SYNTHESIS OF ULTRAFINE GAHNITE ($ZnAl_2O_4$) NANOCRYSTALS BY COPRECIPITATION METHOD

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ABSTRACT

Nanocrystalline zinc aluminate $ZnAl_2O_4$ has been obtained by coprecipitation method at two different temperatures (800°C and 900°C). The precursors used in coprecipitation synthesis of $ZnAl_2O_4$ were zinc nitrate hexahydrate and aluminum nitrate nonahydrate. As a basic source sodium hydroxide was used. The obtained samples were analyzed by X-ray diffraction (XRD) and by energy dispersive spectroscopy (EDAX). Optical properties of nanocrystalline zinc aluminate were also determined by UV/VIS/NIR spectroscopy. The band gap for sample obtained at 800°C was 3,88 eV while for sample obtained at 900°C was 3,97 eV.

Keywords: zinc aluminate, coprecipitation, spinels

INTRODUCTION

Zinc aluminate ($ZnAl_2O_4$) with a cubic, normal crystal structure is widely used as ceramic, electronic and catalytic material [1,2]. The normal spinel $ZnAl_2O_4$ has general formula AB_2O_4, where A and B stands for divalent and trivalent ions, respectively. In this structure, unit cell contains 8 tetrahedral cations (A sites), 16 octahedral cations (B sites) and 32 oxygen anions within the close-packed face-centered cubic unit cell with Fd3m space group symmetry. In normal spinel $ZnAl_2O_4$ structure, the divalent cations Zn^{2+} are at the A sites and the trivalent cations Al^{3+} at the B sites. The band gap of $ZnAl_2O_4$ nanocrystals is 3.8 – 3.9 eV [3,4]. In the literature, many synthesis methods for the obtaining of $ZnAl_2O_4$ have been described, such as: coprecipitation [5], hydrothermal method [6,7], sol–gel [8,9], microwave assisted hydrothermal method [10].

Herein, nanocrystalline zinc aluminate ($ZnAl_2O_4$) particles with a spinel structure were prepared by coprecipitation method at two different temperatures (800°C and 900°C) using zinc nitrate hexahydrate and aluminum nitrate nonahydrate as precursors and sodium hydroxide as the basic source.

MATERIALS AND METHODS

$ZnAl_2O_4$ powders were prepared by coprecipitation method. As precursors $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used. The precursors were mixed in distilled water, then, the appropriate amount of sodium hydroxide solution was added. The mixture was stirred at room temperature for few hours. The resulting suspension was filtrated and washed many times with distilled water and ethylic alcohol, then dried in an oven at 80°C for 6 hours. After drying resulting powders were heated at 800°C and 900°C for 5h. The characterization of the obtained materials was achieved by X-ray diffraction (XRD) using an X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.5418 Å) incident radiation and by energy

dispersive spectroscopy (EDAX) using an scanning electron microscopy (SEM + EDAX; Model INSPECT S). UV/VIS/NIR measurement was carried out using an UV/VIS/NIR spectrophotometer (Model Lambda 950).

RESULTS

X-ray diffraction patterns of the powder samples obtained by coprecipitation method at two different temperatures (800°C and 900°C) are shown in Figure 1 (a) and (b). The observed peaks can be indexed as (111), (220), (311), (400), (331), (422), (511), (440), (620) and (533) crystal planes of the cubic crystalline structure of $ZnAl_2O_4$, respectively, in accordance with the standard JCPDS card of cubic spinel-type $ZnAl_2O_4$ (JCPDS no. 05-0669). X-ray diffraction patterns showed a single phase $ZnAl_2O_4$. The average crystallite size was calculated using Schererr's equation. It was found that average crystallite size increase from 24 nm (for sample heated at 800°C for 5h) to 28 nm (for sample heated at 900°C for 5h). For both samples the cubic lattice parameter was calculated from X-ray diffraction patterns. It was found that this parameter increases with the temperature, as $a = 8{,}0725$ Å for sample heated at 800°C for 5h and $a = 8{,}0786$ Å for sample heated at 900°C for 5h.

