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Synthesis and characterization of colourful aluminates based on nickel and zinc

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ABSTRACT

Gradual changes in the chemical composition of spinel cause variations in the distribution of cations in sites, which affects their properties and colouration. Thus, pigments with nickel-zinc spinel structures $(Ni_xZn_{1-x}Al_2O_4)$ were synthesized by combustion and characterized by varying the chromophore ion content (x = 0; 0.1; 0.2; 0.4 and 1) and calcination temperature (600°, 800° and 1000°C). Characterization of aluminates through thermal analysis (TGA) showed a less than 10% mass loss until approximately 500 °C in not-calcined samples, indicating the combustion reaction could be classified as adequate. The spinel phase was confirmed in all samples by X-ray diffraction (XRD) with segregated phases: ZnO in samples with x = 0 and NiO in samples with x = 0.4 and 1. The post-synthesis thermal treatment at high temperature led to higher crystallinity of the material and the incorporation of secondary phases into the spinel structure. The crystallite size varied between 22.9 and 43.2 nm. Scanning Electron Microscopy (SEM) analysis indicated that the pore size increased with the increasing calcination temperature, and infrared spectroscopy indicated the displacement of the AlO6 band (665 cm⁻¹) to AlO4 (730 cm⁻¹) after the addition of Ni²⁺ ions, revealing the inversion of the crystalline structure. Colorimetric analysis by the CIELab method showed the colour of the zinc-nickel pigments ranged between white (x = 0) and cyan tones $(0 < x \le 1)$. Furthermore, the significant influence of the chromophore ion content and calcination temperature on the colouration of the synthesized pigments was verified by the Tukey test at 5% in terms of the luminosity (L^*) and chromaticity (a^* and b^*). The difference between dry powder and that dispersed in varnish was considered evident. The colorimetric data were used to develop a mathematical model to satisfactorily describe the values of L*, a* and b* as functions of the calcination temperature and nickel load.

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1. Introduction

Natural and synthetic pigments have important applications as colouring agents in industries including ceramics, paints, plastics, varnishes, and others. The main properties of pigments are influence aesthetic colouring, and users search for new and exclusive high-quality products. To meet this demand, it is necessary to focus research on more resistant materials and exclusive colourings in

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A good pigment has particular features, such as a crystalline structure, thermal and chemical stability, adequate granulometry, stable colour, homogeneity, reproducibility and low toxicity whenever possible [4]. In this context, spinel appears to be a material possessing all of these characteristics [5]. Spinel has a general chemical formula $(A_{1-x}B_x)[A_xB_{2-x}]O_4$ with a CFC unit cell, where A is a bivalent cation and B is a trivalent cation; the parentheses represent tetrahedral sites, while the brackets represent octahedral sites, and X is the inversion parameter. In normal spinel, A^{3+} ions occupy octahedral positions and B^{2+} ions occupy tetrahedral positions and material positions a

half of the trivalent cations are in octahedral positions, and the remaining trivalent cations are in tetrahedral positions. Between the two extremes, an intermediate stage exists with a random distribution of cations [6,7]. These materials have refractory, magnetic, semiconducting and chromatic properties in addition to stability even under harsh thermal conditions and redox industry treatments [8]. The gradual incorporation of transition metal ions into spinel structures and the synthetic route affect their physical, optical and chemical properties. The most visible alteration is in terms of the colouring, and therefore, complex oxides are widely used to form new ceramic pigments [5,6,9].

One subgroup of such materials contains aluminates, an important materials class, due to their high thermal stability, ductility, hardness, hydrophobicity, superficial low acidity, low temperature of synthesis and high cation diffusion. These properties are particularly interesting when spinel is used as an inorganic ceramic pigment in high temperature and/or catalytic materials (support or catalyst) [10,11].

