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Effect of zirconium oxide crystalline modifications on lead zirconate synthesis

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Reactivity of zirconium oxide in various crystalline modifications (monoclinic, tetragonal, and cubic) in lead zirconate synthesis has been studied. Using dilatometry and X-ray diffraction analysis, it has been shown that synthesis of lead zirconate involving the monoclinic zirconium dioxide is essentially completed at 800°C. The lowered synthesis temperature favors lowering of the ceramic sample sintering temperature and increasing their shrinkage.

Исследована реакционная способность оксида циркония различной кристаллической модификации (моноклинной, тетрагональной и кубической) при получении цирконата свинца. С помощью дилатометрического и рентгенофазового анализов показано, что получение цирконата свинца с участием моноклинной модификации оксида циркония практически завершается при 800°C. Более низкая температура синтеза цирконата свинца способствует снижению температуры спекания керамических образцов и увеличению их усадки.

There are two main instances that cause a considerable interest in lead zirconate-titanate (PZT) solid solutions for over 40 years [1–3]. First, various phase transformations occur in that system, thus making it possible to study comprehensively the nature of ferroelectric (FE) and antiferroelectric (AFE) ordering as well as the mechanisms providing high piezoelectric characteristics of a material. Second, the ferroelectric PZT ceramics is used in many technical fields due to their pronounced piezoelectric and pyroelectric properties, the ceramics application being extended continuously.

The solid phase synthesis being used mainly in the modern industrial production is studied well enough, so that no surprises occur in laboratory conditions. In the mass production of the ceramics, difficulties arise that are believed to be connected with the use of different grades of zirconium oxide (ZrO_2) as raw materials. Therefore, continuous studies are in progress to elucidate factors influencing to a greatest extent the whole technologic cycle of PZT ceramic pieces manufacturing. The purpose of this work was to study the solid phase synthetic process using zirconium oxide of three known crystalline modifications, namely, monoclinic (M), tetragonal (T), and cubic (C) ones. Zirconium oxide in so-called nanodispersed state (the powder grain size of 150 to 180 nm) was used.

The PZT synthesis is known to include three steps, namely, lead titanate formation; lead zirconate formation; and formation of PZT solid solution due to mutual

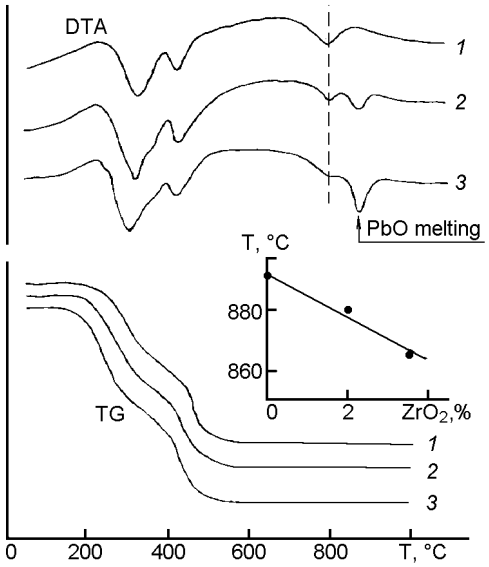

Fig. 1. DTA (top) and TG (bottom) curves for equimolar $PbO–ZrO_2$ mixtures with ZrO_2 modifications: monoclinic (*1*), tetragonal (*2*), cubic (*3*). Inset: M.p. of ZrO_2 solid solution in PbO as function of ZrO_2 concentration (mole per cent).

