Regulation of gahnite crystal size during hydrothermal synthesis

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Abstract.
Gahnite with various particles size was synthesized from boehmite of different particles sizes via interaction with zinc oxide or zinc acetate. It was found that the decrease of the size of gahnite particles is accompanied by decrease of the crystallite size, change of the state of oxygen vacancies and optical properties. The UV light absorption decreases, the blue-shift of an absorption edge is observed, the luminescence of gahnite and Eu$^{3+}$ ions in gahnite changes.

1. Introduction
Zinc aluminate (gahnite, ZnAl$_2$O$_4$) is used as a ceramic, electronic and catalytic material. Gahnite, doped with europium is of special interest as a luminescent material [1, 2]. Gahnite can be synthesized by using conventional ceramic processing techniques [3], sol-gel method [4], coprecipitation method or alumina impregnating method [5] followed by calcination at temperatures (800-1000°C). Various variants of hydrothermal synthesis of zinc aluminate have been also described in the works [1, 6, 7]. Ultrasonic spray pyrolysis technique [2] and flame synthesis [8] of gahnite were also reported.

The authors previously determined that formation of gahnite from a mixture of zinc oxide and aluminum hydroxide during hydrothermal and thermovaporous treatment at 180-400°C and water vapor pressure 10 ÷ 26 MPa runs in accordance with the solid-phase mechanism [9]. It has been found that Zn$^{2+}$ ions diffuse in the alumina matrix and then nucleation and growth of gahnite crystals occurs. Based on this consideration it was assumed that the size of particles of a formed gahnite should decrease along with decrease of the aluminium component particles size. The present work provides the experimental confirmation of the guess that the particles size of produced zinc aluminate should depend on the particles sizes of the parent aluminium oxide or hydroxide. The effect of the particles size on optical properties of zinc aluminate was investigated.

2. Experimental
Zinc oxide and zinc acetate (chemically pure grade), Al(OH)$_3$ – hydargillite (GD18) or AIOOH – boehmite synthesized from it at 370°C as well as boehmite of the mark Apyral AOH 180 DS (from Nabaltec GmbH) and Disperal P2 (from Sasol), and also Eu$_2$O$_3$ (h. p.) were used in this work. The single-phase finecrystalline zinc aluminate was synthesized in medium of ammonia water solution via the treatment of a stoichiometric mixture of zinc oxide and hydargillite or boehmite in a laboratory autoclave (volume 16 cm$^3$) at temperatures 220-400°C (table 1). When synthesizing the Eu$^{3+}$ (2 wt%)-doped gahnite, the europium oxide was added into the precursors mixture. The single-phase nanosized zinc aluminate was synthesized via interaction of boehmite with zinc acetate in medium of ammonia.
water solution at 220°C. The mixture of boehmite and zinc acetate was placed into the autoclave container with an ammonia solution. The degree of autoclave filling with water was 0.2. The product of synthesis was extracted from the container after cooling an autoclave with the help of wash-out. The finecrystalline zinc aluminate was washed with distilled water and then dried at 70°C. The nanosized zinc aluminate was extracted from the container in the form of a colloid solution. The water solution of ammonia was then added into it. The coagulated precipitate was separated by centrifuging with subsequent drying up. Influence of the synthesis conditions on the samples state were explored by methods of X-ray diffraction (diffractometer DRON-3M in filtered Cu-Kα radiation), electron microscopy (Cam Scan Series 2), diffuse reflection (DR) spectroscopy (spectrometer Specord M40 in the region of 220-800 nm), photoluminescence, PL, (S DL-2M at room temperature). Distribution on the crystals sizes of samples was determined from the analysis of the SEM and TEM images by the method of linear segments.

| Table 1. | Conditions of synthesis of undoped and Eu³⁺(2wt%)-doped gahnite |
|-----------|---------------------------------------------------------------|
| Sample    | Precursors                                               | T°C  |
| 1         | Al(OH)₃ + ZnO + Eu₂O₃                                        | 400  |
| 2         | (Boehmite from hydargillite GD18) AIOOH + ZnO               | 260  |
| 3         | (Apyral AOH 180 DS) AIOOH + ZnO                             | 260  |
| 4         | (Disperal P2) AIOOH + ZnO                                  | 260  |
| 5         | (Disperal P2) AIOOH + Zn(C₂H₃O₂)₂ + Eu₂O₃                   | 220  |

