Effect of Fe^{3+} and Y^{3+} Cations on the Crystallization of Tetragonal Zirconia under Mechanical Activation of Amorphous Zirconium Hydroxide

PETER N. KUZNETSOV[1], LYUDMILA I. KUZNETSOVA[1], ANATOLIY M. ZHYZHAEV[1], GENNADIY L. PASHKOV[1] and VLADIMIR V. BOLDYREV[2,3]

[1]*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)*

[2]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

[3]*Novosibirsk State University, Ul. Pirogova 2, Novosibirsk 630090 (Russia)*

E-mail: kuzpn@krsk.info

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Abstract

The effect of mechanical activation of amorphous zirconium hydroxide in centrifugal planetary mill on the formation of crystalline zirconia in the presence of Fe^{3+} and Y^{3+} cation additives is investigated. It is established that the pulsed mechanical impact stimulates dehydration and crystallization of the nanosized metastable form of tetragonal zirconia in a mechanochemical apparatus at the room temperature. The solid-phase mechanochemical synthesis proceeds with a high rate through sequential and parallel routes with the intermediate formation of stable monoclinic modification of ZrO_2. Introduction of additives favours the formation of the tetragonal form; in the presence of small amount of Y^{3+} cations, the process is completed within 2–5 min. The formation of metastable phase in the mechanochemical apparatus can occur due to the pulsed mode of powerful mechanical impact, resulting in the creation of thermodynamically and kinetically favourable conditions, and also due to small crystallite size (12–16 nm) as a result of efficient grinding.

INTRODUCTION

At present, materials based on zirconia, which possesses high thermal stability, mechanical strength and unique surface properties, are widely used in advanced areas of technology. Zirconia exists in the forms of several polymorphous modifications: monoclinic, which is thermodynamically stable below 1172 °C, tetragonal, which is stable within temperature range 1172–2347 °C, cubic, which is stable above 2347 °C (till melting point which is 2680 °C), and rhombic, which exists at high pressure and temperature. High-temperature modifications of ZrO_2 are efficiently used for obtaining construction and ion-exchange materials, selective absorbents and components of heterogeneous catalysts. Special attention is attracted to the catalytic systems containing tetragonal ZrO_2 promoted by sulphate anions or the anions of heteropolyacids and other additives which catalyse many chemical reactions, for example skeletal isomerization of *n*-paraffins at relatively low temperature (below 250 °C) providing high yield of highly branched isomers possessing enhanced octane characteristics [1–3].

Several approaches to the synthesis of metastable high-temperature zirconia are known. Widely spread methods for the synthesis of tetragonal and cubic forms of ZrO_2 are those where the high temperature (above 1200 °C) is used, which is thermodynamically favourable for the reaction [4, 5]. The high-

temperature phases can be produced successfully in metastable forms by fast quenching of the product. Metastable modifications can also be obtained under explosion conditions at high temperature and pressure [5, 6]. For catalyst preparation, the most widespread method is based on the precipitation of fine hydroxide precursors, from which the oxide phase of tetragonal or cubic modification is formed by long thermal activation (at 500–700 °C) [2, 3]. In all the referred methods, formation and stabilization of high-temperature forms of ZrO_2 are promoted by admixtures of polyvalent Y^{3+}, Fe^{3+}, Mn^{2+}, Ca^{2+} cations and/or SO_4^{2-}, WO_4^{2-}, MoO_4^{2-} anions. It is assumed [2, 7, 8] that the introduction of these additives retards the crystallization of ZrO_2 at the temperature below 500–700 °C. According to [8, 9], in the case of crystallite sizes within nanosize range, high-temperature forms are thermodynamically more favourable than the monoclinic modification, because of lower surface energy ($7.7\ 10^{-5}$ J/cm^2 for the tetragonal form [10] against $11.3\ 10^{-5}$ J/cm^2 for monoclinic one [9]). The critical crystallite size for the existence of tetragonal form at the room temperature is 30 nm [8, 9].

