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Evolution of structural and optical properties in the course of thermal evolution of sol–gel derived cobalt-doped gahnite

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ABSTRACT

Thermal evolution of sol–gel derived gahnite ($ZnAl_2O_4$) with 4, 8 and 12 at.% of Zn replaced with Co was studied by thermal analysis techniques (DTA/TGA), X-ray diffraction (XRD) and UV–vis diffuse reflectance spectroscopy (DRS). Zinc–cobalt spinel powders were produced by gel heat treatment at temperatures as low as 400 °C. Crystal structure was characterized using Rietveld refinement of X-ray diffraction patterns for the samples annealed at 800 °C, simultaneously with the analysis of diffraction line broadening. It was found out that the distribution of Co^{2+} ions in tetrahedral and octahedral sites of zinc cobalt aluminate crystal lattice, crystallite size and lattice strain depend on Co loading. The green color of samples thermally treated at $T < 800$ °C has been explained as a consequence of partial oxidation of Co^{2+} ions at lower temperatures and accommodation of Co^{3+} ions in octahedral sites. Thermal treatment at higher temperatures promote gradual change of color from green to blue, characteristic for tetrahedrally coordinated Co^{2+} ions. The spectra evolution could be interpreted as a progressive reduction of Co^{3+} to Co^{2+} ions at higher temperatures.

1. Introduction

Majority of blue ceramic pigments are based on cobalt ion, and one of most common crystalline material used for this purpose is cobalt aluminate ($CoAl_2O_4$). This intense blue color pigment, known as Thénard blue is characterized by its thermal and chemical stability, and also by its stability to solar exposure and atmospheric agents [1]. Beside ceramic, it is widely used for the coloration of plastics, paint, fibers, paper, rubber, glass and cement [1]. Cobalt and its salts are widely considered to be toxic and environmentally hazardous substances. The scarcity of Co and its difficult metallurgy make the use of cobalt raw materials expensive [2]. In order to minimize the use of cobalt in the preparation of blue ceramic pigments, the zinc aluminate, $ZnAl_2O_4$ (known by mineral name gahnite), proves to be a convenient host lattice allowing the development of intense blue colors with small amounts of cobalt ions substituting for zinc ions [3]. Zinc is considerably more abundant in nature and much less toxic than cobalt. Thus, partial replacement of cobalt by zinc in gahnite, producing of $(Zn,Co)Al_2O_4$ solid solutions can reduce the negative health, environmental, sustainability and economic considerations [2].

Both, zinc aluminate and cobalt aluminate have a normal spinel-type structure of the general formula AB_2O_4. Spinels crystallize in the cubic system, space group $Fd\bar{3}m$. The unit cell of the normal spinel structure contains 32 O^{2-} anions, 8 divalent cations A^{2+} in 8 tetrahedral interstices (of 64 available), and 16 trivalent cations B^{3+} in 16 octahedral interstices (of 32 available). On the other hand, the unit cell of the ideal inverse spinel structure contains 32 O^{2-} anions, 8 divalent cations A^{2+} in the octahedral interstices, while 16 trivalent cations B^{3+} are evenly divided between tetrahedral and octahedral interstices. Spinels can also possess some degree of cation disorder, which Verwey and Hellmann [4] described by introducing an inversion parameter, δ. This parameter is defined as a fraction of trivalent cation B^{3+} on tetrahedral cation site. The majority of spinels show some degree of cation disorder. Any intermediate partly disordered state may be expressed as a mixture of these two end members (the ideal normal spinel and the ideal inverse spinel, respectively) with a general formula $^{IV}[A_{1-\delta}\ B_{\delta}]\ ^{VI}[B_{2-\delta}A_{\delta}]\ O_4$, where δ is the inversion parameter.

Different chemical processing methods are used for the preparation of spinels [5] such as solid state reaction, co-precipitation, hydrothermal, combustion, sol–gel, etc. Compared with other techniques, the sol–gel method is a useful and attractive technique for the preparation of nanocrystalline materials for advanced technological applications, because it enables production of pure, homogeneous and ultra fine powders at low temperatures and

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Table 1
Selected structural parameters for samples GC04, GC08 and GC12 heat treated at 800 °C resulted from Rietveld structure refinement.

