

# Structural and thermal characterization of $Ni_xZn_{1-x}Al_2O_4$ synthesized by the polymeric precursor method

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**Abstract** Oxides with  $Ni_xZn_{1-x}Al_2O_4$  spinel structures (x = 0, 0.05, 0.10, 0.15 and 1.0) have been synthesized by a simple polymeric precursor method. The samples were calcined at 600, 800 and 1000 °C for 2 h. The thermal decomposition of materials has been investigated by TG and DTA. X-ray diffractogram showed that the synthesis is efficient to produce spinel structures with no significant interfering phases. Materials characterization also revealed that these oxides had surface areas (BET) in the range of  $8-156 \text{ m}^2 \text{ g}^{-1}$ . The absorption bands in the infrared spectroscopy (IR) were related to  $(ZnO_4)$  and  $[AlO_6]$  stretching vibration, and the UV-Vis spectrograms indicated the presence of Ni<sup>2+</sup> in tetrahedral sites. The colorimetric analysis (CIELab) results showed that the color of the pigments is blue and becomes lighter with increasing synthesis temperature. All these structural and thermal properties indicated that the materials have potential applications as pigments, catalysts and so on.

Keywords Spinel · Pigments · Nickel · Thermal behavior

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#### Introduction

The development of high stable pigments with intense tonalities has attracted the interest of the ceramic industries [1, 2]. Mixed metal oxides with a spinel structure ( $AB_2O_4$ ) can be considered as a subcategory of complex inorganic color pigments that show high thermal stability and high mechanical resistance [3, 4]. Therefore, these oxides can provide potential ceramic pigments [5], magnetic devices [6], thin films [7], catalysts and supports for a wide range of applications [8, 9]. This type of spinel compounds have also received much attention for their capacity to accommodate different cations in their structure, allowing for several types of doping, and consequently providing a wide range of colors [10].

Spinels can be classified into three categories: normal, inverse and intermediate. In the case of normal spinel,  $A^{2+}$  ions occupy tetrahedral sites and  $B^{3+}$  ions occupy octahedral sites.  $A^{2+}$  ions and  $B^{3+}$  ions are surrounded by four and six oxygen ions, respectively. In the inverse spinel, the cations distribution occurs by inverted (B)[AB]O<sub>4</sub> arrangement, in which all the tetrahedral sites are occupied by  $B^{+3}$  cations, while an equal number of  $A^{2+}$  and  $B^{3+}$  cations share the octahedral sites. The intermediate spinel can be represented by  $(A_{1-x}B_x)[A_xB_{2-x}]O_4$  formula, where x is the degree of inversion and  $(A_{1-x}B_x)$  and  $[A_xB_{2-x}]$  represent the tetrahedral and octahedral sites, respectively [11, 12].

The chemical and physical properties of the metal oxides depend on the synthetic route employed. Thus, several methods like co-precipitation [13], hydrothermal synthesis [8], solid-state reactions [14] and polymeric precursor [15] have been reported in the literature to prepare metal oxides with spinel structures. Compared to these chemical methods of synthesis, the polymeric precursor method, which is

based on production of polyesters of metallic citrates, has some advantages, such as high reproducibility, low crystallization temperature, accurate stoichiometric control and relatively low cost [16].

Lisboa-Filho et al. [17] synthesized Ni<sub>x</sub>Zn<sub>7-x</sub>Sb<sub>2</sub>O<sub>12</sub> spinel by the polymeric precursor method and studied the distribution of  $Zn^{2+}$  and  $Ni^{2+}$  ions in tetrahedral and octahedral sites as a function of the amount of nickel incorporated into the spinel. They concluded that up to x = 3, nickel substitutes zinc in octahedral sites. For x > 3, Ni<sup>2+</sup> also occupies tetrahedral sites. Porta et al. [18] also studied the distribution of  $Ni^{2+}$  in  $Ni_xZn_{1-x}Al_2O_4$  spinel obtained by a solid-state reaction process, with x ranging from 0.05 to 0.90. They have found that Ni<sup>2+</sup> preferentially occupies octahedral sites and that it shifts a little toward a random distribution (intermediate-type spinel) with increasing temperature from 800 to 1200 °C. In the study of  $Co_x Zn_{7-x}Sb_2O_{12}$  spinel (x = 0-7), synthesized by the polymeric precursor method, Gouveia et al. [19] stated that the blue color of the pigment depends on the sites that the chromophore ions occupy.

