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Microwave Plasmochemical Synthesis of Nanopowders in the System Pb–Zr–Ti–O

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Abstract–Conditions for building up the composition and structure of mixed Pb, Zr, and Ti oxides in a microwave plasma-chemical process were studied. As starting substances $Pb(C_2H_5)_4$, $Ti(C_4H_9O)_4$, and a 80% $Zr(C_4H_9O)_4$ solution in 2-propanol were used. To avoid stratification of the components the initial temperature of the flow should not exceed 1000ºC. Under these conditions the crystallization of a complex structure requires a combination of a plasma-chemical synthesis with subsequent thermal treatment of the resulting powders. After the thermal treatment an average particle size of lead zirconate-titanate nanopowder was 120 nm.

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Lead zirconate–titanate with unique ferroelectric properties was chosen as a subject to be studied in this work. Recently a demand emerged for the preparation of this material in the form of nanodispersed powders, what makes it possible, in particular, to lower the temperature of its transformation to a ferrielectric phase [1] and to improve its caking [2]. Traditional methods of producing lead zirconate–titanate applied up till now [3–5] involve a multistage preparation of monophase powders and their annealing at a considrably high temperature that results in a partial caking of powders with the formation of conglomerates. To overcome the specified difficulties, we applied in this work the plasma-chemical method of the lead zirconate–titanate preparation, which makes it possible to control flexibly characteristics of resulting nanopowders (dispersity, chemical and phase composition, etc.). As a rule, traditional subjects for plasma_chemical synthesis are simple compounds (oxides, nitrides, and carbides) of high melting points and relatively simple crystal structures. The preparation of a complicated polyelemental material with a required chemical composition of a target phase crystallized in the necessary structural form under conditions of a high-rate non-isothermal plasma flow and short times of heat and mass exchange run into real problems connected with a possibility of formation of several phases in a complicated system. The main task of this work was the study of opportunities and conditions of the formation of the composition and structure of lead zirconate–titanate in a microwave plasma: chemical process.

Thermodynamic calculations of the equilibrium composition of the chemical systems under study at various temperatures were fulfilled by the method developed by B.G. Trusov at Bauman Moscow State Engineering University and based on the minimization of Gibbs energy of the system. In view of the absence of thermodynamic parameters for lead zirconate–titanate in the database of the program in use, a possibility of its formation in the system was judged by the simultaneous presence of equilibrious individual oxides.

In the first stage we have calculated the system $2Pb(C_2H_5)_4 + TiCl_4 + ZrCl_4 + 170O_2$ where the corresponding highest titanium and zirconium chlorides that proved to be efficient in plasma–chemical processes of oxides preparation and highly volatile tetraethyl lead were taken as the starting reagents. When selecting the desired starting reagents we took into account their accessibility, a possibility of

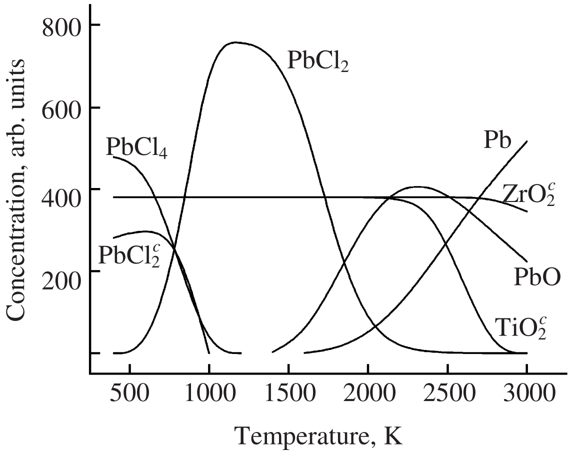

Fig. 1. Temperature dependences of equilibrium concentrations of metal-containing gaseous and condensed (*c*) components in the system $2\ Pb(C_2H_5)_4 + TiCl_4 + ZrCl_4 + 170\ O_2$.

