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# Thermovaporous synthesis of fine crystalline gahnite ($ZnAl_2O_4$)

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In the present paper the formation mechanism of zinc aluminate (gahnite, $ZnAl_2O_4$) under hydrothermal and thermovaporous conditions has been investigated. The gahnite was obtained by treatment in water medium of a mixture of zinc oxide and oxide or hydroxide of aluminum at 180–400°C and under pressure of water vapor 1–26 MPa. It was found that formation of gahnite goes in accordance with the solid-phase mechanism. The impurities added into the reaction medium have an influence upon the rate of transformation. In this case the rate of reaction is controlled by nucleation. The impurities incorporate into the structure of gahnite and change the structural characteristics of the microcrystals, defects concentration and the optical properties of gahnite. The luminescence of $Eu^{3+}$ ions is sensitive to the change of gahnite structure. Gahnite synthesized in ammonia medium has photoluminescence bands at 382 and 547 nm with the excitation band at 267 nm. These PL bands are attributed to oxygen vacancies.

## 1. Introduction

Zinc aluminate (gahnite, $ZnAl_2O_4$) is widely used as ceramic, electronic and catalytic material. It can be synthesized by using conventional ceramic processing techniques, sol-gel method, coprecipitation method or alumina impregnating method with following calcination at relatively higher temperatures (800–1000°C). Recently, ultrasonic sprey pyrolysis technique [1] and flame synthesis [2] of gahnite were used. The various variants of hydrothermal synthesis of zinc aluminate are also described in the works [3–6].

Earlier, it was found that under thermovaporous treatment (TVT)—in an atmosphere of water vapor at temperatures of 200–400°C and pressures of 1.5–30 MPa the structuring of simple metal oxides and synthesis of complicated oxides occurs [7–11]. The basis for these processes is the ability of oxides to transform into a state with high mobility of solid-phase. It occurs due to breakage and formation of metal-oxygen bonds in the quasi-equilibrium processes of hydroxylation—dehydroxylation of oxides under conditions of increased temperature and pressure [10]. As a result the powder of well-edged small single crystals of simple or complicated oxide will be obtained. Size of the particles depends on the process parameters and it can be varied within an interval of 0.5–400 microns.

In the present paper the formation mechanism of zinc aluminate under hydrothermal conditions and thermovaporous treatment is suggested.

## 2. Experimental methods

The stoichiometric mixture of starting materials, such as aluminum oxide (highest purity grade), aluminum oxyhydroxide (boehmite) or hydroxide (hydrargillite of the trademark GD00) with zinc oxide (graded as chemically pure) were placed into the stainless steel receptacle, which was put into autoclave (volume 16 cm$^3$) on support. The water was added into the receptacle or into the autoclave bottom outside of the receptacle. The degree of autoclave filling with water was equal to 0.2. The boehmite, utilized in operations, was previously obtained by heating of hydrargillite in thermovaporous conditions up to 400°C.

Doping element (chromium, manganese, yttrium or europium) was added into reaction medium as salt solution or oxide. The process was carried out both in water and in water vapor at 180–400°C. Then the autoclave base

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was quenched with water. In this case the water vapor was condensed on the bottom of the autoclave and the dry product was unloaded.

The synthesized products were characterized by various methods: X-ray (diffractometer DRON—3M in filtered Co or Cu-K$\alpha$ radiation), scanning electron microscopy (Cam Scan Series 2), photoluminescence (PL) (SDL-2M at room temperature in the interval 260–800 nm by exciting light with wavelength 254 nm), diffuse reflection spectroscopy (spectrometer Specord M40 in the region of 220-800 nm). The content of impurity elements in hydrargillite and gahnite was determined by chemical analysis. The degree of transformation was determined by the relation of integrated intensities of diffraction peaks to maximum value at the end of transformation. The lattice parameters were determined. Perfection of gahnite structure was estimated on the size of Bragg scattering zone (D, nm), which was determined by a profiling of diffraction peak (220).

