Synthesis of Eu-Doped Gahnite in Water and Water-Ammoniac Fluids

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In present paper the effect of ammonia contained in water fluid on synthesis and properties of gahnite ($ZnAl_2O_4$) doped with (0.4-4 mol%) europium was investigated. It is revealed that the synthesis of oxide in water-ammoniac fluid proceeds with formation of single-phase product that has a smaller size of crystal, than in case of synthesis in water fluid. The gahnite synthesized in water-ammoniac fluid has intensive luminescence bands of oxygen vacancies. In its structure the bound nitrogen is detected. However, during synthesis in water fluid the europium ions are more effectively incorporated into structure of nascent gahnite. The europium ions form complexes with oxygen vacancies. The excitation efficiency of Eu^{3+} ions luminescence in absorption band of oxygen vacancies is increased with the content of Eu^{3+} in gahnite. After annealing on air of gahnite samples synthesized in fluid of various compositions the changes of their luminescence differ. It has been supposed that in the gahnite synthesized in a fluid of various compositions the environment around Eu^{3+} ions differs outside the first coordination sphere. It is concluded that ammonia participates in processes of gahnite formation and provokes increasing of nucleation rate and is remained in its structure.

INTRODUCTION

Earlier [1] authors were revealed that the formation of gahnite passes in accordance with the solid-phase mechanism from a mixture of zinc oxide and aluminum hydroxide under hydrothermal and thermovaporous treatment at 180-400°C and pressure of water vapor 1 - 26 MPa. The impurities added into the reaction medium influence upon the rate of transformation. The maximum effect of the formation acceleration of $ZnAl_2O_4$ was observed in the ammonia solution medium. The gahnite synthesized in water ammonia medium has photoluminescence bands at 382 and 547 nm. These PL bands are attributed to oxygen vacancies. The luminescence of Eu^{3+} ions is sensitive to the change of gahnite structure. This property of Eu^{3+} ions luminescence is known [2,3] and can be used for the analysis of structure local changes [3, 4].

In the present work the peculiarities of europium ions incorporation into gahnite structure during formation in medium of water (SCW) and water-ammoniac (SCW-Am) fluid were studied and Eu^{3+} ions were used as a luminescent structural probe.

1 - MATERIALS AND METHODS

The stoichiometric mixture of aluminum hydroxide (hydrargillite of the trademark GD18), zinc oxide (graded as chemically pure) and 0.4 - 4 mol% europium oxide (highest purity grade) were placed into the stainless steel container, which was put into autoclave (volume 16 cm^3) on support. The water was added into the autoclave bottom outside of the container. The ethyl alcohol (1%) was added into water for creation of reducing conditions of synthesis. At treatment in a water-ammoniac fluid the water solution of ammonia (25%) was added inside of the container with an intermixture of reagents. The degree of autoclave filling with water was equal to 0.2. The autoclaves are heated at 400 C within 24 hours. The synthesized products were characterized by methods: X-ray powder diffractometry (diffractometer DRON - 3M in filtered Co or Cu-Kα radiation), scanning electron microscopy (Cam Scan Series 2), excitation and emission photoluminescence (PL) (SDL-2M at room temperature), diffuse reflection (DR) spectroscopy (spectrometer Specord M40 in the region of 220-800 nm). The impurities of water and gases in sample of Eu (0.4 mol%)-doped gahnite are measured using the mass-spectrometric quantitative analysis of gases evolved into high vacuum at a stepwise heating of sample from room temperature up to 1400 C with an interval in 200 C and duration of each step 40 minutes.

2 - RESULTS AND DISCUSSION

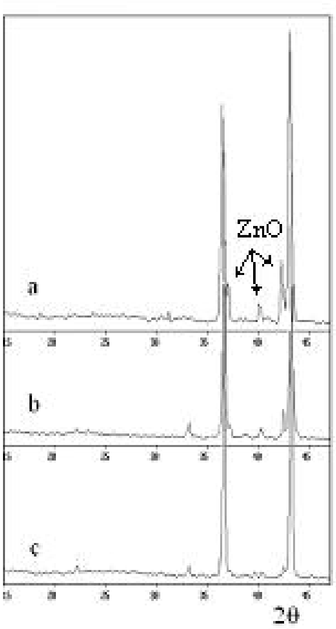


Figure 1: XRD patterns for Eu (1.2 mol%)-doped $ZnAl_2O_4$ samples synthesized in SCW: (a) as prepared, (b) after annealing at 1000 C, (c) at 1200 C.

