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SCIENTIFIC BASIS OF TECHNOLOGY OF FINE-CRYSTALLINE QUARTZ AND CORUNDUM

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Authors have investigated the mechanism and the kinetics of fine-crystalline quartz and corundum synthesis in supercritical water. The thermovaporous treatment of raw materials has been carried out in laboratory ($v = 20$ ml) and technical ($v = 2\,m^3$ and $v = 4\,m^3$) autoclaves at temperatures between 390 and 410°C and vapor pressures of water from 20 to 27 MPa in the presence of microadditives of activators. The samples of products after thermovaporous treatment have been studied by X-ray diffraction, optical and electron microscopy, mass-spectroscopy, ESR-, IR-spectroscopy, thermal analysis and pycnometry. It was shown that microadditives of activator into silica or alumina might not only accelerate the attainment of the best hydroxylation, but also initiate the transformation of precursors in an ordered way. The control of the transformation mechanism by introducing activators into the starting materials has allowed us to obtain fine-crystalline quartz and corundum with desired properties: various habitues and size of crystals. On the basis of these data, technology of fine-crystalline quartz and corundum has been developed.

Keywords: Quartz; Corundum; Synthesis; Thermovaporous treatment; Supercritical water

INTRODUCTION

Authors have developed the technology of fine-crystalline materials, which is based upon thermovaporous treatment of oxides or

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hydroxides with the addition of small amounts of activators [1,2]. In particular, processes of solid-phase transformation of silica and alumina in supercritical water (t = 390–410°C; P_{H_2O} = 20–27 MPa) were studied [3–5]. Authors made an emphasis on the investigation of mechanism and kinetics of quartz synthesis (α-SiO_2) and corundum (α-Al_2O_3), because these products are widely used in industry [6–8].

EXPERIMENTAL

The synthesis of quartz or corundum is carried out in laboratory (v = 20 ml) and standard autoclaves volume 2 m^3 or 4 m^3, inside of which the containers with raw materials are inserted. The raw material for production of quartz was amorphous silica (SiO_2), and for synthesis of corundum – alumina (Al_2O_3) or gibbsite ($Al(OH)_3$). The pressure of water vapour is generated due to evaporation of water, which is poured in the bottom of the autoclave. By heating the autoclave up to 390–410°h the pressure of water vapour reaches 20–27 cPw. The pressure is kept constant due to the use of a special by-pass valve. The raw material is treated within 24–90 hours. The activators were added in the water. The product of synthesis is a powder with sizes of crystals from 1 to 500 microns. The samples of products after thermovaporous treatment have been studied by X-ray diffraction, optical and electron microscopy, mass-spectroscopy, ESR-, IR-spectroscopy, thermal analysis and pycnometry.

RESULTS AND DISCUSSION

The essential role during the synthesis of fine-crystalline quartz and corundum is played by the addition of small amounts ($1 \cdot 10^{-3}$–$5 \cdot 10^{-1}$%) of special substances (activators of transformation), which are capable to influence not only the rate of synthesis, but also the size and habitus of synthesized crystals. Thus, this method allows controlling the process of synthesis with the purpose of producing powders with special properties [9].

Our experiments allowed us to conclude that the mechanism of formation of quartz and corundum in supercritical water is governed

by the following general rules:

- the process of transformation of initial material (raw material – silica and gibbsite) occurs through a solid-phase mechanism with formation of intermediate compound with a certain degree of hydroxylation (Fig. 1);
- the kinetics of quartz and corundum formation satisfies the Avrami–Erofeev equation $\alpha(t) = 1 - \exp[-(kt)^n]$, where k is the rate constant and n the crystalline seeds nucleation mechanism parameter, which characterises dimensional growth of crystals [5].

In the case of silica samples, extreme hydroxylation occurs at 400°C and $P_{H_2O} = 20$ MPa, during thermovaporous treatment within about 2 h (Fig. 2). At this moment the minimum of density of silica is fixed, and this corresponds to a maximum disordering of the structure of SiO_2 [10]. During hydroxylation the structure of amorphous SiO_2 becomes more reactive. In conditions of quasiequilibrium of the processes of hydroxylation and dehydroxylation in supercritical water, the restructuring of SiO_2 into a more thermodynamically stable intermediate phases (at first cristobalite and keatite) and then in quartz begins. The direction of the process of the synthesis of quartz through different intermediate phase (cristobalite or keatite) can be adjusted due to the addition of the activators of various nature [1]. So, nitrogen-containing additives (N_2H_5OH) direct the structural processes through intermediate crystalline phase, primarily of cristobalite, and the final crystals of quartz have isometric bipyramidal habitus (Fig. 3). In this case crystals have size of 200 to 500 microns.