Considering that  $ZnAl_2O_4$  spinel may be used as a chromophore ion support, and also that Ni<sup>2+</sup> is an ion that can color ceramic materials, this manuscript reports on the synthesis of  $ZnAl_2O_4$  spinel, by the polymeric precursor method. The influence of the temperature and the different degrees of substitution of  $Zn^{2+}$  by Ni<sup>2+</sup> ion in the spinel lattice were also investigated. The obtained oxides were characterized by different structural and spectroscopic techniques.

### Experimental

#### Materials

The chemicals were: nickel acetate (99 %, Vetec, Brazil), zinc nitrate (97 %, Cromoline, Brazil), aluminum nitrate (98 %, Dinâmica, Brazil), citric acid (CA, 99 %, Vetec, Brazil) and ethylene glycol (99 %, Vetec, Brazil). All of the reactants were used as supplied.

# Sample preparation

Ni<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> oxides (x = 0, 0.05, 0.10, 0.15 and 1.0) were synthesized by a polymeric precursor method [10]. In a typical procedure to synthesize 10 g of a sample with the composition of Ni<sub>0.15</sub>Zn<sub>0.85</sub>Al<sub>2</sub>O<sub>4</sub>, 42.38 g of aluminum nitrate, 14.28 g of zinc nitrate and 2.09 g of nickel acetate were slowly dissolved in 100 mL of distilled water. An aqueous solution of citric acid, prepared using 98.12 g of citric acid diluted in 100 mL of water, was added to this system under vigorous stirring. The stirring was kept, and

the system was heated at 70 °C. After 1 h, 58.75 mL of ethylene glycol was slowly added. The heating was kept until the volume was reduced to the half. With increasing viscosity of the solution, the polymeric gel was formed. The precursor powders were obtained by submitting the resulting polymeric gels to a thermal treatment at 300 °C in an oven, under air flow, for 2 h. Then, the precursor powders were grounded and lastly calcined at 600, 800 and 1000 °C for 2 h in an oven. The other samples (Ni<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>, x = 0, 0.05, 0.10 and 1.0) were synthesized following the same procedure described for the Ni<sub>0.15</sub>Zn<sub>0.85</sub>Al<sub>2</sub>O<sub>4</sub> sample, only adjusting the amounts of metal sources to obtain the desired metal molar ratio in the sample.

#### Instrumental analysis

X-ray diffraction (XRD), using powder method, was performed on a PANalytical X'PERT PRO MPD (PW 3040/60) diffractometer, model PW 3710 BASED. Radiation Cu  $K_{\alpha}$  (0.15406 nm) was used. The  $2\theta$  scanning speed was  $0.02^{\circ}$  s<sup>-1</sup>.

Infrared spectra were recorded in the  $800-400 \text{ cm}^{-1}$  spectral region by means of a Thermo IR100 spectrometer.

The surface area, diameter and pore volume were calculated according to Brunauer–Emmett–Teller and Barret– Joyner–Halenda (BET/BJH) method using a Quantachrome NOVA 1200 equipment. Before the analysis, the samples were heated at 250 °C for 2 h.

The thermal decomposition of the samples was investigated by thermogravimetric analysis (TG) and differential thermal analysis (DTA). It used a Thermal Sciences thermobalance (TG/DTA), model PL-STA. About 10 mg of the samples was placed in platinum pans and heated from room temperature to 1000 °C, at a heating rate of  $10 \text{ °C min}^{-1}$  and using a synthetic air flow of 40 mL min}^{-1}.