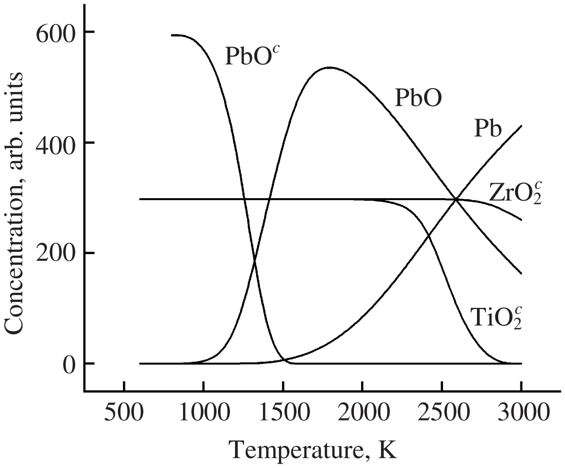

Fig. 2. Temperature dependences of equilibrium concentrations of metal-containing gaseous and condensed (*c*) components in the system $2\ Pb(C_2H_5)_4 + Ti(C_4H_9O)_4 + Zr(C_4H9O)_4 + 240O_2$.

gasification at sufficiently low temperatures, and a possibility of precision simultaneous dosed injection of the three components in a necessary proportion into a reactor. The amount of oxygen in calculations exceeded a stoichiometrically necessary quantity approximately by a factor of six and corresponded to a real consumption of plasma_forming air in a microwave process.

The calculations have shown (Fig. 1) that condensed titanium and zirconium oxides are present in the system within the entire temperature interval characteristic for plasma_chemical synthesis, whereas lead oxide is observed only in the gaseous state and only at temperatures above 1600 K. On decreasing temperature the total lead in the system is bound into chloride. The absence of a temperature range of simultaneous existence of three oxides in the condensed state practically excludes a possibility of the formation of a ternary oxide in a high-temperature process.

Hence in the second stage we calculated the system $2\ Pb(C_2H_5)_4 + Ti(C_4H_9O)_4 + Zr(C_4H_9O)_4 + 240\ O_2$ free of chlorine where tetraethyl lead, titanium tetrabutoxide, and zirconium tetrabutoxide were chosen as starting substances. It is seen from Fig. 2 that in this system oxides of three elements are present in equilibrium within the whole temperature range under consideration. It allows us to affirm that lead titanate–zirconate can be formed in the system under consideration, therefore we used the above-mentioned starting substances in the experimental study. The favorable thermodynamics is not a unique necessary condition for the formation of the ternary oxide in a plasma–chemical reactor. It is important to select such conditions for the process that provide a complete simultaneous condensation of three oxides, strongly differing in boiling points, from a high-temperature flow.

We designed a segmented plasma_chemical reactor with a compulsory tempering of reaction products, and also special devices for injecting reagents into a reactor both in the form of a vapor–gas mixture and in the form of liquid droplet aerosol. The scheme of the experiment is shown in Fig. 3. To dose zirconium acetylacetonate, we used a powder loader (*7*). For other starting substances fluid-flow loaders (*8*) were used, and these substances were supplied in a reaction zone either in a vapor form (as in the case of tetraethyl lead and titanium tetrabutoxide) using evaporators (*9*) and gas-carrier (*15*) or in the droplet aerosol form in the case of individual organic liquids and their mixtures. In the latter case a specially constructed injector was used for aerosol prepartion. The place of injecting reagents (*3*) longwise a reactor (*4*) could be varied according to experimental tasks. As a plasma-forming gas, and in this case also a reacting gas, we used air or oxygen that was heated in a plasma generator to 2500°C. A powder-gas flow was cooled longwise a reactor mainly due to thermoexchange with relatively cold walls of a quartz tube inserted inside a reactor, and in the case of short lengths of a reactor, due to additional injection of air (*16*) at a flow rate of 1.5 m^3 h^{-1}. Further cooling to a temperature of no more than 150°C took place in a fissured water-cooled cooler (*5*).

The use of a segmented plasma–chemical reactor allowed us variation of the place of injecting reagents longwise a reactor and thereby to inject them into zones with various temperatures of a plasma flow. The temperatures longwise the reactor with a useful power of 4 kW is given below.