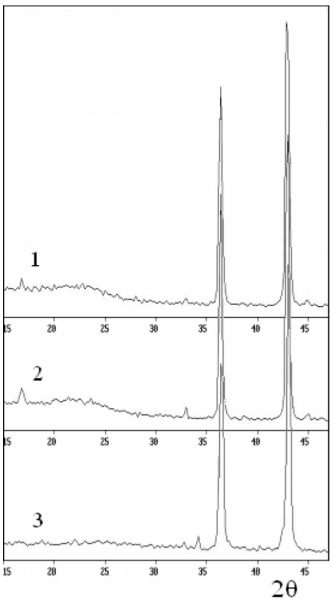


Figure 2: XRD patterns for $ZnAl_2O_4$:Eu samples synthesized in SCW-Am as a function of the doping concentration in reaction medium: (1) 0.8; (2) 1.2; (3) 1.6 mol%.

At synthesis of zinc aluminate in SCW fluid the obtained product contains the surplus of zinc oxide and gahnite has a deviation of stoichiometry with partial inversion of spinelic structure [1]. After annealing such samples in air at 1000°C and 1200 C for 1 hour the surplus zinc oxide disappears (fig. 1). At synthesis of zinc aluminate in a water-ammoniac fluid at once is formed single-phase gahnite (fig. 2). One can note that at increase of the content of europium up to 4 mol% in a synthesized product there is an impurity of europium hydroxide $Eu(OH)_3$.

In fig. 3 are shown the typical shape of gahnite samples synthesized in SCW (fig. 3,a) and SCW-Am fluids (fig. 3,b). It is visible that gahnite crystals synthesized in SCW fluid have the sizes up to 10 microns, while at synthesis in SCW-Am fluid do not exceed 1 micron. The smaller size of gahnite crystals synthesized in SCW-Am fluid testifies to increase of nucleation rate in this medium.

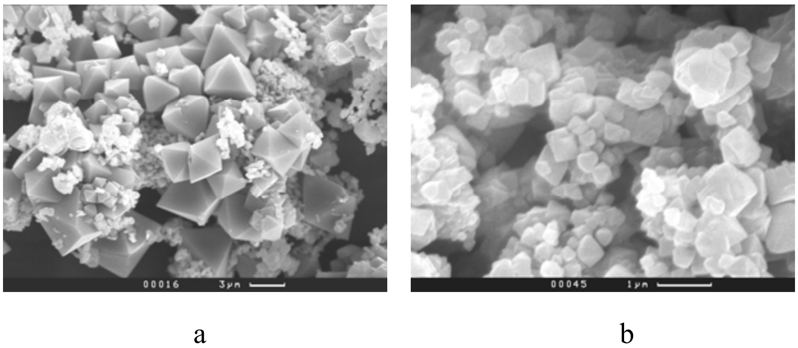


Figure 3: SEM micrographs of Eu (1.6 mol%)-doped gahnite samples synthesized: (a) in SCW, (b) in SCW-Am.

In fig. 4 are shown the diffuse reflection spectra of Eu (0.4-4 mol%)-doped gahnite samples synthesized in water-ammoniac (fig. 4, a) and water (fig. 4, b) fluids. The shift of band edge of fundamental light absorption for gahnite samples (solid lines in fig. 4, a) concerning zinc oxide (dotted line in figure 4, a) approximately corresponds to a relation of band-gap energy for gahnite (3.8 eV [5]) and zinc oxide (3.2 eV [6]). For gahnite samples synthesized in a water fluid such shift is imperceptible.

The narrow light absorption bands by Eu^{3+} ions (they are well visible on a inset in fig. 4, a) there are in both cases on DR spectra.

