

# Synthesis of nanocrystalline $(\text{Zn}_{1-x}\text{Co}_x)\text{Al}_2\text{O}_4$ solid solution: structural and optical properties

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## ABSTRACT

New inorganic pink pigments based on nanocrystalline  $(\text{Zn}_{1-x}\text{Co}_x)\text{Al}_2\text{O}_4$  solid solution, were prepared using the hydrothermal method, obtaining nanoparticles below 8 nm. The spinel  $\text{ZnAl}_2\text{O}_4$  was chosen as host hue to introduce Co(II) ions, because zinc aluminate is colorless and presents great thermal stability.

The most straightforward way to obtain blue colors in bulk ceramics is by means of cobalt, Co(II) ions exhibit, when tetrahedrally coordinated, highly saturated blue shades, nevertheless these nanoparticles show a brilliant pink color due to partial substitution of Al(III) ions in octahedral sites. The samples characterization was performed by X-ray diffraction and diffuse reflectance spectroscopy. The morphology of the nanoparticles was studied by high-resolution transmission electron microscopy.

The effects of Co(II) concentration and heating temperature on the spinel structure and the optical properties of the solid solution were systematically studied.

**Keywords:** nanoparticles, spinel pigments, solid solutions, optical properties

## 1 INTRODUCTION

During the last decades, much attention has been focused on the rational synthesis of nanocrystals ranging in size from 1 to 100 nm, which can exhibit very interesting size-dependent electrical, optical, magnetic and chemical properties compared with those of bulk counterparts [1].

Zinc aluminate ( $\text{ZnAl}_2\text{O}_4$ ), naturally occurring as the mineral ghanite, is a member of the spinel family. At present, zinc aluminate is used as a catalyst for the dehydration of saturated alcohols to olefins, methanol and higher alcohol synthesis, preparation of polymethylbenzenes, synthesis of styrenes from acetophenons and isomerisation of alkenes.

Zinc aluminate have high thermal stability, high mechanical resistance, hydrophobicity, and low surface acidity. It is widely used as a high temperature material, catalysts and

catalyst support, optical coating and as ceramic pigment when is doped with transitional cations [2-4]

Besides, as a wide band gap semiconductor (3.8 eV)  $\text{ZnAl}_2\text{O}_4$  can be used as transparent conductor, dielectric and optical material [5].

The crystal structure of spinel ( $\text{MgAl}_2\text{O}_4$ ) has been determined by Bragg [6] and Nishikawa [7] in 1915. It has the space group  $\text{Fd}\bar{3}\text{m}$  and has a cubic structure made of eight molecular units ( $\text{AB}_2\text{O}_4$ ). The A cation is divalent and the B cations trivalent, one unit cell of a compound with the spinel structure is built up from 32 oxygen ions arranged in a fcc-lattice, giving 64 tetrahedral and 32 octahedral sites. The divalent A cations occupy eight tetrahedral sites and the trivalent B cations occupy 16 octahedral sites. This distribution of the cations is designated as normal, however, this is thermodynamically not always the most stable situation, since the configurational entropy counteracts the site preference energy. Therefore, in spinels A and B cations may interchange sites via diffusion, eventually leading to the situation where all the A cations are in octahedral sites, this structure is designated as inverse.

All distribution between the two extremes are possible and the degree of inversion is given by the inversion parameter  $\gamma$ , which is defined as the fraction of A cations in octahedral sites.

$\text{ZnAl}_2\text{O}_4$  has the chemical formula of  $\text{AB}_2\text{O}_4$  with the normal spinel structure [8].

The main aspect of spinels is the presence of two metallic cations,  $\text{A}^{2+}$  and  $\text{B}^{3+}$ , in tetrahedral and octahedral sites, respectively. The manner in which such sites are occupied depend on the calcining temperature [9]

To prepare  $\text{ZnAl}_2\text{O}_4$  powders, scientists have put forward various synthetic routes, generally including the traditional method of solid-solid reaction, wet chemical route such as co-precipitation, sol-gel and hydrothermal synthesis [10].

