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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Low-Temperature Synthesis of Phases of the System $PbTiO_3$–$PbZrO_3$ and Electrical Properties of Materials Based on These Phases

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Abstract—New low-temperature methods for synthesis of phases of the system $PbTiO_3$–$PbZrO_3$ were developed and the effect of a method employed to synthesize these phases on electrical properties of ceramic materials on their base was studied.

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At present, the method of solid-phase reactions (MSPR) remains the main method for synthesis of phases of the oxygen-octahedral type. To difficultly eliminated disadvantages of this technique belong: (a) evaporation of *p*-element oxides (PbO, Bi_2O_3, Sb_2O_5) from the stock in the course of high-temperature synthesis; (b) changes in the composition of *d*-element oxides (Fe_2O_3, Cr_2O_3, MnO_2, CoO, V_2O_5) contained in the stock via their full or partial decomposition at the synthesis temperature of the target phase; and (c) low rate of solid-phase reactions, multistage nature of the processes involved, and polydispersity of the powdered reaction products. Therefore, a ceramic synthesized from a stock of this kind has a nonuniform macrostructure (grain size and shape, and size, shape, and concentration of pores) and varied composition of the grain surface and bulk. As a consequence, samples of even the same batch show a wide scatter of their electrical parameters, density, and mechanical characteristics. These disadvantages stimulate development of alternative, low-temperature methods for synthesis of these phases and new technologies for fabrication of ceramic articles with a desired set of properties.

A possible way to solve this problem is to use as precursors ole forms of *p*-and *d*-element hydroxides, which are amphoteric and can, under certain conditions, interact with acids, alkalis, salts, and oxides of various elements [1–3]. This method, gel technology, have been successfully used to synthesize titanates, zirconates, stannates, and manganates(IV) of s- and p-elements [3–5].

The aim of this study was to develop ϕ low-temperature mode of synthesis of phases in the $PbTiO_3$–$PbZrO_3$ (PTZ) system and to examine the effect of a method used to synthesize these phases on the electrical properties of a ceramic prepared from these phases.

EXPERIMENTAL

Powders of composition $PbTi_xZr_{1-x}O_3$ ($0 \le x \le 1$) with a step of 0.02–0.1 were prepared (depending on the region of the system under study) by three different methods: (1) by MSPR with PbO (analytically pure), TiO_2 (special purity), and ZrO_2 (analytically pure) as starting substances; mixtures calcined in the following mode: at 550°C for 1 h, 650°C for 2 h, 800°C for 2 h, and 900°C for 1 h, with reburdening after each isothermal stage of synthesis and XPA control over the completeness of the process; (2) by reacting α-$Ti_xZr_{1-x}O_2 \cdot zH_2O$ with 1.5 M solutions of $Pb(NO_3)_2$ and $Pb(CH_3COO)_2$ at T = 20–25°C [4]; and (3) by reacting α-$Ti_xZr_{1-x}O_2 \cdot zH_2O$ with PbO at T = 20–25°C [5].

The reaction products formed in the low-temperature synthesis are X-ray amorphous. To obtain

crystalline phases, these products were calcined at 300–800°C for 1–3 h.

The phases $TiO_2 \cdot zH_2O$, $ZrO_2 \cdot zH_2O$, and $Ti_xZr_{1-x}O_2 \cdot zH_2O$ were precipitated from Ti(IV) and Zr(IV) nitrate solutions with a 10% NH_4OH solution at T = 0–10°C and pH 8. The starting solutions were, in turn, produced by dissolution of α-forms of titanium(IV) and zirconium(IV) hydroxides precipitated from 2 M solutions of $H_2[TiCl_6]$ in 30% nitric acid [6].

The precipitates obtained were separated from the mother liquor by filtration or centrifugation at temperature below 10°C to diminish the oxolation rate and then were reacted with solutions of Pb^{2+} salts or PbO. The sorption properties of α-forms of the hydroxides were studied at T = 5–7°C by measuring the residual concentration of Pb^{2+} ions in the sorbate and by determining the chemical composition of a sorbent at definide intervals of time.

An X-ray phase analysis of the powders and of the surface of the ceramic was performed on a DRON-2.0 diffractometer (CuK_α radiation, Ni-β-filter). The relative sizes of crystallites and microheterogeneities were estimated by half-widths of the diffraction peaks B200 and B002 [7].

DTA and TG studies of amorphous samples were performed with MOM (Hungary) and Perkin–Elmer Diamond TG/DTA derivatographs; nano- and microscopic objects were visualized with a Solver Pro-M (NT–MDT, Moscow) scanning probe microscope.