## 3. Results and discussion

### 3.1. Synthesis of gahnite without addition of activator into reaction medium

During the treatment of a mixture of hydrargillite with zinc oxide, the formation of gahnite both in thermovaporous and under hydrothermal conditions starts at temperatures about 200°C. With the use of alumina of the special purity (or boehmite obtained from it) the formation of gahnite in these conditions does not occur. The impurities influence on rate of transformation. The hydrargillite of the trademarks GD00 contains about 0.08% of impurities (Table I). Due to the influence of these impurities the gahnite synthesis from hydrargillite and zinc oxide at 200°C proceeds in 144 h by 50%. With the addition of impurity (0.1% of chromium) the synthesis of gahnite is completed in 87 h. The impurities of manganese, iron or yttrium also activate the transformation.

TABLE I The content of impurity elements in hydrargillite, ppm

| | |
|---|---|
| Fe | 4 |
| Co | 0.02 |
| Mn | 0.07 |
| Cr | 0.3 |
| Zn | 4 |
| Ni | 0.05 |
| Cu | 0.4 |
| Pb | 0.2 |
| Bi | 0.8 |
| Cd | <0.005 |
| Ga | 50 |
| Ca | 30 |
| Mg | 2 |
| Ba | 0.4 |
| Na | 600 |
| K | 100 |

TABLE II The content of impurity elements in samples of gahnite undoped (S1) and doped by yttrium (S2), ppm

| Impurity | S1 | S2 |
|---|---|---|
| Fe | 80 | 1 |
| Cr | <1 | <1 |
| Cu | 100 | 2 |
| Ga | <10 | <10 |
| Ca | 10 | 10 |
| Mg | 5 | 3,5 |
| Ba | 0.3 | <0.2 |
| Na | 150 | 100 |
| K | 20 | 20 |
| Y | — | 200 |

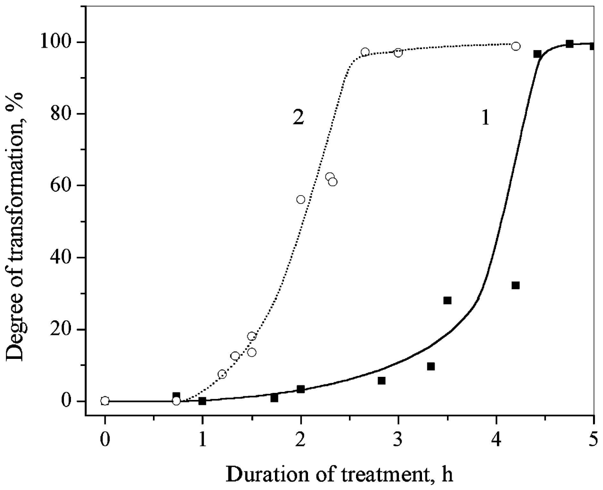

*Figure 1* The kinetics of hydrargillite to boehmite transformation at 180°C. 1—in water, 2—in water vapor.

During treatment of the hydrargillite or alumina is converted into boehmite that interacts with zinc oxide. The transformation rate of hydrargillite at 180°C in water vapor is higher, than in water. The time of transformation differs twice (Fig. 1). It was found that at 140–160°C the transformation of hydrargillite into boehmite in water occurs 6–7 times slower than in the water vapor pressure [5]. The structure of formed boehmite is perfected and the content of structural water is decreases [4, 6, 7]. At temperatures about 400°C in the absence of zinc oxide, boehmite is transformed to corundum [3].

High solid-phase mobility of the zinc oxide structure also appears in water vapor at temperatures about 200°C in the presence of impurities. Under these conditions the morphology of the particles varies and the growth of ZnO microcrystals starts [8]. Formation of gahnite also starts during thermovaporous treatment of boehmite mixture with zinc oxide at temperatures higher 200°C.