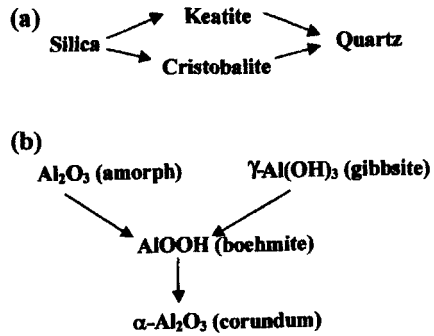

FIGURE 1 The stages of formation of (a) quartz, (b) corundum.

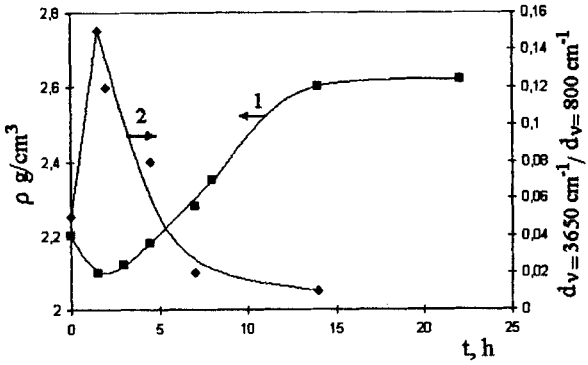

FIGURE 2 Time dependencies of silica density (curve 1) and of hydroxyls content (curve 2) during thermovaporous treatment (400°C, 20 MPa, activator $(CH_3)_4NOH$).

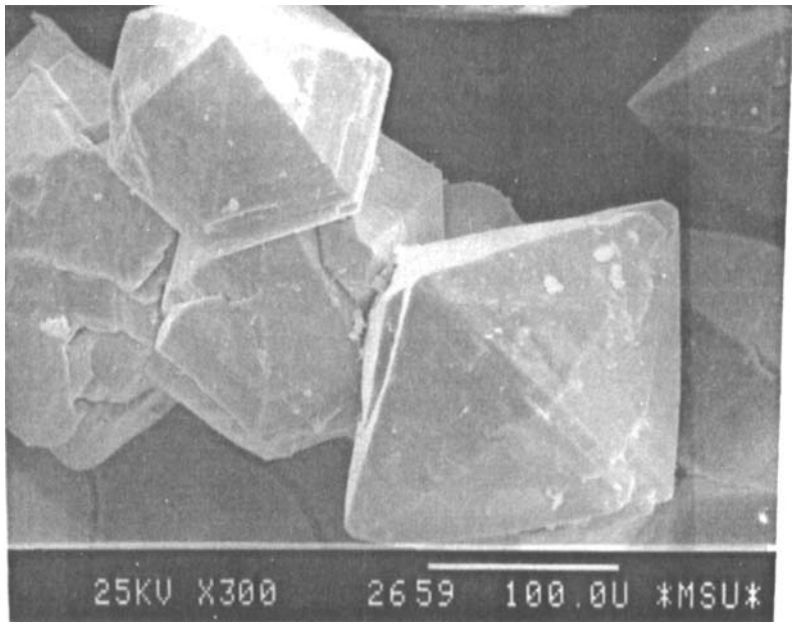

FIGURE 3 Microcrystals of quartz synthesized by using nitrogen-containing activator $N_2H_4 \cdot H_2O$.

By using aliphatic alcohols the process occurs mainly with the formation of keatite, from which then are formed needle-prismatic crystals with a size of 5 to 30 microns (Fig. 4).

