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Role of precursor compaction and water vapour pressure during synthesis of corundum in supercritical water

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Abstract

The present paper is devoted to studying the influence of water vapour pressure on the α -Al₂O₃ phase nucleation process and on the size distribution and doping level of the synthesized fine crystalline corundum. The effect of preliminary compaction of precursors and pressure variation on the corundum synthesis process in water vapour was also investigated. The products of synthesis were studied by various physical and chemical methods. It was found that the rise of water vapour pressure during synthesis leads to diminution of the concentration of nucleation centres and promotes increase of the corundum crystal size. The higher the pressure the more perfect the corundum crystals that are formed, having lower concentration of defects.

1. Introduction

Modern industry demands provision of certain physical characteristics of fine crystalline materials it uses. One of these characteristics is crystal size and size distribution of crystalline powders. Both doped corundum and undoped corundum are used as abrasive powders for industrial, optical or lapidary polishing. In their earlier works the present authors have investigated the mechanism and kinetics of the process of forming corundum in water vapour at sub- and supercritical conditions [1, 2].

The present paper is devoted to study of the influence of water vapour pressure on the size distribution of the synthesized fine crystalline doped or undoped corundum. The influence of water vapour pressure on parameters of doping of the corundum produced is also investigated. It was found that the α -Al₂O₃ phase nucleation process depends on the pressure of the water vapour. Additionally, the effect of preliminary compaction of different precursors on the process of corundum synthesis in water vapour was examined.

2. Experimental methods

Two kinds of raw material were used in the present work. These were hydrargillite of tradename 'GD 00', with sodium impurity content of up to 0.48% by mass, and hydrargillite of tradename 'GD 00M', with sodium impurity content of not more than 0.08% by mass.

Corundum synthesis was carried out in a laboratory autoclave having reaction volume of 18 cm³. Two ways of preparation of the reaction mixture were used. In the first method, dry hydrargillite was placed into container, and a pre-calculated amount of water or a dopant containing solution was added to the container. This allowed provision of a certain pressure of water vapour during synthesis. The container was put into the autoclave. Then the autoclave was closed and heated up to the required temperature, which was maintained for a certain time. In the second method, the same amount of the dopant (Cr or Mn) containing solution was placed in the container with dry hydrargillite. The produced suspension was carefully mixed. An additional amount of water was placed between the inner wall of the autoclave and the container. This allowed provision of a certain pressure of water vapour in the autoclave.

To investigate the effect of preliminary compaction of precursor on the corundum synthesis process mixtures (1:1) of hydrargillite with alumina or boehmite with alumina were used as precursors. The alumina consisted of a mixture of amorphous phases of aluminium oxide with admixture of fine weakly ordered corundum. The precursors were compacted by a hydraulic press at a pressure of 20 MPa.

The synthesized products were explored by x-ray methods (diffractometer DRON-3M in filtered Cu K α radiation), photoluminescence (SDL-2M at room temperature in the interval 260–800 nm using excitation of corundum luminescence by light with wavelength of 254 nm), IR spectroscopy (IR Fourier spectrometer EQUINOX 55/S in the range of 4000–400 cm⁻¹), optical spectroscopy (the diffuse reflection spectra were measured on a Specord-M 40 spectrophotometer) and electronic microscopy (Cam Scan Series 2). The mass-spectrometry investigations were carried out using an MI-1311 mass spectrometer.

3. Results

As was reported earlier [1] the hydrargillite is transformed in an atmosphere of super-critical water vapour to corundum through an intermediate substance—boehmite: $\text{Al}(\text{OH})_3 \rightarrow \text{AlOOH} + \text{H}_2\text{O} \rightarrow \alpha\text{-Al}_2\text{O}_3$. The rate of formation, habitus and size of corundum crystals depend on the temperature, pressure and composition of the dopants.

The influence of vapour water pressure on synthesized crystal size was investigated in an interval of pressures of 20–27.7 MPa. Synthesis of corundum was performed from hydrargillite (GD 00) containing 0.48% of sodium impurity. The corundum synthesis was carried out at 400 °C over 14.5 h.

Figure 1 shows that the product of synthesis (corundum) obtained at a pressure of 12.5 MPa and a temperature of 400 °C contains 15% of the intermediate (boehmite), and products of synthesis obtained at pressure higher than 24 MPa contain only corundum.

