

# INFLUENCE OF MOLAR RATIO WATER FLUID/ $\text{Al}_2\text{O}_3$ ON SOLID PHASE COMPOSITION

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In the present work it was shown that a diminution of a molar ratio - water in fluid/ $\text{Al}_2\text{O}_3$  - slows down the process of the formation of boehmite and corundum from hydrargillite. In case values of this molar ratio less than 2, the tohdite ( $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) in products of alumina or of hydrargillite transformation in SCWF appears.

In case values of this molar ratio 1 - 0.7 the hydroxylation of  $\text{Al}_2\text{O}_3$  proceeds in direction of tohdite formation only. Thus, depending on a relation of water fluid moles to alumina moles the solid-phase transformation at the temperature of  $400^\circ\text{C}$  on various paths runs. In this work the tohdite was obtained in more soft conditions than by other authors.

## INTRODUCTION

Earlier with the participation of authors [1] the technology of fine-crystalline oxides was developed. This technology is based on thermo treatment in a water fluid of oxides, hydroxides and oxyhydroxides to obtain e.g. quartz or corundum. The transformation of oxides starts with formation of a partially hydrated intermediate. Due to quasi-equilibrium of processes of hydroxylation - dehydroxylation the coordination of structural ions changes with frequency inversely proportional energy of bond. The mechanism of selection of coherent positions of structural ions in lattice consists in accumulation of positions with a maximal lifetime [2].

## MATERIALS AND METHODS

The raw material, oxide, oxyhydroxide (boehmite, of the mark Apyral AOH 180DS) or aluminum hydroxide (hydrargillite, of the mark GD00) was put in the container inside of autoclave, and the water was filled in an autoclave (volume  $15 \text{ cm}^3$ ) outside of the container.

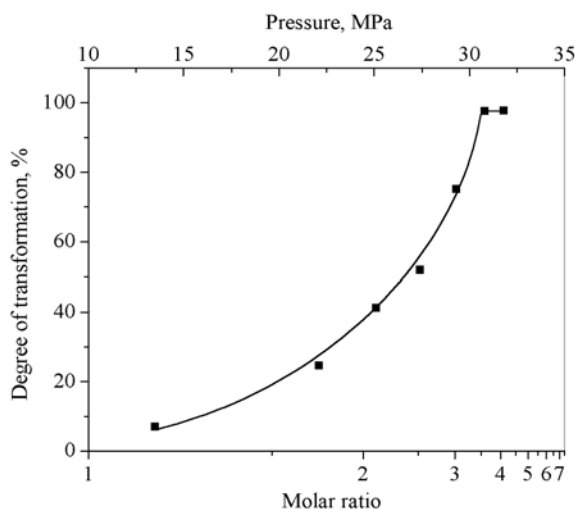
The process was realized in medium of water vapor. The necessary pressure of water vapor can be generated at the expense of structural water of boehmite or aluminum hydroxide.

In that case an autoclave was not filled with water. The autoclave was chilled. The transformation products were explored by X-ray methods (diffractometer DRON 3M), by IR-spectroscopy (spectrometers IR-75, EQUINOX 55/S in a region of  $4000\text{-}400 \text{ cm}^{-1}$ ) and by morphological analysis (electron microscope "Cam Scan Series 2"). The photoluminescence spectrums were measured at room temperature in the region of  $260\text{-}800 \text{ nm}$  at light excitation  $254 \text{ nm}$  using spectrometer SDL-2M.

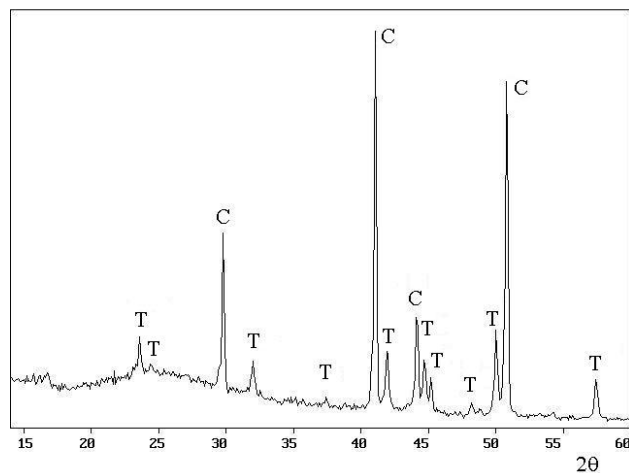
## RESULTS AND DISCUSSION

During treatment of oxide or oxyhydroxide of aluminum in a water fluid at the temperature of  $400^\circ\text{C}$  and molar ratio the water fluid/ $\text{Al}_2\text{O}_3$  more than 2 at first is obtained a boehmite. Then the corundum is formed of it due to a quasi-equilibrium dehydroxylation [2].