Progress in developing of experimental equipment and methods of mechanical activation opened new possibilities for an increase in the reactivity of solids, stimulation of solid-phase chemical reactions and development of new reagent-free methods of obtaining finely dispersed materials in metastable state on this basis [11–13]. For instance, the authors of [14–18] showed that the tetragonal (T) form of ZrO_2 could be obtained from thermodynamically stable monoclinic (M) oxide form by mechanical grinding. According to the data reported in [14], long grinding of M-form of ZrO_2 in ball mill (for 50 h) results in a partial (45 %) phase transition into the T-form after achieving its crystallite size about 10 nm. Introduction of oxide additives Y_2O_3, Fe_2O_3, CoO (6–10 %) and increase in the power of mechanical pulse caused substantial acceleration of the phase transition [17, 18].

We have showed previously [19] that nanostructured ZrO_2 of tetragonal modification can be produced within several minutes from finely dispersed amorphous zirconium hydroxide, as well as from well-crystallized oxide of the stable monoclinic modification in high-energy mechanochemical apparatus like centrifugal planetary mill. The goal of the present work is to investigate the effect of Fe^{3+} and Y^{3+} cation additives on the dynamics of the formation of crystalline zirconia under mechanochemical activation in centrifugal planetary mill.

EXPERIMENTAL

Zirconium hydroxide was prepared by precipitation from the aqueous solution of zirconyl chloride (15 % $ZrOCl_2$) by a 12 % ammonia solution under intense mixing at the room temperature. The gels prepared were kept for 3 h; the precipitate was washed by decanting, then filtered and washed with distilled water till negative reaction for Cl^- ions in the washing water. The cake was dried in the air and then in drying oven at 110 °C for 15 h. Doping with Fe^{3+} and Y^{3+} cations was performed by adding of the solutions of their nitrates to zirconyl chloride solution before hydroxide precipitation. The amount of promoters in the solid dried precipitate was varied from 0.7 to 4.7 % (calculated for metal).

Thermal activation of the zirconium hydroxide and that promoted by Fe^{3+} cations was performed in a quartz reactor in the air at 350–700 °C. Mechanochemical activation was carried out in AGO-2 activator mill of centrifugal planetary type with two tightly closed steel drums of 150 ml volume. Steel balls (∅ = 3 mm) with total mass 106 g and 3 g of zirconium hydroxide were loaded into each drum. Mechanical load was varied by the time of treatment (from 0.5 to 30 min). The drums were cooled with water while operating to exclude substantial heating of the material under treatment.

The X-ray diffraction patterns of the products of thermal and mechanical activation were recorded with DRON-3 diffractometer using filtered CuK_α radiation, with scanning rate 1 degree/min under strictly identical conditions. The dynamics of mechanochemical processes was estimated using relative changes in the intensities of diffraction peaks of each phase.

The size of crystallites was determined by the standard Debye–Sherrer procedure using the broadening of X-ray diffraction lines. The lines for small reflection angles were used (low-index reflections with d = 2.99 Å for the tetragonal form and d = 3.16 Å for monoclinic form). Correction for physical and instrumental broadening was introduced using the lines of the standard annealed oxide. Specific surface of the samples was measured using thermal desorption of nitrogen (BET procedure). Using the values of specific surface area the average particle size was calculated assuming spherical (cubic) shape of the particles.

RESULTS AND DISCUSSION

Crystallization of the ZrO_2 oxide phases on calcination of non-promoted zirconium hydroxide starts at the temperature about 500 °C with the formation of monoclinic and tetragonal modifications. The tetragonal phase is metastable under these conditions; with the increase in calcination temperature up to 600–700 °C it is transformed into monoclinic phase. The temperature at which crystallization starts decreases to 350 °C as a result of zirconium hydroxide doping with Fe^{3+} cations. For small amount of dopant (0.7 %, calculated for metal), at first a mixture of T- and M-modifications is formed (Fig. 1, curve *2*). The increase in dopant concentration to 2.3–4.7 % stabilizes T-form (see Fig. 1, curves *3, 4*); monoclinic phase in the product is almost completely absent. With calcination temperature increased to 700 °C, the degree of crystallinity increases substantially. In the case of low promoter content, M-form is predominant in the product (see Fig. 1, curve *6*). With an increase in promoter content, mainly T-form is produced (see Fig. 1, curves *7, 8*). According to the XRD data, other crystalline phases in the products of thermal activation, including iron oxide phases, were not detected.