Recently, a new application of the spinels as ceramic nanopigments has been explored, owing to their high mechanical resistance, high thermal stability, low temperature sinterability and the easy incorporation of chromophore ions into the spinel lattice, allowing for

different types of doping, thus producing ceramic pigments with different colors [11].

The traditional and unavoidable source of blue in a ceramic pigment is the cobalt ion. All the blue ceramic pigments known currently (except vanadium-zircon) classified with the DCMA number, contain cobalt to some extent: the  $\text{Co}_2\text{SiO}_4$  olivina (DCMA 5-08-2), the  $(\text{Co,Zn})_2\text{SiO}_4$  willmenite (DCMA 7-10-2), and the cobalt spinels  $\text{CoAl}_2\text{O}_4$  (DCMA 13-26-2),  $\text{Co}_2\text{SnO}_4$  (DCMA 13-27-2),  $(\text{Co,Zn})\text{Al}_2\text{O}_4$  (DCMA 13-28-2) and  $\text{Co}(\text{Al,Cr})_2\text{O}_4$  (DCMA 13-28-2).  $\text{Co}^{2+}$  cation is known as a chromophore which usually develops blue color, the coloring performance depends very much on the coordination of  $\text{Co}^{2+}$  ions.

The  $\text{ZnAl}_2\text{O}_4$  is a normal spinel,  $\text{Zn}^{2+}$  ions occupy tetrahedral sites, while  $\text{Al}^{3+}$  cations occupy octahedral positions. When  $\text{Co}^{2+}$  is added to this structure, substituting  $\text{Zn}^{2+}$  in bulk systems usually occupy tetrahedral sites and develop blue color.

E.F. da Costa et al [12] observed that the  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  ( $x = 0-1$ ) system develops violet, blue and cyan, centered in the blue colors.

Accordingly, the present work aims at prepare the nanocrystalline  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  ( $x = 0-1$ ) system by the hydrothermal route, and the optical properties of the samples were analyzed.

## 2 EXPERIMENTAL

The  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  ( $x=0, 0.2, 0.4, 0.6, 0.8, 1.0$ ) system was synthesized using the hydrothermal method, in this experiment,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (99% Sigma-Aldrich),  $\text{ZnCl}_2$  (98% Sigma-Aldrich) and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (99% Sigma-Aldrich) were used as starting materials. Firstly, stoichiometric amounts of start materials were dissolved in deionized water, mixed well with each other, the pH was adjusted via dropping 28 wt%  $\text{NH}_4\text{OH}$  solution to 10-11, obtaining a white gel, which was washed with deionized water and then dried at room temperature for one week. Subsequently dried and grinded the gel, was calcined in air at  $600^\circ\text{C}$  2h.

Six samples were prepared according to the stoichiometry:  $\text{ZnAl}_2\text{O}_4$ ,  $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.6}\text{Co}_{0.4}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.4}\text{Co}_{0.6}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.2}\text{Co}_{0.8}\text{Al}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$

Phases in the resultant powders were identified by X-ray diffraction, the patterns were obtained at room temperature with  $\text{Cu K}_\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) by using a D5000 Siemens diffractometer. UV-Vis electronic absorption spectra was measured in diffuse reflectance mode in the 200–1200 nm wavelength range with an Ocean Optics HR4000 fiber optic spectrometer.

High-resolution transmission electron micrographs (HR-TEM) were obtained in a JEOL 2010 FASTEM analytical microscope operating at 200 kV.

## 3 RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of the compositions synthesized for the  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  solid solution calcined at  $700^\circ\text{C}/2\text{h}$ . At this temperature for all the values of  $x$  studied, the characteristic peaks of the spinel structure were noticed.