Length from the reactor heading, mm	0	100	200	360	580
Flow temperature, °C	2400	1500	1100	980	810

Powder samples to be studied were selected separately from various sections of the installation.

According to the X-ray analysis, a powder obtained in the system Pb–Ti–O and collected from reactor walls (Fig. 4, *1*) is $PbTiO_3$ with a perovskite structure and a small admixture of a non-identified phase (lines at 2θ: 28.95, 36.4, and 49.2). This admixture was completely removed by treating the powder by a 5% acetic acid solution (Fig. 4, *2*). In a powder collected from the filter (Fig. 4, *3*), aside from crystalline $PbTiO_3$, a significant amount of a phase with a low crystallization degree was found, that obviously originated from a low temperature in the reactor and an insufficient time of particles residence in a flow. Such powder can be converted to a crystalline state by annealing at 700°C for 2 h (Fig. 4, *4*), however in this case its specific surface area decreases from 12 up to 6.6 m^2 g^{-1}.

Average particle size of the powder taken from the filter was 62 nm. The shape of powder particles is close to spherical (Fig. 5, photo *1*). Rodlike crystals are observed on the surface of some particles (Fig. 5, photo *2*), which obviously correspond to lead oxide, as after treating a powder with acetic acid they disappear simultaneously with disappearence of the PbO lines from the diffractogram.

Zirconium tetragonal oxide is mainly found in the diffractogram of the powder obtained in the Pb–Zr–O system and taken from the filter (Fig. 6, *1*), whereas no perovskite lead was observed. This fact is attributable to a much higher refractoriness of zirconium oxide resulting in its primary condensation in the form of an individual phase that then has no time to react with lead oxide within a short residence time of particles in the reactor. The annealing of such powder in a furnace at 850°C within 2 h results in the formation of lead zirconate (Fig. 6, *2*). The average particle size determined by measuring a specific surface area increases twice up to 120 nm upon the thermal treatment.

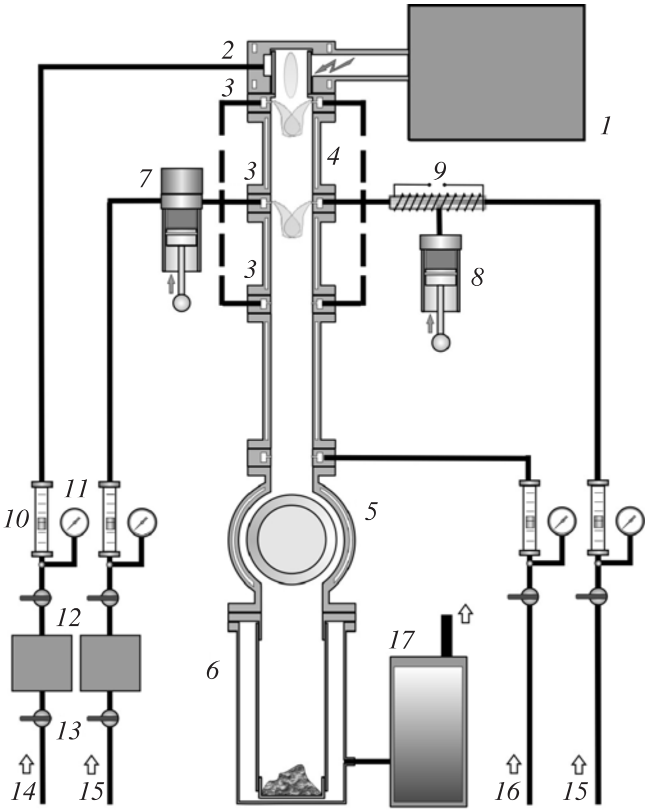

Fig. 3. Scheme of the plasma–chemical installation: (*1*) microwave generator; (*2*) plasmatron; (*3*) devices for injecting reagents; (*4*) reactor; (*5*) heat exchanger; (*6*) filter-collection of a powder; (*7*) dosing unit for powder; (*8*) dosing unit for liquids; (*9*) evaporator; (*10*) rotameters; (*11*) manometers; (*12*) gas purification system; (*13*) valves; (*14*) plasma-forming gas entry; (*15*) gas-carrier entry; (*16*) tempering gas entry; (*17*) scrubber.