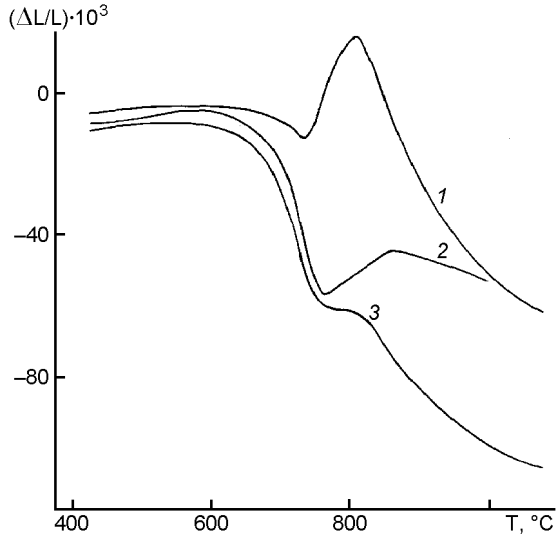

Fig. 2. Dilatometric curves for raw equimolar $PbO–ZrO_2$ mixtures with ZrO_2 modifications: monoclinic (*1*), tetragonal (*2*), cubic (*3*).

diffusion of the components [4]. It is just the second step that defines the product quality to the greatest extent. Therefore, the main attention in this work is given to lead zirconate (PZ) formation.

PZ was prepared by solid phase synthesis from lead carbonate and zirconium dioxide mixed in stoichiometric ratio. The finely dispersed (150 to 180 nm) ZrO_2 powder was obtained by co-precipitation of zirconium and yttrium hydroxides from solutions of their nitrates using aqueous ammonium solution [5, 6]. After filtration and drying, the ZrO_2 precipitate was calcined at 500°C and 700°C. The various crystalline modifications of ZrO_2 were obtained using doping with yttrium oxide (tetragonal modification, 3 mole per cent, cubic one, 6 mole per cent).

The PZ synthesis conditions were studied using thermogravimetry, dilatometry, and X-ray analysis. The differential thermal analysis (DTA) was carried out using a D-103 derivatograph (MOM) within 20–1100°C temperature interval at heating rates of 5 to 10°C/min. For X-ray phase analysis (XPA), a DRON-3 diffractometer with filtered copper emission was used in the continuous recording mode. The phase composition was quantitatively determined to within ±3 %. The dilatometric measurements were carried out using a NETZSCH 402 ED dilatometer within 20–1300°C temperature interval at heating rates of 5 to 10°C/min.

Fig. 1 presents the DTA curves and mass change (thermogravimetric) ones obtained at heating of lead carbonate equimolar mixtures with zirconium oxide of three crystalline modifications (monoclinic, tetragonal, and cubic). The DTA curves for all samples show a double-step endotherm within 300 to 450°C temperature range caused by lead carbonate decomposition. The further temperature elevation gives rise to an endotherm at 800°C (for mixtures containing any ZrO_2 modification). In the shrinkage curves (Fig. 2, curves 1, 2), this endotherm is accompanied by an anomalous sample expansion within 750 to 850°C temperature range for monoclinic and tetragonal ZrO_2 modifications while for cubic one, a bend is observed (see Fig. 2, curve 3). The anomalous sample expansion maximum tends to decrease down to disappearance when passing from monoclinic ZrO_2 modification to cubic one.

At even higher temperatures (about 870°C), one more endotherm is seen in DTA curves for tetragonal and cubic ZrO_2 modifications only (Fig. 1, curves 2, 3). This effect increases when passing from the tetragonal to cubic ZrO_2. This effect is absent when monoclinic ZrO_2 is used. The last endotherm in the DTA curves is within the PbO melting range, but its temperature differs from the PbO melting point reference value. To characterize this high-tempera-

ture endotherm, we have determined the melting temperatures of $PbO:ZrO_2$ solid solutions. The inset in Fig. 1 presents the temperature dependence for PbO containing up to 4 mole per cent of dissolved ZrO_2. The increasing ZrO_2 content is seen to cause the melting temperature down to values corresponding to the high-temperature endotherms shown in Fig. 1.