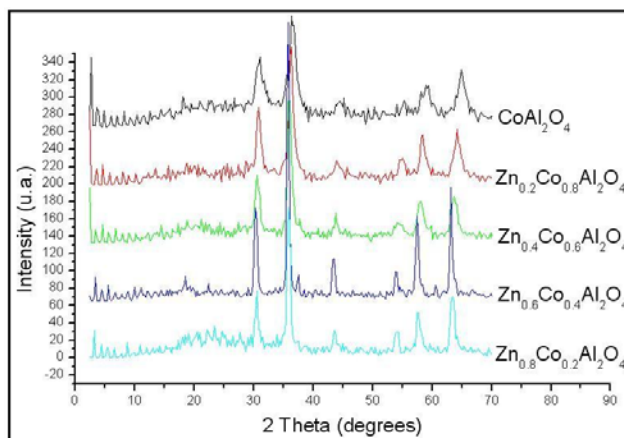


Figure 1. XRD diffraction patterns of powder samples heat treated at  $700^\circ\text{C}$

The XRD patterns showed that zinc aluminate structure was formed as a single phase in all samples. In these samples, Co ions seem to be completely incorporated into the spinel lattice, in agreement with the atomic radii for divalent cations Co and Zn, both in tetrahedral coordination.

All reflections of the XRD pattern of the white powders of  $\text{ZnAl}_2\text{O}_4$  (Fig.2) can be readily indexed to a spinel zinc aluminum oxide (JCPDS, 74-1136) which indicates the high purity of the nanocrystalline  $\text{ZnAl}_2\text{O}_4$ . This zinc aluminate has a cubic crystalline structure with a unit symmetry described by space group  $\text{Fd}\bar{3}\text{m}$  and lattice parameter  $a = 8.083 \text{ \AA}$ .

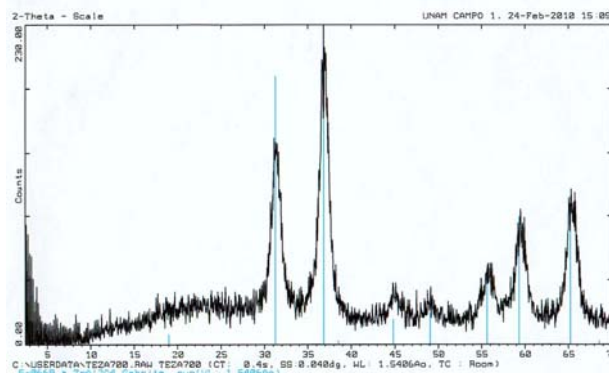


Figure 2. XRD pattern of  $\text{ZnAl}_2\text{O}_4$  nanoparticles

It can be observed that the diffraction peaks are markedly broadened, which is indicative of a fine crystallite. In all

samples, no peaks of impurity are observed in the XRD patterns.

In order to determine the  $\text{Co}_3\text{O}_4$  nanoparticles average size, the peak broadening method using the classical Scherrer equation over the (3 1 1), (2 2 0), (4 2 2), (5 1 1) and (4 4 0) reflections was employed.

$\text{ZnAl}_2\text{O}_4$  nanoparticles have an average size of  $6.4 \pm 1.2$  nm

Fig. 3 illustrates the UV-vis spectra in the range from 220-800 nm, for the  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  samples heated  $700^\circ\text{C}/2\text{h}$ .