The UV–Vis absorption spectra were obtained in a Shimadzu 2550 spectrophotometer. All data were collected in the 300–800 nm region.

The CIELab chromatic coordinates were taken by means of a Gretac Macbeth Color-eye 2180 colorimeter, using a D65 illumination.

### **Results and discussion**

#### **Characterization by XRD**

The development of the spinel structure of  $ZnAl_2O_4$  and  $NiAl_2O_4$  was confirmed by XRD technique (Fig. 1), revealing that the synthesis route applied in this work (the polymeric precursor method, at a relatively low temperate) was efficient to produce the oxides. The XRD patterns



Fig. 1 XRD patterns of a ZnAl<sub>2</sub>O<sub>4</sub> and b NiAl<sub>2</sub>O<sub>4</sub> at 600, 800 and 1000 °C

show the characteristic peaks of ZnAl<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub> spinels (JCPDS files 73-1962 and 10-0339 for ZnAl<sub>2</sub>O<sub>4</sub> and NiAl<sub>2</sub>O<sub>4</sub>, respectively). The XRD reflections suggested that ZnAl<sub>2</sub>O<sub>4</sub> (Fig. 1a) is monophasic at all temperatures and that NiAl<sub>2</sub>O<sub>4</sub> (Fig. 1b) presented a secondary phase related to NiO. As can be seen in Fig. 1b, as the calcination temperature increased the intensity of the characteristics peaks of this secondary phase decreased. These results indicated that the recrystallization process might eliminate oxygen and suggested that nickel was restructured into the NiAl<sub>2</sub>O<sub>4</sub> spinel. The crystallinity of these systems increased. This conclusion was reached given that welldefined and more intense diffraction peaks were observed. With increasing nickel doping (Ni<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub>, x = 0.05, 0.10 and 0.15), no differences in the XRD patterns were noticed. Average crystallite sizes of the samples are displayed in Fig. 2. It was found that crystallite size increases in accordance with the nickel content in the sample, and it



Fig. 2 Crystallite size of  $Ni_xZn_{1-x}Al_2O_4$  (x = 0.05; 0.10 and 0.15), heat-treated at 600, 800 and 1000 °C

is also important to point out that there is a linear relationship between the crystallite size and synthesis temperature.

#### Characterization by infrared spectroscopy (IR)

The IR spectra of the  $ZnAl_2O_4$  spinel at different calcination temperatures are given in Fig. 3. All samples presented absorption bands at about 505, 548 and 650 cm<sup>-1</sup> that were ascribed to [AlO6] (octahedral) stretching vibration [12]. The ZnAl<sub>2</sub>O<sub>4</sub> spinel showed an absorption band at 430 cm<sup>-1</sup> that can be attributed to the ZnO stretching vibration [20]. The absence of the band at around 730 cm<sup>-1</sup>, related to (AlO<sub>4</sub>; tetrahedral) stretching vibration, showed that ZnAl<sub>2</sub>O<sub>4</sub> spinel is normal, with the divalent metal ion in tetrahedral sites, and the trivalent metal ion in the octahedral sites [21].

The bands at around 430 and 410 cm<sup>-1</sup> became more evident as the temperature increased. So, it was possible to conclude that a better spinel structure can be obtained at higher temperatures. Ni<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> (x = 0.05; 0.10 and



Fig. 3 IR spectra of ZnAl<sub>2</sub>O<sub>4</sub> at different calcination temperatures

0.15) spinels calcined at 800 °C showed absorption band at around 430 and 410 cm<sup>-1</sup> that can be attributed to the Nitetrahedral (NiO<sub>4</sub>) stretching vibration. These findings were also observed by other researchers like Souza et al. [12], who considered that, in general, the spinel structures display metal–oxygen absorption bands (M–O–M or O–M–O) in the range of 500–900 cm<sup>-1</sup>.

