

The PZT system ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, $0.0 \leq x \leq 1.0$): Specific features of recrystallization sintering and microstructures of solid solutions (Part 1)

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Abstract

This work is concerned with the specific features of sintering of solid solutions of the PZT system ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, $0.0 \leq x \leq 1.0$) depending on composition. The microstructure of the solid-solution ceramics has been found to be a fairly homogeneous, mosaic, sufficiently close packing of isometric crystallites with a range of section from 3 to 11 μm , but there exists a number of special features related to the component and phase composition of the objects. It has been found that the changes in multifractal parameters of grain structure of these ceramics reflect with high sensitivity the processes of phase transformations in the solid solutions. The obtained results are useful in developing piezoelectric materials based on the PZT system.

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1. Introduction

The $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) solid solutions find increasing use in various piezoelectric devices. The majority of industrial functional ferro-piezoelectric ceramic materials (FPCM) are based on these solid solutions. Taking into account the fact that the properties of these FPCM's are mainly determined by their crystal structure (which forms at $T=(870\text{--}1070)$ K), by their microstructure (which forms at $T=(1070\text{--}1370)$ K, i.e., when the structural motive already exists) and by the density of sintered ceramics, it is useful to determine the influence of the composition on the latter as well as on the size of crystallites. This is important from the point of view of determining the correlation between the phase and grain structures of solid solutions as well as due to the possibility of governing the microstructure by varying the composition, i.e., the

position of the solid solution on the phase diagram of the system.

2. Objects under study, their synthesis and studying methods

The objects under study are the solid solutions $(1-x)\text{PbZrO}_3-x\text{PbTiO}_3$ ($0.0 \leq x \leq 1.0$). In the ranges $0.0 \leq x \leq 0.12$, $0.30 \leq x \leq 0.36$, $0.37 \leq x \leq 0.42$ and $0.52 \leq x \leq 0.57$ the concentration step, Δx , was 0.01, whereas in the ranges $0.42 < x \leq 0.52$ and $0.60 < x < 0.90$ it was 0.005 and 0.0025, respectively.

The samples of solid solutions were prepared according to the conventional ceramic technology (solid-state synthesis, sintering without applied pressure). The synthesis was performed in two stages with intermediate grinding and granulation of the powders. The first and the second annealing temperatures, T_1 and T_2 , were 1140 K and 1170 K, respectively. Isothermal ageing at both temperatures was conducted during 7 h. The optimal sintering temperature, T_{sint} , was chosen from three sintering temperatures in the range of (1470–1530) K. The densest sintered samples were obtained at

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$T_{\text{sint.}}=(1490\text{--}1510)\text{K}$ after 3 h sintering time (depending on composition).

The x-ray studies were carried out by means of the powder diffraction method using the DRON-3 diffractometer (Fe K_{α} -radiation; Mn-filter; Fe K_{β} -radiation; Bragg–Brentano focusing scheme). The study was conducted on the bulk and ground ceramic objects, which enabled one to preclude the influence of surface effects, stresses and textures arising in the process of preparation of ceramics. The x-ray density ($\rho_{\text{x-ray}}$) was calculated using the formula: $\rho_{\text{x-ray}}=1.66 \cdot M/V$, where M is the formula unit weight in grams and V is the perovskite cell volume in \AA^3 . The homogeneous deformation parameter, δ , was calculated using the following formulae: $\delta=\cos\alpha$ (for the Rh-phase) and $\delta=\frac{2}{3}(\frac{c}{a}-1)$ (for the T-phase). The measurement errors of structural parameters were estimated to be as follows: $\Delta a=\Delta b=\Delta c=\pm(0.002\text{--}0.004)\text{ \AA}$ for the linear ones; $\Delta\alpha=3'$ for the angular ones, and $\Delta V=\pm 0.05\text{ \AA}^3$ for the volume ($\Delta V/V \cdot 100\%=0.07\%$).

The experimental density (ρ_{exp}) of the samples was determined by the hydrostatic weighing technique with octane used as the liquid medium. The experimental density was calculated using the formula: $\rho_{\text{exp}}=(\rho_{\text{oct}} \cdot m_1)/(m_2-m_3+m_4)$, where ρ_{oct} is the octane density, m_1 is the mass of the dry sample, m_2 is the mass of the octane-saturated sample, m_3 is the mass of the saturated sample weighed in octane with a suspension, and m_4 is the mass of the suspension for the sample. The relative density (ρ_{rel}) was calculated using the formula $(\rho_{\text{exp}}/\rho_{\text{x-ray}}) \cdot 100\%$.

