DOPING OF CORUNDUM WITH CERIUM DURING SYNTHESIS IN WATER FLUID

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ABSTRACT

Doping of fine crystalline corundum has performed during synthesis in water fluid at T=415°C and P=21.6-31.6 MPa with concentration of cerium in interval 0.001 – 0.25 % in reaction medium. Kinetics and mechanism of corundum (α-Al_2O_3) formation from $Al(OH)_3$ (hydrargillite) in supercritical water fluid (SCWF) in presence of cerium ions were investigated. The hydrargillite was transformed into Ce-doped boehmite, which then into the powder of fine crystalline corundum doped with cerium at 415°C is transformed. An induction period precedes the formation of corundum from boehmite, as in the case of a presence of dopant, so also without it. The size of corundum crystals was growing with an increase of pressure and content of cerium ions. The doping of boehmite and corundum results in appearance of absorption bands of cerium ions in the diffuse reflection spectra. At lighting in the absorption band the luminescence of cerium ions as in samples of boehmite and corundum is observed. The luminescent emission of cerium ions in corundum (at 370 nm) is increased with the fluid pressure during synthesis. The heating in vacuum at 1400°C leads to decrease of the luminescence intensity. It is evidence that in the medium of supercritical water the cerium ions form in the structures of boehmite and corundum a complex with hydroxyl groups, which is a luminescence center of Ce-doped corundum synthesized in supercritical water fluid.

INTRODUCTON

Due to boom in development and manufacture of new light sources, for example light emitting diodes (LED), the technologies of the UV-light-emissive luminophors production are of great importance. Cerium-doped corundum is one of such materials. Only few works devoted to the synthesis of the Ce^{3+}-doped corundum are presented in the literature [1-3]. During last two decades the method of the oxide synthesis in the supercritical water fluid was developed in our laboratory. We applied this method for the synthesis of corundum doped with such elements as Co, Mn, Cr as well as for the synthesis of the complex oxides [4]. In this report we developed the method of the synthesis of fine crystalline α-Al_2O_3:Ce in supercritical water fluid. Also kinetics, mechanism features and some unusual properties of the product were investigated. The best of our knowledge, this is the first example of cerium-doped corundum obtaining with the using SCWF-method.

MATERIALS AND METHODS

Cerium-doped corundum was synthesized in laboratory autoclaves (12 – 18 ml). All starting materials purchased from commercial sources were of high purity grade. $Al(OH)_3$ (Hydrargillite GD00 of Pikalevo alumina plant) was used as starting material. Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) was used as doping agent. For corrosion prevention 0.2 ml of

morpholine aq. solution (0.02 % v/v) was added into reaction mixture. Ce^{3+} concentration in reaction media was calculated relative to aluminum oxide.

Initial water suspension of the reagent mixture was placed into an autoclave in a stainless steel vessel. Water was poured inside this vessel. The autoclaves were heated to 415 °C (heating rate ~ 3°/min) and held at this temperature for indicated time period. Water fluid pressure reached 21.6 to 31.6 MPa at this temperature and strongly depends on filling degree. The X-ray diffraction patterns of synthesis products were collected from STOE and DRON-3M diffractometers using Cu$K\alpha$ radiation. The photoluminescence spectra of the samples were obtained on SDL-2M spectrometer. DRK 120 (glow discharge conditions, the main band 254 nm) and DKsSh (210–800 nm) light sources were used for luminescence excitation. The size and shape of the crystals were studied using a Cam Scan Series 2 scanning electron microscope. The diffuse reflection spectra were studied over the range 220–900 nm on a Specord M40 spectrophotometer with $BaSO_4$ as reference. The additional absorption spectra were obtained by subtracting the diffuse reflection spectrum of a sample with a low dopant concentration from the diffuse reflection spectrum of a sample with a higher dopant concentration.

The thermal analyses were carried out in dynamic argon atmosphere (20 mL/min^{-1}) using Netzsch STA 449C thermal analyzer coupled with Netzsch Aeolos QMS 403C quadroupole mass-spectrometer. Differential scanning calorimetry (DCS), thermogravimetry (TG) and differential thermogravimetry DTG curves were obtained from the samples.