# $Characterization \ by \ N_2 \ adsorption-desorption \ (BET \ and \ BJH)$

Surface area, pore diameter and pore volume were determined by N<sub>2</sub> adsorption–desorption technique (see Table 1). The obtained pore diameters were similar and indicated that the oxides are mesoporous [22]. NiAl<sub>2</sub>O<sub>4</sub> spinel calcined at 600 °C exhibited the largest surface area (156 m<sup>2</sup> g<sup>-1</sup>), and it can be observed that the surface area decreased as the temperature increased. This result was expected since the calcination promotes the sinterization of the crystallites, which produces materials with lower surface areas [23].

# Thermal analysis (TG and DTA) characterization

The TG and DTA curves of the as-synthesized  $Ni_xZn_{1-x}Al_2O_4$  (x = 0, 0.05, 0.10, 0.15 and 1.0) samples

 Table 1
 BET and BJH results of the spinels

are shown in Fig. 4a, b, respectively. All TG curves exhibited three distinct mass loss regions. The first one (about 8 %), between 42 and 180 °C, was associated with desorption of water and gases physically adsorbed in the structure of the materials. These results can be confirmed by DTA curves that showed an endothermic peak in the same temperature range. The second and the third ones (about 48 %), in the range from 180 to 800 °C, and that exhibited exothermic peaks, can be associated with the consecutive thermal decomposition of the carbon chain [24]. Except NiAl<sub>2</sub>O<sub>4</sub> precursor powder sample, no mass losses can be seen above 800 °C, indicating that pigments are stable at high temperatures. The mass loss (about 4.53 %) observed above 800 °C for the NiAl<sub>2</sub>O<sub>4</sub> precursor powder was related to the elimination of oxygen due to the structural rearrange of nickel in the NiAl<sub>2</sub>O<sub>4</sub> spinel, which is assigned by X-ray results.

#### Characterization by UV-Vis Spectroscopy

Figure 5 shows the absorption spectra in the UV–Vis region of samples  $Ni_xZn_{1-x}Al_2O_4$  (x = 0.05, 0.10 and 0.15) heat-treated at 1000 °C. The absorption band at approximately 632 nm can be related to the v4<sub>Td</sub> transition ( ${}^{3}T_1 \rightarrow {}^{3}T_2$  ( ${}^{3}P$ )), and the small band around 780 nm can

Sample	Surface area/m <sup>2</sup> $g^{-1}$	Pore volume/cm <sup>3</sup> g <sup><math>-1</math></sup>	Pore diameter/nm
ZnAl <sub>2</sub> O <sub>4</sub> 600 °C	77	0.027	3.4
ZnAl <sub>2</sub> O <sub>4</sub> 800 °C	44	0.022	3.7
ZnAl <sub>2</sub> O <sub>4</sub> 1000 °C	8	0.004	3.0
NiAl <sub>2</sub> O <sub>4</sub> 600 °C	156	0.087	3.3
NiAl <sub>2</sub> O <sub>4</sub> 800 °C	71	0.040	3.0
NiAl <sub>2</sub> O <sub>4</sub> 1000 °C	37	0.016	3.7
Ni <sub>0.05</sub> Zn <sub>0.95</sub> Al <sub>2</sub> O <sub>4</sub> 600 °C	83	0.075	3.3
Ni <sub>0.10</sub> Zn <sub>0.90</sub> Al <sub>2</sub> O <sub>4</sub> 600 °C	78	0.077	3.3
$Ni_{0.15}Zn_{0.85}Al_2O_4 600 \ ^{\circ}C$	122	0.139	3.4