To fabricate ceramics, powders of the synthesized phases were compacted into disks 12 mm in diameter (compaction pressure 70 MPa) and sintered at 1100–1250°C for 1–2.5 h [optimal sintering modes for a stock of certain kind was chosen using the sample density as a criterion (>90%)]. Samples 1 mm high and 10 mm in diameter (with fired-in Ag electrodes) were polarized in a silicone oil at 80–120°C in fields of 30–80 kV cm^{-1}. Their electrical properties were determined 7 days after the polarization in conformity with GOST (State Standard) 1230–80 (d_{31} by dynamic, and d_{33} by quasistatic methods; dielectric parameters and capacitance, with an R-581 bridge at a frequency of 1 kHz).

According to the results of tunneling microscopy, the phases $TiO_2 \cdot zH_2O$, $ZrO_2 \cdot zH_2O$, and $Ti_xZr_{1-x}O_2 \cdot zH_2O$, precipitated from Ti(IV) and Zr(IV) nitrate solutions, are composed of ellipsoidal grains, whose principal axis does not exceed 2 μm (Fig. 1), and

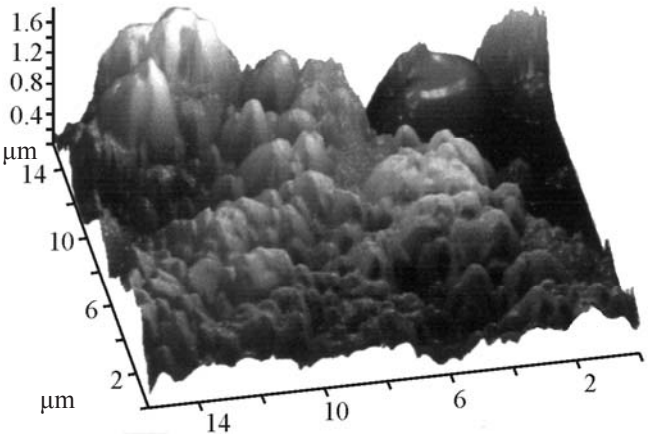

Fig. 1. Micrograph of a $Ti_{0.5}Zr_{0.5}O_2 \cdot zH_2O$ phase freshly precipitated from nitrate solutions of Ti(IV) and Zr(IV) with a 10% NH_4OH solution at T = 7–10°C.

contain, according to TG data, 65–80 wt % H_2O (Fig. 2) and up to 5 mol % NH_4^+ and NO_3^- [8].

The curves of sorption of Pb^{2+} ions by these phases from nitrate and acetate solutions are shown in Fig. 3. Curves *1* and *2* in this figure are in qualitative agreement with the data of [1]; however, the interpretation of the rise in the sorption capacity on passing from nitrate to acetate solutions in [1] seems to be insufficiently correct. As shown previously [9], sorption on α-forms of *p*- and *d*-element hydroxides occurs by two principal mechanisms: (a) joint sorption of the cation and anion and (b) substitution of H^+ ions in hydroxy functional groups OH^- by M^{n+}. In the latter case, the pH value of the sorbate deceases in the course of sorption, which suppresses the exchange of H^+ and M^{n+} ions, and an equilibrium determined not only by the concentration $c(M^{n+})$, but also by $c(H_3O^+)$ is attained in the systems. Consequently, for the sorption capacity of the sorbents to be raised, it is necessary to make higher the pH of the sorbate in the course of sorption, which can be done by introducing a buffer solution into the system (Fig. 3, curve *3*).

Another method consists in neutralization of H_3O^+ ions in the system by introduction of lead(II) oxide instead of a lead(II) salt. As already noted, the gel-like phase contains NH_4^+, whose hydrolysis yields H_3O^+ ions. Therefore, in grinding of a gel with PbO, the latter phase gradually dissolves, which starts the process of sorption of lead(II) ions by titanium(IV) and zirconium(IV) hydroxides. In turn, the sorption of Pb^{2+} ions favors removal from the sorbent of H_3O^+ ions, which are neutralized via reaction with PbO. The process repeats to the point of complete dissolution of

