



# Cobalt and nickel aluminate spinels: Blue and cyan pigments

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## Abstract

$M^{2+}$ -doped aluminate spinels ( $M = \text{Co}$  or  $\text{Ni}$ ) were prepared by a polymeric route leading to pure phases for synthesis temperatures equal to 800 or 1200 °C and characterized by UV–vis–NIR spectroscopy,  $^{27}\text{Al}$  NMR and XRD refinements. Coloration of the synthesized pigments is clearly sensitive to the distribution of doping ions in the aluminate spinel lattice. As the synthesis temperature increased, a color shift from green to blue has been observed for  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  compound while coloration of  $\text{Zn}_{1-x}\text{Ni}_x\text{Al}_2\text{O}_4$  compound remains greenish-gray. Hence, to improve pigment coloration and/or synthesis cost, two different strategies have been proposed: (i) the synthesis of aluminum over-stoichiometric spinel with  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{Al}_{2.2}\text{O}_{4+\delta}$  formal composition in order to force  $\text{Co}^{2+}$  to be located in tetrahedral sites and (ii) changing from  $\text{ZnAl}_2\text{O}_4$  to  $\text{MgAl}_2\text{O}_4$  as host lattices for  $\text{Ni}^{2+}$  doping ions in order to force  $\text{Ni}^{2+}$  to be located in octahedral sites.

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## 1. Introduction

Synthetic blue pigments are widely used in the ceramics industry as coloring agents for glazes or porcelain stoneware [1–2]. The traditional source of blue color in a ceramic pigment remains the divalent cobalt ion ( $\text{Co}^{2+}$ ) in tetrahedral coordination site [3], especially inside the  $\text{CoAl}_2\text{O}_4$  spinel phase [1–16]. However, recent publications have focused on the elaboration of aluminate spinels for cyan pigments (one primary color in subtractive system) with  $\text{Ni}^{2+}$  as chromophore ion [17–19].

The main drawback of  $\text{CoAl}_2\text{O}_4$  blue pigment lies in the large range of colorimetric parameters depending on material thermal history. Indeed, the  $\text{CoAl}_2\text{O}_4$  composition (known as Thenard's blue) is known for exhibiting a sky-blue hue more intense after high temperature treatment [6–12] than after moderate annealing. Previous literature work [6–10,20–22] and more especially our own previous study [16] on  $\text{Zn}_{1-x}\text{Co}_x\text{Al}_2\text{O}_4$  oxides have underlined the influence of thermal history on the pigment coloration and reported this “becoming-green” phenomenon with decreasing synthesis temperature. Presently, a clear consensus [16,20–24] shows

that the effect is due to the variation of the distribution of the cobalt cations between octahedral and tetrahedral sites of the spinel network, with the possibility to obtain a pink ceramic as an extreme effect when  $\text{Co}^{2+}$  ions are entirely located in octahedral site [21].

In this study,  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$  powder was elaborated by a Pechini route [25] and thereafter annealed at various temperatures between 800 and 1200 °C. Combined analysis of diffuse reflectance spectra, X-Ray diffraction patterns and  $^{27}\text{Al}$  NMR spectra clearly shows that the green color of pigments issued from low temperature treatments is due to cationic and anionic deficient spinels with tetrahedral vacancies accompanied by a partial fraction of  $\text{Co}^{2+}$  in octahedral sites as shown in our previous study [16]. In this paper, it is shown that the solution to this “problem”, considering that high thermal treatments increase the production cost significantly, is to synthesize aluminum over-stoichiometric spinel with  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{Al}_{2+d}\text{O}_4$  formulation.

Another study is devoted to the preparation  $\text{Zn}_{0.9}\text{Ni}_{0.1}\text{Al}_2\text{O}_4$  compounds by the same Pechini route as previously, with thermal treatments varying between 800 and 1200 °C. As for the zinc–cobalt aluminates, color evolution is observed with the zinc–nickel pigments thermal history. Furthermore, poor colorations besides pigment application: greenish grays, are only obtained and linked to the cationic distribution of the

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$\text{Ni}^{2+}$  chromophore ions in the spinel framework. In a parallel way to the case of zinc–cobalt aluminates, a strategy was found in order to synthesize beautiful cyan pigments with coloration arising from the occurrence of  $\text{Ni}^{2+}$  ions only in octahedral sites: synthesizing  $\text{Mg}_{0.9}\text{Ni}_{0.1}\text{Al}_2\text{O}_4$  spinel compounds instead of the  $\text{Zn}_{0.9}\text{Ni}_{0.1}\text{Al}_2\text{O}_4$  compounds.

## 2. Experimental

The nickel and cobalt pigments were synthesized by the Pechini route [25]. This chemical process is based on cations chelation by citric acid (CA) and on polyesterification between CA and ethylene glycol (EG) which leads to the formation of a polycationic resin. Aqueous solutions of citrate were prepared by dissolving CA in a minimal volume of water. Then, cationic salts:  $\text{ZnCl}_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were added in stoichiometric proportion to the acid solution. CA/cations molar ratio equal to 3/1 was used. After complete dissolution of the metallic salts, EG was added with a 4/1 EG/CA molar ratio. EG–CA polymerization was promoted by removing water with continuous heating on a hot plate. Then, the highly viscous mixtures were thermally treated in two steps: a first calcination at  $300^\circ\text{C}$  for 10 h, then, an annealing step for 20 h between  $800^\circ\text{C}$  and  $1200^\circ\text{C}$ ; the annealing and cooling rates were fixed to  $2^\circ\text{C min}^{-1}$  while it is known that cooling rate can slightly the cationic distribution inside spinel compounds [26].