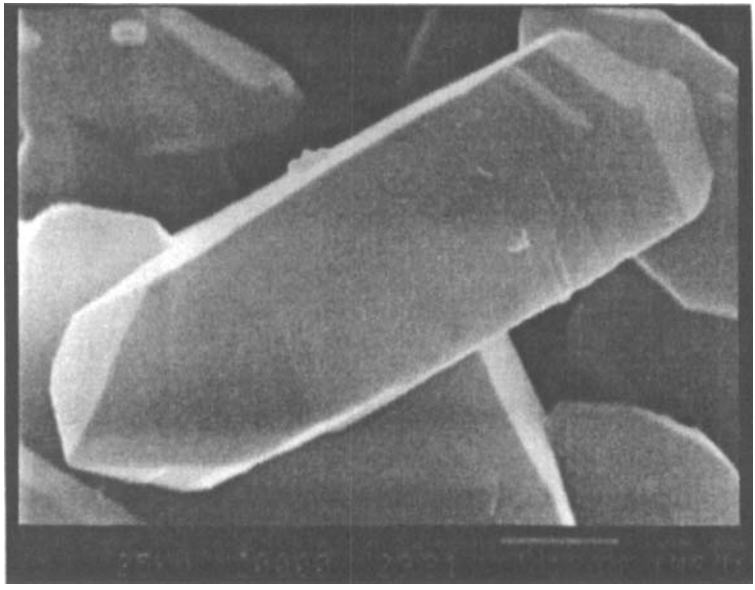

FIGURE 4 Microcrystals of quartz synthesized by using ethanol as activator.

During the processes of synthesis of corundum from alumina (amorphous Al_2O_3) or aluminum hydroxide ($Al(OH)_3$-gibbsite) in both cases intermediate phase is boehmite, which transforms into corundum (Fig. 1). The formation of corundum from boehmite starts after 6 h of delay period. From the beginning of the induction period the removal of excess water content from the structure of boehmite occurs. Then the removal of structural water from hydroxylgroups with the rise of corundum seeds happens. The activators are able to accelerate or to slow down the process of corundum formation (Fig. 5). The addition of Cr-containing activator results in a shortening of the delay period and does not change the rate constant k and the value of parameter n equal to 3. The value of parameter n equal to 3 corresponds to the three-dimensional growth of corundum crystals. In this case corundum crystals have isometric habitus (Fig. 6). The process of corundum formation in the presence of B-containing additives is characterised by $n = 2$. This value n corresponds to the two-dimensional growth of corundum. The main habitus type of corundum crystals in this case was indeed hexagonal plate (Fig. 7).

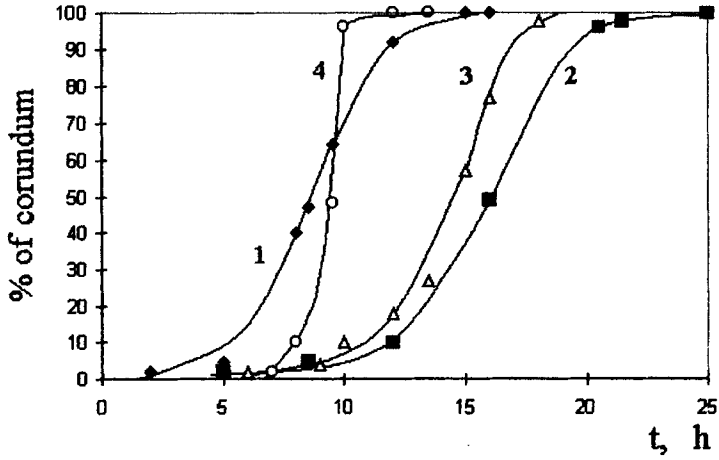

FIGURE 5 Kinetics of corundum formation during thermovaporous treatment at 400°C and 21 MPa in the presence of small amounts of Cr^{+3} ions (1), B^{+3} ions (2), in the absence of activators (3), after mechanical treatment of the precursor in vibratory mill (10 min) (4).

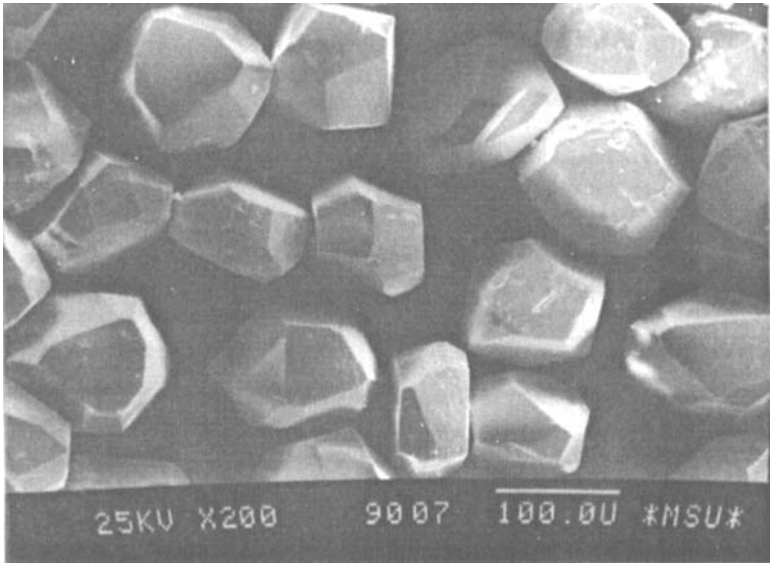

FIGURE 6 Microcrystals of corundum synthesized by using Cr-containing activator.