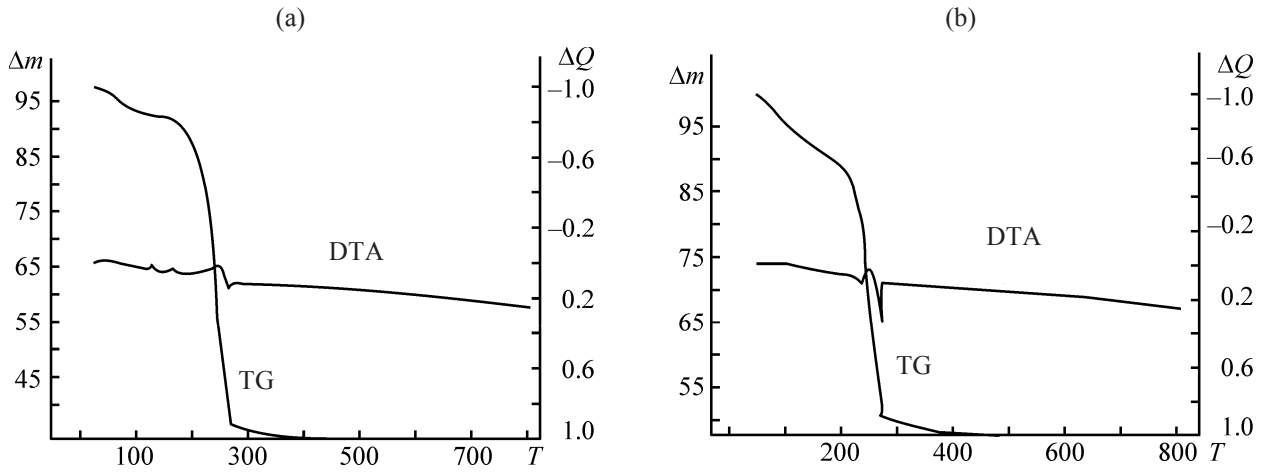

Fig. 2. DTA and TG curves of the phases (a) $TiO_2 \cdot zH_2O$ and (b) $Ti_{0.5}Zr_{0.5}O_2 \cdot zH_2O$. ($\Delta m$) Loss of mass, ($\Delta Q$) heat effect, and ($T$) temperature; the same for Fig. 4.

PbO and transfer of Pb^{2+} ions to the sorbent. As a result, stratification is observed in the systems and a solid semitransparent colorless amorphous phase is formed, which resembles in its outward appearance the magnesia cement. The amorphous phases synthesized by the sorption method and by the reaction with PbO decompose in the temperature range 50–550°C (Fig. 4).

According to XPA data, cubic phases with a perovskite structure start to be formed in these systems at 280–300°C, which is favored by the exothermal decomposition at 280°C of NH_4NO_3, which crystallizes in the systems upon removal of H_2O from samples (T = 50–200°C), and by the energy released in crystallization of the amorphous phase. The size of the coherent scattering region (CSR) of particles appearing in the first stage is 10–25 nm. As temperature is raised, the primary crystals increase in size at the expense of the amorphous phase surrounding these crystals. The final size of powder particles can be varied within the range 50–800 nm by changing the rate at which the temperature of samples is raised and the time of their isothermal treatment.

As the CSR increases in size (to 50–80 nm), cubic phases are transformed into tetragonal phases, irrespective of the values of x in solid solutions of composition $PbTi_xZr_{1-x}O_3$. Further increase in the annealing temperature results in that the c/a ratio of the tetragonal phases increases for samples with $0.5 \le x \le 1$, and the tetragonal phases are converted into rhombohedral phases at compositions with $0 \le x \le 0.35$.

The $PbTi_xZr_{1-x}O_3$ phases from the central part of the system ($0.36 \le x \le 0.48$), synthesized at 500–650°C, belong to the morphotropic region (MR) whose width gradually decreases as temperature is raised and the

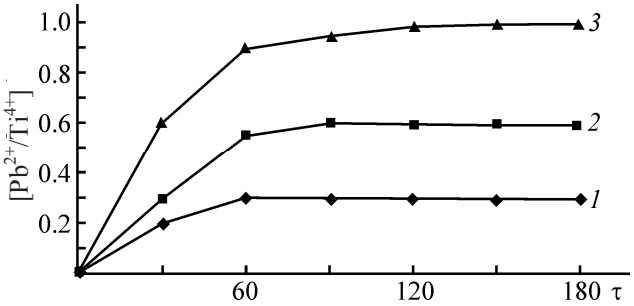

Fig. 3. Curves of Pb^{2+} sorption by the $Ti_{0.5}Zr_{0.5}O_2 \cdot zH_2O$ gel. ($[Pb^{2+}/Ti4+]$) Sorbate/sorbent ratio and (τ) time. Composition of a 1.5 M solution: (*1*) $Pb(NO_3)_2$, (*2*) $Pb(CH_3COO)_2$, and (*3*) $Pb(NO_3)_2$ in the presence of NH_4OH–NH_4NO_3.