Fig. 2 shows the change in products composition during thermovaporous treatment of boehmite mixture with zinc oxide within 24 h, in the temperature range 230–400°C. At different conversion level in the diffraction pattern of

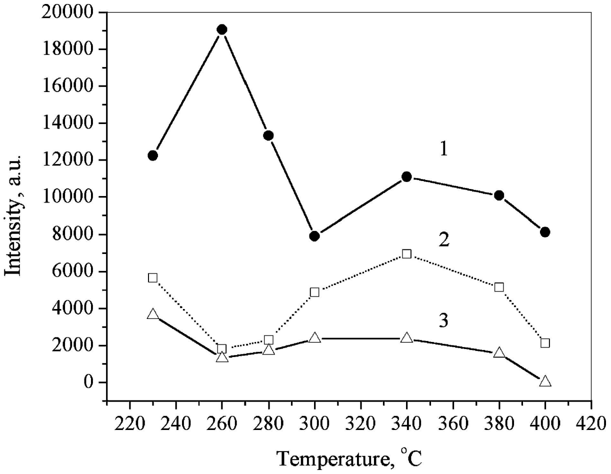

*Figure 2* Temperature dependence of products composition of TVT of ZnO/AlOOH mixture. TVT time: 24 h. 1—gahnite (113), 2—zinc oxide (101), 3—boehmite (020).

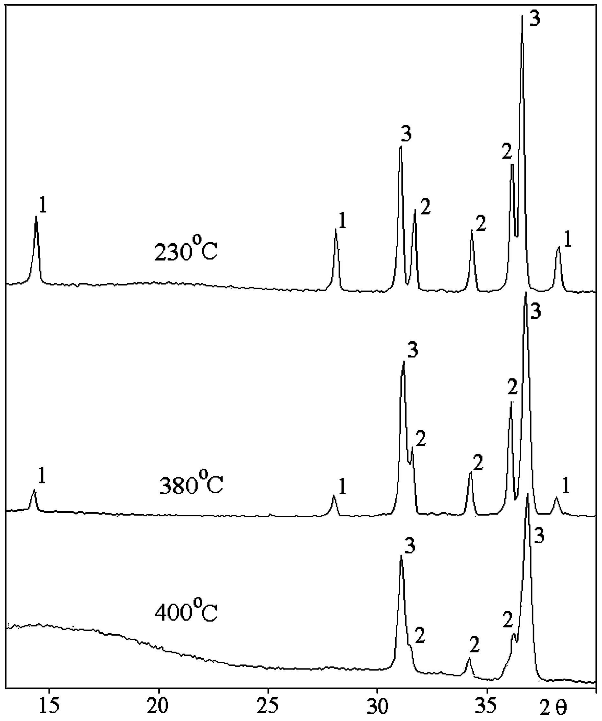

*Figure 3* XRD patterns (Cu-K$_a$ radiation) of ZnO/AlOOH mixture treated in thermovaporous conditions at the some temperatures. TVT time: 24 h. 1—boehmite, 2—zinc oxide, 3—gahnite.

products are peaks of boehmite, zinc oxide and gahnite. Other intermediate phases were not observed. The generation rate of gahnite at first increases with increasing of temperature. Then it is retarded in the range 260–340°C and passes through a minimum about 300°C. The transformation completes in 24 h at 400°C. The complicated dependence of gahnite formation rate on temperature of process can be determined by change of boehmite state or by recrystallization of zinc oxide with a diminishing reactivity. The decrease of gahnite peaks intensity (Fig. 2) at temperatures of synthesis 340–400°C is conditioned by a structure disordering of nascent gahnite.

The broadening of gahnite X-ray peaks testifies to it. The comparison of a position and resolution of diffraction peaks of gahnite and zinc oxide within the $2\theta$ region 30–38° exhibits the broadening of gahnite peaks at the rise of synthesis temperature up to 400°C (Fig. 3). It is necessary to mark that gahnite synthesized hydrothermally at higher temperature 650°C [9], differs by broader diffraction peaks.