RESULTS

Kinetics

The kinetic curves of cerium-doped corundum formation in a supercritical water fluid at 415°C and $C(Ce^{3+})$= 0.02 or 0.5 % are shown in **Figure 1**. Transformation of hydrargillite into corundum occurs through the stage of boehmite formation. Full conversion of the hydrargillite into boehmite achieves at the temperatures above 200 °C. Initial point of the kinetic curves corresponds to the temperature 415 °C and the pressure of SCWF 29.6 MPa and, therefore, these curves describe isothermic boehmite transformation into corundum.
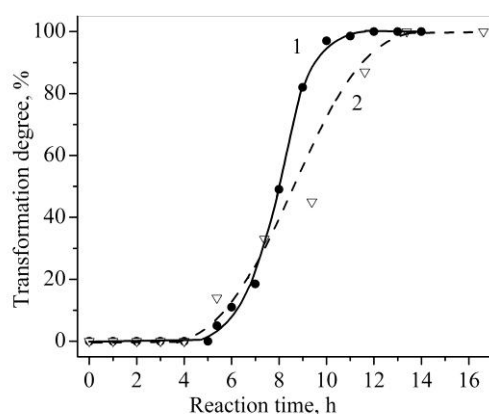

Figure 1. Kinetic curves of doped corundum formation. P_{H_2O} = 29.6 MPa, T = 415 °C.
1 – $C(Ce^{3+})$ = 0.02 %; 2 – $C(Ce^{3+})$ = 0.25 %.

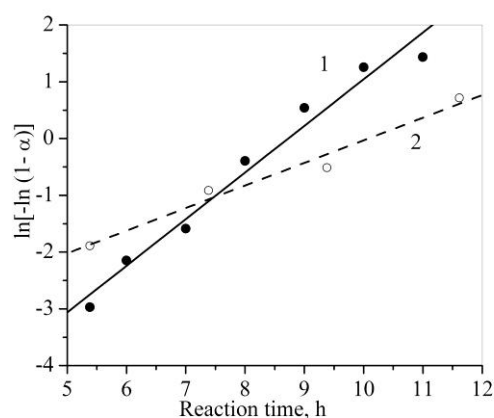**Figure 2.** Kinetic curves linearization.
1 – $C(Ce^{3+})$ = 0.02 % ;
2 – $C(Ce^{3+})$ = 0.25 %.

5 h-long induction period preceded the formation of crystals of corundum. According to **Figure 1** samples with higher concentration of cerium are characterized with prolonged reaction times necessary for full conversion achievement (13.5 h for samples with $C(Ce^{3+})$ = 0.5 % versus 11 h for samples with $C(Ce^{3+})$ = 0.02 %). Obtained kinetic curves could be linearized [5] in coordinates *ln[–ln(1 – α)] – t* (**Figure 2**). Decreasing the slope angle with increase of cerium concentration in the reaction medium denotes a decrease of corundum nucleation rate. The kinetics of the process corresponds to the solid-phase transformation mechanism. In medium of SCWF the intensive hydroxylation – dehydroxylation processes of hydrargillite and boehmite occur. This ensured that dehydroxylation their structures proceed in quasi-equilibrium condition and is accompanied by appearance of high solid phase mobility [5].

Transformation of boehmite into corundum is accompanied by increase of coherent-scattering regions (CSR) of both phases (**Figure 3**). Fast boehmite CSR increase during the induction period corresponds to structure ordering with followed corundum crystals formation, their ordering and growth. However when comparing the CRS dependencies in **Figure 3a** and **3b** can be seen that the increase of the cerium content in the reaction medium makes difficult a perfection of the boehmite and corundum structures.
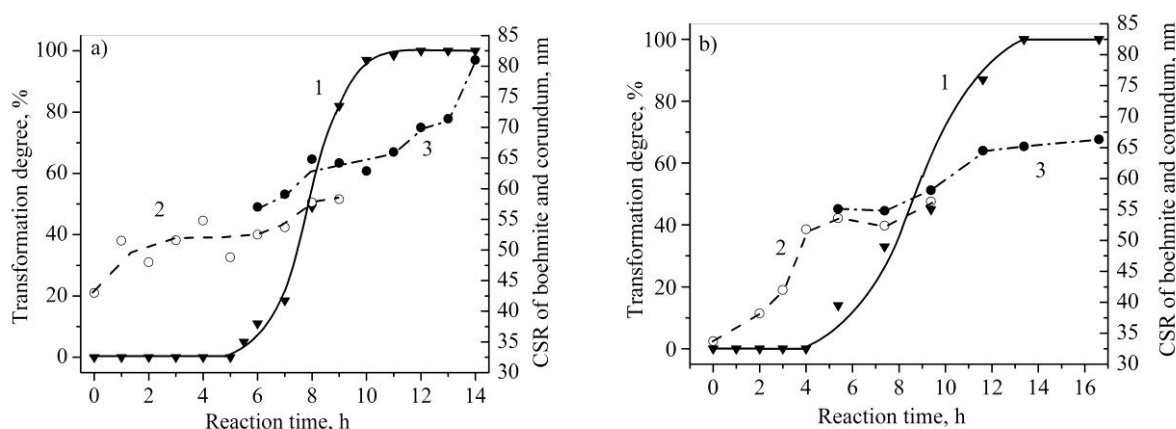

Figure 3. CSR change of corundum and boehmite during boehmite transformation into corundum at T = 415 °C, P_{H_2O} = 29.6 MPa. **a)** $C(Ce^{3+})$ = 0.02 %; **b)** $C(Ce^{3+})$ = 0.25 %.
1 – kinetic curve of corundum formation; 2 – boehmite CSR; 3 – corundum CSR.