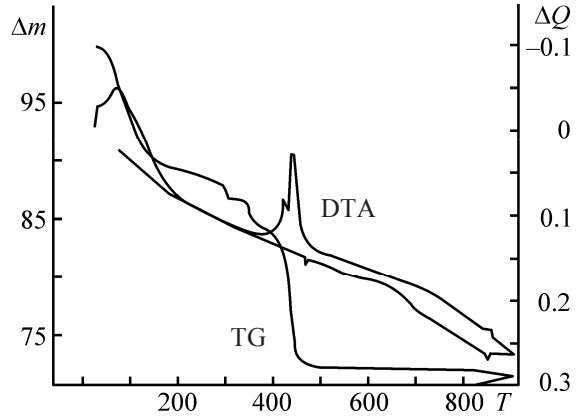

Fig. 4. DTA and TG curves of the amorphous phases synthesized by the sorption method.

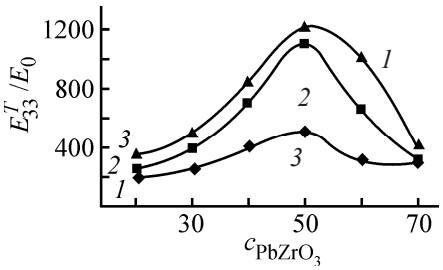

Fig. 5. Dependence of E_{33}^T/E_0 of PTZ ceramics on composition. [c($PbZrO_3$)] Concentration. Ceramic produced from a stock synthesized by (*1*) a solid-phase reaction, (*2*) sorption, and (*3*) reaction of $Ti_xZr_{1-x}O_2 \cdot zH_2O$ with PbO.

calcination time is made longer. However, even upon sintering of the samples (T = 1100–1150°C), the width of the MR in the system for phases produced by the gel technique is about 4 mol %, which substantially exceeds that in the system whose phases are synthesized by MSPR.

The ceramic was fabricated using a stock synthesized by methods 2 and 3 (preliminary thermal treatment at T = 650°C for 1 h). Data on the electrical parameters of the samples obtained are presented in Fig. 5. The microstructure of their surface demonstrated that, with the low-temperature stock, the average grain diameter of finished articles is 200 to 400 nm (method 3) and 350 to 700 nm (method 2), whereas the average grain size of a ceramic fabricated from the stock synthesized by MSPR is about 5000 nm, with a scatter of 900 to 15500 nm in the observation region.

The increase in the electrical parameters of the ceramic fabricated from the stock synthesized by methods 2 and 3 (type 1), compared with the ceramic produced by the conventional technology (type 2), is due to a number of factors: (a) the density of the type-1 ceramic is 94% and more relative to the theoretically possible value, whereas the density of the type-2 ceramic is 5–9% lower, which predetermines the lower elastic compliance of type-1 samples and their higher dielectric constant; (b) the grain size of the type-1 ceramic is comparable with the size of domains, and, therefore, it can be suggested that part of grains in this ceramic are single-domain (which is a factor raising the polarization efficiency); and (c) the type-1 ceramic is more stable against breakdown and cracking in polarization, which enables, in some cases, polarization of samples in fields of up to 80 kV cm^{-1} at 120–150°C.

Analysis of dielectric hysteresis loops shows that the type-1 ceramic surpasses the type-2 ceramic in the value of the coercive electric field by 50–70%, which is presumably due to an increase in the total area of intergrain boundaries. Therefore, the electrical parameters of the type-1 ceramic are more thermally stable, compared with the type-2 ceramic.

CONCLUSIONS

(1) It was demonstrated that low-temperature synthesis of any phase of the PTZ system can be performed by reacting $Ti_xZr_{1-x}O_2 \cdot zH_2O$ with a $Pb(NO_3)_2$ solution (in the presence of an ammonium nitrate buffer solution) or with lead(II) oxide in joint grinding.

(2) Cubic, tetragonal, and rhombohedral phases of the $PbTiO_3$–$PbZrO_3$ system with particle sizes in the range from 10 to 800 nm were obtained by varying the temperature and rate of decomposition of the primary amorphous product.

(3) The method of low-temperature synthesis was used to fabricate samples with electrical parameters surpassing those of a ceramic of the same composition, prepared by the conventional technology: by 40–50% for $\varepsilon_{33}^T/\varepsilon_0$, 25–35% for d_{33}, and 25–38% for d_{31}.

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