The synthesis at temperatures lower 380°C (Fig. 3) results in the shift of gahnite peaks towards lower angles. This suggests that the unit cell parameter of gahnite is increased. Two gahnite samples synthesized at 400°C have unit cell parameter 8.067(4) and 8.074(4) Å, and gahnite synthesized at 270°C — 8.115(4) Å. One can note that after the complete transformation at 400°C the synthesized product contains the surplus of zinc oxide. After annealing this product at 1050°C, the peaks of gahnite are narrowed, peaks intensity increases and surplus zinc oxide disappears. These results testify the deviation of stoichiometry and partial inversion of spinelic structure of gahnite at temperatures of synthesis above 380°C. In this case the aluminum ions occupy also the tetrahedral positions. A similar deviation of stoichiometry is well known for spinel [10] and has been observed also for gahnite [11]. For non-stoichiometric zinc aluminate, (Zn$_{0.3}$Al$_{0.7}$)Al$_{1.7}$O$_4$ in [11] the lattice parameter $a = 8.006(2)$ Å was found. For stoichiometric gahnite the lattice parameter near to the known value 8.0848 Å [12, 13] is usually obtained.

## 3.2. Synthesis of gahnite with the addition of activator into reaction medium

The additive of yttrium or europium oxide to a mixture of hydrargillite with zinc oxide allows to obtain doped gahnite (Table II) by TVT at 400°C. The doping by yttrium ($1\cdot10^{-2}$ %) accelerates transformation and allows to obtain gahnite with more perfect structure. The size of Bragg scattering zone (D) of gahnite synthesized in water vapor at 400°C is increased at the addition of yttrium with 30.3 up to 44.8 nm. The obtained gahnite has the form of well-edged octahedral crystals with the size 2–8 microns (Fig. 4).

In synthesis of gahnite, the dopants are conveniently added into the reaction medium as water solution of salt. The addition of manganese $1\cdot10^{-1}$–$1\cdot10^{-2}$%, iron or chromium ions accelerates the transformation at 400°C and allows to obtain a single-phase gahnite, whereas under the hydrothermal treatment in water a residue of zinc oxide is obtained. Especially strong activating effect appeared in the synthesis of gahnite in aqua ammonia medium. When the autoclave is heated up to 380°C the gahnite formation completes, and up to 260°C it is

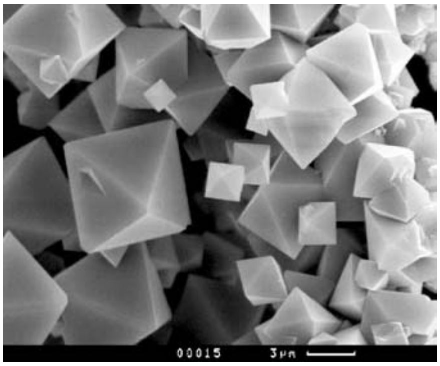

*Figure 4* SEM microphotograph of gahnite doped by yttrium (Sample S2).

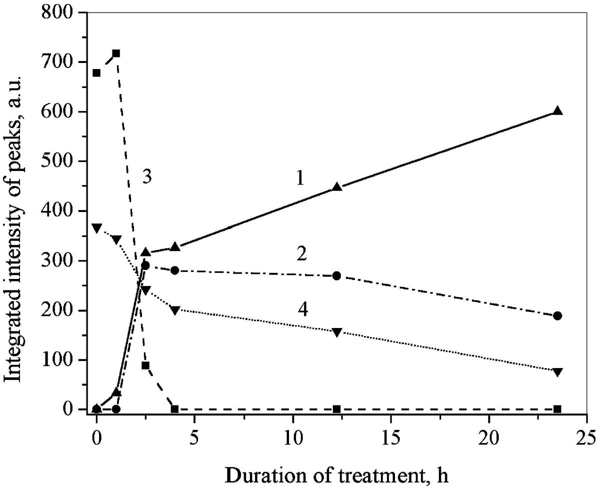

*Figure 5* Kinetics of interaction of hydrargillite with zinc oxide mixture during treatment in ammonia solution at 180°C. 1—gahnite, 2—boehmite, 3—hydrargillite, 4—zinc oxide.