The investigation of the mechanism of transformations has shown, that at diminution of a molar ratio a water fluid/ $\text{Al}_2\text{O}_3$  the process of formation of a boehmite and corundum from hydrargillite is retarded (**Figure 1**), and at values of a molar ratio less than 2 in transformation



**Figure 1.** Dependence of degree of transformation of boehmite into corundum on a molar ratio a water fluid/ $\text{Al}_2\text{O}_3$  during 1.5 hours at the temperature of  $422^\circ\text{C}$ .



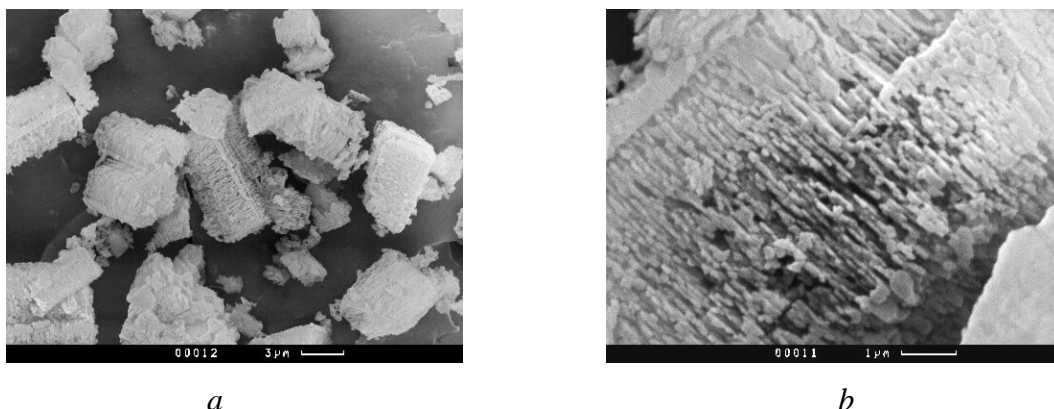
**Figure 2.** X-ray powder diffraction pattern of product of treatment of boehmite Apyral AOH 180DS at  $417^\circ\text{C}$  in water vapor with a molar ratio water fluid/ $\text{Al}_2\text{O}_3$  equal to 1.

C - diffraction reflexes of corundum, T - diffraction reflexes of tohdite - phase  $71651\text{-}5\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ . Co radiation.

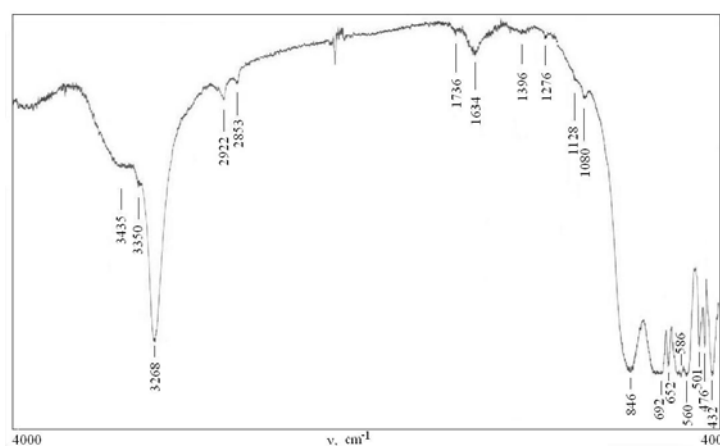
broad peak of IR-absorption decreases in the field of  $3600\text{-}3000\text{ cm}^{-1}$ , the peaks of absorption at  $3268$  and  $1080\text{ cm}^{-1}$  vanish, and in the field of  $900\text{-}400\text{ cm}^{-1}$  the spectrum becomes complicated (**Figure 4**). At temperature rise of heating-up on air up to  $1100^\circ\text{C}$  tohdite transforms into  $\alpha\text{-Al}_2\text{O}_3$ .

products there is a particularly hydrated alumina - tohdite ( $5\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ ) (**Figure 2**). At values of a molar ratio 1-0.7 during 3-20 hours a process proceeds only on a path of formation tohdite. And even increase of a molar ratio (and pressure of water fluid up to 23 MPa) the formed tohdite phase is conserved, not transforming into corundum.

