Synthesis of lead zirconate: influence of zirconium oxide crystal modification

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Specific features of lead zirconate synthesis from zirconium oxide of various crystal modifications (monoclinic, tetragonal, and cubic) have been studied. The monoclinic zirconium oxide has been shown to exhibit thehighest reactivity and its use results in decreased temperatures of lead zirconate synthesis and the ceramic sample sintering. A physical mechanism is proposed to explain the dependence of the lead zirconate synthesis temperature on the zirconium oxide crystal lattice type.

Изучены особенности процесса получения цирконата свинца из оксида циркония различной кристаллической модификации (моноклинной, тетрагональной и кубической). Показано, что моноклинная модификация оксида циркония является наиболее реакционно способной: ее использование ведет к понижению температуры синтеза цирконата свинца и температуры спекания керамических образцов. Предложен физический механизм, определяющий зависимость температуры синтеза цирконата свинца от типа кристаллической решетки оксида циркония.

The process of solid-phase synthesis of lead titanate-zirconate (PZT) is studied well enough, and at the obtaining of this material under laboratory conditions there arise no unexpected problems. However, mass production of ceramic articles is often accompanied with certain difficulties connected with the use of different kinds of zirconium oxide raw material. Therefore, investigations aimed at elucidation of the factors, which manifest themselves most largely in the whole of the technological cycle of the production of PZT-based ceramic articles, are being constantly carried out.

PZT synthesis is realized in three stages: formation of lead titanate, formation of lead titanate, formation of PZT solid solution due to mutual diffusion of titanium and zirconium ions. To the largest extent the quality of the final product is limited by the second stage of the process. That is why the main goal of the present work is investigation of lead zirconate (PZ) synthesis using zirconium oxide of different crystal modification. PZ was synthesized from the mixtures of lead carbonate and zirconium dioxide taken in the stoichiometric proportion. Fine-grained (150–180 nm) ZrO_2 powder was obtained by the method of mutual precipitation of zirconium and yttrium hydroxides from the solutions of their nitric acid salts by ammonia water solution [1, 2]. After filtration and drying ZrO_2 sediment was calcinated at 500 and 700°C. The tetragonal and cubic ZrO_2 crystal modifications were obtained by doping with yttrium oxide (3 mol% and 6 mol%, respectively).

The conditions of ZT synthesis were studied using thermogravimetric, dilatometric and X-ray methods. Differential thermal analysis (DTA) was realized on MOM QD-103 derivatograph in (20–1100)°C temperature interval at a heating rate of
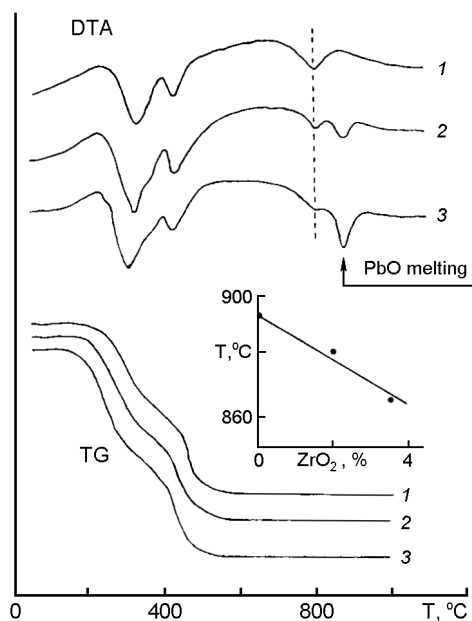
Fig. 1. DTA (above) and TG (below) curves for equimolecular $PbCO_3$–ZrO_2 mixtures. ZrO_2 modification: *1* — monoclinic, *2* — tetragonal, *3* — cubic. In the insert — melting temperature of PbO containing ZrO_2 vs ZrO_2 concetration (mol%).

Fig. 2. Dependence of PZ content (mass %) on the synthesis temperature for monoclinic (above) and tetragonal (below) ZrO_2 modifications. ZrO_2 calcination temperature, °C: *1* — 500, *2* — 700.

5–10°C/min. X-ray investigations (X-ray phase analysis - XRPA) were carried out on DRON-3 diffractometer in filtered CuK_α-radiation under the conditions of continuous registration. The accuracy of quantitative phase composition measurement was ±3 %. Dilatometric measurements were carried out on NETZSCH 402 ED dilatometer in (20–1300)°C temperature region at a heating rate of 5°C/min.

Presented in Fig. 1 are the DTA curves obtained in the process of heating of equimolar lead carbonate and zirconium oxide mixtures of three crystal modifications (monoclinic, tetragonal and cubic). The DTA curves for all the samples are characterized by two-step endothermal effect in (300–450)°C temperature interval caused by decomposition of lead carbonate. At further increase of the temperature endothermal effect is observed in the region of 800°C (for all ZrO_2 modifications).