Figure 2 shows the dependence of time needed for the complete transformation of hydrargillite into corundum on temperature. Comparison between figures 1 and 3 shows that dependences of the conversion of the hydrargillite to corundum on water vapour pressure have similar form at both tested temperatures (400 and 422 °C). This dependence of degree of hydrargillite transformation to corundum on pressure can be described by the following equation:

$$\alpha = 0.7 \exp(P/6.25) \quad (1)$$

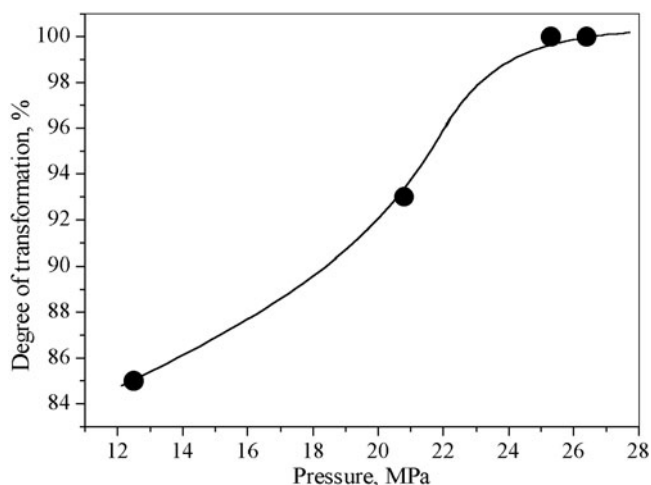


Figure 1. Conversion of hydrargillite 'GD 00' into corundum versus water vapour pressure. $T = 400\text{ }^{\circ}\text{C}$; $\tau = 14.5\text{ h}$.

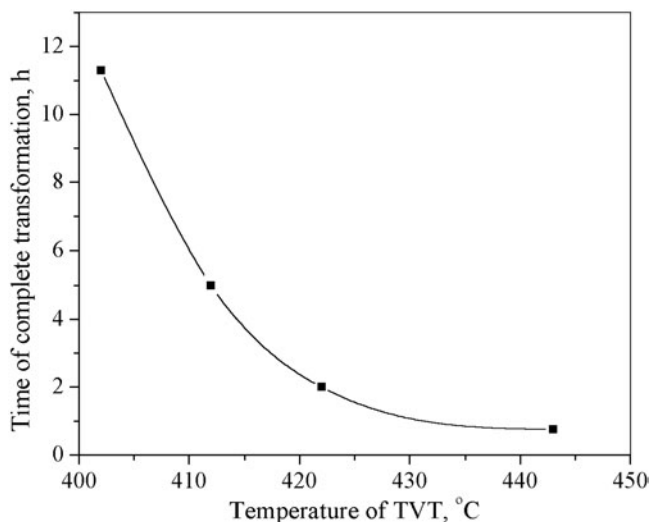


Figure 2. Dependence of time to complete formation of corundum on temperature; $\gamma = 20$.

where α is the degree of transformation and P is the water vapour pressure at $422\text{ }^{\circ}\text{C}$ and different fillings of the autoclave by water.

The rate of the hydrargillite transformation to corundum increases with a rise of pressure and temperature.

The habitus of formed corundum crystals depends on water vapour pressure and temperature very weakly. Figure 4 represents the electron microphotographs of the undoped corundum synthesized from hydrargillite 'GD 00M' at pressures of 20.0 MPa (a) and 27.7 MPa (b). The crystals have bipyramidal form in both cases.

An increase of the crystal size was observed as the pressure rose. Thus the pressure decreasing to very low values (2 MPa) results in formation of corundum crystals having a size of about a micron. These crystals also have bipyramidal form (figure 5). Such low pressure

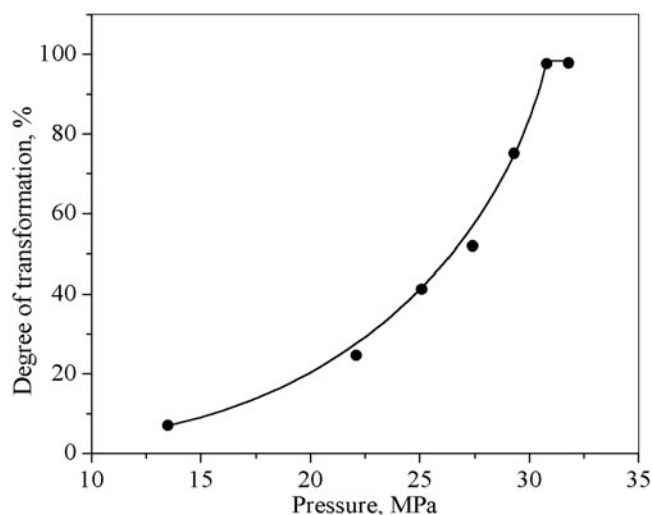


Figure 3. Conversion of hydrargillite 'GD 00' to corundum versus water vapour pressure; $T = 422^\circ\text{C}$; 1.5 h TVT.