The diminution of a molar ratio water fluid/ $\text{Al}_2\text{O}_3$  is accompanied by decreasing of pressure of water vapour and accordingly by decrease of intensity of processes of hydroxylation - dehydroxylation of alumina structure, and also diminution of mobility of structure. The depressing of solid-phase mobility appears in diminution of morphological perfection of formed particles tohdite contrary to boehmite (**Figure 3**). It is shown that the particles of tohdite conserve the shape of starting crystals of a hydrargillite, and the separate particles tohdite are of fine plates. The depressing of solid-phase mobility of tohdite structure as contrasted to boehmite is conditioned also by greater bond energy of hydroxyl groups in structure of tohdite. The removing of hydroxyl groups from structure of a boehmite happens in interval of temperatures  $450\text{-}490^\circ\text{C}$  [2], and from structure tohdite at  $750^\circ\text{C}$  [3]. Really, under heating-up of synthesized tohdite on air up to temperature  $600^\circ\text{C}$  in an IR-absorption spectrum of tohdite conserve characteristic for hydroxyls band of absorption at  $3268\text{ cm}^{-1}$ . At temperature rise of heating up to  $800^\circ\text{C}$  a sample loses 3.6 weights. %, and the



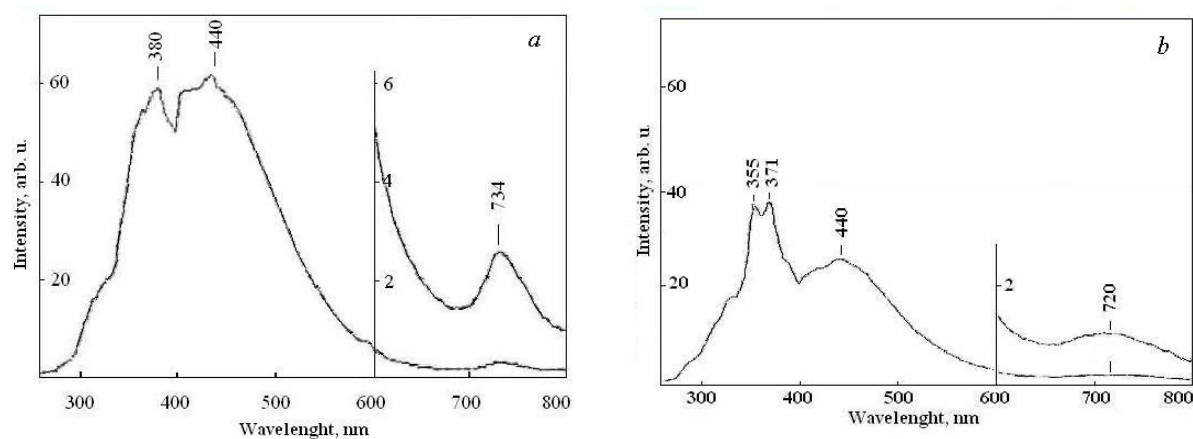
**Figure 3.** Morphology of tohdite particles: *a* - general view of particles, *b* - view of plates crystals of tohdite.



**Figure 4.** Infrared spectrum of tohdite.

The absorption band at  $3268\text{ cm}^{-1}$  can be assigned [4] to the stretching frequency for OH groups. She is similar to strong absorption band hydroxylgroups in structure of hydrogarnet ( $3600\text{ cm}^{-1}$ ), assigned [5] to valence vibrations of "free" OH - groups.

Other peculiarity of synthesized tohdite is the availability of a band in red area of luminescence spectrum (**Figure 5, a**) about 734 nm. The intensity of this band is incremented



**Figure 5.** Luminescence spectra: *a* - synthesized tohdite, *b* – after annealing at  $800^{\circ}\text{C}$

at temperature rise of annealing on air up to  $600^{\circ}\text{C}$ . After annealing at  $800^{\circ}\text{C}$  this band is sharply depressed (**Figure 5, b**). The luminescence band about 734 nm can be assigned to not

bridging atoms of oxygen. They will be formed during dehydroxylation of alumina structure, as we watched it in case of silicon dioxide [6]. The bands about 380 and 440 nm caused by oxygen vacancies (F-centers). The repressing them during annealing of tohdite is conditioned by interaction of oxygen vacancies with not bridging atoms of oxygen incipient at removing from structure tohdite of hydroxyl groups [6]. It is possible to explain maintenance of both kinds of defects - both oxygen vacancies and not bridging atoms of oxygen in structure of tohdite by low mobility of tohdite structure in our conditions of synthesis.

It is necessary to mark that the formation of tohdite from alumina in water vapor proceeds in more soft conditions of synthesis then under hydrothermal synthesis [4], which one demand temperatures 450-500°C and a filling of an autoclave about 80 % and durations of treatment 20-100 hours.

## CONCLUSION

The diminution of a molar ratio water fluid/ $\text{Al}_2\text{O}_3$  up to values less than 2 result to retardation of processes, both hydroxylation, and dehydroxylation of a solid phase during thermovaporous treatment of oxides or oxyhydroxides of aluminum. Thus, the direction their transformations vary: instead of a boehmite and then corundum will be forms a tohdite. In structure of tohdite the defects - oxygen vacancies and not bridging atoms of oxygen caused by the mechanism of formation of a phase  $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  are conserved.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge ISTC for financial support (pr. N 1381).

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