The characteristics of particle size of the products of thermal activation of zirconium hydroxide promoted by Fe^{3+} cations are presented in Table 1. Specific surface area of the hydroxide samples was about 363–368 m^2/g, which corresponds to the particle size of 4.1 nm. During calcination specific surface decreases

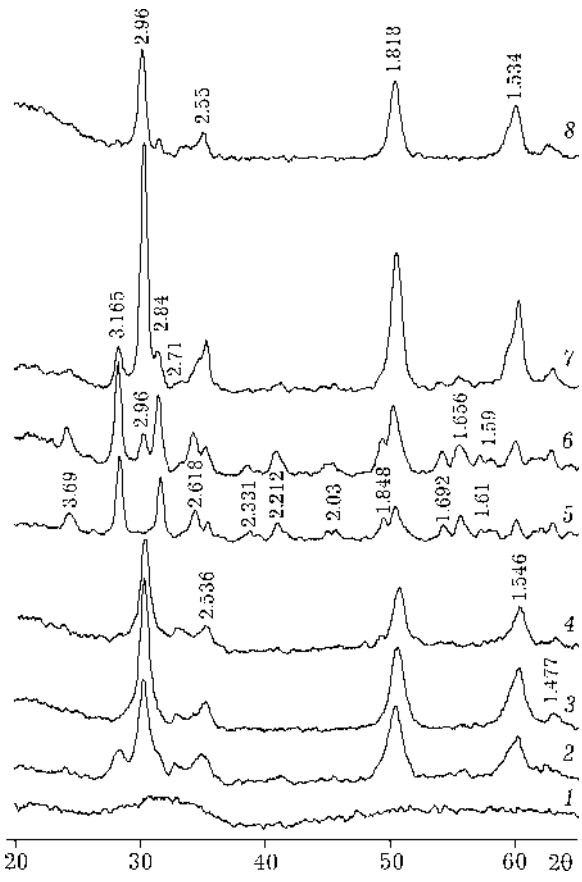

Fig. 1. Diffraction patterns of products obtained by annealing amorphous zirconium hydroxide promoted by Fe^{3+} cations at 350 (*1–4*) and 700 °C (*5–8*). Fe content, mass %: 0 (*1, 5*), 0.7 (*2, 6*), 2.3 (*3, 7*), 4.7 (*4, 8*).

substantially; and after 700 °C, it is about 32–33 m^2/g, so particle size being 30–31 nm. The size of crystallites of the tetragonal ZrO_2 formed as a result of calcination at 700 °C of the hydroxide containing 2.3 % Fe^{3+} did not exceed 20 nm.

Mechanochemical activation of dry X-ray amorphous non-promoted zirconium hydroxide powder in centrifugal planetary mill stimulates dehydration and crystallization of the oxide phases. Even after a short treatment (for 2 min) weak and broadened reflections of crystalline zirconia of monoclinic and tetragonal modifications are detected in the diffraction patterns (Fig. 2, curve *1*). Increase in mechanical load leads to increase in crystallinity degree. This process is completed for 15 min; tetragonal ZrO_2 is predominant in the crystal product; M-form is almost absent (see Fig. 2, curve *5*). Other crystalline phases are absent, according to the XRD data. The size of T-form

TABLE 1
Particle size of the products of thermal activation of zirconium hydroxide promoted with Fe^{3+} cations

Content of Fe^{3+}, %	Crystallization temperature, °C	Specific surface, m^2/g	Mean particle size*, nm	Mean T-crystallite size**, nm
0.7	–	363	4.1	–
0.7	350	109	9.4	12
0.7	600	44	22.7	15
0.7	700	32	31.2	20
2.3	–	368	4.1	–
2.3	350	125	8.0	13
2.3	600	–	–	14
2.3	700	33	30.0	20

*Estimation according to the data on specific surface.
**On the basis of broadening of X-ray lines.

crystallites did not exceed 16 nm after 15 min; their specific surface was about 20 m^2/g (Table 2). This corresponds to the mean particle size of 49 nm.