Morphological studies
SEM imiges of initial hydrargillite particles, intermediate boehmite aggregates and corundum crystals formed are shown in **Figure 4**. Hydrargillite particles (**a, b**) morphology retains during initial transformation into boehmite aggregates (**c, d**). The primary crystals of corundum appear at the end of the induction period (**e, f**). Then they grow, them habit varies (**f**, **g**, **h, i**) [5]. High solid phase mobility determines the perfect faceting of crystals during their nucleation and growth. Corundum crystal size distributions were calculated from the microphotographs using method of linear segments. Data describing dependence of the mean size of the crystals formed on pressure and cerium ions concentration are summarized in **Figure 5**. SCWF pressure and dopant concentration increase both lead to significant rise of the crystal size. The increasing of fluid pressure leads to increase of growth rate of crystals, and increase of the cerium ions concentration suppresses the rate of corundum nucleation.
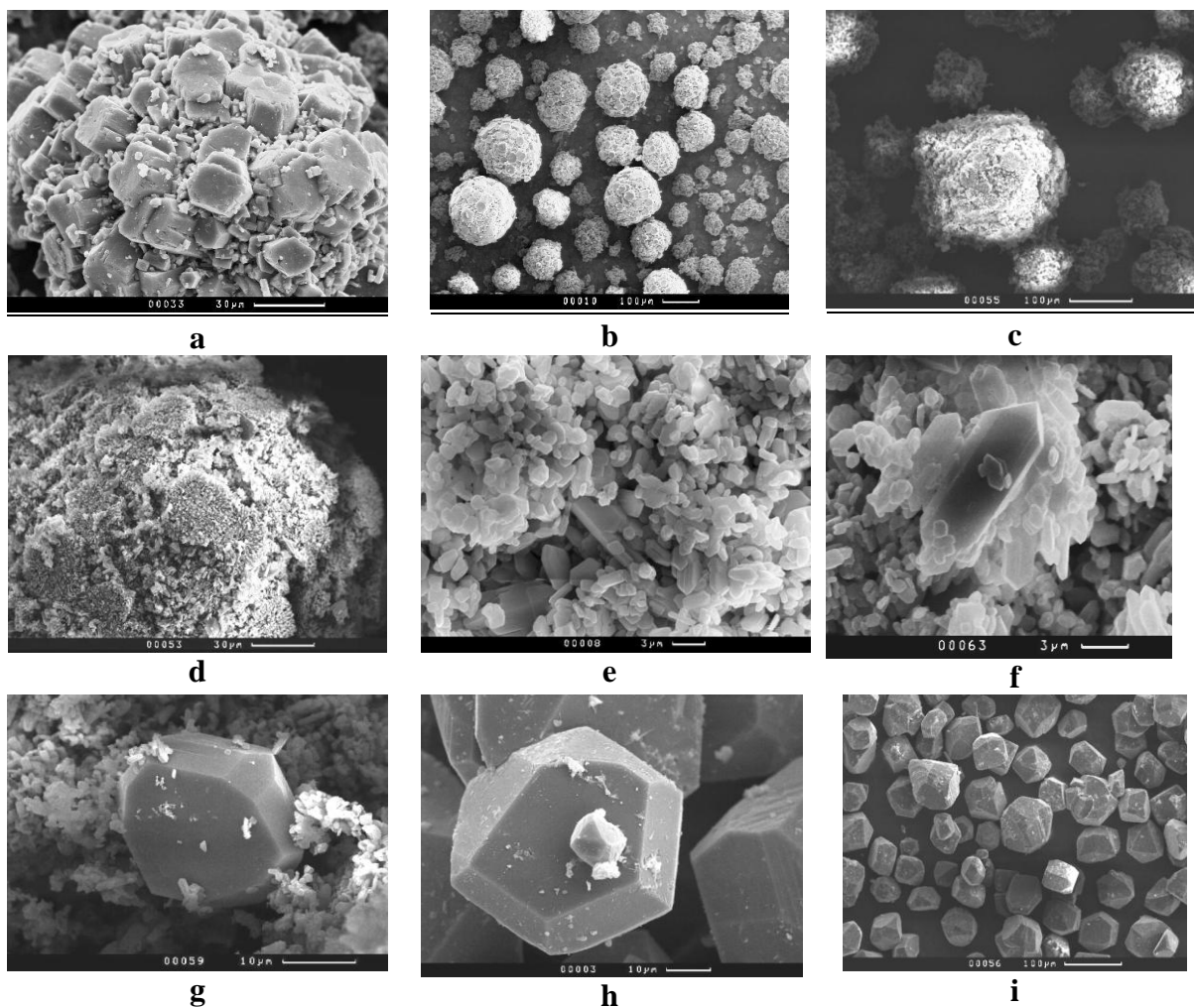
Figure 4. Initial hydrargillite particles (**a, b**), intermediate boehmite aggregates (**c, d**) or single particles (**e**) and corundum crystals formed (**f-i**). T = 415 °C; P_{H_2O} = 29.6 MPa
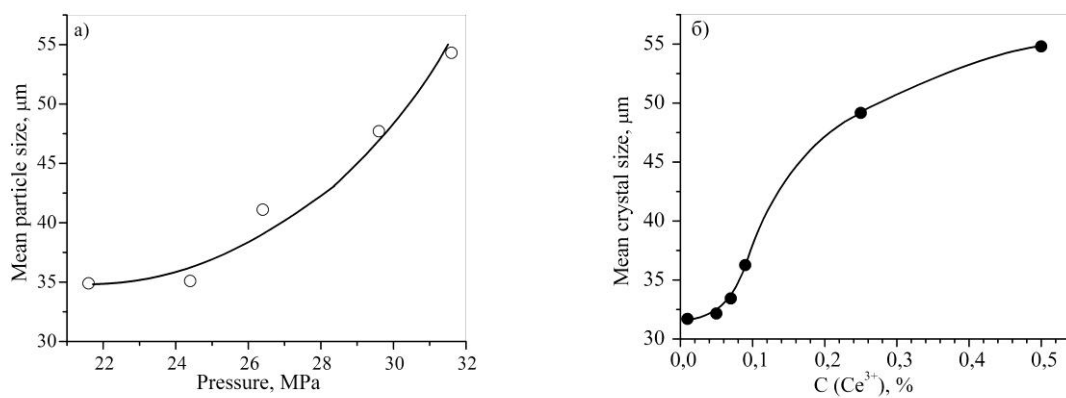