No perovskite phase was formed immediately in the plasma-chemical process when powders in the system Pb–Ti–Zr–O were obtained, which was also the case with lead zirconate (Fig. 7, *1*). After a thermal treatment of the powder gathered from the filter in air at 850°C for 2 h the average size of its particles increased up to 120 nm. Therewith changes in its diffractogram (Fig. 7, *2*) are observed, which can be attributed to the appearance of an insufficiently crystallized perovskite phase with a poor resolution of

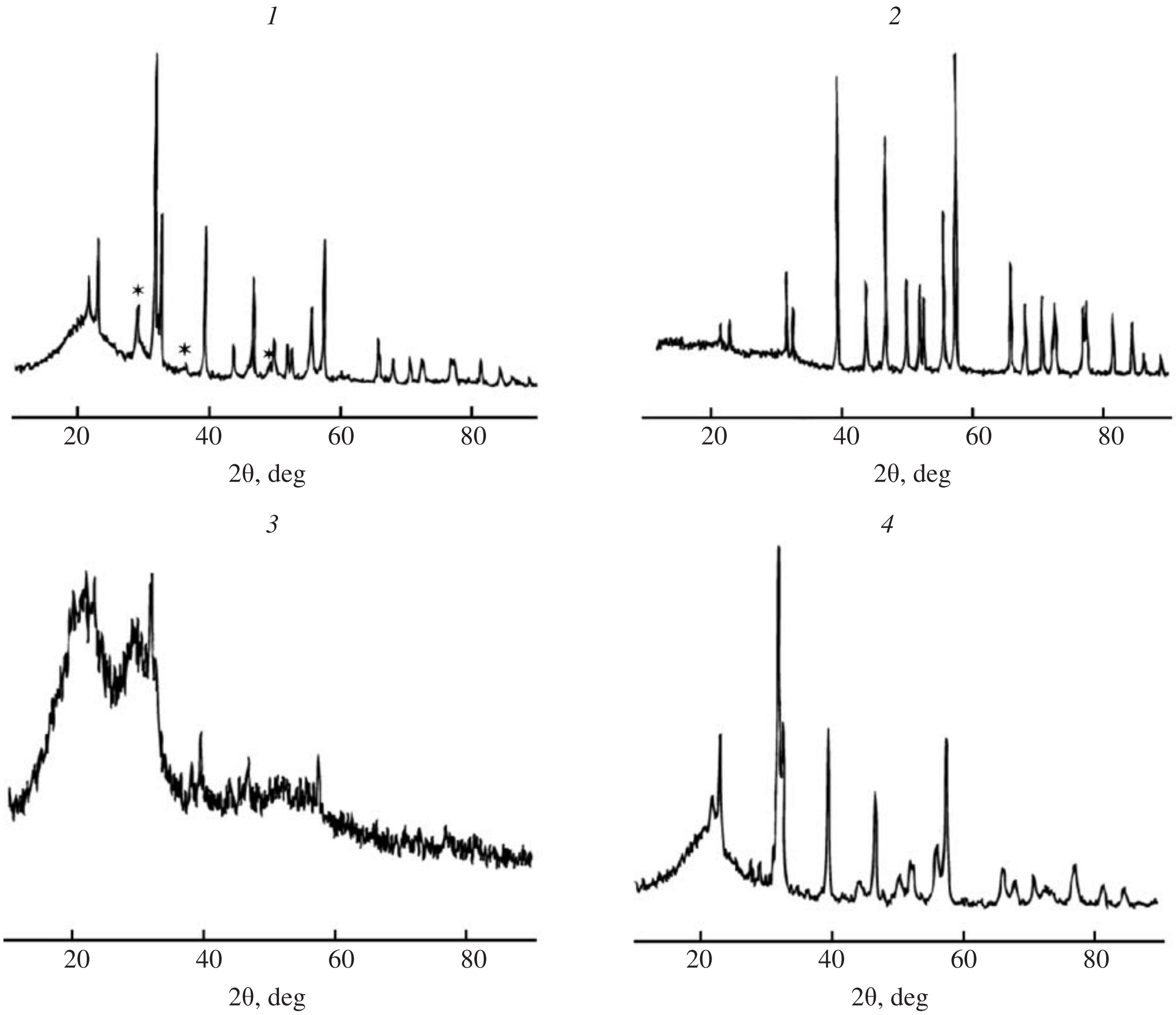

Fig. 4. Diffractograms of Pb–Ti–O powders. Reflexes of the admixed phase are marked off by asterisks.

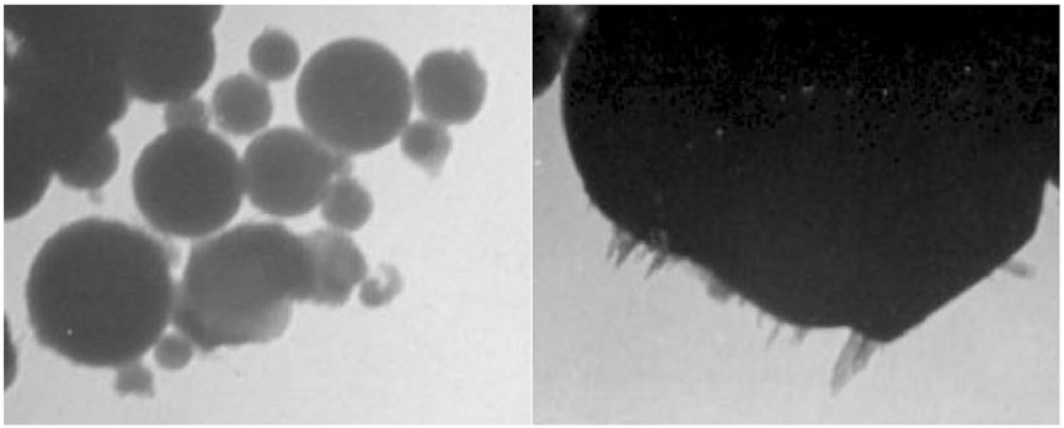

Fig. 5. Microphotographs of $PbTiO_3$ powder particles (64.5 nm in 1 cm).

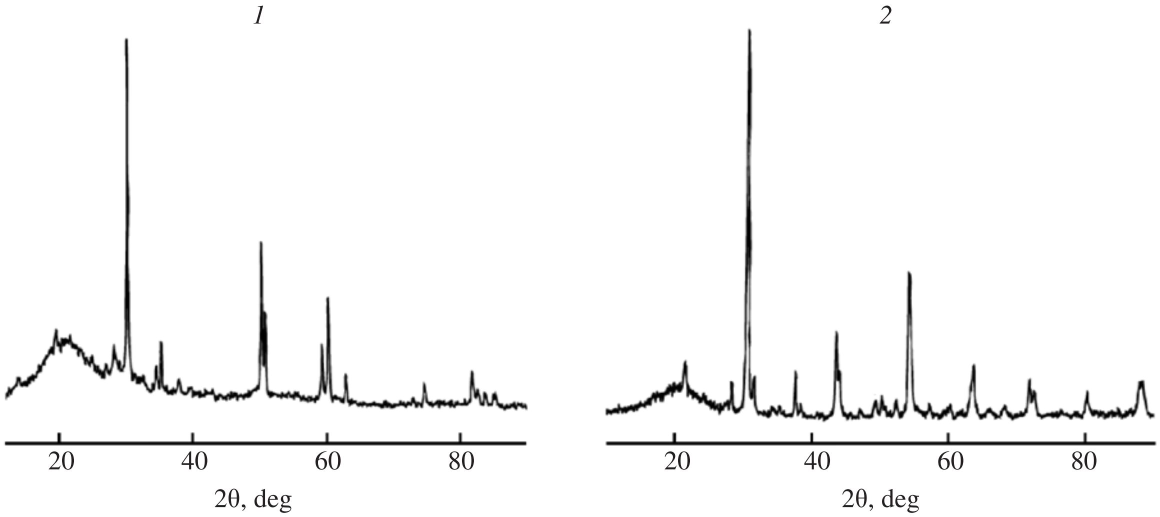

Fig. 6. Diffractograms of Pb–Zr–O powders.