At higher temperatures (~870°C) one more endothermal effect occurs for the tetragonal and cubic modifications of ZrO_2 (Fig. 1, curves 2, 3). The effect itself becomes more pronounced when passing from the tetragonal modification to the cubic one. In the case of the monoclinic modification the mentioned effect is absent.
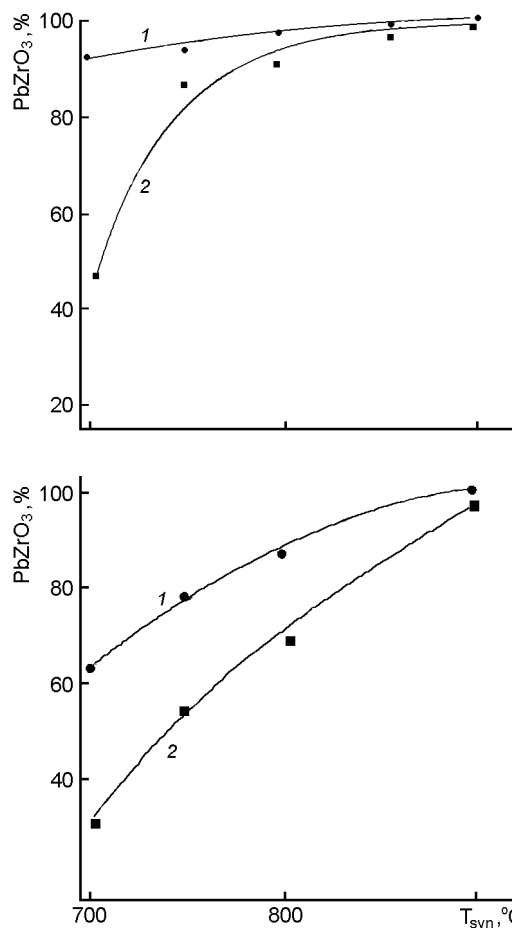
The last endothermal effect on the DTA curves is located in the region of lead oxide (PbO) melting, but its temperature differs from the T_{melt} value contained in reference literature. To identify the high-temperature endoeffect, we determined the melting temperature of PbO:ZrO_2 solid solution. As the content of ZrO_2 dissolved in PbO increased, the melting temperature decreased down to the values at which high-temperature endothermal effects shown in Fig. 1, were observed.

The results of XRPA show that the degree of the completeness of solid-phase reaction of PZ formation depends on the crystal modification of the used ZrO_2. Shown in Fig. 2 are the dependences of the content of PZ (mass %) on the synthesis temperature for ZrO_2 of monoclinic and tetragonal modifications (in all the cases the duration of the procedure of synthesis was 2 h). As seen
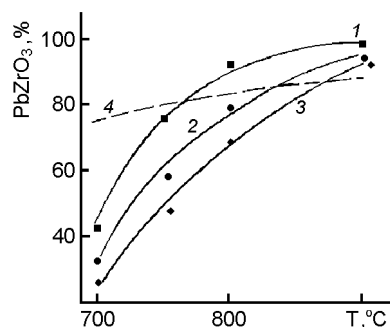
Fig. 3. Dependence of PZ content (mass %) on the synthesis temperature. ZrO_2 modification: *1* — monoclinic, *2* — tetragonal, *3* — cubic, *4* — monoclinic with Y_2O_3 addition (3 mol%).

from the results presented in the figure, the degree of the reaction completeness depends not only on the crystal modification of the used zirconium oxide, but also on the conditions of its preparation (calcination temperature).

Since the modification of zirconium oxide can be changed only by introduction of doping oxides (in our case its is yttrium oxide), for determination of the contribution of yttrium, there were realized the procedures of PZ synthesis from pure zirconium oxide and lead carbonate, but the raw material contained 3 mol% of yttrium oxide introduced additionally. The results of these experiments are shown in Fig. 3.

The most significant result obtained in the present research is the dependence of the completeness of the solid-phase reaction on the crystal modification of ZrO_2. This result is non-trivial, and additional investigations are required for its understanding. But the physical factor, which must be taken into account for interpretation of the obtained results, may be pointed to just now.

Different modifications of zirconium oxide can be obtained only by means of stabilization of different crystal structures by doping elements. In the present work for this purpose yttrium oxide was used. As a consequence, the performed experiments are essentially many-factor ones. In particular, the final result may be influenced by increased imperfection of the crystal lattice caused by different valence of zirconium and yttrium ions as well as by grain-boundary impurity effects. Both of these factors may lead to changes in the efficiency of diffusion transport and, consequently, to changes in the solid-phase synthesis kinetics.