completed by 55%. Fig. 5 shows the kinetics of gahnite synthesis at 180°C from hydrargillite and zinc oxide in ammonia solution. Under these conditions of synthesis the hydrargillite (Fig. 5, the curve 3) is converted to boehmite in 4 h (Fig. 5, curve 2). By that time the gahnite synthesis is completed already by 43%. Then the gahnite formation is continued from zinc oxide and boehmite. In Fig. 6 are shown the kinetic curves of gahnite formation at 180, 200 and 260°C and also the kinetic curve for 200°C in coordinates ln(1-$\alpha$)-$\tau$.

The curves are satisfactorily straightened in coordinates ln(1-$\alpha$)-$\tau$ of the equation of solid-phase transformation with a limiting stage of nucleation with permanent rate [14]. The temperature dependence of transformation rate, determined from slope angles of the linearized kinetic curves, allows to obtain apparent activation energy value of 85.9 kJ/mol (Fig. 7).

The permanent nucleation rate suggests that the diffusion of zinc ions in an aluminous matrix occurs rapidly. On reaching certain concentration of zinc ions, the nucleation of a gahnite phase starts. The morphology of crystals formed depends on the transformation conditions. In the synthesis under water vapor medium, the hydrargillite at first transforms into fine crystalline boehmite (with the particles size of 0.5–1 microns [3]), and then the small crystals of gahnite (Fig. 4) are formed. At the case of synthesis in ammonia water solution medium the zinc ions diffuse into hydrargillite crystals and the obtained gahnite particles conserve the shape of initial particles of hydrargillite (Fig. 8). During synthesis of gahnite without addition of activator into reaction medium the low mobility of structure impedes the diffusion of zinc ions. Due to this the nucleation of gahnite occurs with the deficiency of zinc ions and leads to the formation of crystals with anomalous stoichiometry. The gahnite with the most perfect structure (D = 50.3 nm) is obtained during the synthesis in ammonia vapor (ammonia solution outside of the receptacle) at 260°C. In ammonia solution at 260°C and

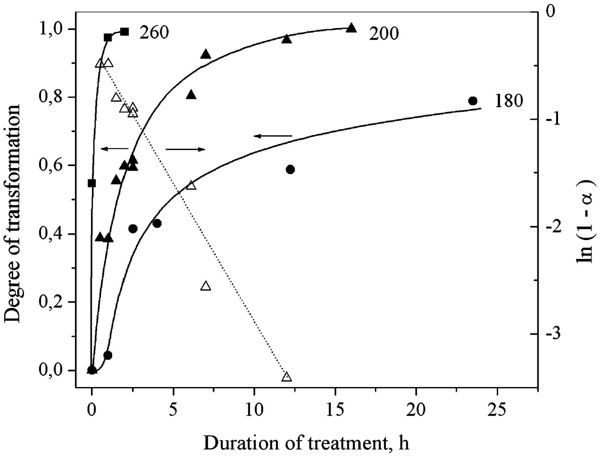

*Figure 6* Kinetics of gahnite synthesis during treatment of hydrargillite with zinc oxide mixture in ammonia solution at some temperatures and kinetic curve for 200°C in coordinates ln(1-$\alpha$)-$\tau$.