Figure 5. Dependences of mean crystal size: (**a**) on pressure of SCWF, $C(Ce^{3+})$ = 0.02 %, t_{synt} = 35 h., T = 415 °C and (**b**) on cerium ions concentration, P_{H_2O} = 29.6 MPa, t_{synt} = 21 h, T = 415 °C.

Doping mechanism

Analysis of the diffuse reflectance (DR) spectra of the samples obtained revealed appearance of the strong band about 310 nm (absent in a spectra of undoped samples) that which can be attributed to Ce^{3+}-ion light absorbance (**Figure 6a**). This fact elucidates the mechanism of aluminum-oxygen matrix doping by cerium ions. We speculate that doping occurred at the stage transformation of hydrargillite into boehmite and followed by conversion of cerium-doped boehmite into cerium-doped corundum (**Figure 6b**). The insets in **Figure 6** show the spectra of additional absorption due to Ce^{3+} ions embedded into the structure of boehmite (**Figure 6a**) and corundum (**Figure 6b**). It is seen that the absorption band of Ce^{3+} ions in corundum, compared with boehmite, is shifted toward the red by 21 nm. In both cases, bands have a complex shape, whose components are more resolved for Ce^{3+} ions in the corundum. The weak band around 236 nm is caused by the formation of F^+-centers. The absorption of Ce^{3+} ions has at least three components about 330 nm, 430 nm and 544 nm.
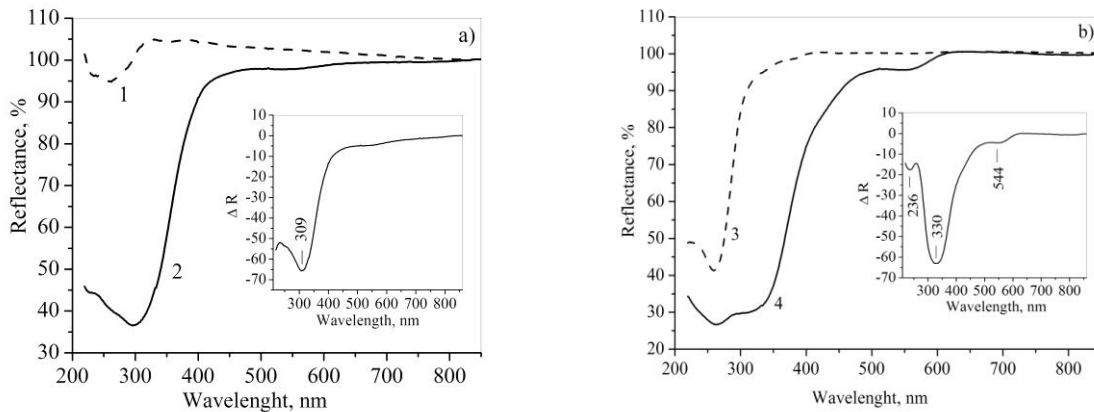