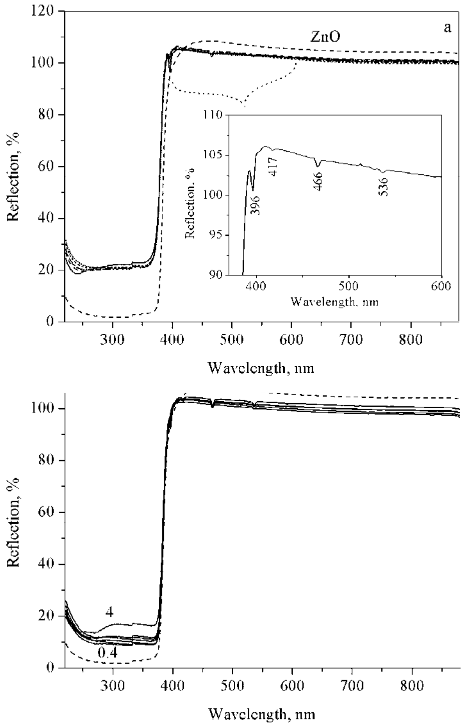


Figure 4: DR spectra initial zinc oxide (dotted line) and samples of Eu (0.4-4 mol%)-doped gahnite synthesized in: (a) SCW-Am., (b) SCW.
In inset is shown the section of DR spectrum for sample Eu (1.6 mol%)-doped gahnite.

In PL spectrum (Fig. 5) of synthesized gahnite an intensive band about 380 nm and broad band about 540 nm are present. We attributed these bands to a luminescence of defects on the basis of oxygen vacancies [1]. From fig. 5 it can be seen that the gahnite synthesized in water-ammoniac fluid has intensive luminescence bands of oxygen vacancies and the gahnite synthesized in a fluid of various compositions differs by a relation of bands about 380 and 450 nm. This difference can be caused by a various environment around oxygen vacancies and/or by known recharge of F-centres. Besides in spectra there are narrow luminescence bands of Eu^{3+} ions, which intensity is higher for gahnite samples synthesized in water fluid. Consequently the europium ions are more effectively incorporated into structure of nascent gahnite during synthesis in water fluid. The luminescence excitation of Eu^{3+} ions occurs in absorption band of oxygen vacancies (at 274 and 277 nm, fig. 6), in fundamental absorption band with an edge maximum about 380 nm and in absorption bands of light directly by europium ions (at 394, 402, 416, 466, 527 and 536 nm). The narrow bands of luminescence excitation (612 nm) at light absorption by Eu^{3+} ions (fig. 6) as well as narrow luminescence bands of Eu^{3+} ions (fig. 5) correspond to well-ordered location of Eu^{3+} ions in determinate structural position of crystal lattice of gahnite. The excitation of Eu^{3+} ions luminescence in absorption band of oxygen vacancies (fig. 6) indicates formation of composite defects out of Eu^{3+} ions interacting with oxygen vacancies.

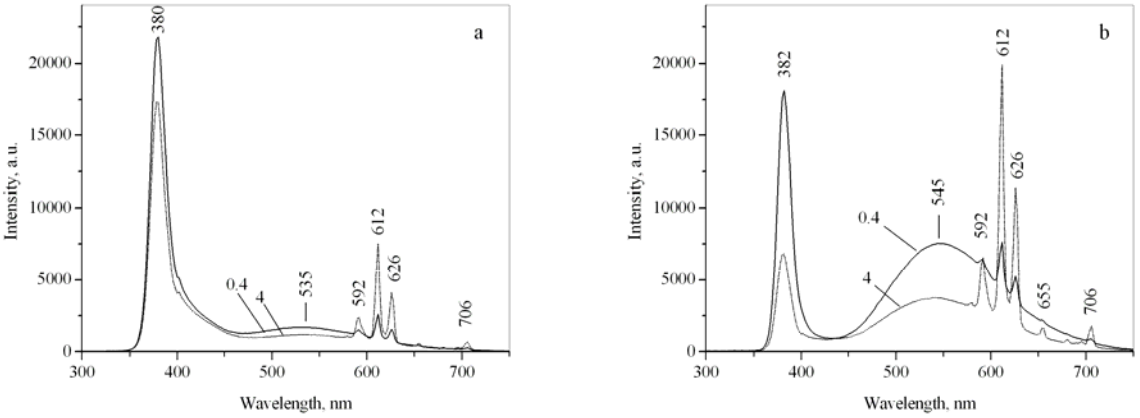


Figure 5: Emission spectra of Eu (0.4 and 4 mol%)-doped gahnite samples synthesized: (a) in SCW-Am, (b) in SCW. (Excitation 254 nm).

However the broadening of bands at 274 and 277 nm (fig. 6) clearly indicates energy inhomogeneity of oxygen vacancies complex with Eu^{3+} ions.