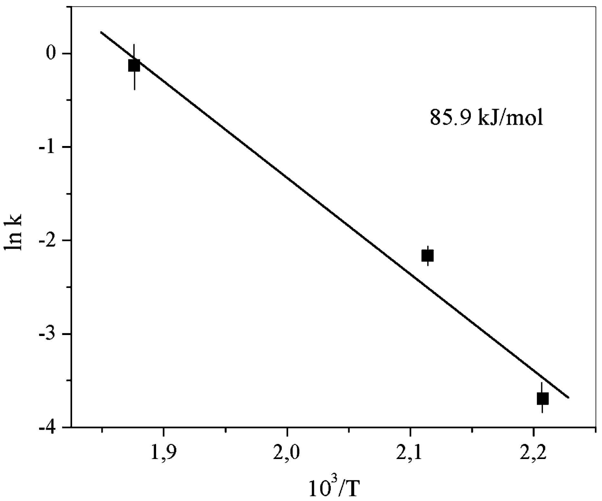

*Figure 7* Temperature dependence of the gahnite formation rate.

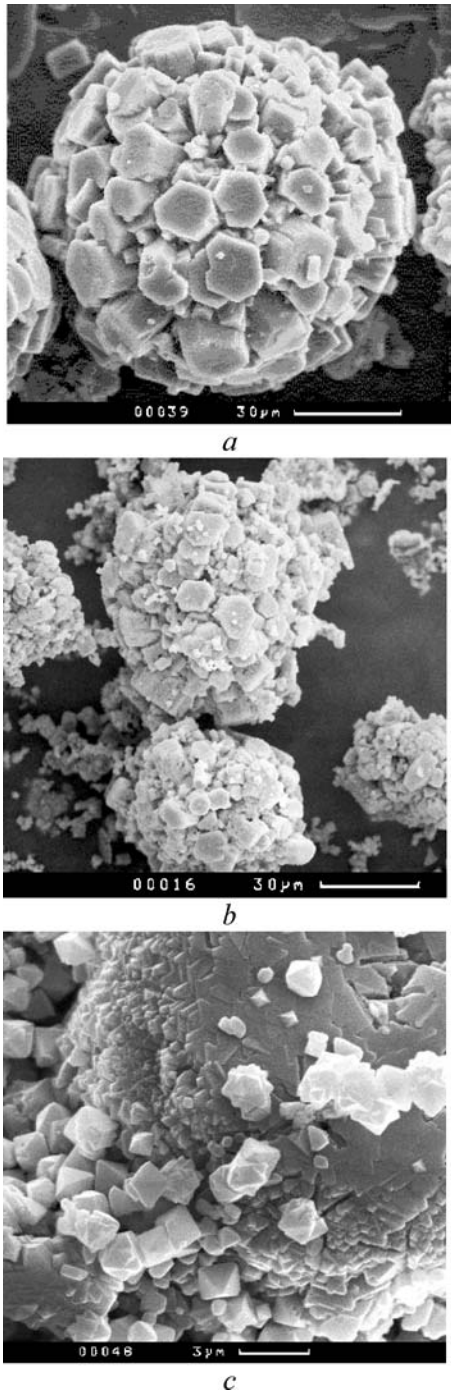

*Figure 8* The morphology of hydrargillite and gahnite particles:
a—aggregate of prismatic crystals of hydrargillite,
b—gahnite particle obtained in medium ammonia at 400°C,
c—transformed in gahnite the initial hydrargillite crystal.

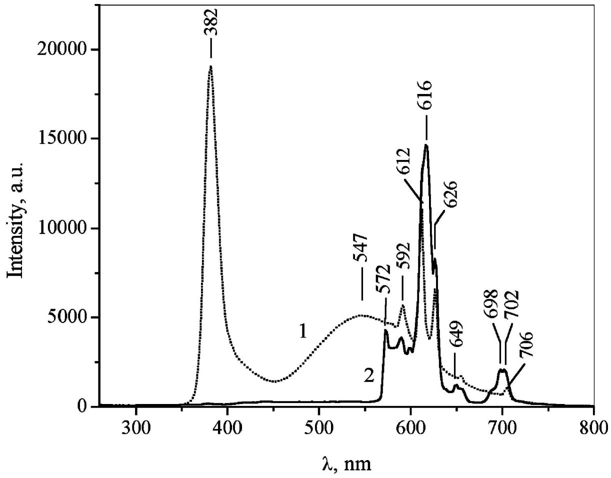

*Figure 9* PL spectra of $Eu^{3+}$ (1 mol%)-doped gahnite: 1—as prepared, 2—after annealing at 1400°C for 2 h. Exciting wavelength is 254 nm.