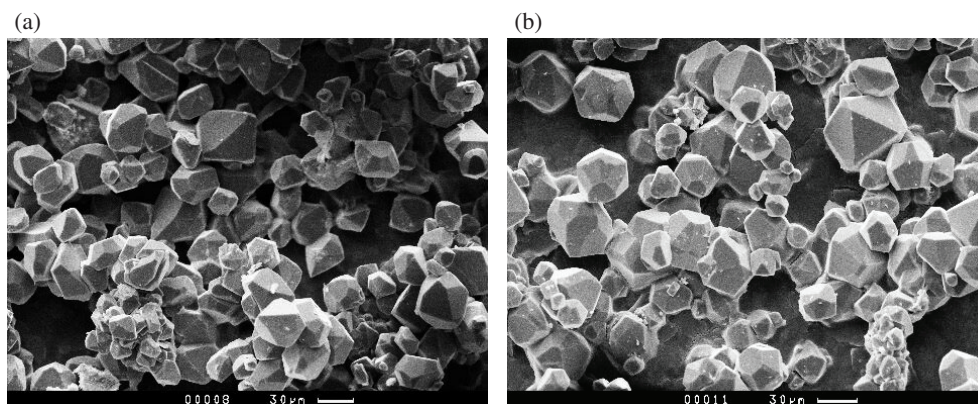


Figure 4. Undoped corundum synthesized at 20.0 MPa (a) and 27.7 MPa (b).

was obtained in the autoclave due to a loss of the water from the boehmite structure the during the corundum formation process. In this case boehmite was used as a raw material, and water was not added to the autoclave. Thermovaporous treatment (TVT) of boehmite containing different concentrations of manganese at low pressure allowed us to obtain well faceted fine crystalline corundum with the crystal size varying in the interval of $0.5\text{--}3\ \mu\text{m}$ regardless of the concentration of manganese (figure 5).

Figure 6 shows the size distribution of corundum crystals synthesized at different pressures. Increasing water vapour pressure leads to upsizing of corundum crystals and broadening of the crystal size distribution. The composition of impurity contained in the raw material and the nature of the dopant influence the corundum formation rate and the crystal size.

Hydrargillite 'GD 00M' with a sodium impurity content of not more than 0.08% was subjected to thermovaporous treatment for 46 h at a temperature of 400°C within the water vapour pressure range of 20.0–27.7 MPa. The synthesis was carried out in the presence

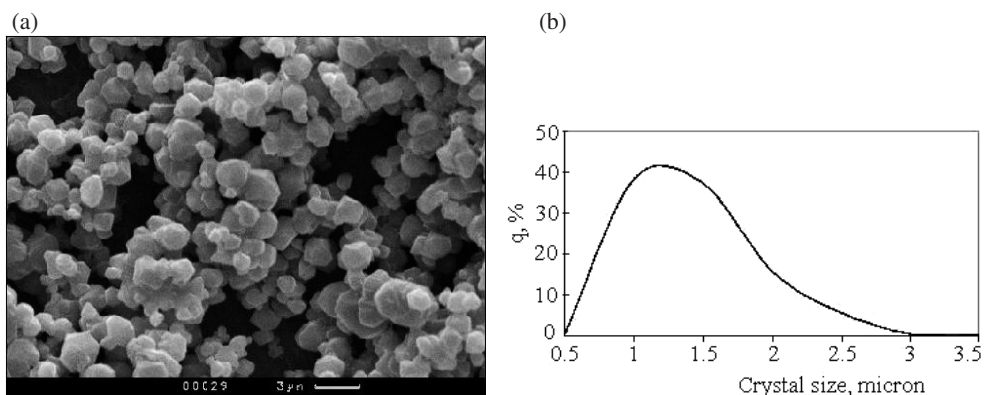


Figure 5. Electron microphotograph and the crystal size distribution curve of corundum obtained by thermovaporous treatment of boehmite doped by manganese at pressure 2 MPa.