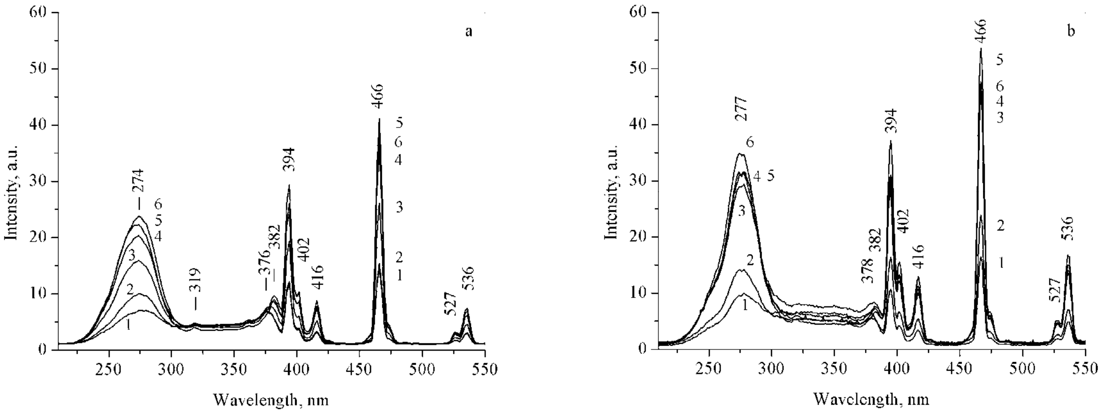


Figure 6:. Excitation spectra of Eu (0.4 and 4 mol%)-doped gahnite samples synthesized: (a) in SCW-Am, (b) in SCW. (Emission 612 nm). Content of europium, mol%: (1) 0.4, (2) 0.8, (3) 1.2, (4) 1.6, (5) 2, (6) 4.

Table 1: Effect of content of the Eu^{3+} ions on the intensity relation of excitation bands at 278 and 466 nm of Eu^{3+} ions luminescence (612 nm)

Europium content, mol%	I_{274}/I_{466}	I_{277}/I_{466}
	Gahnite synthesized in SCW-Am	Gahnite synthesized in SCW
0.4	0.23	0.22
1.2	0.47	0.49
4	0.5	0.65

The increase of europium ions content influences their interaction with oxygen vacancies (Table 1). As can be seen in Table 1 the excitation of Eu^{3+} ions luminescence in absorption band of oxygen vacancies is more effective when the doping concentration is increased. It means that the incorporating of each new Eu^{3+} ion into structure of composite oxide in SCW fluid is accompanied by formation of a complex with more number of oxygen vacancies.

After annealing in air of gahnite samples synthesized in fluid of various compositions the change of Eu^{3+} ions luminescence differ (fig. 7, 8). In fig. 7, 8 it is visible that after samples annealing the intensity relation of luminescence bands corresponding to transitions $^5D_0 \rightarrow {}^7F_2$ (612, 616, 628 nm [3, 4, 7]) as well as $^5D_0 \rightarrow {}^7F_1$ (588, 592, 598 nm [4, 7]) and $^5D_0 \rightarrow {}^7F_0$ (574 nm [3, 4]) differs. Usually it is interpreted in the terms of change of ligands covalence or distortion of Eu^{3+} ions sites [2, 4]. Dissimilar distortion of Eu^{3+} ions sites arises from various environments around these ions. Since the Eu^{3+} ions luminescence bands of the as-prepared samples are identical (fig. 5), the various environments around these ions apparently concerns to the second coordination sphere. It is necessary to note that with increase of the europium content the differences of the spectral distribution of Eu^{3+} ions luminescence decrease and at the content of europium 4 mol% practically disappear (fig. 8).

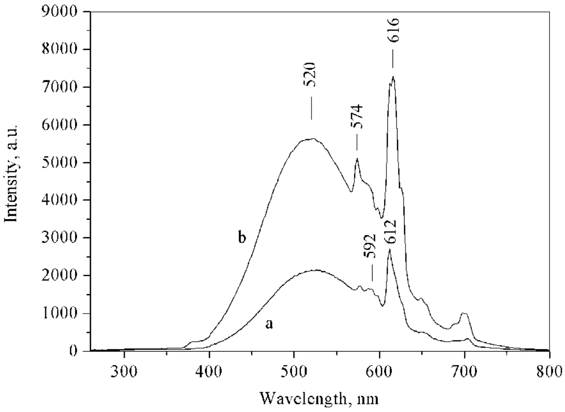


Figure 7. Emission spectra after annealing in air at 1200 C for 1 h of Eu (0.4 mol%)-doped gahnite samples synthesized: (a) in SCW-Am, (b) in SCW. (Excitation 254 nm).