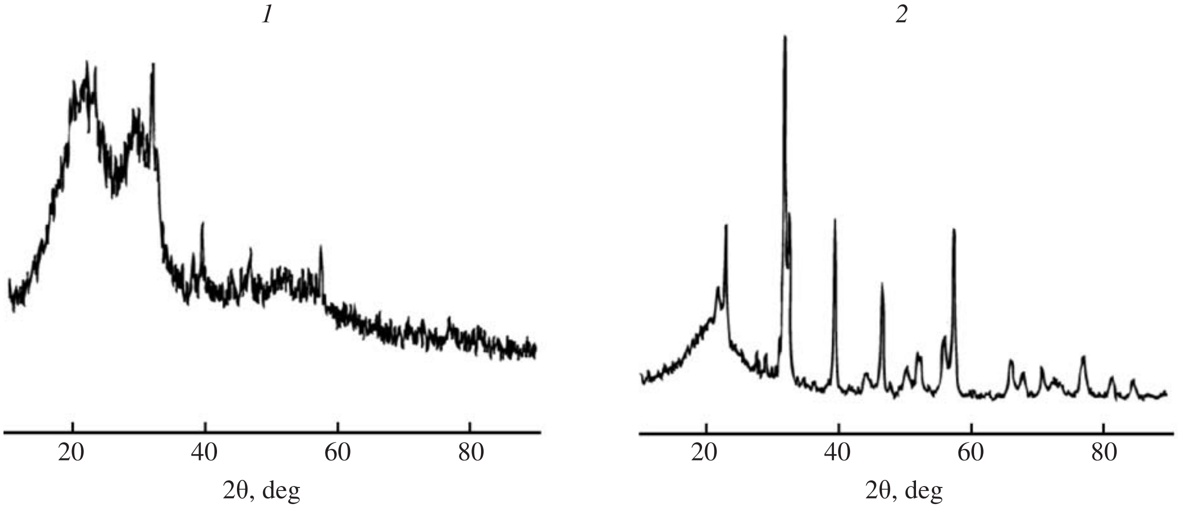

Fig. 7. Diffractograms of Pb–Ti–Zr–O powders.

closely located reflexes of the synthesized lead zirconate-titanate powder.

To determine probable conditions for the formation of the ternary oxide, in the first stage of the work we have studied the synthesis of individual lead, titanium, and zirconium oxides in the plasma-chemical reactor.

EXPERIMENTAL

The X-ray analysis was carried out using an ADP2-01 X-ray diffractometer (“Burevestnik” scientific production association, Russia) equipped with a program for automation of the processes of obtaining, handling, and analysis of X-ray data developed for DRON or analogous X-ray diffractometers. Operating conditions: an X-ray tube with a BSV-27 copper anode, U 34 kV, I 14 mA, working slits on a primary beam in the input collimator: vertical 0.1 mm, horizontal 4 mm; slits in front of the detection block in the output collimator: horizontal 1 mm, vertical 0.1 mm. To determine phase compositions, diffractograms were recorded in steps (0.05º) with an exposure of 3 s in the interval of 2θ angles 20–90º. The scale range of an intensimeter (I) was 2000 imp/s.

We used an EM-100 BR transmission supermicrocope (“Elektronmash,”,Ukraine) for electron microscopy.

The specific surface area was determined with an AUTOSORB-1 adsorber (Quantachrome, USA). The procedure of the determination of a specific surface area and porosity is based on measuring the amount of gaseous nitrogen adsorbed on or desorbed from a surface and pores of solid substances at specified equilibrium pressures. The analysis was carried out by a volumetric method. The instrument was calibrated using a set of standard samples (Quantachrome, USA) with a known specific surface area: TiO_2 with the specific surface area of 13.6 m^2 g^{-1} and Al_2O_3 with the specific surface areas of 109 and 237 m^2 g^{-1}.