X-Ray diffraction (XRD) measurements were carried out on a PANalytical X'PERT PRO diffractometer equipped with a X-celerator detector, using  $\text{Cu}(\text{K}\alpha_1/\text{K}\alpha_2)$  radiation. Diffractograms have been analyzed by Rietveld refinement method using FULLPROF<sup>®</sup> program package [27]. Unit cell parameters, atomic positions and occupancies as well as the Debye Weller factors (isotropic displacement factors) were refined in space group  $Fd-3m$  corresponding to the spinel structure.

$^{27}\text{Al}$  MAS (spin rate 30 kHz) NMR spectra were recorded with a Bruker 500 solid state spectrometer at 130.3 MHz. A single pulse sequence was used with a  $1\ \mu\text{s}$  pulse width (corresponding to a  $\pi/12$  flip angle for a liquid sample) and a 30 s recycle delay. The 0 ppm reference was set to a 1 M aluminum nitrate solution using the secondary solid state reference  $\text{Al}(\text{PO}_3)_3$  ( $-21.4$  ppm).

Diffuse absorption spectra were recorded at room temperature from 200 to 800 nm (1 nm step; 2 nm band length) with a Cary 17 spectrophotometer using an integration sphere. Halon was used as white reference. Mathematic treatment of the obtained spectra allowed the determination of colorimetric parameters in RGB space. The first step consists in obtaining XYZ tri-stimulus values (defined by the CIE, 1964) from integration (on the visible range, i.e. from  $\lambda = 380$  nm up to 780 nm) of the product of  $x(\lambda)$ ,  $y(\lambda)$  or  $z(\lambda)$  functions (CIE-1964) with the diffuse reflectance spectra function:  $X = \int x(\lambda)R(\lambda)d\lambda$ . Thereafter, the transfer equations defined by the CIE, 1976, from XYZ space to the RGB space, were used in order to obtain RGB chromatic parameters. RGB is used herein (instead of the commonly used  $L^*a^*b^*$  chromatic parameters) in order to allow everyone to simulate the corresponding coloration with common drawing software.

## 3. Results and discussion

### 3.1. $\text{Zn}_{0.9}(\text{Ni}_{0.1}/\text{Co}_{0.1})\text{Al}_2\text{O}_4$ pigments

Reflectance spectra were recorded in the near-UV/visible/near-IR range for  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$  compounds prepared at  $800^\circ\text{C}$  and  $1200^\circ\text{C}$  (Fig. 1). The d–d bands appearing at about 600 nm are well known to be relative to the  $\text{Co}^{2+}$  ion in tetrahedral coordination: these bands were indexed as  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  transition, which can be decomposed as a triplet due to the L–S Russel–Saunders coupling. The intensity of this triplet drastically increases with annealing temperature between  $800^\circ\text{C}$  and  $1200^\circ\text{C}$ . This phenomenon already reported in literature [16,21,23] is related to the increase of cobalt fraction in tetrahedral site. A series of convoluted gaps with ligand oxygen-to-metal cations ( $\text{Co}^{2+}$  or  $\text{Zn}^{2+}$ ) charge transfers can be observed near the UV–vis frontier. A blue coloration adequate for pigment applications can thus be achieved for this chemical composition only when high annealing temperature is performed ( $1200^\circ\text{C}$ ).

For  $\text{Zn}_{0.9}\text{Ni}_{0.1}\text{Al}_2\text{O}_4$  compounds prepared at  $800^\circ\text{C}$  and  $1200^\circ\text{C}$ , reflectance spectra recorded in the near-UV/visible/near-IR range (Fig. 2) exhibit intense convoluted bands in UV–vis range due to oxygen to  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  charge transfers, and a doublet at about 600 and 630 nm. These d–d bands, as a doublet, can be attributed to  $\text{Ni}^{2+}$  in octahedral field according to literature on nickelate spinels [17–19]. Nevertheless, this attribution remains subjective and open to criticism without more detailed investigations in the infrared range. However, the low intensity of these d–d bands is consistent with an attribution to centro-symmetric sites. Actually, the colors which are reached, are unsaturated (greenish gray) and not adequate for pigments applications.

Rietveld refinements of X-ray diffraction patterns were performed for cobalt and nickel-doped compounds obtained after annealing at  $800^\circ\text{C}$  and  $1200^\circ\text{C}$ . A graphical illustration of experimental, calculated and difference signals is reported in Fig. 3, for the nickel-doped samples. Obviously the peak width decreases as annealing temperature increases, revealing an increase in crystallite size. Crystallite size can be roughly

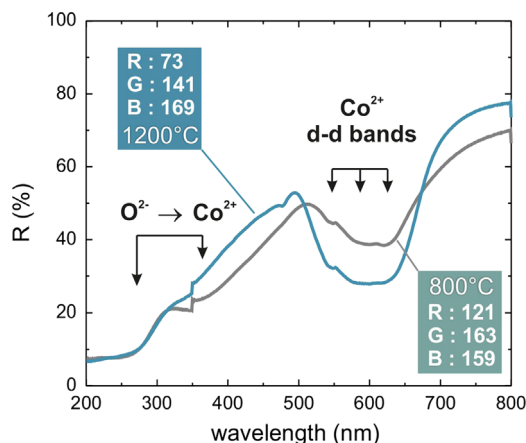


Fig. 1. Diffuse reflectance spectra ( $R\%$ ) of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$  compound prepared at  $800^\circ\text{C}$  and  $1200^\circ\text{C}$ .

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