ceramic samples were performed led by the electron microscope method. The Raman spectra were excited by argon laser light ($\lambda = 0.488\,\mu\text{m}$).

3. Results

At the first stage, the dependencies of the piezoelectric and dielectric parameters on the conditions of the sample preparation of the PZT compositions from the MPB region were investigated. The results for one sample are presented in Fig. 2.

From the data given in Fig. 2, it results that the small differences in the conditions of preparation of the ceramic material can lead to significant differences in the physical properties. If the methods of control of the ceramic materials had not been applied during the preparation, the results of measurements of the physical properties of the fabricated ceramic samples would be rather irrational because spoilt ceramic materials hardly meet the requirements for a given application.

Control of the microstructure is done, as a rule, for the characterization of the ferroelectric ceramics at various stages of its sintering [11 – 13].

As an example in Fig. 3 the correlations between some electrophysical parameters, dimensions of the crystallites and total density (for samples obtained by hot-pressing method) are shown. It was expected that the influence of the hot pressing on the microstructure would be larger that in the case of conventional sintering.

It was found that the influence of the time and temperature of the sintering on the dimensions of grains is noticeable (Fig. 3a).

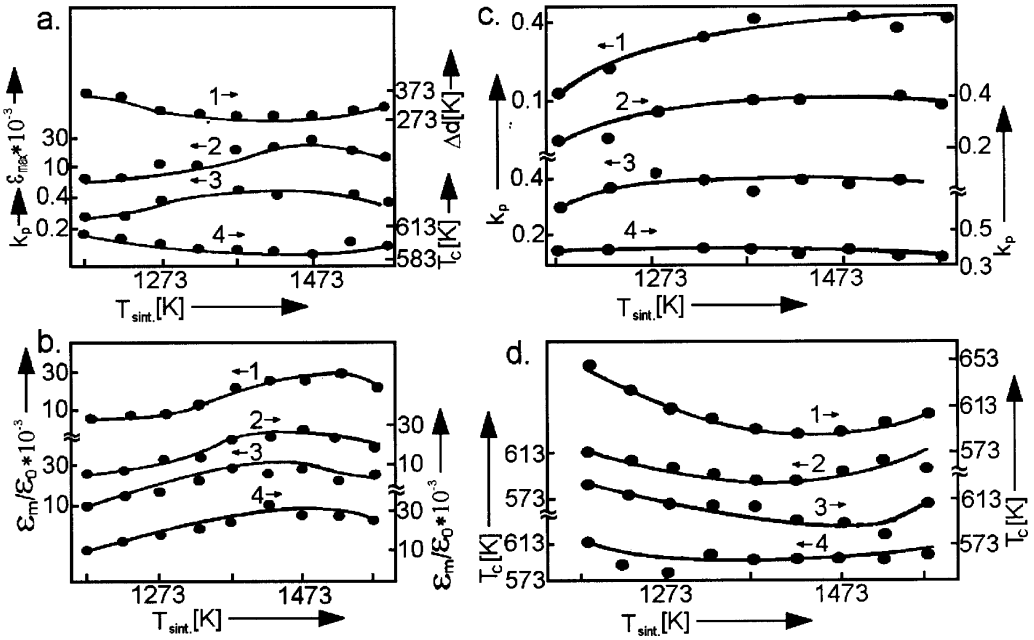

Fig. 2. The dependencies of the dielectric permittivities ($\varepsilon_{\max}$), electromechanical coupling coefficients (k_p), Curie temperature (T_c) and phase transition diffuseness parameters (Δ_d) on the sintering temperature (T_{sint}) (sintering time, $t_{\text{sint}} = 2$ hours); a) the dependencies of $\varepsilon_{\max}$, ε_0, k_p, T_c on the sintering temperature and time (t_{sint}: 1-0.25; 2-2; 3-3; 4-5 hours) (b, c, d).

The decrease in the dielectric permittivities ($\varepsilon/\varepsilon_0$) with increasing grain sizes (Fig. 3b) is due to a decrease in the internal strains of the specimen brought about by an increased domain twinning in the larger grains.

The electromechanical coupling coefficient (k_p) was practically independent of the dimensions of the grains but its value is related to the bulk density (Fig. 3c).

It is possible to explain the decrease of coercive field E_c and the monotonic decrease of the Q_m values by the grain size increase (Fig. 3d). This effects could be explained also as a result of the increased twinning during the grain size increase. The latter causes an increase in the number of the domain walls which lead to higher mechanical losses and thereby to a lower Q_m.

At the same time the analysis of the microstructure may be in general effectively used only at the stage of sintering. Its possibilities are limited to the control of other stages of preparation of the ferroelectric elements (synthesis, polarization etc).