Figure 6. DR spectra of **a)** boehmite и **b)** – corundum (T_{synt}= 415 ^{o}C, P_{H_2O} = 29.6 MPa T_{synt}= 415 ^{o}C),
1 – undoped boehmite, (t_{synt} =1 h); 2 – doped boehmite (C(Ce) = 0.25%, t_{synt} = 1 h, T_{synt}= 415 ^{o}C)
3 –undoped corundum (t_{synt} =23 h); 4 – doped corundum (C(Ce^{3+}) = 0.25 %, t_{synt} =16.5 h, T_{synt}=415) ^{o}C
The insets show the spectra of additional absorption.

These results lead to the conclusion, that doping ions are adsorbed on particles of hydrargillite and boehmite and are involved into structural rearrangement along with aluminum ions. As a result, cerium ions uniformly distributed in the structure of crystals both boehmite and corundum.

Differential thermal analysis

Samples synthesized during induction period (0 – 4 hours, T_{synt}= 415 ^{o}C) were analyzed by differential thermal analysis. Typical thermogram of cerium-doped boehmite sample is shown in **Figure 7**. Analysis of TG curve revealed two-step weight loss of the samples during heating. In the beginning of induction period boehmite structure is enriched with water due to active hydroxylation process occurred before induction period (during autoclave heating to 415 ^{o}C). First step of the weight loss resulted from removal of excess water from boehmite with preservation of its structure (340 – 350 ^{o}C). Second step of the weight loss (555 – 565 ^{o}C) concerned with removal of water from the boehmite structure correspond to its full decomposition.

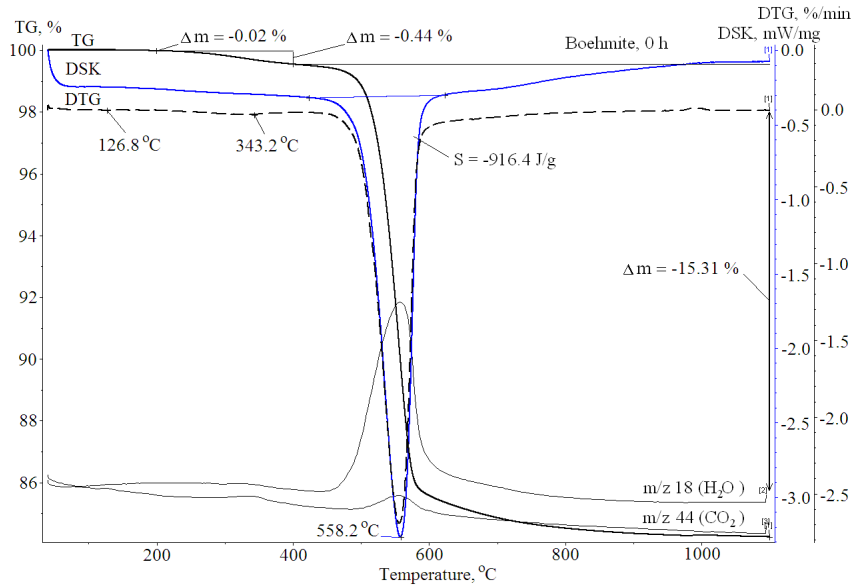**Figure 7.** Typical boehmite thermogram.
$C(Ce^{3+}) = 0.25\%$, $T_{synt} = 415$ °C, $P_{H_2O} = 29.6$ MPa, $t_{synt} = 0$ h

Dependence of boehmite mass change from reaction time is shown on Figure 8. Hence the structural water of this boehmite consist of two types - strongly bound structural hydroxyl groups and weakly bound water molecules in the interplanar space of the structure of boehmite.