Presented in Fig. 3 are the dependences of the end product yield on the synthesis temperature obtained for the three modifications of zirconium oxide (remind that the tetragonal and cubic modifications of yttrium oxide are stabilized by 3 mol% and 6 mol% of yttrium oxide, respectively). Shown for comparison is the corresponding dependence for the raw material obtained using the monoclinic modification of zirconium oxide (not containing yttrium oxide) with the addition of 3 mol% of yttrium oxide introduced into the raw material in pure form. All the dependences, which characterize the raw material with no yttrium oxide introduced in pure form, are of similar shape. At the same time, they qualitatively differ from the curve obtained for the raw material, which contains yttrium oxide introduced in pure form. In the latter case we do not observe completely terminated synthesis process even at high temperatures. This may be referred to the grain-boundary impurity effect, which restricts diffusion processes. In our opinion, it is not the effect that defines the synthesis peculiarities revealed in the present work.

Increase of the content of yttrium oxide caused by its lower valence lowers the oxygen index (the chemical formula of the oxide used in this case is $(Zr_{1-x}Y_x)O_{2-\delta}$, $\delta(x) \geq 0$ and increases with x). According to the present-day ideas, in this case raise of the crystal lattice imperfection degree must lead to increase of the diffusion coefficients and to more efficient process of solid-phase synthesis. However, experiments show the opposite situation. As seen from Fig. 2 and 3, as the content of yttrium oxide in zirconium oxide increases, the synthesis is shifted towards high-temperature region. Thus, changes in the degree of imperfection of zirconium oxide crystal lattice do not define the observed synthesis peculiarities neither.

The perovskite crystal structure of PZ is a three-dimensional frame formed by [ZrO_6] octahedrons joined by the vertexes where oxygen ions are located. The crystal structure of titanates is a frame formed by [TiO_6] octahedrons. Lead ions lie in the dodecahedron hollows of the octahedron frame. The crystal structure of ZrO_2 (or TiO_2) is a frame formed by the same [ZrO_6] (or [TiO_6]) octahedrons joined partially by the edges and partially by the faces. This oxygen octahedron structure of oxides is more closely packed than that of perovskite.

At the synthesis of the mixture of zirconium (or titanium) oxide and lead oxide and the perovskite structure formation, the octahedrons of the closely packed zirconium (titanium) oxide structure "open up" and turn around. Then similar "new" structure is formed up by lead (or barium) ions. As is seen, in the process of solid-phase synthesis of complex-composition oxides there participate two main mechanisms: breakage of the chemical bonds in simple zirconium (titanium) oxides followed by turn of basic structure elements, i.e. oxygen octahedrons, and diffusion of lead ions to their "new" location in the newly formed perovskite structure.

As seen from the experimental results presented in Fig. 2, PZ powders calcinated at 500°C provide lower synthesis temperatures. X-ray investigations [3, 4] show that the crystal structure of such powders is not completely formed. In particular, in the diffraction patterns obtained for the powders calcinated at 500°C some duplet lines are not resolved. It is only after calcination at 700°C that these lines become completely resolved. While the raw material is being kept at the synthesis temperature there take place several processes such as termination of crystallization and complete formation of the crystal structure typical of each particular ZrO_2:Y composition, breakage of the chemical bonds and turn of the oxygen octahedrons, appearance of lead ions in the crystal structure. As a result, the perovskite crystal structure is formed. Due to the fact that the said processes are simultaneous, the required energy expenditure turns out to be less than that corresponding to the case when there are used the powders with the preliminarily formed crystal structure (those annealed at 700°C).

Now let us explain raise of the temperature of PZ synthesis in the process of passing from the monoclinic modification to the tetragonal and then to the cubic ones. Different modifications of zirconium oxide are characterized by different intensities of the chemical bonds. At the changeover from the cubic modification to the tetragonal and then to the monoclinic ones the symmetry degree of the elementary crystal cell decreases and the reduced parameter of deformation increases. The bonds unequal in length (but crystallographically equivalent in the initial cubic modification) may be considered to be a consequence of extension or compression of the bonds which exist in the high-temperature cubic modification. Deformation of the chemical bonds (change of the interior distances) causes additional mechanical energy typical of the crystal lattice in the low-symmetry state.

Mechanical stresses, which take place in the distorted lattice of lead zirconate of the tetragonal and monoclinic modifications promote breakage of the bonds in the oxygen octahedron frame. This results in decrease of the temperature of PZ synthesis at the changeover from the cubic to the monoclinic modification of lead zirconate. The considered mechanisms of solid state reactions (of the diffusion and block structure types ones) are competing as concerns their influence on the change of the synthesis temperature. Unfortunately, at present there are no reliable methods (and the corresponding physical models) which allow to separate the contributions of these mechanisms. However, experiments show that in the process of PZ synthesis the structure mechanism predominates.

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Синтез цирконату свинця:
вплив кристалічної модифікації оксиду цирконія

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Досліджено особливості процесу синтезу цирконату свинцю з оксиду цирконію різної кристалічної модифікації (моноклинної, тетрагональної та кубічної). Показано, що моноклинна модифікація оксиду цирконію є найбільш реакційно здатною: її використання призводить до зниження температури синтезу цирконату свинцю та температури спікання керамічних зразків. Запропоновано фізичний механізм, що пояснює залежність температури синтезу цирконату свинцю від типу кристалічної гратки оксиду цирконію.