The most suitable method of the production process control is the X-ray powder diffraction methods by that one can determine: i – the crystal phases and their concentrations in specimens; ii – the crystal phase symmetries and the cell parameters; iii – the values of spontaneous deformations; iv – mechanical and electrical (domain) texture parameters; v – microinhomogeneities (microdeformations); vi – values of coherent scattering regions (CSR).

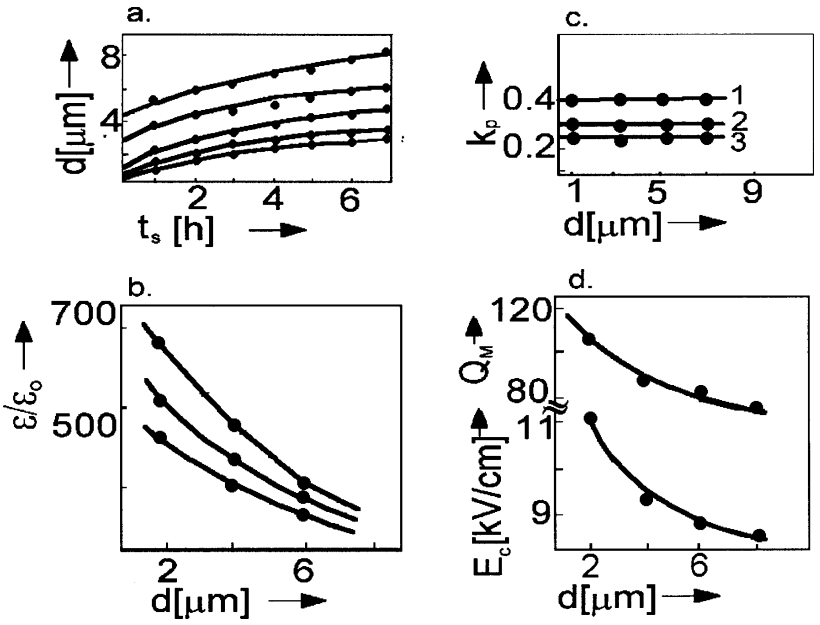

Fig. 3. The dependencies of the grain size on the sintering temperature and time (a), the dependencies of $\varepsilon/\varepsilon_0$, the electromechanical coupling (k_p), coercive fields (E_c), and mechanical quality factors (Q_m) on the grain sizes of the ceramics (b, c, d).

For the determination of the structural parameters of powder (ceramic) specimens the mathematical treatment of the diffraction profiles (Fig. 4a) has been used. Different methods of such a treatment are described in [14, 15]. Figure 4b demonstrates two examples of separation of the three diffraction peaks related to the R — (200^R), T — (200^T, 002^T) phases which coexist in MPB of the PZT-type materials.

A comparison of the diffraction profiles obtained for ceramics sintered at different τ_{sint} and T_{sint} indicates that high degree of homogeneity is possible at lower T_{sint} if the sintering time is increased. Figure 4 shows a decrease of the amount of the R-phase and narrowing of the diffraction peak of the T-phase.

A separation of the overlapped peaks allows both the determination of the cell parameters and the evaluation of the microinhomogeneities $\eta = \Delta d/d$ and the coherent scattering region (CSR) dimensions by the analysis of full width of the half maxima (FWHM) of the diffraction peaks. These parameters are very sensitive to the real state of the ferroelectric materials.

The estimation performed is due to the fact that the microinhomogeneity value in the paraelectric cubic phase does not exceed 10^{-4} and the CSR dimensions, as a rule, are found to be larger than 100 nm (for ceramics produced under the optimal conditions).

Changes of the CSR values are observed at the MPB transitions to the ferroelectric T- and R-phases.

The conditions of sintering of the ceramic materials from MPB have an influence on both the percentage of the ratio of the R to the T phases and of the FWHM as shown