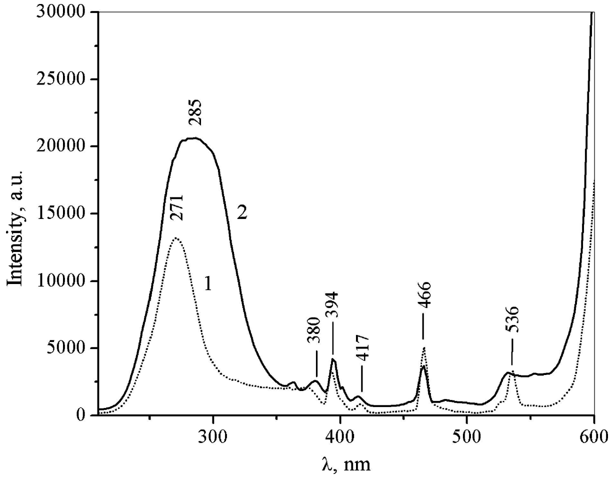

*Figure 10* Excitation spectra of $Eu^{3+}$ (1 mol%)-doped gahnite: 1—as prepared ($\lambda_{PL} = 612$ nm), 2 — after annealing at 1400°C for 2 h ($\lambda_{PL} = 616$ nm).

400°C, the gahnite is formed with less perfect structure 36.5 and 38.3 nm respectively.

It is possible to estimate a point defects in gahnite samples by photoluminescence. In PL spectrum (Fig. 9, spectrum 1) of gahnite synthesized in the ammonia medium an intensive band at 382 nm and broad band of weak intensity centered at 547 nm are present. Both PL bands are excited in band at 267 nm. These PL bands are absent in the gahnite synthesized in medium of water vapor. They occur, if the water vapor contains mixture (1–2%) of ethanol. Similar luminescence bands in quartz glass [14] and corundum [15] are attributed to intrinsic defects of lattice—oxygen vacancies. Such attribution of the PL bands at 382 nm and at 547 nm of gahnite corresponds to the reducing conditions of synthesis. On the whole the intensity of PL bands of the oxygen vacancies at 382 nm and 547 nm is increased for samples with high gahnite formation rate and therefore with high mobility of its structure.

The gahnite doped by europium, has also characteristic series of PL bands (Fig. 9, spectrum 1) with the basic maximum at 612 nm and maxima of weak intensity at 592, 626 and 706 nm. After annealing this sample in air

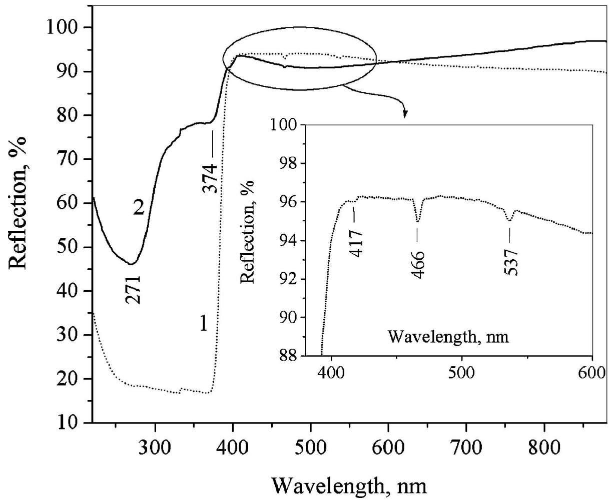

*Figure 11* Reflection spectra of $Eu^{3+}$ (1 mol%)-doped gahnite. 1 — synthesized at 400°C in water vapor, 2 — after annealing of this sample in air at 1400°C for 2 h.