Spinel synthesis is traditionally realized by conventional methods [12,13] due to their ease of implementation at the industrial level. By contrast, alternative routes allow for better characterized pigments and/or lower environmental impacts. Most unconventional techniques use water; these include coprecipitation [14,15], sol-gel processes [16], polymeric precursor methods (Pechini) [17] and combustion [18,19]. The last is based on an exothermic reaction and is self-supporting between the reductant propellant and oxidant agent within a homogeneous solution in addition to being an easy, cheap and efficient method to product homogeneous and pure nanometric materials [18–21]. The gas released in the synthesis is essential for the nanometric material size, and the amount of released gas depends on the fuel used [22,23]. Glycine is one of the most commonly used fuels because it is a low-cost amino acid and a large molecule that hinders the contact between metallic ions in solution, resulting in materials with nanometric particle sizes [24–26].

Currently, blue pigments are mostly produced starting with cobalt ions, but these ions are toxic, scarce and costly [27]. Souza et al. [28] synthesized blue pigments based on the cobalt-containing $Co_xZn_{1-x}Al_2O_4$ (x = 0; 0.1; 0.3; 0.5; 0.7; 0. 9 and 1) using the polymeric precursor method, with the aim of reducing the cost of production and lowering the amount of toxic chromophore ions; they found a blue colouring in many shades, which became more intense with the increasing amount of cobalt. Tang et al. [29] synthesized blue pigments of cobalt in high purity without a dopant by a sol-gel method in jet printing applications for roofing tile ceramic decorations.

Currently, nickel is being investigated as an alternative to cobalt in the production of blue pigments. Visinescu et al. [30] studied the synthesis of $Ni_xZn_{1-x}Al_2O_4$ (x = 0.1, 0.2, 0.4, 0.6, 0.8, 1) by a sol-gel method for application as the catalyst in oxidative methane reforming. The colours obtained varied between blue and green, with the best characterization of colours at x = 0.6. Lorenzi et al. [5] synthesized nickel-doped gahnite (ZnAl₂O₄) to measure blue and green products separately to explain the colouration. It was concluded that the Ni²⁺ in the tetrahedral sites determines the blue colour even in small amounts and that NiO is responsible for the greenish colouration. Therefore, considering that zinc aluminate can be used to support ions and nickel is a chromophore ion, this work describes the synthesis of Ni_xZn_{1-x}Al₂O₄ spinels by combustion, using glycine as the propellant. The structural, morphological and colorimetric properties were found to be functions of the dopant ion concentration and the calcination temperature. Furthermore, a mathematical model is proposed to describe the behaviour of the variables L*, a* and b* by the CIELab method for the evaluation of the final synthesized pigment.

2. Experimental

In the synthesis of colourful aluminate pigments, the chemical reagents were purchased from commercial sources: nickel nitrate $[Ni(NO_3)_2.6H_2O, Vetec-Brazil]$, zinc nitrate $[Zn(NO_3)_2.6H_2O, Synth-Brazil]$, aluminium nitrate $[Al(NO_3)_3.9H_2O, Synth-Brazil]$, and glycine $[NH_2CH_2COOH, SIGMA-Brazil]$. All materials were used as received, and experiments were carried out with distilled water.

2.1. Sample preparation

Spinels (Ni_xZn_{1-x}Al₂O₄) were synthesized by a combustion method. Metal nitrates and the fuel were dissolved in water and heated at 80 °C under constant stirring until total water evaporation and full gel formation. When the gel formed, the temperature of the hot plate was increased to achieve the ignition temperature of the propellant. The time of the combustion reaction was approximately 10 s until reaching the high flame temperature. Therefore, to investigate the influence of the calcination temperature on the final properties, each material was separated into four portions; three were calcined in a muffle furnace at three different temperatures (up to 600° , 800° and 1000° C) for 6 h. The solid calcined materials were ground with an agate mortar and pestle. Finally, the powders were stored for further characterization and application.

The amount of fuel and nitrates used in the preparation of the aluminates was based on a stoichiometric balance by the following equation: $\sum n_i v_i = 0$, where n_i is the number of moles of each reactant and v_i is the oxidation number, so that the fuel/oxidizer ratio corresponds to the stoichiometric ratio. The combustion reactions can be described as follows:

 $\begin{array}{l} xNi(NO_3)_2.6H_2O + (1-x) \\ Zn(NO_3)_2.6H_2O + 2Al(NO_3)_3.9H_2O + 4.4NH_2CH_2COOH \rightarrow Ni_xZn_{1-x}Al_2O_4 + 35.1H_2O + 8.9CO_2 + 6.2N_2 \end{array}$

The powder materials were prepared with nominal compositions of x = 0; 0.1; 0.2; 0.4 and 1. According to the preparation, they were identified by the composition of nickel (x) and the calcination temperature (y). For example, Ni0.1Zn600 refers to a sample containing 0.1 nickel and calcined at 600 °C. Furthermore, samples without thermal treatment are designated as "SC".