According to the data of analysis of impurities introduced in the products of mechanical activation as a result of wall drums and balls friction erosion the metal iron has appeared in activated matter after the treatment for 30 s (0.5 %, Table 3). Iron content was straight dependent on the treatment time and after 15 min it was 8.1 %. The content of other impurities like Cr, Ni, Mn, Mo, Ti, and V was less than 0.03–0.05 % in most cases.

The diffraction patterns illustrating the effect of Fe^{3+} cations, introduced into zirconium hydroxide during co-precipitation, on the formation of crystal phases under mechanochemical activation are shown in Fig. 2. One can see that up to 2 min of treatment small amounts of promoter (0.7 %) have almost no effect on crystallization: similarly to the case of non-promoted hydroxide, M- and T-forms of crystalline zirconium oxide are observed (see Fig. 2, curves *1, 2*). For higher concentration of the introduced Fe^{3+} (2.3 and 4.7 %), the T-form is prevailing (see Fig. 2, curves *3, 4*). The crystalline product obtained after 15 min is, almost independently on the quantity of promoter, represented by the single phase of tetragonal ZrO_2 (see Fig. 2, curves *5–8*) with the crystallite size near 16 nm (Table 4).

The effect of iron added to amorphous zirconium hydroxide on ZrO_2 crystallization into the tetragonal form under mechanical and thermal activation is compared in Fig. 3. One can see that the thermal process is characterised by higher sensitivity to promoter added, in

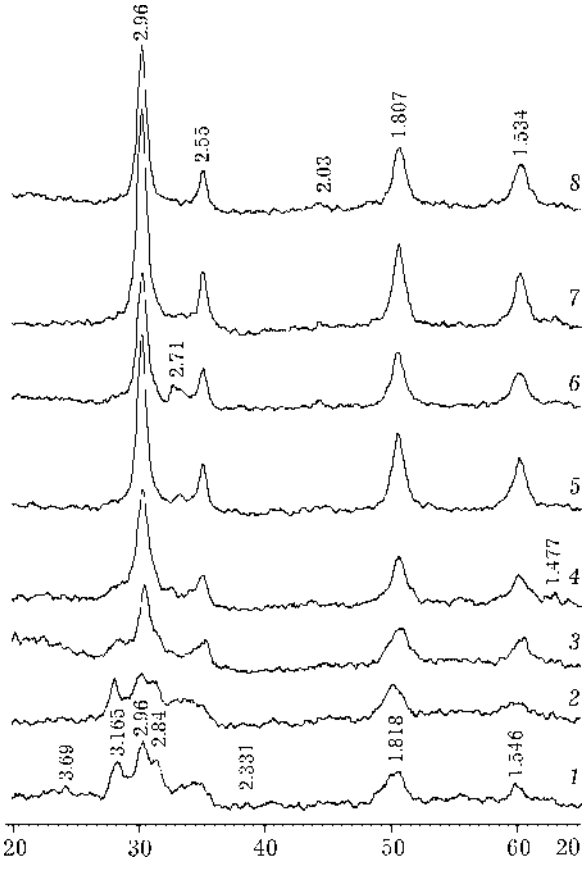

Fig. 2. Diffraction patterns of the products of mechanical activation of amorphous Fe^{3+} promoted zirconium hydroxide for 2 (*1–4*) and 15 min (*5–8*). Fe content, mass %: 0 (*1, 5*), 0.7 (*2, 6*), 2.3 (*3, 7*), 4.7 (*4, 8*).

TABLE 2

Effect of mechanical load on particle size of the product of mechanical activation of zirconium hydroxide

Activation time, min	Specific surface, m^2/g	Mean particle size, nm	Mean size of T-crystallites, nm
2	25	39	–
5	19	51	12
15	20	49	16

TABLE 3

Metal impurity content of the products of mechanical activation of zirconium hydroxide

Activation time, min	Content, mass %						
	Fe	Cr	Ni	Mn	Mo	Ti	V
0.5	0.5	–	–	–	–	–	–
2	1.0	0.01	0.02	0.01	0.0003	None	None
5	3.0	0.02	0.02	0.03	0.0009	»	»
15	8.1	0.1	0.03	0.05	0.003	»	»

comparison with the mechanochemical one. Under thermal activation at 700 °C, the introduction of 0.7 % iron shows only insignificant effect on the formation of the T-form; with the increase in its content up to 2.3 %, the content of T-form increases sharply (in 10 time). Under mechanochemical activation, the effect of Fe^{3+} additives on the crystallization of the T-form is much lower.