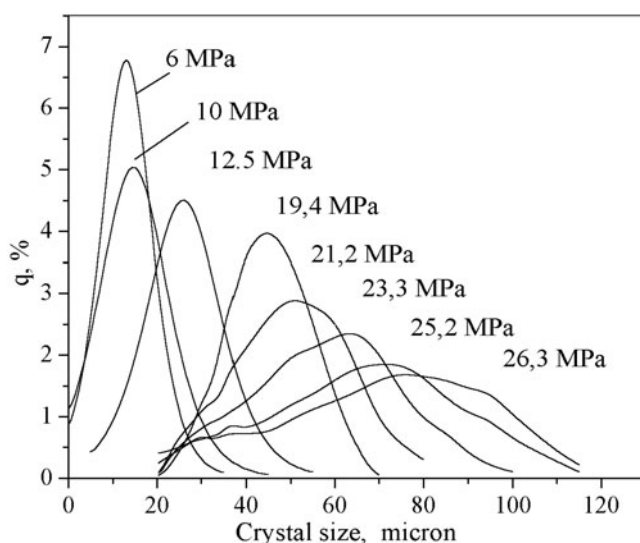


Figure 6. Size distribution of corundum crystals synthesized at different pressures; $T = 400\text{ }^{\circ}\text{C}$; $\tau = 92\text{ h}$.

of a dopant (chromium, Cr). Chromium was added to the reacting system as a solution of ammonium dichromate. The chromium content in the solution was 0.4% by mass of the corundum formed. X-ray analysis of synthesized products showed 100% of corundum. Decreasing sodium content in the raw material and chromium addition lead to the formation of finer crystals in the same range of pressure and temperature. At the same time increasing water vapour pressure leads to upsizing of the corundum crystals synthesized (figure 7).

Optical reflection spectra of the doped corundum synthesized at various water vapour pressures were studied. This allowed us to investigate the effect of pressure on the process of corundum doping by chromium during its synthesis.

Figure 8 shows the diffuse reflection spectra (DR spectra) of fine crystalline corundum doped by chromium. The corundum samples were synthesized at water vapour pressures of 20.0 and 27.7 MPa respectively. The DR spectra of these samples have three absorption bands

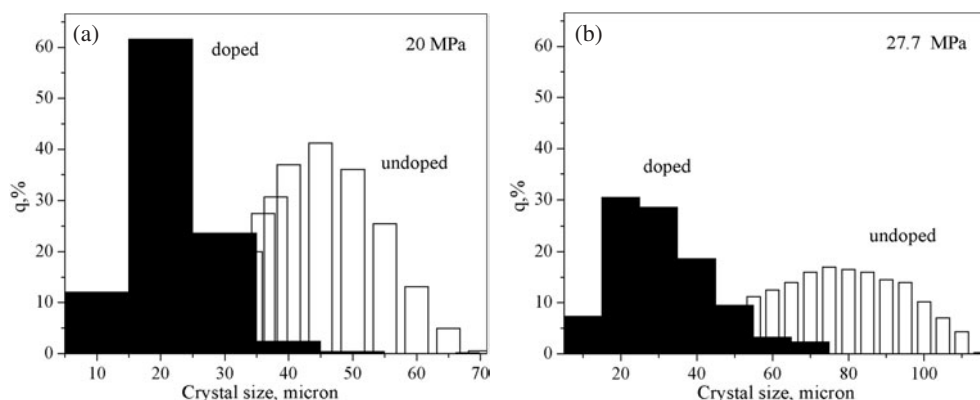


Figure 7. Size distribution of doped corundum crystals (Cr), synthesized under different pressures (20 and 27.7 MPa). Raw material is hydrargillite 'GD 00M'; $T = 400^\circ\text{C}$; $\tau = 46$ h.