2.2. Thermodynamic calculation of flame temperature

To calculate the adiabatic flame temperature of combustion, Eqs. (1)-(3) were used [31]. The flame temperature is the highest temperature achieved during the combustion reaction.

$$\Delta H^{o} = \sum n \Delta H^{o}_{P} - \sum n \Delta H^{o}_{R} \tag{1}$$

$$|\Delta H^{o}| = \int_{T_{o}}^{T} nC_{P} dT$$
⁽²⁾

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$$
(3)

Where n is the number of moles; ΔH_R^0 and ΔH_P^0 are the standard enthalpies of formation of the reactants and products, respectively; and T is the adiabatic flame temperature and starting temperature (298 K). Cp is the heat capacity of the products at constant pressure. The thermodynamic data of the reactants and products [31,32] are available from the literature and listed in Tables 1 and 2. Due to a

Table 1

Thermodynamic data required for the calculation of the adiabatic flame temperature [32].

Compound	Entalphy of formation (kcal.mol ⁻¹)
Ni(NO ₃) ₂ .6H20(c)	-534.83
Zn(NO ₃) ₂ .6H20(c)	-551.30
Al(NO ₃) ₃ .9H20(c)	-897.57
NH ₂ CH ₂ COOH(c)	-126.31
$ZnAl_2O_4(c)$	-493.26
$NiAl_2O_4(c)$	-457.60
$Ni_{0,1}Zn_{0,9}Al_2O_4(c)^a$	-489.69
$Ni_{0,2}Zn_{0,8}Al_2O_4(c)^a$	-486.13
$Ni_{0,4}Zn_{0,6}Al_2O_4(c)^a$	-479.0
$H_2O(g)$	-57.80
CO ₂ (g)	-94.05
N ₂ (g)	0

(c): crystalline; (g): gas.

^a the entalphy of formation was calculated in the appropriate stoichiometric proportions of pure spinel: NiAl₂O₄ and ZnAl₂O₄.

Table 2 Constants of equation (5) [21]

Chemical Species	Α	10 ³ B	10 ⁶ C	10 ⁻⁵ D			
CO ₂	5.457	1.045	_	-1.157			
N ₂	3.280	0.593	_	0.04			
H ₂ O	3.470	1.450	_	0.121			

lack of information on the thermodynamic properties of spinels, the heat capacity of $MgAl_2O_4$ (1.90613 cal mol⁻¹ K⁻¹) [33,34] is used because the compounds are isostructural and their divalent metallic radii [Ni²⁺, Zn²⁺ and Mg²⁺] are nearly the same [35].

2.3. Characterization

The thermal behaviour of aluminate was determined using thermogravimetric analysis (NETZSCH-STA 449 F3 Jupiter model) with a heating rate of 10 °C/min from 25 °C to 700 °C in an alumina crucible (sample holder) with a nitrogen atmosphere at a flow rate in 50 mL/min.

The crystalline phases were determined by X-ray diffraction (XRD) using the powder method. The diffraction patterns were determined with a D8 ADVANCE Bruker diffractometer equipped with a goniometer (theta/theta) and Cu anode ceramic X-ray tube (K α_1 1,54058A), model 10190376 (2 kW/60 kV). The diffractograms were based on the detection range of $10^\circ \le 2 \theta \le 80^\circ$ with a step size of 0.02° and a speed of $0.01^\circ s^{-1}$. The crystallite sizes were calculated using the Scherrer formula. The quantified phases and lattice parameters were calculated by the Rietveld methodology.

A scanning electron microscope (SEM), VEGA3 System Shimadzu model, was used to investigate the microstructure of the powders. The secondary electron beam was used, and the samples were previously metalized by the deposition of gold film.