The diffraction patterns of the products of mechanical activation of zirconium hydroxide promoted by Y^{3+} cations, which are known to be the most efficient stabilizers of the T-form of ZrO_2 [2, 3], are shown in Fig. 4. One can see from the comparison of the diffraction patterns that the introduction of Y^{3+} at the mass fraction of only 1.1 % (which corresponds to 1.5 atomic %) causes a substantial increase in the rate of T-form formation. Crystallization process proceeds selectively; after 15 min, the product of mechanical activation is represented by single T-form of ZrO_2. For higher Y^{3+} content (3.6 %), metastable ZrO_2 is formed as early as after the activation for 5 min. For comparison, let us note that the addition of the same (1.5 %) atomic fraction of Fe^{3+} (which corresponds to the mass fraction of Fe^{3+} equal to 0.7 mass %) had almost no effect on the mechanochemical process. For mechanical activation of the hydroxide with Y^{3+} mass fraction 3.6 % for 15 min (see Fig. 4, curve *3*), we observed a noticeable decrease in the intensity

TABLE 4

Effect of Fe^{3+} cations and duration of mechanical treatment on the size of crystallites of T-form of ZrO_2

Content of Fe^{3+}, mass %	Treatment time, min	Mean crystallite size, nm
0.7	2	–
2.3	2	12
4.7	2	11
–	15	16
0.7	15	16
2.3	15	16
4.7	15	15

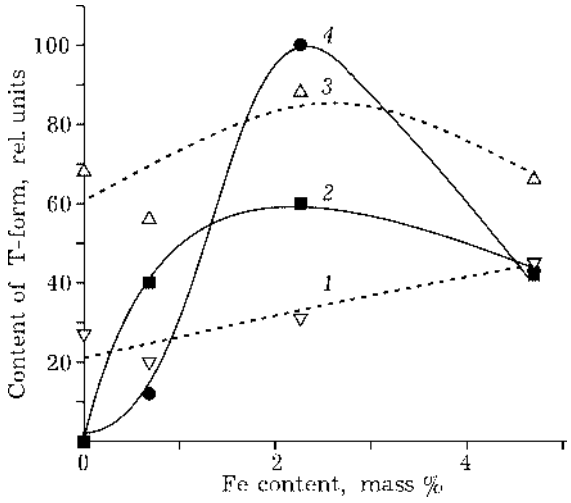

Fig. 3. Formation of tetragonal ZrO_2 form from amorphous zirconium hydroxide promoted by Fe^{3+} cations, under the action of mechanical activation (*1, 3*) and thermal activation (*2, 4*). Time of mechanical activation, min: 2 (*1*), 15 (*3*); temperature of thermal activation, °C: 350 (*2*), 700 (*4*).

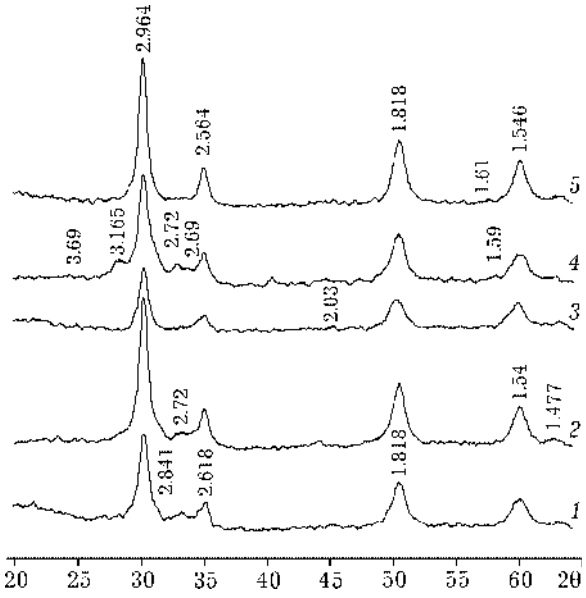

Fig. 4. Diffraction patterns of the products of mechanical activation of amorphous zirconium hydroxide promoted by Y^{3+}, activated for 2 (*1, 4*), 5 (*2*) and 15 min (*3, 5*). Content of Y, mass %: 3.6 (*1–3*), 1.1 (*4, 5*).

of diffraction reflections of the T-form in comparison with the intensity of reflections after treatment for shorter time. This is likely to be due to the fact that the product is in crystallized state after mechanical treatment for several minutes. During further loading of mechanical energy into the system, a reverse process of the amorphization of crystalline particles starts. The size of the crystallites of T-form is only slightly dependent on the fraction of promoter Y^{3+} and is within 12–16 nm (Table 5).