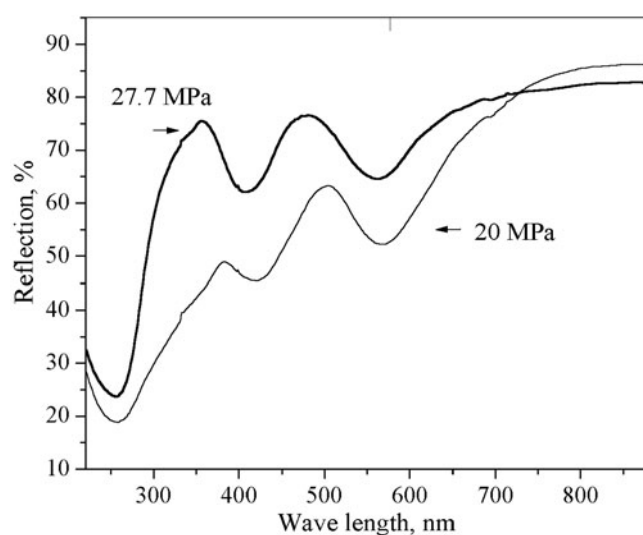


Figure 8. The electron reflectance spectra of doped corundum (Cr) synthesized at pressures of 20 and 27.7 MPa respectively. Raw material is hydrargillite 'GD 00M'; $T = 400^\circ\text{C}$; $\tau = 46$ h.

with reflection minima near 260, 410 and 560 nm. These absorption bands can be attributed to Cr(III) ions, which are in a feebly distorted octahedral oxygen environment. The distortion is stipulated by a small contribution of a trigonal crystalline field [3].

The DR spectra of all samples of corundum doped by chromium were registered after ablation of the samples. The synthesized corundum powders were washed out multiple times in hot distilled water to remove chromium ions adsorbed at the surface of the crystals. From the DR spectra the chromium content in doped corundum was determined. The chromium concentration was calculated using the parameter R of the Kubelka–Munk equation [4].

$$F(R) = (1 - R)^2 / 2R = 2.303ac/s \quad (2)$$

where R is reflectance; a is the extinction factor; c is the concentration of the absorbent component Cr(III) ions and s is a scattering coefficient. The extinction factor was found from DR spectra of the standard corundum samples with fixed content of chromium. The basic

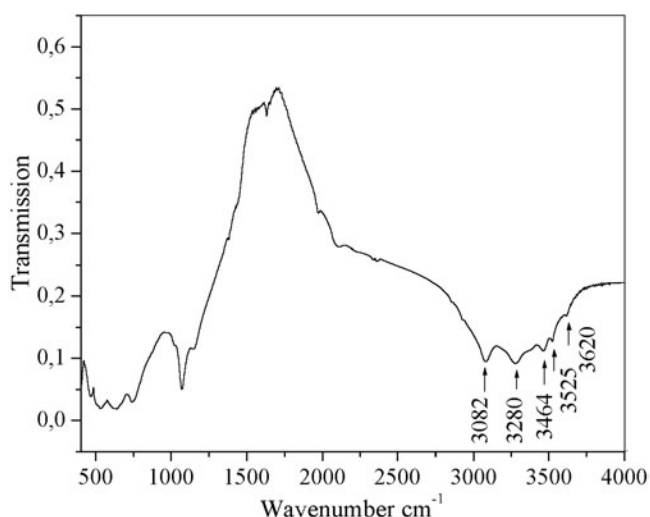


Figure 9. IR spectrum of the corundum synthesized at a vapour pressure of 12.5 MPa.

Table 1. The chromium concentration in doped corundum versus water vapour pressure.

	20	27	20	24.8	27.7
	(water in	(water in	(water in	(water in	(water in
	container)	container)	autoclave)	autoclave)	autoclave)
<i>P</i> (MPa)	0.10	0.04	0.10	0.095	0.08
Cr (% mass)					

fraction of crystals (up to 80%) in the standards was in the size range of 10–50 μm . This size distribution corresponds to the investigated samples and the scattering coefficient was a constant in all cases. The values of chromium content in the corundum samples were calculated using amplitudes of two absorption bands with wavelength reflection minima near 410 and 560 nm. The concentrations calculated for one sample using two bands were equal. The results of the calculation are presented in table 1.

The data in table 1 show that the increase of water vapour pressure during synthesis leads to a decrease of the chromium content in the corundum.

The peculiarity of the method of corundum synthesis used is the formation of corundum crystals in the atmosphere of a water fluid. The presence of residual hydroxyls in the structure of corundum synthesized at various water vapour pressures was investigated by means of IR spectroscopy.