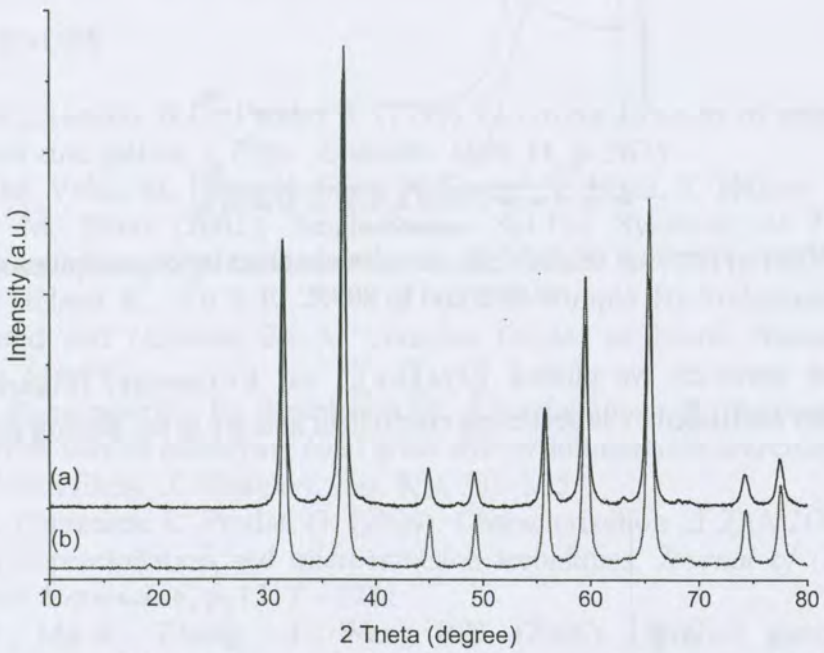
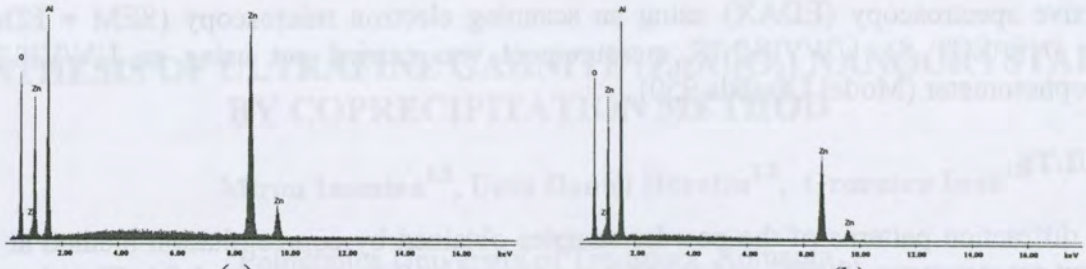


Figure 1 XRD patterns of $ZnAl_2O_4$ samples obtained by coprecipitation method: a) 800°C and b) 900°C

To analyze chemical composition of obtained zinc aluminate nanoparticles energy dispersive X-ray analysis (EDAX) was performed. A typical EDAX spectrum of $ZnAl_2O_4$ samples obtained by coprecipitation method is presented in Figure 2 (a) and (b). EDAX measurements were performed in different points of the powders and then an average of the results was made. The results confirmed the uniformity and the closely stoichiometric composition with the precursor material.



(a) (b)

Figure 2 The qualitative EDAX analysis of $ZnAl_2O_4$ samples obtained by coprecipitation method: a) 800°C and b) 900°C

The absorbance was calculated from the diffuse reflectance spectrum using Kubelka–Munk equation. The optical absorbance spectrum (Figure 3) of $ZnAl_2O_4$ is detected in the 250-400 nm region at room temperature.

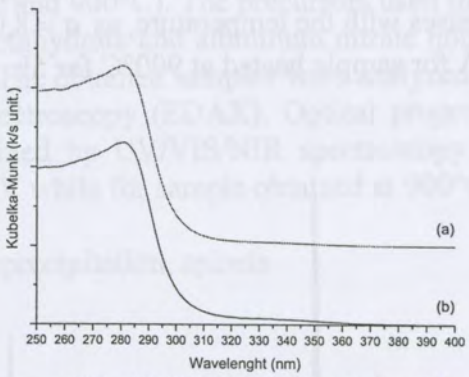


Figure 3 Absorbance spectrum of $ZnAl_2O_4$ samples obtained by coprecipitation method: a) 800°C and b) 900°C

From absorbance spectrum we plotted $\{(k/s)(h\nu)\}^2$ vs. $h\nu$ (energy) (Figure 4), where k denotes absorption coefficient, s is scattering coefficient and $h\nu$ is the photon energy.

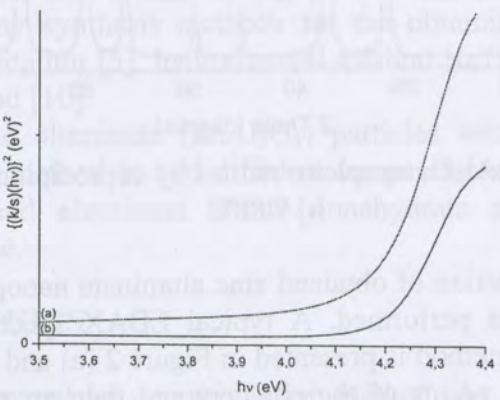


Figure 4 Plot of $\{(k/s)(h\nu)\}^2$ vs. $h\nu$ (energy) of $ZnAl_2O_4$ samples obtained by coprecipitation method: a) 800°C and b) 900°C

The band gap of $ZnAl_2O_4$ were determined from the absorbance spectra. The band gap value depends strongly by temperature used. One can see that the band gap for sample obtained at 800°C is 3,88 eV and for sample obtained at 900°C is 3,97 eV.

CONCLUSIONS

- In this research, $ZnAl_2O_4$ nanoparticles were successfully prepared by coprecipitation method at different temperatures using zinc nitrate hexahydrate and aluminum nitrate nonahydrate as precursors.
- From X-ray diffraction, one can see that $ZnAl_2O_4$ spinel was single phase crystallized and the particle size depends strongly by heating temperature.
- EDAX measurements confirmed the uniformity and the closely stoichiometric composition with the precursor material.
- Morevover, the band gap for sample obtained at 800°C was 3,88 eV while for sample obtained at 900°C was 3,97 eV.

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