Fig. 5 Absorption spectra in the UV–Vis region of the  $Ni_xZn_{1-x}$ Al<sub>2</sub>O<sub>4</sub> (x = 0.05, 0.10 and 0.15) samples calcined at 1000 °C

be assigned to the spin-forbidden  $v3_{Td}$  transition  $({}^{3}T_{1} \rightarrow {}^{1}T_{2}, {}^{1}E ({}^{1}D))$ , which is generally observed in solid materials [25]. According to the Tanabe–Sugano diagram, besides the prohibited spin transitions observable in the near-UV–Vis region, a d<sup>8</sup> ion like Ni<sup>2+</sup> in cubic coordination has three d–d allowed spin transitions, which may occur in tetrahedral and octahedral electronic spectra [26]. According to Lorenzi et al. [10], the absorption bands observed from 300 to 800 nm are the fingerprint of tetrahedral Ni<sup>2+</sup>, and that the blue color, which is characteristic of this ion, was attributed to the occupation of Ni<sup>2+</sup> ions in this kind of site. No signals related to Ni<sup>2+</sup> in octahedral sites were observed. These results indicated that the Ni<sup>2+</sup> ion in the Ni<sub>x</sub>Zn<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> pigments occupied tetrahedral sites and that these pigments are blue.

#### Colorimetric analysis (CIELab)

The pigment colors were qualitatively and quantitatively characterized by the CIELab method, where  $L^*$ ,  $a^*$  and  $b^*$ parameters measure the brightness and the intensity of red-green and yellow-blue colors, respectively. The coordinates of Ni<sub>0.05</sub>Zn<sub>0.95</sub>Al<sub>2</sub>O<sub>4</sub> pigment, treated at different temperatures (Table 2), showed that both  $a^*$  and  $b^*$ values decreased as the calcination temperature increased. In contrast, the values of  $L^*$  increased as the calcination temperature increased. With the obtained results, it was possible to conclude that the lower the temperature, the lighter the pigment. The chromatic coordinate values  $(L^* \cdot b^* \cdot a^*)$  of the pigments Ni<sub>0.05</sub>Zn<sub>0.95</sub>Al<sub>2</sub>O<sub>4</sub>,  $Ni_{0.10}Zn_{0.90}Al_2O_4$ ,  $Ni_{0.15}Zn_{0.85}Al_2O_4$  and  $NiAl_2O_4$ , calcined at 1000 °C, are given in Table 3. As can be seen, the value of  $b^*$  parameter indicates that the color of the pigments can be either yellow or blue, and that its intensity decreased as the amount of nickel increased in the materials [27].

Table 2 Colorimetric analysis of the Ni<sub>0.05</sub>Zn<sub>0.95</sub>Al<sub>2</sub>O<sub>4</sub> samples

Temperature/°C	$L^*$	<i>a</i> *	$b^*$
600	71.35	-1.21	6.10
800	77.00	-5.27	5.83
1000	77.39	-7.00	4.03

Table 3 Colorimetric analysis of the  $Ni_xZn_{1-x}Al_2O_4$  at 1000  $^\circ C$  samples

x value in the $Ni_xZn_{1-x}Al_2O_4$ formula	$L^*$	<i>a</i> *	$b^*$
0.05	72.01	-7.23	9.11
0.10	77.39	-7.00	4.03
0.15	69.52	-8.97	1.56
1.0	56.44	-8.40	-14.73

### Conclusions

The precursor polymeric method is efficient for obtaining  $Ni_xZn_{1-x}Al_2O_4$  pigments of spinel-type structure. The obtained spinels were thermally stable, crystallized at relatively low temperatures and had not significant interfering phases. The results of the thermal analysis indicated that these pigments are stable at high temperatures. UV–Vis results showed that Ni<sup>2+</sup> occupied tetrahedral sites. The colorimetric coordinates showed that the intensity of the blue color of the pigments depends on the amount of Ni<sup>2+</sup> incorporated into the spinel-type structure. The calcination temperature also influenced the color of the obtained ceramic pigments, indicating that pigments (x = 0.05, 0.10, 0.15 and 1.0) are blue when they are calcined at high temperatures.

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