at 1400°C for 2 h the PL spectrum (Fig. 9, spectrum 2) contains only bands of europium. However, position of the most intensive band shifts to 616 nm. The relation of intensities and position of some other bands also change. It testifies [21] to change of the crystal environment of $Eu^{3+}$ ions. The similar differences of PL spectra $ZnAl_2O_4$:Eu are shown in [12]. The high-temperature annealing of gahnite produces also appreciable changes in excitation spectrum of $Eu^{3+}$ ions (Fig. 10). The narrow bands of weak intensity may be attributed to light absorption by $Eu^{3+}$ ions. Their positions coincide with absorption bands of $Eu^{3+}$ ions in a reflection spectrum (Fig. 11) of this gahnite sample.

The intensive excitation band of $Eu^{3+}$ ions at 271 nm (Fig. 10, spectrum 1) is located in the absorption band of oxygen vacancies. After annealing sample at 1400°C the state of oxygen vacancies and their interaction with $Eu^{3+}$ ions change. The part of oxygen vacancies after annealing sample of gahnite disappears (Fig. 11), and in excitation spectrum of $Eu^{3+}$ ions (Fig. 10, spectrum 2) the band of oxygen vacancies broadens, increases and its maximum shifts to 285 nm. It testifies that the number of oxygen vacancies, with which the $Eu^{3+}$ ions interact, increases, and their energy inhomogeneity broadens. It is possible to suppose (as in [21]) that the hydroxyl groups participate in changes of gahnite structure at annealing.

## 4. Conclusion

The synthesis of gahnite through the treatment of mixture of hydrargillite or boehmite with zinc oxide in hydrothermal and thermovaporous conditions proceeds on the solid-phase mechanism. The $Zn^{2+}$ ions diffuse in the alumina matrix. On reaching the indispensable saturation, nucleation occurs and the growth of gahnite crystals begins. The synthesis of gahnite in water or in water vapor is observed at 400°C in 24 h. Because of poor solid-phase mobility under these conditions of synthesis, the nonstoichiometric zinc aluminate with partial inversion of spinel structure is obtained. The rate of transformation at thermovaporous conditions of synthesis considerably increases at the presence of activators: impurities of $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Y^{3+}$ ions. The maximum effect of the formation acceleration of $ZnAl_2O_4$ was observed under treatment of hydrargillite mixture with zinc oxide in the ammonia medium solution. In this case the complete transformation occurs at 200°C within 16 h. The process is limited by nucleation with constant rate. The apparent activation energy value is 85.9 kJ/mol. In the gahnite synthesis conditions ensuring heightened mobility of its structure, the gahnite contains oxygen vacancies with PL bands at 382 nm and 547 nm and a band of PL excitation at 267 nm. The impurities ions added into reaction medium are incorporated into the structure of gahnite. During treatment of the mixture hydrargillite with zinc oxide and europium oxide, the doped gahnite is obtained. The luminescence of $ZnAl_2O_4$ doped with europium is characteristic for the $Eu^{3+}$ ion. The basic PL excitation band of the $Eu^{3+}$ ions is located in the absorption region of oxygen vacancies, with that the $Eu^{3+}$ions interact. Due to this the luminescence of the $Eu^{3+}$ ion is sensitive to the change of gahnite structure. The annealing $ZnAl_2O_4$:Eu in air at 1400°C results in the disappearance of a part of oxygen vacancies and change of interaction of $Eu^{3+}$ ions with the remaining vacancies. As a result of it, the PL intensity of $Eu^{3+}$ ions increases and shift to the red region of position of basic bands of excitation and luminescence is observed.

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