The XPA results show that the extent of solid-phase PZ formation depends on the crystalline modification of ZrO_2 used. Fig. 3 shows dependence of PZ content (per cent mass) on the synthesis temperature for monoclinic and tetragonal ZrO_2 modifications (the synthesis duration was 2 h in all cases). The reaction completion extent is seen to depend not only on the zirconium oxide crystalline modification but also on the preparation conditions thereof (calcination temperature). Since the zirconium oxide modification can be changed only by introducing oxide dopants (in our case, yttrium oxide), PZ was synthesized from pure zirconium oxide and lead carbonate but with 3% (mol.) yttrium oxide added to the initial blend in order to reveal just the effect of yttrium. The results of those experiments are shown in Fig. 4.

The results obtained show that the final result depends mainly on the synthesis temperature, the raw material pre-history (calcination temperature of the co-precipitated hydroxide), and the ZrO_2 crystalline modification. The first mentioned factor is easy to understand and well studied. It should be noted, however, that the use of monoclinic ZrO_2 modification with grain size of 150 to 180 nm provides the final product manufacturing at lower temperatures than are required if stock-produced batches of that oxide are used. The most important result of this work that is worth to emphasize consists in that the solid-phase reaction run depends on the ZrO_2 crystalline modification used. This is a non-trivial result, and further investigation are necessary to understand it.

In this work, the tetragonal and cubic zirconium oxide modifications have been obtained using yttrium oxide as a dopant. Thus, the experiments carried out are substantially multifactor ones. In particular, the final results may be influenced by increased imperfection of the crystal lattice due to different valences of zirconium and yttrium ions as well as impurity effects at grain boundaries. The both factors may result in changed efficiency of the diffusion

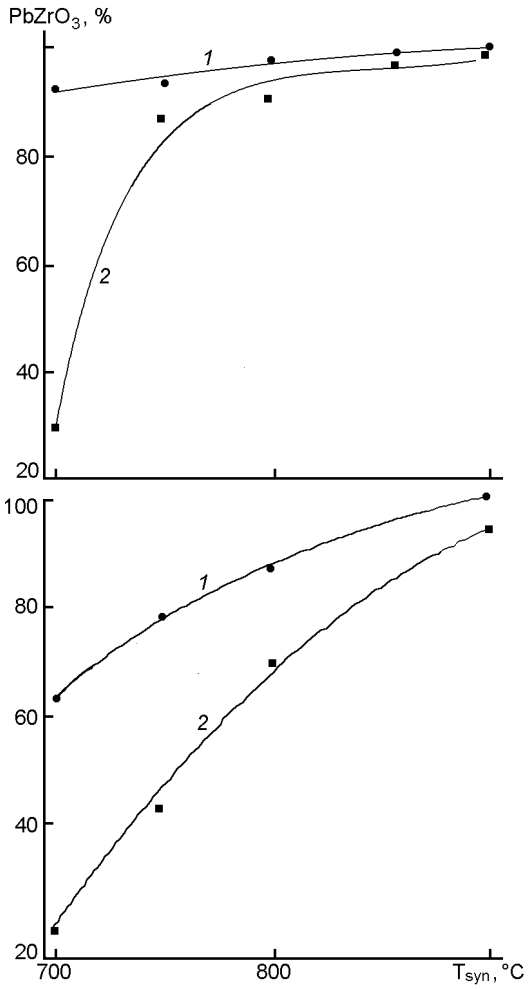

Fig. 3. PZ content (per cent mass) as a function of synthesis temperature at monoclinic (top) and tetragonal (bottom) equimolar $PbO–ZrO_2$ mixtures with ZrO_2 modifications. ZO_2 calcination temperature, °C: *1* – 500, *2* – 700.

transport and thus in changed kinetics of the solid phase synthesis. Therefore, let the second-order factors be determined at first and then disregarded.