The results show that the content of both types of hydroxyl groups decrease during the induction period. Consequently perfection of boehmite structure takes place during reversible dehydroxylation in state of quasi-equilibrium with SCWF. It should be noted that content of structural water in Ce-doped boehmite increases by about 0.5% compared with the undoped boehmite [6].
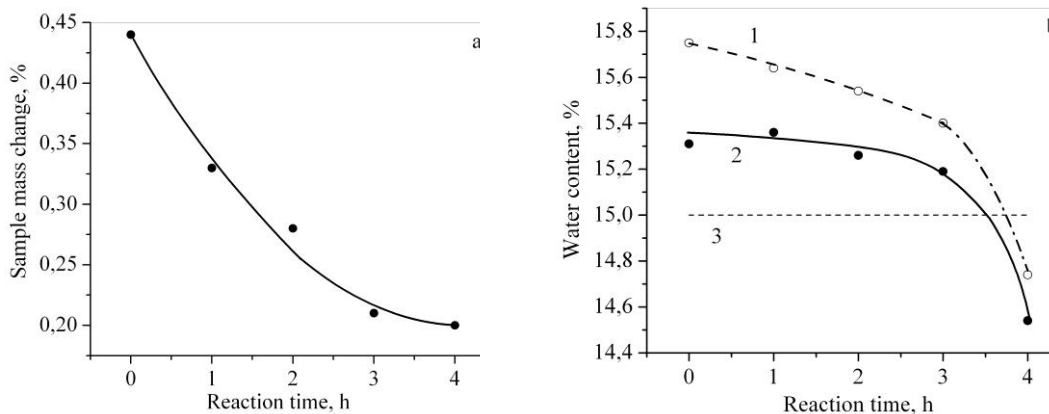

Figure 8. Dependence of boehmite mass change from reaction time, $C(Ce^{3+})=0.25\%$, $T_{synth} = 415$ °C, $P_{H_2O} = 29.6$ MPa; **a)** first step of the weight loss (removal of weakly bound water); **b) 1** – changes in full water content; **2** – second step of the weight loss (removal of water from the boehmite structure); **3** – stoichiometric line of undoped boehmite.

6

Luminescence

Typical luminescence spectra of the obtained samples are presented in the Figure 9 and 10. Excitation light with the wavelength 254 nm was used. The boehmite and corundum both have broad absorption band about 200 – 400 nm. Doping boehmite with cerium leads to appearance a strong band of luminescence (Figure 9) with characteristic doublet spectrum of Ce^{3+} [7, 8] emission at 311 and 332 nm. In the luminescence spectrum of the cerium-doped corundum strong band with maximum about 350 nm appears (Figure 10). It also has a complex shape, but the components are more broadened that in the case of boehmite. Around 420 nm the luminescence band of F-centers [9-11] located. In the red region of the corundum luminescence spectrum are clearly visible the bands of impurity Mn^{4+} and Cr^{3+} ions. In contrast to the cerium ions, they do not have the luminescence bands in boehmite.
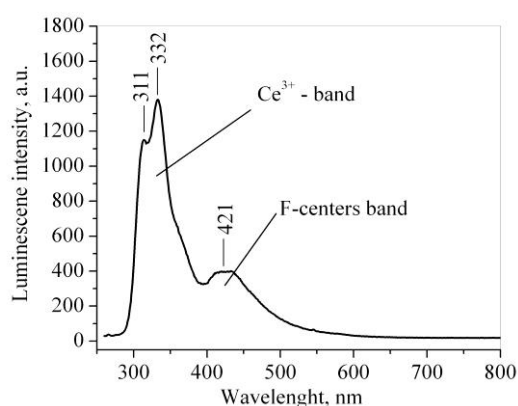

Figure 9. Typical luminescence spectrum of cerium-doped boehmite. $C(Ce^{3+}) = 0.02\%$, $T_{synt} = 415\ ^{o}C$, $P_{H_2O} = 29.6$ MPa, $t_{synt} = 2$ h.

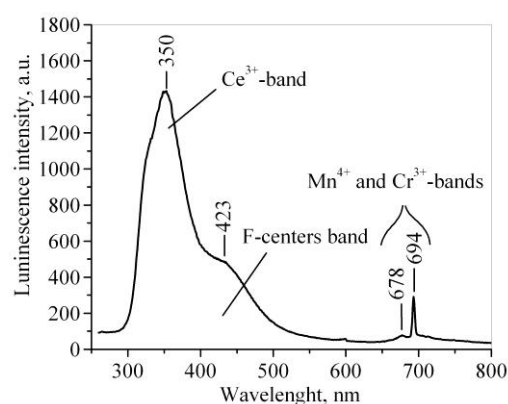**Figure 10.** Typical luminescence spectrum of cerium-doped corundum. $C(Ce^{3+}) = 0.02\%$, $T_{synt} = 415\ ^{o}C$, $P_{H_2O} = 21.6$ MPa, $t_{synt} = 35$ h.

To investigate dependence of Ce^{3+}-luminescence in boehmite and corundum from reaction time a set of samples with $C(Ce^{3+}) = 0.02$ % was synthesized. Results are presented in the Figure 11. The intensity of Ce^{3+}-luminescence reduces during induction period. Over this time Ce^{3+}-band has a form specific to boehmite. Maximal luminescence quenching occurs after 5-6 h treatment with SCWF. During this time dehydroxylation of boehmite (**Figure 8**) and perfection its structure occur (**Figure 3a**). During boehmite structure dehydration the luminescence of cerium ions is significantly reduced.