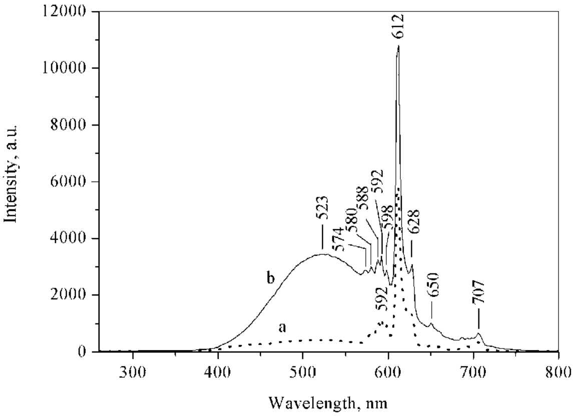
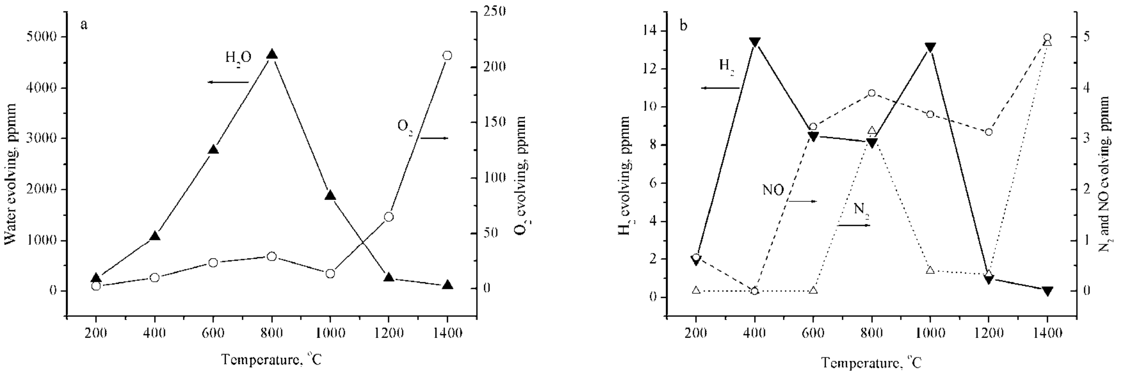


Figure 8. Emission spectra after annealing in air at 1200 C for 1 h of Eu (4 mol%)-doped gahnite samples synthesized: (a) in SCW-Am, (b) in SCW. (Excitation 254 nm).

For Eu (0.4 mol%)-doped gahnite was measured the gases evolve into vacuum at stepwise heating of sample (fig. 9). The majority fugitive impurity is water (as hydroxyl groups). Its content is 1.1 wt%. The sharp increasing of oxygen evolving at temperatures higher 1000 C is caused by dissociation of gahnite with evaporation of oxygen and zinc. The evolving of hydrogen ($4.7 \cdot 10^{-3}$ wt%) indicates complicated oxidation-reduction processes, in which the oxygen vacancies and hydroxyl groups can participate. The evolving of N_2 and NO (total content of nitrogen is $1.8 \cdot 10^{-3}$ wt%) are caused by presence in gahnite structure of bound nitrogen.

The presence of bound nitrogen in structure, more small size of crystals and effective formation of oxygen vacancies in gahnite structure synthesized in SCW-Am fluid allows to assume that ammonia participates in processes of gahnite formation and provokes increasing of nucleation rate and is remained in its structure.



a b

Figure 9: Gases evolving at stepwise vacuum heating of Eu (0.4 mol%)-doped gahnite samples synthesized in SCW-Am.: H_2O and O_2 – a, H_2, N_2, NO – b.

CONCLUSION

The treatment of initial mixture of hydrargillite, zinc oxide and europium oxide in medium SCW-Am fluid corresponds to reducing conditions of gahnite synthesis. Ammonia participates in synthesis, causes effective formation of oxygen vacancies and acceleration of transformation. The europium ions are incorporated in gahnite structure forming a complex with oxygen vacancies. At annealing of gahnite on air at 1200 C the environment of Eu^{3+} ions varies due to the elimination of OH-groups and bound nitrogen.

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