3. Results and discussion

Figure 1 shows the morphology of gahnite samples synthesized via treatment of a mixture of zinc oxide and europium oxide with hydargillite at 400°C. The gahnite formed in these conditions of synthesis conserves the shape of the parent hydargillite particles [9] and contains particles from 2-3 up to 10 microns by size. Figure 2 shows the morphology of gahnite samples synthesized via treatment of a mixture of zinc oxide with boehmite of different dispersity at 260°C. The relation of the particles size of boehmite and synthesized gahnite is presented in table 2.

| Table 2. | The average particles size (µm) of boehmite and synthesized from it gahnite. |
|-----------|-----------------------------------------------------------------------------|
| Sample    | Raw material                        | Boehmite | Gahnite |
| 2         | Boehmite from hydargillite GD18    | 1        | 1.59    |
| 3         | Boehmite Apyral AOH 180DS          | 0.2      | 1.22    |
| 4         | Boehmite Disperal P2              | 0.05     | 0.65    |

One can see from figure 2 and table 2 that sizes of the gahnite particles decrease with decrease of the particles size of parent boehmite. Nano dimensional gahnite is possible to be synthesized if one changes the relation of a nucleation and growth rates of gahnite particles due to decreasing of synthesis temperature and facilitation of a diffusion stage of zinc ions to a surface of boehmite particles when using zinc acetate instead of zinc oxide. The figure 3 shows a typical TEM image of synthesized nanocrystalline gahnite.

Figure 4 shows the DR spectra of synthesized gahnite samples with different particles size. One can see that the UV absorption decrease and also the band shape of fundamental absorption changes when the size of particles decreases.
The absorbance edge shifts toward short wavelength. It corresponds to the known dependence of the band gap $E_g \sim 1/d$ on the nanocrystalline particle size $d$ [10]. However, the observed changes of absorbance spectra with the size of particles exhibit the more complicated nature rather than a simple shift of the absorption edge towards the shorter wavelengths. The similar change of UV-absorption was observed when changing the stoichiometry and when employing the mechanical grinding of zinc aluminates [3]. It is necessary to note that synthesis of zinc aluminates with the decrease of the size of particles is accompanied by decrease of the crystallite size (table 3).

As the gahnite crystallites size decrease the intensity of UV luminescence band also reduces and the band position varies (figure 5). In the visible spectral region the position of the wide band shifts from 520 up to 440 nm. As a result, UV-band of nanogahnite luminescence (figure 6, sample 5) is suppressed and the band at 440 nm becomes more intensive. We attributed these bands to luminescence of the defects on the basis of oxygen vacancies [9]. The luminescence of these defects is excited in bands at 294, 304 and 315 nm (figure 7) which are characteristic for light absorption by oxygen vacancies. Eu-doped gahnite has a series of narrow luminescence bands of Eu$^{3+}$ ions (figure 6) in the red spectrum region. As compared with the finecrystalline gahnite the position of the most intensive luminescence band of Eu$^{3+}$ ions in nanocrystalline gahnite shifts from 612 nm to 614 nm. The relative of intensities and position of some other bands also change. It testifies to a change of the crystal environment of Eu$^{3+}$ ions. The change of the bands intensity ratio is observed also in excitation spectra of Eu$^{3+}$ ions luminescence (figure 8). The basic difference of excitation spectrum of Eu$^{3+}$ ions in nanocrystalline gahnite is the absence of a band at 270 nm originated from absorption of light by oxygen vacancies.

![Figure 2. SEM image of gahnite samples synthesized at 260°C from boehmite of different particle size: 1 µm (a), 0.2 µm (b) and 0.05 µm (c).](image)

![Figure 3. TEM image of gahnite (sample 5) synthesized from boehmite Disperal P2 and zinc acetate at 220°C. The average size of crystals is 36 nm.](image)

![Figure 4. DR spectra of synthesized gahnite samples: finecrystalline Eu-doped - 1, undoped gahnite different particle size - 2 (1.59 µm), 3 (1.22 µm), 4 (0.65 µm); nanocrystalline Eu-doped gahnite -5.](image)

| Sample | $D$, nm |
|--------|---------|
| 1      | 32±3    |
| 2      | 44±4    |
| 3      | 33±3    |
| 4      | 28±3    |
| 5      | 18±2    |

**Table 3.** The crystallite size of gahnite samples.
Conclusion
Using of boehmite with various particle sizes allows to synthesize in hydrothermal conditions finecrystalline and nanocrystalline gahnite, both the pure or doped one. As the size of gahnite particles is decreased the state of oxygen vacancies changes, the UV absorption decreases, a blue-shift of an absorption edge occurs, and the luminescence spectra of pure and Eu-doped gahnite vary.

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