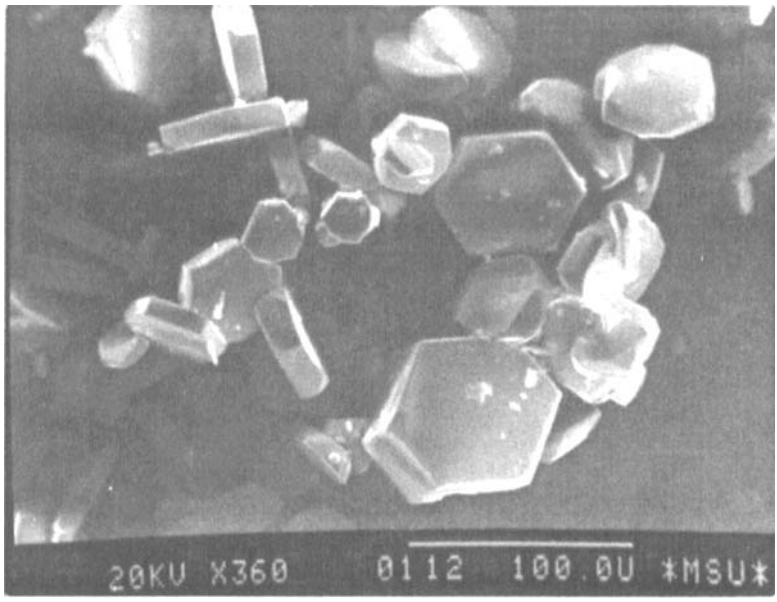

FIGURE 7 Microcrystals of corundum synthesized by using B-containing activator.

The formation of corundum in water vapour is facilitated after mechanical activation of precursor $Al(OH)_3$ [11]. Even after a short duration (10 min) of treatment of gibbsite in vibration ball mill the rate of transformation of boehmite into corundum increases more than two times in the same conditions of reaction. Mechanical treatment of gibbsite leads to its destruction with the formation of intrinsic defects (oxygen and hydroxyl vacancies), which were studied by photoluminescence. It has been shown that the intensity of blue luminescence ($\sim$ 330 nm) of boehmite is increased after mechanical treatment. Redundant energy results in decreased potential barriers of the phase transitions and decomposition process.

The rate of formation of corundum slightly depends on the pressure of supercritical water. But pressure strongly influences the size and habitus of formed crystals. The experiments have shown that on a low bound of range of used pressures (18–20 MPa) during the synthesis of corundum mainly the small-sized platelets (1 – 10 μm) are formed. In case of high-pressures (26–27 MPa), big-sized corundum crystals

(100–400 μm) with bipyramidal habitus are formed. Figure 8 demonstrates that the size and distribution of crystal sizes depend on the pressure of supercritical water.

The pH of the fluid in the range of values from 5.4 to 9.5 weakly influences the size and habitus of crystals of corundum, but the influence of pH becomes stronger when it exceeds 10. In these conditions the size of synthesised crystals decreases.

During the transformation of boehmite into corundum the removal of water molecules together with the part of mineral impurities from boehmite structure occurs. The introduction into fluid of substances