IR spectra were recorded for samples synthesized at pressures of 12.5 and 26.4 MPa correspondingly. The investigation of residual hydroxyls in the corundum synthesized was carried by the IR-spectroscopy method using an 'EQUINOX 55/S' spectrometer. It is seen (figure 9) that in the IR spectra of the sample synthesized at a pressure of 12.5 MPa (15% boehmite) the characteristic absorption bands of boehmite traces ($\nu\text{-OH}$, 3280 and 3080 cm^{-1}) present. The other three absorption bands relate to hydroxyl vibration in the corundum structure.

Indeed, the absorption trace bands with maxima 3280 and 3080 cm^{-1} are absent in spectra of the sample produced at the pressure of 26.4 MPa (figure 10). The sample represents 100% corundum. Two absorption bands in spectra of this sample with the wavelength maxima at 3464, 3525 and 3620 cm^{-1} correspond to oscillations of residual hydroxyls in the structure of

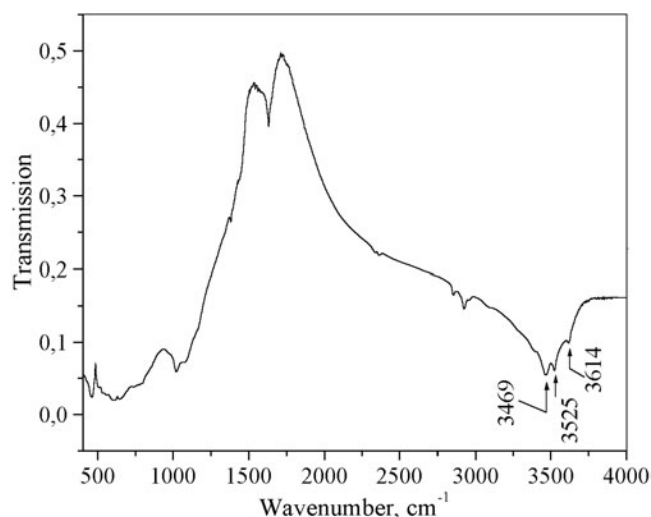


Figure 10. IR spectrum of the corundum synthesized at a water vapour pressure of 26.4 MPa.

the corundum. The region of the spectra at 400–650 cm^{-1} relates to the structural vibrations (Al–O) of corundum. The absorption bands have low resolution in this region. One can assume that the structure of this corundum sample has many vacancy defects, and the hydroxyl groups are placed in these defects. Increase of the synthesis duration is usually accompanied by an ordering of the corundum structure, healing of the defects and decrease of hydroxyl content. The increase of pressure results in the decrease of the content of vacancies and hydroxyls.

During doping of corundum the metal ion displaces hydroxyl in a vacancy. As the mass-spectrometric studies have shown, the doped corundum contains only a few hydroxyls.

The vacancies in corundum can be exhibited as optically active F-centres. In the corundum luminescence spectrum (excitation by light of wavelength 254 nm) the F-centres (the oxygen vacancies with two entrapped electrons) are characterized by a band in the range of 410–420 nm; F⁺-centres (the oxygen vacancies with one entrapped electron) have a band in the spectrum of luminescence in the wavelength interval of 327–335 nm. Figure 11 shows the spectra of luminescence of corundum samples synthesized at different water vapour pressures. The band at 678 nm is caused by Mn⁴⁺ ions; the band at 694 nm is caused by Cr³⁺ ions imparted to the corundum structure during synthesis as an impurity. The intensity of corundum luminescence bands depends on the water vapour pressure during synthesis. It is shown that as of the pressure increases the vacancy concentration decreases just as the quantity of optically active centres on the basis of Mn⁴⁺ and Cr³⁺.

As has been shown [5], the process of corundum crystal formation in supercritical water fluid proceeds in a solid phase. One can assume that the mass transfer process takes place on the phase boundary during contact of particles. So the effect of compaction of the precursor on the crystal size of corundum synthesized was investigated. The pressing was performed at a pressure of 20 MPa. As a raw material an intermixture of boehmite and alumina (1:1) with crystals of 1–5 μm was used. Conditions of synthesis and results of the experiments are represented in table 2. In all cases corundum was produced.

One can see that irrespective of whether precursor was compacted or not the addition of alumina results in formation of corundum with the particle size of 1–5 μm such as the crystals of alumina.