After the induction period the transformation of the boehmite into corundum started. Corundum formation is attended by appearance and growth of intensity of Ce^{3+} luminescence band. The spectra of samples synthesized in 6, 7, 10, 14 h of treatment by SCWF (11, 18.5, 80 and 100 % of corundum in the reaction products respectively) are presented in the Figure 12. It can be seen that as the formation of corundum the structure the luminescence band of Ce^{3+} ions takes the form characteristic for the Ce^{3+} doped corundum.

Set of samples with Ce^{3+}-concentration from 0.001 to 0.5 % was synthesized to investigate the concentration dependence of Ce3+-luminescence in corundum. Results are presented in the **Figure 13**. Maximal Ce^{3+}-luminescence intensity is observed at $C(Ce^{3+}) = 0.005$ % (**Figure 13, curve 1**). Significant red shift of the Ce^{3+}-band from 337 to 373 nm in $0.001 - 0.1$ % concentration range occur (**Figure 13, curve 2**). At cerium concentration about 0.1 % is

observed full quenching of Ce^{3+} ions luminescence. The Ce^{3+}-band red shift can be caused by local change of crystalline field at the formation of ions associates with increase their concentration in the corundum structure.
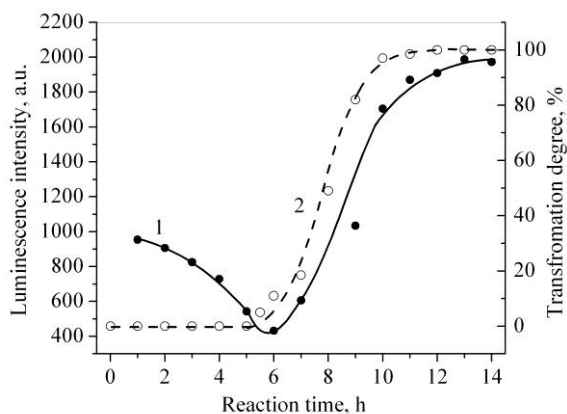

Figure 11. 1 - Dependence of the Ce^{3+} luminescense of boehmite and corundum on reaction time. 2 – kinetic curve of the cerium-doped corundum formation. $C(Ce^{3+}) = 0.02$ %, $P_{H_2O} = 29.6$ MPa, $T_{synt} = 415$ ^{o}C
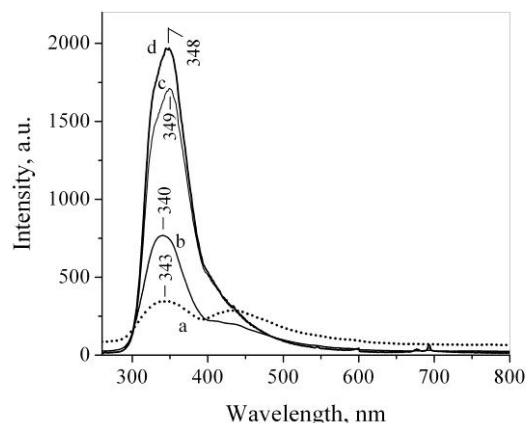

Figure 12. Luminescence spectra of the samples synthesized at different reaction times:

a) 6 h; b) 7 h; c) 10 h; d) 14 h;

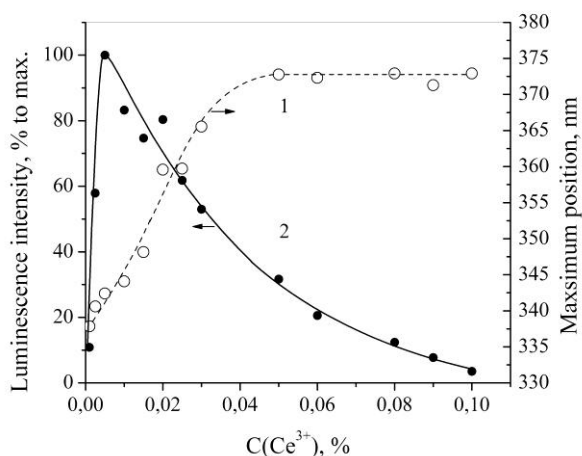$C(Ce^{3+}) = 0.02\%$, $P_{H_2O} = 29.6$ MPa, $T_{synt} = 415$ ^{o}C