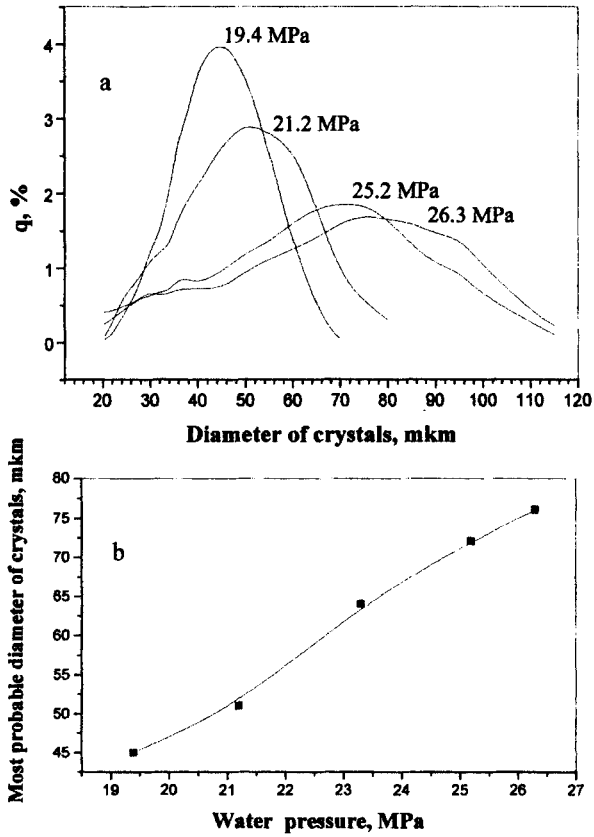

FIGURE 8 The distribution of sizes (a) and most probable diameter (b) of corundum crystals as a function of pressure of water vapour at 393°C.

forming volatile compounds with these impurities can intensify the removing of the mineral impurities.

In Table I the content of impurities in initial material (gibbsite) and in final product (corundum) synthesized from this material are listed. In the process of synthesis, special additives were used. Besides, at the stage of formation of boehmite, doping metal ions can easily enter the structure. These ions are placed in the interlayer space and in defects of vacancy type. During transformation of boehmite into corundum such ions as Fe^{+3}, and Cr^{+3} take isomorphic places in lattice corundum.

Tables II and III present the mechanical properties of fine-crystalline corundum. It is necessary to note the high mechanical strength of sample 7. It corresponds to corundum doped by lanthanum ions. Pure corundum shows a mechanical strength close to that of synthesized diamonds of DS 4–6 classes. The doped corundum exceeds in mechanical strength the synthetic diamond of the higher class (DS 15).

TABLE I Impurity contents (%) in the inital material and in synthesized corundum

Impurity	*Starting material* γ-$Al(OH)_3$	*Corundum* α-Al_2O_3
Si	$1 \cdot 10^{-3}$	$5 \cdot 10^{-4}$
Mn	$< 3 \cdot 10^{-4}$	$< 3 \cdot 10^{-4}$
Mg	$7 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
Fe	$1 \cdot 10^{-3}$	$5 \cdot 10^{-4}$
Ni	$5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Cr	$< 5 \cdot 10^{-4}$	$< 5 \cdot 10^{-4}$
Cu	$5 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
Ca	$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
Co	$< 1 \cdot 10^{-4}$	$< 1 \cdot 10^{-4}$
Ti	$5 \cdot 10^{-4}$	$< 5 \cdot 10^{-4}$
Pb	$< 5 \cdot 10^{-5}$	$< 5 \cdot 10^{-5}$

TABLE II Mechanical strength of fine-crystalline corundum and diamond

	Crystals size,	*Mechanical strength, N*		
N	*μm*	*Corundum*	*Diamond*	*Type of diamond*
1	200/160	10.1	8.0	DS 6
2	80/50	3.8	4.4	DS 6
3	80/63	3.9	4.4	DS 6
4	125/100	3.9	4.1	DS 4
5	100/80	3.3	3.6	DS 4
6	100/63	2.3	1.8	DS 2
7	250/200	20.3	17.3	DS 15

TABLE III Abrasive ability of fine-crystalline corundum

N	*Crystals size* μm	*Form of crystals*	*Abrasive ability* g/30 min	*Relative abrasive ability*	
				Ratio to diamond	*Ratio to electrocorundum*
1	4/3	Isometric bipyramids	0.066	0.76	1.4
2	7/5	Hexagonal plates ($d/l=10$)	0.070	0.8	2.9
3	12/8	Isometric bipyramids	0.36	0.52	
4	15/13	Truncated bipyramids ($d/l=5$)	0.47	0.68	
5	20/15	Hexagonal plates ($d/l=7-10$)	0.72	0.59	
6	30/26	Hexagonal prisms ($d/l=1$)	1.33	0.75	
7	40/30	Isometric bipyramids	0.65	0.36	1.9
8	180/100	Thickening hexagonal plates ($d/l=5-7$)	0.73	0.24	

In Table III the data obtained during the tests of abrasive ability of synthesized fine-crystalline corundum is listed. Platelets of corundum with size of 5 to 7 microns have abrasive ability similar to the one of synthetic diamond.

On the basis of these data on transformations of silica and alumina in supercritical water, new technologies of fine-crystalline quartz and corundum have been developed [12]. These technologies are carried out at plants of Russian Federation.

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