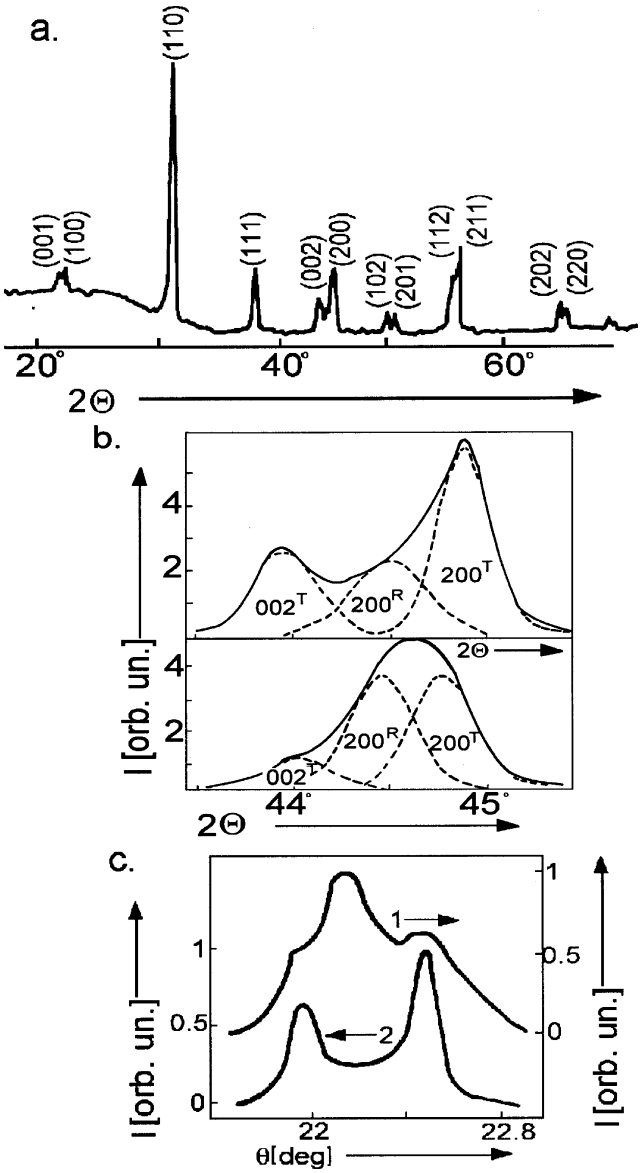

Fig. 4. The X-ray powder diffraction profile (a) and the separation method of overlapped peaks (b): 1 – sample hot pressing, 2 – classic sample technology; the change of the diffraction profile as a result of different sintering times (1 – $t_{\mathrm{sint}} = 0.25\,\mathrm{h}$; 2 – $t_{\mathrm{sint}} = 5\,\mathrm{h}$; $T_{\mathrm{sint}} = 1223\,\mathrm{K}$) (c).

in Fig. 4. With an increase in the sintering temperature up to 1398 K the concentration of the T phase at room temperature increases and the FWHM of the difraction peaks decreases.

The influence of the electric fields of polarization on the structure and the physical properties of the PZT-type ceramics was discussed elsewhere [16 – 18].

The spectra of the Raman scattering are sensitive to the dynamical state of the crystals [19 – 20]. In particular, by means of the IR methods, the Raman- and Brillouin-spectroscopy it is possible to investigate the softening of the transverse optical (ferroelectric) mode above the phase transition.

In this paper the preliminary results of the Raman investigations of the PZT-system samples are presented. It is worthy of noting that all samples were obtained under the same conditions of the synthesis and sintering (Fig. 5).

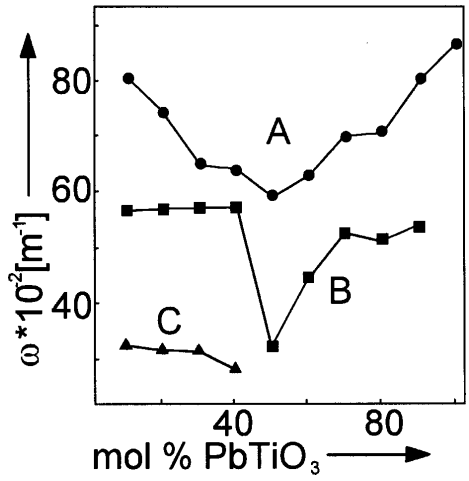

Fig. 5. The dependencies of the mode frequencies of the PZT systems on the $PbTiO_3$ concentration obtained by the Raman spectroscopy (argon laser).

It seems reasonable to assume that the A-mode is the ferroelectric E(TO) one. It becomes softer while approaching to the MPB (concentration phase transition at room temperature). The B mode may be treated as the TA-transverse acoustic one. The C-mode appears in the rhombohedral phase of the solid solutions only and may be related to RLT($R3c$) phase. It may be caused by the M_3- or R_{25}-type phase transitions.

In our opinion the further investigations of the specific vibration spectra of the PZT-type ferroelectric materials obtained under various conditions allow to separate the dependencies of the corresponding parameters on the quality of the crystallites. As a result it should give the possibility to apply the combinational light scattering method to the operative control of the quality of the material at all stages of the production.

4. Conclusion

The results of the studies of the PZT-type ceramics with compositions from MPB presented above demonstrate that the variation of preparation conditions strongly determine the physical properties of the piezoelectric ceramic sensors.

An effective control of the ceramics fabrication at the different stages of the production can be performed by the X-ray powder diffraction methods.

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Keywords: PZT, piezoceramics, electro-acoustic sensors, Raman spectroscopy, XRD.

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