Sample	Atom site	Occupancy [8]	δ [8]	Crystallite size (nm)	Lattice strain (%)
GC04	^{IV}A	0.003 Co + 0.96 Zn + 0.037 Al	0.037(4)	22.3	0.04
	^{VI}B	0.0185 Co + 0.9815 Al			
GC08	^{IV}A	0.029 Co + 0.92 Zn + 0.051 Al	0.051(3)	21.6	0.05
	^{VI}B	0.0255 Co + 0.9745 Al			
GC12	^{IV}A	0.065 Co + 0.88 Zn + 0.055 Al	0.055(4)	20.3	0.08
	^{VI}B	0.0275 Co + 0.9725 Al			

short calcinations times [6]. The use of nanoparticles can improve the pigment performance enhancing tribological and mechanical properties [7]. Another effect of nanoparticles, being smaller than the wavelengths of visible spectrum, is that no scattering and no reflection occur in the visible-light range, so the nanocomposite is transparent [7].

In this work nanoparticles of (Zn,Co)$\mathrm{Al_2O_4}$ spinel pigment were prepared by sol–gel method. Samples were prepared in which 4, 8 and 12 at.% of zinc in the gahnite lattice was replaced with cobalt with the aim to obtain a blue ceramic pigment having reduced negative environmental impact and lower production costs.

2. Material and methods

2.1. Sample preparation

Three gels with composition $\mathrm{Zn_{1-x}Co_xAl_2O_4}$, where x = 0.04, 0.08, 0.12 (denoted as GC04, GC08 and GC12, respectively) were prepared. For the preparation of gels the chelating agent ethyl-acetoacetate, $\mathrm{C_6H_{10}O_3}$ (99%, Fluka, Germany), was firstly added to the sec-butanol, ^{s}BuOH (99%, Kemika, Croatia), and then the appropriate amount of aluminium sec-butoxide, $\mathrm{Al(O^sBu)_3}$ (97%, Aldrich, Great Britain), was firstly dissolved in the $\mathrm{^sBuOH/C_6H_{10}O_3}$ solution. $\mathrm{Al(O^sBu)_3}$ was added to the solution using syringe to minimize exposure to air humidity. The appropriate amounts of zinc nitrate hexahydrate, $\mathrm{Zn(NO_3)_2{\cdot}6H_2O}$ (99%, Kemika, Croatia), and cobalt nitrate hexahydrate, $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$ (99%, Kemika, Croatia), were also dissolved in ^{s}BuOH. Both solutions were stirred for 1 h before the nitrate salts solution was added drop wise to the $\mathrm{Al(O^sBu)^3/C_6H_{10}O_3}$ solution. The molar ratio of $\mathrm{Al(O^sBu)_3{:}C_6H_{10}O_3{:}[Zn(NO_3)_2{\cdot}6H_2O + Co(NO_3)_2{\cdot}6H_2O]{:}{}^sBuOH}$ was 2:2:1:10. The mixture was stirred in a closed reactor for 24 h at room temperature. No precipitation was observed during that period. The clear red-colored sols were poured into a large Petri dish in order to maximize exposure to air moisture and kept at room temperature. After 2 days the gelation occurred and completely transparent gels were obtained. Drying of the gels for five more days at room temperature enabled the evaporation of solvent and the release of alkoxy groups resulting in a dry product. The obtained samples were then subsequently grinded to fine powders. The powders were heated in the furnace with static air at a heating rate of 10 °C/min and calcined at various temperatures between 200 and 900 °C for 2 h. Afterwards they were slowly cooled to RT in the furnace. The prepared samples were denoted GC04, GC08 and GC12 (Table 1).

2.2. Characterization

The thermal behavior of powder precursors was characterized by differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) using a simultaneous DTA/TGA analyzer Netzsch STA 409. For the thermal analysis ~50 mg of material were placed in Pt crucibles and heated at a rate of 10 °C min^{-1}.