At first, let the role of yttrium oxide be considered. Fig. 4 presents the dependences of the final product yield on the synthesis temperature obtained using three zirconium oxide modifications (it is to remind that tetragonal and cubic modification are stabilized with 3 and 6% (mol.) of yttrium oxide, respectively). To compare, the corresponding dependence is shown for the raw blend obtained with monoclinic zirconium oxide (yttrium oxide free) and with that containing 3% (mol.) pure yttrium oxide introduced into the blend. All the curve characterizing the blends where yttrium oxide was not added separately are similar

Table. Unbound lead oxide (PbO, p.c.mass) concentration in $PbZrO_3$ synthesized at different temperatures

T_{syn}, °C	ZrO_2 modification and calcination temperature, °C				
	monoclinic 500	monoclinic 700	tetragonal 500	tetragonal 700	cubic 700
700	6.7	61	37.5	65	77
750	5.8	8	21.3	44	56
800	1.5	6	12.7	17	30
900	0.6	–	–	1.8	5.9

to each other and differ from the curve corresponding to the blend containing pure yttrium oxide. The most substantial difference consists in that, in the latter case, the completed synthetic process is not observed even at high temperatures. It is just that effect that can be related to the grain boundary impurity effect limiting the diffusion processes. In our opinion, that effect does not define the synthesis features observed in this work.

Now let us consider how the change in oxygen non-stoichiometry (due to zirconium oxide stabilization with different amounts of yttrium oxide) may influence the synthetic process. An increase in yttrium oxide content is known to result in decreased oxygen index (due to the lower yttrium valence). In this case, the oxide in use is characterized as $(Zr_{1-x}Y_x)O_{2-\delta(x)}$ ($\delta(x) \geq 0$ and increases in parallel with x). According to modern concepts, the increased imperfection of the crystal lattice must cause increased diffusion coefficients and improved efficiency of the solid synthesis process. The experiment, however, proves the opposite effect. It is seen from Figs. 3 and 4 that as the yttrium oxide content in the blend rises, the synthesis is shifted towards higher temperatures. Thus, the changes in zirconium oxide crystal lattice imperfection do not define the observed features of the synthesis process.

Let the mechanisms defining the solid phase synthesis processes in PZ be considered in more detail. Those are similar to those in $PbTiO_3$ and $BaTiO_3$. The perovskite PZ structure is a three-dimensional framework of $[ZrO_6]$ octahedrons coupled together at their vertices where oxygen ions are arranged. In titanates, the framework consists of $[TiO_6]$. Lead ions are arranged in dodecahedral voids of the octahedral framework. The crystal ZrO_2 (or TiO_2) structure is the same framework of $[ZrO_6]$ (or $[TiO_6]$) octahedrons coupled together in part with

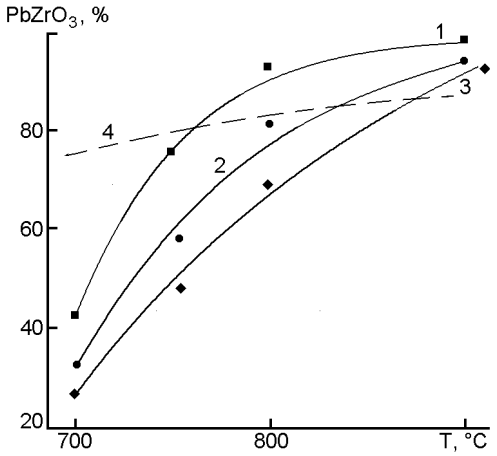

Fig. 4. PZ content (mass.%) vs synthesis temperature for zirconium oxide calcined at 700 °C. ZrO_2 modification: *1* – monoclinic, *2* – tetragonal, *3* – cubic, *4* – monoclinic with the addition of 3 mol. % Y_2O_3 in the blend before synthesis.

edges and in part with faces. Such oxygen-octahedral structure of oxides is packed more closely than that of perovskite. In the synthesis process of a mixture of zirconium (or titanium) oxide and lead oxide and the perovskite structure formation, the octahedrons of the close-packed zirconium (or titanium) oxide structure are "open" and rotated. Then, lead (or barium) ions are embedded into that "new" structure. In the solid phase synthesis of complex perovskite type oxides, two main mechanisms are seen to be involved: breakdown of chemical bonds in simple zirconium (or titanium) oxide with rotation of the basic structure elements (oxygen octahedrons) and diffusion of lead ions to their "new" sites in the forming perovskite structure.