Figure 13. Concentration dependence of the maximum position of Ce^{3+}-luminescence band 348 nm (1) and emission intensity (2) of the doped corundum synthesized at $P_{H_2O} = 29.6$ MPa, $T_{synt} = 415$ ^{o}C, $t_{synt} = 20 - 25$ h.
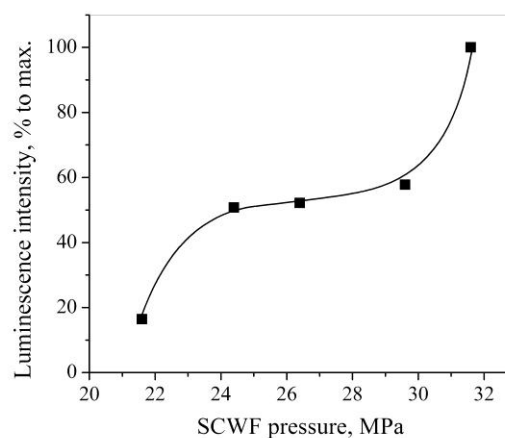

Figure 14. Dependence of the intensity of band 348 nm on SCWF pressure during Ce-doped corundum synthesis under conditions: $C(Ce^{3+}) = 0.02\%$, $T_{synt} = 415$ ^{o}C, $t_{synt} = 20 - 25$ h.

SCWF pressure dependence of corundum Ce^{3+}-luminescence was investigated in the range 21.6 – 31.6 MPa (**Figure 14**). It is seen that increase of the SCWF pressure leads not only to increase the size of the obtained crystals but also to luminescence intensity rise.

8

It allows concluding that the Ce^{3+} ions interact with hydroxyl groups and form complex defect and slow down the dehydroxylation of structure. As result the cerium ions influence on the rate of corundum formation and the size of crystals.
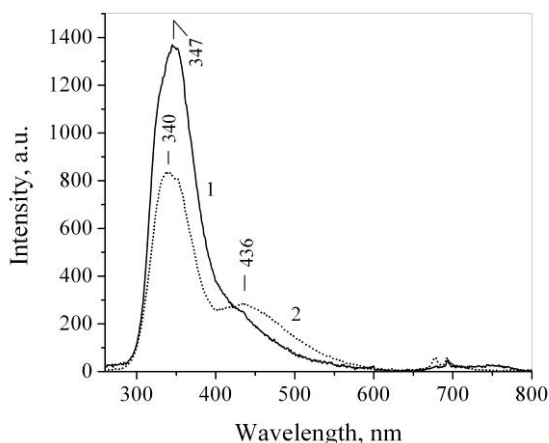

Figure 15. Influence of corundum annealing under vacuum at 1800 °C for 1 hour on luminescence of Ce^{3+} ions. 1 - before, 2 - after annealing.

The annealing of cerium-doped corundum at 1800 °C for 1 hour in a vacuum leads to the removal of residual hydroxyl groups and causes suppression of the cerium ions luminescence (**Figure 15**). Formation of oxygen vacancies during dehydroxylation of corundum at the annealing causes intensity increase of F-centers band (about 436 nm). It should be noted that annealing of the same sample in air at 1400 °C for 1 hour leads to a complete quenching of the Ce^{3+} ions luminescence apparently due to oxidation in Ce^{4+} ions. Therefore we can conclude that the hydroxyl groups stabilize the state of the cerium ions in synthesized corundum and boehmite samples in the form of Ce^{3+}.

CONCLUSION

The peculiarity of the transformation process of a solid-phase oxides and hydroxides in SCWF is the active participation of water molecules. Therefore reaction products contain residual hydroxyls in its structure. In process of doping this leads to the formation of the characteristic defect structure comprising ion-dopant and hydroxyl. In this regard, the optically active centers in Ce^{3+} doped corundum are very sensitive to heat treatment.

The investigation of kinetics and mechanism of corundum formation from hydrargillite in supercritical water fluid in presence of the Ce^{3+}-ions through the stage of boehmite formation occurred. Crystals size of synthesized corundum rises at the increase of Ce3+-concentration and pressure of SCWF. The doping with Ce3+-ions occurs at the stage of formation of boehmite from hydrargillite, followed during transformation of cerium-doped boehmite into cerium-doped corundum. Interaction of Ce^{3+}-ions with the structural hydroxyl groups influences on the formation of boehmite and corundum. The hydroxyl groups in structure of boehmite and corundum stabilize the state of the cerium ions in the form of Ce^{3+}.

The boehmite and corundum doped with cerium during synthesis in water fluid have the typical characteristics Ce^{3+}-ions luminescence. Maximal Ce^{3+}-luminescence intensity in corundum is observed at $C(Ce^{3+}) = 0.005$ %. It was found that SCWF pressure increase led to Ce^{3+}-ions luminescence intensity rise.

It is possible to make the conclusion, as a result of the carried out researches, that using SCWF as reaction medium, fine crystalline corundum doped with cerium having the wholly satisfactory optical characteristics can be obtained.

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