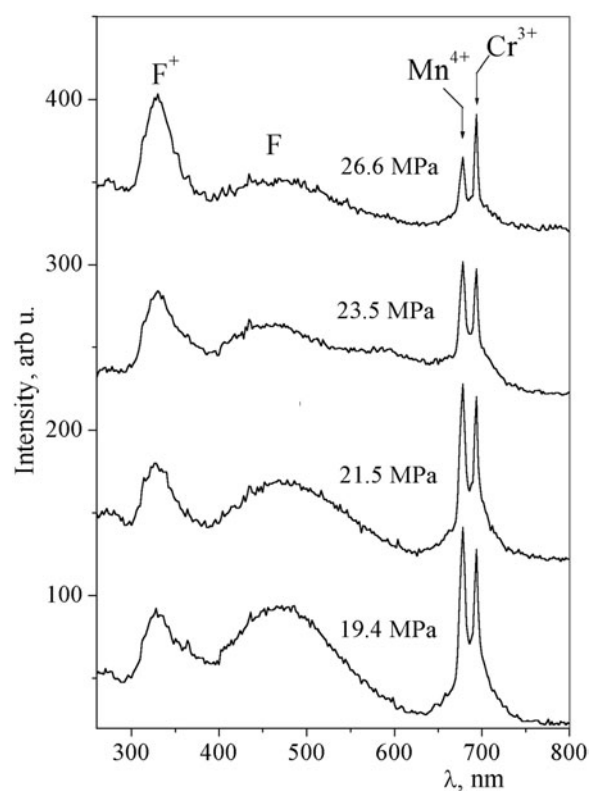


Figure 11. Spectrum of luminescence of corundum synthesized at different water vapour pressures. (Exciting light wavelength—254 nm.)

Table 2. Effect of precursor compaction on corundum crystal size.

Precursor	Compaction	TVT conditions			Size of crystals (μm)
		T ($^{\circ}\text{C}$)	P (MPa)	τ (h)	
1 Boehmite/alumina	+	400	27.5	90	1–3
2 Boehmite	+	400	27.5	90	20–30
3 Boehmite/alumina, 0.2% Cr	+	400	27.5	90	2–5
4 Boehmite/alumina, 1% NaOH,	+	400	27.5	90	2–3
5 Boehmite/alumina, 1% NaOH,	–	400	27.5	90	2–5
6 Hydrargillite/alumina, 1% NaOH	–	400	27.5	48	1–5
7 Hydrargillite/alumina	–	400	27.5	48	1–5

4. Discussion

The present authors [6, 7] earlier reported that during synthesis of corundum in a water vapour atmosphere the dehydration of the precursor and intermediate takes place in the quasi-equilibrium conditions. Because of that, the water vapour pressure will affect the process of

corundum formation. Sizes of the corundum crystals synthesized depend on the relation of the α -Al₂O₃ phase nucleation rate and the growth rate of the crystals.

The production rate of corundum and its properties are determined, to a great extent, by the conditions of formation of boehmite (the intermediate) from hydrargillite. In the water fluid that reaches a temperature of 400 °C the structural water present in the boehmite begins to be lost before the traces of corundum are detected by x-ray methods. In the boehmite crystal lattice fragments of oxide structures appear first. Then they transmute into centres of formation of a new phase—corundum. The quantity of such centres is determined by the water pressure. At identical temperatures and thermovaporous treatment times the quantity of such centres is higher at lower pressures.

Generation of nucleation centres was stimulated by admixture with boehmite of fine alumina. It results in the formation of fine crystalline corundum (1–5 μ m). The same effect was obtained in the case of compaction of precursor with the addition of alumina. In this case fine crystals were also formed despite contact between particles. A similar effect was observed on preheating of hydrargillite in ambient air at a temperature of 300–400 °C. Moreover, due to preliminary elimination of water from the hydrargillite structure after thermovaporous treatment, fine crystals (1–5 μ m) of corundum were obtained. The rise of the water vapour pressure during thermovaporous treatment of precursor (boehmite or hydrargillite) results in diminution of concentration of nucleation centres and promotes an increase of the corundum crystal size (figure 6).

The rise of pressure results not only in an increase of the crystals size, but also in obtaining a more perfect structure of crystals: the concentration of vacancies—defects and residual hydroxyl groups decreases (figures 9 and 10). Moreover, formation of crystals having more perfect structure with a smaller content of vacancies makes penetration of the doping ions into the crystal lattice more difficult.

As a result of increasing pressure the quantity of doping ions incorporated into the corundum lattice decreases (figure 8; table 1).

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