It is to note that in the lead zirconate-lead titanate system, $PbZrO_3$-$PbTiO_3$, not only perovskite type compounds but also the pyrochlore structure ones may be formed. The latter structure is also a framework of

oxygen octahedrons but coupled with edges. In this case, the synthesis temperature is much lower (400 to 450°C) than that of perovskite compounds . This fact indicates that such temperatures are quite sufficient to provide the effective diffusion of lead ions from the lead oxide granules to their new sites and their embedding into inter-octahedral voids with pyrochlore crystal lattice. Those temperatures are, however, insufficient to break the chemical bonds and to rotate the octahedrons. The energy providing the latter processes and the perovskite structure formation is provided only by higher temperatures (700°C and above).

It is seen from the above that it is not diffusion processes that are critical in the perovskite type lead zirconate. Therefore, let us consider in more detail the synthesis process concept based on the block structure mechanism of perovskite type oxide formation. It is seen from the experimental results (Fig. 3) that the lead zirconate powders calcined at 500°C provide the PZ synthesis at lower temperatures. This can be explained in an unambiguous and non-contradictory manner taking into account the above considerations. The X-ray examinations have shown that the crystal structure of those powders is not yet formed completely [6]. The powders could be characterized as "amorphous in part" (there is a short-range order while the long-range one is not expressed clearly). During the heat treatment at the synthesis temperature, several processes occur, including the completion of crystallization, formation of full-crystal structure characteristic of each specific ZrO_2:Y composition, the chemical bond breakdown and the oxygen octahedron rotation, and the lead ion embedding into the structure, resulting at the end in formation of the perovskite crystal structure. Since the processes mentioned run simultaneously, the required energy is lower than in the case when powders of pre-formed crystal structure (calcined at 700°C) are used.

Now let the phenomenon of the PZ synthesis temperature increase when passing from the monoclinic zirconium oxide modification to the tetragonal one be considered. The phenomenon mechanism is not clear although, in our opinion, it is defined also by the block-structure formation process of perovskite type oxides. Zirconium oxide in various modifications is characterized by different stress levels of chemical bonds. When passing from the monoclinic modification to the tetragonal one, the unit cell symmetry is lowered and the reduced strain parameter increases. The bonds of different lengths (but equivalent crystallographically in the initial cubic modification) can be considered as those resulting from the tension or compression of bonds existing within the high-temperature cubic modification. The chemical bond straining (the ion spacing changes) provides an additional mechanical energy inherent in the low-symmetry crystal lattice.

The mechanical stresses (or rather the excess elastic energy) in the distorted PZ lattice (of monoclinic and tetragonal modification) favor the bond breakdown in the oxygen-octahedral framework. As a result, the PZ synthesis temperature becomes lower when passing from the monoclinic modification to the tetragonal one. The mechanisms considered (diffusion and block-structure) are competitive in the effect on the synthesis temperature change. Unfortunately, there are no reliable methods (as well as suitable physical models) to discriminate the contributions from both mechanisms. Experimental data show, however, that it is the second mechanism that predominates in the PZ synthesis.

Thus, reactivity of three zirconium oxide crystalline modifications in PZ preparation has been studied. The calcination temperature elevation at ZrO_2 preparation results in a decreased chemical activity. For solid-phase PZ synthesis, use of monoclinic ZrO_2 modification is to be preferred. The use of such blend results in lowered sintering temperature of ceramic samples.

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Вплив кристалічної модифікації оксиду цирконію на синтез цирконату свинцю

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Досліджено реакційну здатність оксиду цирконію різних кристалічних модифікацій (моноклінної, тетрагональної та кубічної) при одержанні цирконату свинцю. За допомогою дилатометричного та рентгенофазового аналізів показано, що одержання цирконату свинцю за участю моноклінної модифікації оксиду цирконію практично завершується при 800°С. Більш низька температура синтезу цирконату свинцю сприяє зниженню температури спікання керамічних зразків та збільшенню їх усадки.