Crystalline phases formed by thermal treatment of the samples were identified by powder X-ray diffraction (XRD) using a Philips MPD 1880 diffractometer with monochromatized CuKα radiation. Diffraction patterns for phase identification were collected between 5° and 70° 2θ in steps of 0.02° and with a fixed counting time of 2 s per step. The samples that were heat treated at 800 °C were additionally scanned in the 2θ range from 10° to 140°, in steps of 0.02°(2θ) with fixed counting time of 7 s per step, for the purpose of structure refinement and line broadening analysis by the Rietveld method. Rietveld method was performed by the program X′Pert HighScore Plus, version 2.1 (PANalytical 2004using a pseudo-Voigt profile function and the polynomial background model. The instrumental line broadening was determined using silicon powder (Koch-Light Lab. Ltd., 99.999% purity, spherical particles with diameter of 1 μm).

UV–vis diffuse reflectance spectra (DRS) of the samples were acquired using an OceanOptics USB 2000 spectrometer equipped with a bifurcated fiber-optic reflection probe. Spectroscopically pure barium sulphate was used as a reference and matrix for sample dilution. Reflectance data were recorded between 300 and 800 nm with a spectral resolution of 0.2 nm. A total of 50 spectra were collected per sample and averaged to increase the signal-to-noise ratio. The measured reflectance data were transformed to Kubelka-Munk function using equation $F(R) = (1-R)^2/2R$, where R is reflectance of the sample.

3. Results and discussion

3.1. Thermal behavior of the dried gels

Fig. 1 shows DTA and TGA curves of the as-prepared gels. Several thermal features took place during the heating of the gels. A wide endotherm in the range between room temperature and ~160 °C, sharp exotherm at ~160 °C and two more exotherms, between 250 and 350 °C as well as between 600 and 700 °C are seen on DTA curve. TG curves show four weight loss steps: a continuous loss of ~18% between room temperature and ~160 °C, a rapid weight loss of 23–31% at ~160 °C followed by weight loss of 15–18% between 180 and 330 °C. An additional small continuous loss at temperatures higher than 300 °C could also be seen on TG curves.

Based on our previous detailed investigation on gahnite synthesis using the sol–gel technique [5] the peaks in DTA-TGA curves could be assigned as follows: the first endothermic DTA peak, accompanied by continuous weight loss seen on TGA curves of the samples (Fig. 1), was induced by evaporation of the residual solvent and physically adsorbed water from the gel. The sharp exothermic peak at ~160 °C on DTA curves of samples accompanied with rapid weight loss is a consequence of an auto-combustion process involving nitrates and organic phase. Weight loss between 180 °C and 300 °C could be attributed to formation of nitrous gasses due to decomposition of nitrates. The peaks in the temperature range 250–350 °C and 600–700 °C indicate crystallization processes. It seems that under dynamic heat-treatment the spinel phase crystallizes in two steps. The two-steps crystallization processes seen on DTA scans can be explained with the fact that the majority of zinc and cobalt content is not at disposal for reaction until the end of nitrate decomposition process.

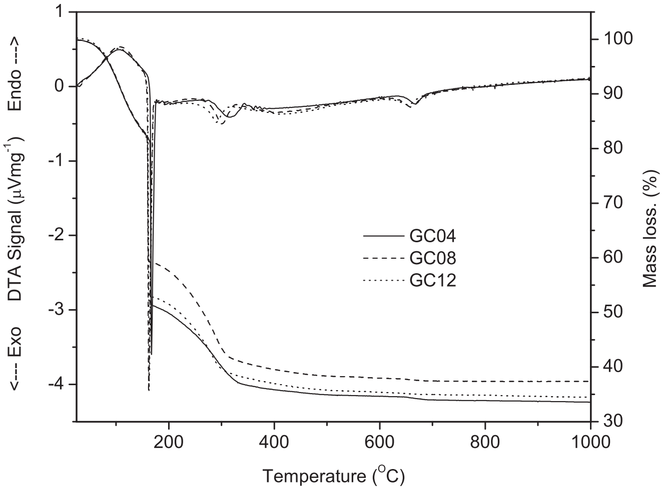

Fig. 1. DTA and TGA patterns of samples GC04, GC08 and GC12.