The microstructure examination was carried out in reflected light using the Neophot 21 and Leica DMI 5000 M optical microscopes. The samples were preliminarily ground using fine-grained abrasive paper. Then, a finer grinding was performed by the abrasive having the particle size $D \leq 5\text{ }\mu\text{m}$ in the presence of aqueous medium. Further polishing was also conducted in the aqueous medium with the Cr_2O_3 powder having the particle size of $(0.1\text{--}0.2)\text{ }\mu\text{m}$. At the two latter steps the quality of processing was controlled with the help of the microscope (light field and polarized light regimes). The visualization of intercrystalline boundaries of the ferroelectric (FE) ceramics was performed by the chemical etching method using the acidic etchant (5% aqueous solution of the concentrated nitric acid with addition of 15 drops of the concentrated hydrofluoric acid per 200 ml of the etchant), which, depending on the reaction activity of individual materials, could be diluted with water. The etching duration as well as the etchant concentrations were chosen depending on character of the obtained results. The average size of crystallites, \bar{D} , was determined by the chord method.

3. Experimental results and discussion

Fig. 1 presents the dependencies of the theoretical (ρ_{theor}), x-ray ($\rho_{\text{x-ray}}$), experimental (ρ_{exp}) and the relative (ρ_{rel}) densities of the PZT system solid solution samples on concentration of the components.

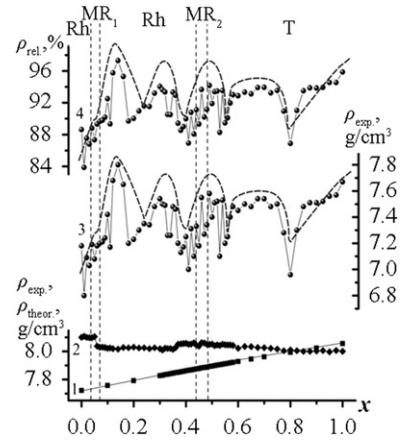
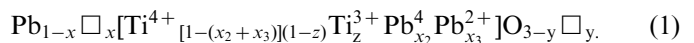


Fig. 1. Concentration dependences of the theoretical (ρ_{theor}) (1), x-ray ($\rho_{\text{x-ray}}$) (2), experimental (ρ_{exp}) (3) and relative (ρ_{rel}) (4) densities of the PZT system solid solution samples.

As can be seen from Fig. 1, the experimental densities have a tendency to increase, like the theoretical ones, but this increase is not monotonous: there are three distinct and one diffuse maxima (see the envelope curve in Fig. 1). The causes of such behavior will be discussed below. The prepared solid solutions possess slightly lowered ρ_{exp} values ($\rho_{\text{exp.aver.}} \approx (0.88 \div 0.94)\rho_{\text{x-ray}}$) compared to those of materials prepared by the traditional ceramic technology ($\rho_{\text{exp}} \approx 0.95\rho_{\text{x-ray}}$). This is especially typical for the solid solutions from the PbZrO_3 -rich region ($\rho_{\text{exp.aver.}} = 0.85 \div 0.92\rho_{\text{x-ray}}$). Here, the “losses” in ρ_{exp} are as high as $\sim 10\%$. This effect manifests itself to a lesser degree in the PbTiO_3 -rich solid solutions having the values of $\rho_{\text{exp.aver.}} \sim 0.92 \div 0.94\rho_{\text{x-ray}}$. In this case, the “shortage” of ρ_{exp} is 1–3%. This observation may be explained with the following considerations taken into account. According to Ref. [1], the vacancy-diffusion processes dominate in the mass transfer mechanism of oxide materials, to which our objects belong. Let us consider the two end members of the system – PbTiO_3 and PbZrO_3 – from these positions.

It follows from Ref. [2] that the real PbTiO_3 crystal resembles in its structure the intrinsic solid solution, or the autoisomorphic substance [3], a composition of which may be qualitatively described by the formula:



here, $x=x_1+x_2+x_3$ is the deviation from the PbO stoichiometry, x_1 is the PbO loss resulting from the lead volatility at the temperatures of solid-phase synthesis and sintering, x_2 is the fraction of Pb^{4+} incorporated into the B-sublattice as a result of Pb^{2+} oxidation, x_3 is the fraction of Pb^{2+} incorporated into the B-sublattice, z is the amount of Ti^{3+} being always present in the composition because of its variable valence, y is the originating deficiency in oxygen, and denotes vacancies. This formula does not reflect all the peculiarities of PbTiO_3 structure but it shows a considerable difference between the real cationic composition of polycrystals and the ideal $\text{Pb}^{2+}\text{Ti}^{4+}\text{O}_3^2-$

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