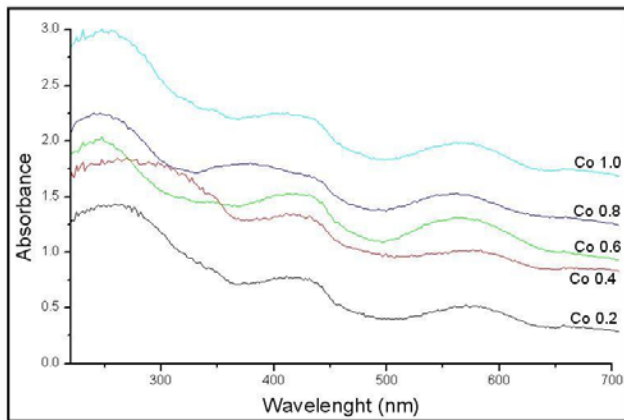


Figure 3. UV-vis absorbance spectra of  $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.6}\text{Co}_{0.4}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.4}\text{Co}_{0.6}\text{Al}_2\text{O}_4$ ,  $\text{Zn}_{0.2}\text{Co}_{0.8}\text{Al}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$

The electronic absorption spectra obtained exhibits three wide absorption bands attributed to  $\text{Co}^{2+}$  in octahedral coordination and particularly to the CF transitions:

${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{2g}({}^4\text{F})$  at 560 nm,  ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{A}_{2g}({}^4\text{F})$  at 420 nm and  ${}^4\text{T}_{1g}({}^4\text{F}) \rightarrow {}^4\text{T}_{1g}({}^4\text{P})$  at 250 nm.

Nano-sized  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  system is expected to have a normal spinel, with  $\text{Co}^{2+}$  situated at the tetrahedral site, however the optical spectra of the nano-sized samples are coherent with a hexa-coordinated  $\text{Co}^{2+}$  ion. It is completely different from the optical spectra of the bulk system, which exhibits the expected intense bands in the 500-600 nm range attributable to the transitions of  $\text{Co}^{2+}$  in 4-fold coordination [13].

All samples present similar spectrum, with absorption bands attributed to  $\text{Co}^{2+}$  in octahedral sites, which implies a change in the structure, inverse spinel is noticed independently on composition.

Typical HR-TEM micrograph obtained from sample  $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Al}_2\text{O}_4$  is shown in figure 4.

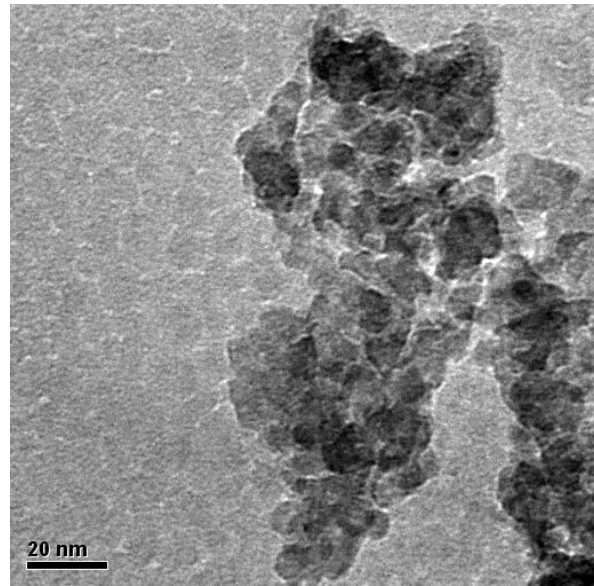


Figure 4. HRTEM micrograph of  $\text{Zn}_{0.8}\text{Co}_{0.2}\text{Al}_2\text{O}_4$

In this micrograph, nanocrystallites with dimensions close to those determined by X-ray diffraction patterns can be observed.

## 4 CONCLUSIONS

Nanocrystalline pink powders of  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  ( $x = 0; 0.2; 0.4; 0.6; 0.8$  and  $1.0$ ) were synthesized by the hydrothermal method, obtaining nanoparticles with average particle size of  $6.4 \pm 1.2$  nm. The UV-vis absorbance spectra of the samples  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  display a three wide absorption bands centered at approximately 560, 420 and 250 nm, which are attributed to  $\text{Co}^{2+}$  in octahedral coordination. It is completely different from the optical spectra of the bulk system, which exhibits the expected intense bands in the 500-600 nm range attributable to the transitions of  $\text{Co}^{2+}$  in 4-fold coordination.

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