Lead oxide is the most low-melting oxide in the system, therefore conditions in a reactor necessary for its condensation in many respects define the formation of the ternary oxide. We used air (at a flow rate of 2.5–4 m^3 h^{-1}) as a plasma-forming gas in the experiments. Starting tetraethyl lead was delivered to a reactor (at a flow rate of 3–5 g min^{-1}) in the form of a vapor–gas carrier (nitrogen) mixture (at a flow rate of 0.3 m^3 h^{-1}). The formation of solid nanoparticles of lead oxide in a flow occurred at a temperature of the reaction zone less than 1000°C that corresponded to the thermodynamic calculations. Incomplete condensation of PbO vapor and, at the same time, a precipitation of a sintered oxide on reactor walls were observed in a reactor section operating at a higer temperature. The resulting powders presented monophase PbO with an average particle size from 60 up to 100 nm depending on the process mode parameters.

Titanium oxide. To obtain titanium oxide, starting titanium tetrabutoxide was delivered to a reactor (at a flow rate of 4 g min^{-1}) in the form of a vapor in a mixture with a gas-carrier (nitrogen). The initial mixture was delivered to a reaction zone with a temperature of 950°C, i.e. to the zone where, according to the results of the previous experiments, the complete PbO condensation is possible while obtaining mixed oxides. In these conditions titanium tetrabutoxide was completely converted to the oxide. The obtained powder consisted of particles with an average size of 85 nm and represented a mixture of anatase and rutile in the ratio 3:2.

Zirconium oxide. In the first stage we tested zirconium acetylacetonate $Zr(C_5H_7O_2)_4$ as a zirconium-containing raw material that was introduced into a reactor as a powder at a flow rate of 2–5 g min^{-1}. As a gas-carrier we used oxygen at a flow rate of 0.3 m^3 h^{-1}. The flow rate of plasma-forming air was 2.5 m^3 h^{-1}. When introduced in the initial high-temperature reactor zone acetylacetonate is oxidized completely in all modes of operation. When introduced in the zone with temperature 950°C the yield of oxide close to 100% was observed only at the flow rate of no more than 3 g min^{-1}. Taking into account the difficulties in the acetylacetonate solid-phase oxidation, we used as a raw material in further experiments a 80% solution of zirconium tetrabutoxide in 2-propanol, a commercial reagent. The solution in the form of an aerosol was delivered into the reactor by an injector. The resulting powder consisted of particles with an average size of 50–70 nm and presented a mixture of tetragonal and monoclinic modifications in the ratio 4:1.

Synthesis of powders in the system Pb–Ti–O. In the synthesis of powders in the system Pb–Ti–O we used a mutual solution of tetraethyl lead and tetrabutyl titanium with the ratio of the components corresponding to the composition of $PbTiO_3$. The solution was delivered into a reactor (at a flow rate of 3 g min^{-1}) in the form of an aerosol. To spray the solution, air at a flow rate of 0.2 m^3 h^{-1} was used. The flow rate of plasma-forming gas (air) was 2.5 m^3 h^{-1}. The reactor consisted of two sections of 200 mm in length each; walls of the lower section were lined with quartz.

Synthesis of powders in the system Pb–Zr–O. As a feed stock we used a mixture of tetraethyl lead and 80% solution of zirconium tetrabutoxide in 2-propanol. The ratio of metals in the initial mixture corresponded to the composition $PbZrO_3$. The other parameters of plasma-chemical process were the same as in the synthesis of $PbTiO_3$.

Synthesis of powders in the system Pb–Ti–Zr–O. The reaction mixture for powders preparation in this system included tetraethyl lead, titanium tetrabutoxide, and 80% solution of zirconium tetrabutoxide in 2-propanol in the ratio necessary for obtaining the target compound $PbTi_{0.5}Zr_{0.5}O_3$. The flow rate of the mixture was 3 g/min. The mixture was delivered into a reactor through an injector with air spraying. Air flow rate for the plasma formation was 2.5 m^3 h^{-1}.

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