It is interesting to note that, according to the data reported in [18], the formation of metastable ZrO_2 form proceeded slower and less selectively under the addition of yttrium promoter in the form of the individual oxide Y_2O_3. For instance, with higher Y_2O_3 concentration and activation for 15 min, the product still contained substantial amount of the monoclinic form. This indicates that the efficiency of stabilizing effect of the promoter depends not only on its chemical properties but also on the method by which it is introduced into the matrix of the initial material and on the homogeneity extent of the mixture under treatment.

It should be underlined that individual crystal oxide phases of dopants (iron and yttrium oxides) are absent in the products of mechanochemical and thermal activation of the doped hydroxide systems, as the XRD data show, although the crystallization of iron oxides was observed during mechanical activation of iron hydroxide [20]. According to the data reported in [2, 3, 5, 6], promoter cations, in particular Y^{3+} (radius: 0.88 Å) and Fe^{3+} (radius: 0.67 Å) get introduced during thermal activation into

TABLE 5

Effect of Y^{3+} cations and duration of mechanical treatment on the size of crystallites of the T-form of ZrO_2

Content of Y^{3+}, mass %	Treatment time, min	Mean crystallite size, nm
1.1	2	12
1.1	5	13
1.1	15	16
3.6	2	15
3.6	5	16
3.6	15	15

the lattice of ZrO_2 which is being formed (the radius of Zr^{4+} cation: 0.82 Å), which results in the formation of solid solution. Using the referred above concentrations of promoters, we did not observe any noticeable regular changes in the lattice parameters of promoted thermally and mechanochemically activated ZrO_2 samples, although the radius of Fe^{3+} and Fe^{2+} cations is smaller while the radius of Y^{3+} cations is larger than that of Zr^{4+} cations. This may be connected with relatively small concentrations of the additives.

So, the data obtained show that the activation of amorphous zirconium hydroxide in high-energy mechanochemical apparatus stimulates fast dehydration and crystallization of zirconia at nearly room temperature. After 15 min, the crystalline product obtained from non-promoted hydroxide is represented by high-temperature nanosized phase of the tetragonal zirconia with the mean crystallite size of 16 nm. As regards the reaction mechanism, there is no reason to assume that the synthesis proceeds as a result of thermal activation which occurs in local sites of a solid as a result of heating to the temperature above 1172–1200 °C. Such a high temperature is improbable in a centrifugal planetary mill [13] and is likely to be impossible in a ball mill, in which this process was also observed [14].

The formation of high-temperature form of ZrO_2 in the mechanochemical apparatus is likely to occur according to a complex mechanism under the influence of many factors. The authors [2, 3] connect the existence of the tetragonal zirconia at low temperature with its fine-dispersed state. When prepared by thermal activation of the hydroxide precursors, small particle size of the T-form is usually achieved by doping with polyvalent cations (with valence below 4), which generate oxygen vacancies thus hindering crystal growth [2, 3, 7]. High-power mechanical action in a mechanochemical apparatus causes intensive crushing of the particles; the mean size of the formed crystallites does not exceed 16 nm that is in the range preferable for the tetragonal form.

Analysis of the products of mechanical treatment of non-promoted zirconium hydroxide showed that friction results in the introduction of a substantial amount of metal iron into the system. The fraction of oxidized iron, which can be formed in the apparatus from the metal iron and cause stabilizing action on the formation of high-temperature phase, is likely to be small due to small volume of oxygen in the drum. On the other hand, the data on doped samples indicate that the promoting effect of Fe^{3+} cations on the mechanochemical process starts at their mass fraction not less than 2.3 %; in the case of smaller dopant content, promotion was not observed. It can be concluded from this comparison that the formation and stabilization of the T-form under mechanochemical activation cannot be connected with the impurity (erosion) of iron, although it may have an effect on the rate and selectivity. This is also confirmed by the data obtained by the authors of [14], who observed the phase transition of monoclinic zirconium oxide into tetragonal one in grinding devices made of different materials: tungsten carbide, corundum, and steel.

The solid-phase synthesis of the T-form from hydroxide in mechanochemical apparatus characterises by high rate and starts from the simultaneous formation of two crystal phases: monoclinic and tetragonal. Under further mechanical action, the monoclinic form undergoes phase transition into the tetragonal one. The introduction of promoting polyvalent cations Fe^{3+} (2.3 mass % and more) and Y^{3+} (1.1 mass % and more) causes an increase in the rate and selectivity of the formation of T-form. In the presence of Y^{3+}, the process is completed as early as within 2–5 min almost without the formation of monoclinic modification. For comparison, let us note that in a vibration ball mill the phase transition of the M-form into T-form started only after activation for 3–15 h (depending on the type of material of the milling bodies); after treatment for 50 h, only 45 % of the monoclinic oxide was transformed into the tetragonal oxide [14]. In similar experiments with vibration mill, which we performed in [19], phase transition was not observed after treatment of the monoclinic oxide for 15 h. Gradual amorphization of the structure occurred; after 15 h, the amount of the initial crystal phase decreased till 15 %, and crystallite size decreased to 35–40 nm. Under powerful pulsed mechanical action in plan-

etary centrifugal mill, the same sample of the monoclinic oxide started to transform into the tetragonal one as early as after the treatment for 30 s [19].

Under mechanical treatment in high-energy apparatus like centrifugal planetary mill, not only the conditions for efficient crushing of the particles are realized. With the high rate of high-power pulse input, high temperature and pressure can be developed in local sites of a solid (mainly in the points of contact with the milling bodies during collisions); substantial shift strain can thus be created, which leads to plastic deformation and intensive generation of defects. This favours the process kinetics [12, 13, 21]. The transition of M-form into the T-form is accompanied by the decrease in molar volume by about 7 %. It may be expected that high pressure coupled with high temperature, developed in local sites of a solid, can provide thermodynamic probability for a denser T-oxide to be formed. According to the thermodynamic calculations performed in [22], a linear dependence exists between the applied external static pressure and phase transition temperature: $dT/dP = -0.032$ °C/bar. This means that at the pressure of 2 GPa, which according to [13, 23] can be achieved in local sites of a solid in a mechanochemical apparatus, the point of M → T phase transition should decrease by 640 °C, up to 560 °C. The possibility to achieve this temperature level under mechanical activation is established elsewhere [13, 23].

According to the available experimental data on the effect of the applied external static pressure on phase equilibrium [24], the transition of monoclinic ZrO_2 into a dense rhombic modification (which also is metastable under normal conditions with respect to monoclinic form) occurs at the pressure of 2.0–2.5 GPa and the temperature of 450 °C. When the pressure was increased to 3.0–3.5 GPa, the temperature decreased to 400 °C. At 3.7 GPa, the transition into the T-form was observed at the room temperature [25]. It should be noted that these relations were established for phase transitions under the action of static pressure. A feature of dynamic transitions under the shock action of high-power pressure pulses is that they occur under a sharp pressure gradient in the shock wave front, which generates a substantial amount of defects and dislocations. Under these conditions, as described in [26], a significant acceleration of the process and a decrease in the pressure of phase transition is observed, in comparison with the process caused by static pressure.

CONCLUSION

The described data indicate that the formation of tetragonal ZrO_2 in a mechanochemical device under the action of a powerful mechanical pressure pulses can be due to the creation of thermodynamically favourable temperature and pressure conditions in separate sites of a solid. Rapid removal of the pulse quenches the formed T-modification, which is non-equilibrium with respect to normal conditions. Under subsequent pulses, the process can propagate over a substantial part of the volume of the solid and further onto whole its volume. The presence of polyvalent promoter cations in the system, in particular Y^{3+} and to a less extent Fe^{3+}, helps stabilizing this form. Additional stabilization effect can be connected with the small size of the crystallites formed under mechanical activation.

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