Infrared spectra were recorded in the 400–4000 cm⁻¹ spectral region by means of a Shimadzu (IRPrestige-21). Analyses were performed on self-supporting pellets diluted with KBr.

The CIELab chromaticity coordinates were taken directly from the calcined powders by means of a Konica Minolta Color Reader CR-10 portable colourimeter using D65 illumination and the 10° standard observer. To verify the paint formulation and properties, the powders were sifted through a 200-mesh sieve and dispersed in a colourless acrylic varnish (ACRILEX) at a proportion of 10%. The CIELab parameters were taken after 48 h drying at room temperature. Finally, the differences in colour between the dry and dispersed powder were calculated using Eq. (4), which is the simple distance between two points in the three-dimensional colorimetric space.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{4}$$

In the CIELab system, L^* is the degree of lightness or darkness, ranging from white ($L^* = 100$) to black ($L^* = 0$). Positive values of a^{*} correspond to red, and negative values correspond to green. Positive values of b^{*} correspond to yellow, while negative values correspond to blue.

3. Results and discussions

3.1. Pigment synthesis

In this study, synthesis of the pigments resulted in materials with a spongy, extremely porous and fragmentary appearance, which is characteristic of this experimental route; the results are shown in Fig. 1. As seen in the literature, the combustion method involves the self-ignition of an aqueous solution containing an oxidizer (the corresponding metal nitrates) and an organic fuel, such as glycine. The rapid evolution and large volume of gases released during the process immediately cool the product, limiting agglomeration and leading to the formation of nanocrystalline powders [18,19]. Furthermore, an evident bluish colouration is observed, provided by the nickel ions, and the dark sections correspond to carbon deposited from an incomplete combustion reaction.

Table 3 presents the adiabatic flame temperature data calculated according to Eq. (2). The values vary slightly but are consistent with the data from the literature [35]. The values slightly varied because the variables that can significantly influence the flame temperature, such as the type of fuel and fuel-oxidizing ratio, were kept constant [22]. In addition, the total number of moles of gases were unchanged when replacing zinc with nickel, as both the nickel nitrate and zinc nitrate used were in their hexahydrate forms.

3.2. Thermal analysis characterization

To evaluate the thermal behaviour of the material and confirm the presence of carbonaceous compounds deposited on the surface of pigments, thermogravimetric analysis was conducted. The results for Ni0Zn, Ni0.4Zn and Ni1Zn are presented in Fig. 2. All samples exhibit similar behaviours, with the mass loss profile following a standard pattern: the first event of mass loss occurred



Fig. 1. Material synthesized by the combustion method.

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 Table 3

 Theoretical adiabatic flame temperature of the nickel series.

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Theoretical adiabatic flame temperature (°C)	Total Number of Gaseous Moles
967.0	50.2
963.4	50.2
959.8	50.2
952.7	50.2
931.7	50.2
	Theoretical adiabatic flame temperature (°C) 967.0 963.4 959.8 952.7 931.7



Fig. 2. Thermal analysis of the prepared powders.

due to the loss of water at approximately 100 °C, and the second event was seen at 500 °C, which corresponds to residual carbon burning from CO and CO₂ left after the incomplete combustion reaction, as confirmed by visual data analysis. From 500 °C onwards, a significant variance of mass was not found, which implies the full cleaning of the surface of the produced pigment. The small lost mass (<10%) presented by the samples can be explained the values of the maximum flame temperatures (Table 3); all were above 900 °C, which makes the combustion reaction practically complete.

3.3. Microstructure and porosity characterization

The effect of the calcination temperature on the morphology of the materials was determined by XRD and SEM analyses. Micrographs of samples Ni0.4ZnSC (Fig. 3a), Ni0.4Zn600 (Fig. 3b) and Ni0.4Zn1000 (Fig. 3c) are shown in Fig. 3. The material, in general, is spongy in appearance and extremely porous. No definite structure can be seen, and isolated particles are not identified, only aggregates. The large aggregation involves nanostructured particles and results from the attractive van der Waals force [36]. It is possible to verify that the calcination process led to an increased number of pores and changes in pore size when comparing the results of fresh samples and those calcined at 600 °C (Fig. 3a and b). This fact is attributed to the superficial cleaning of the sample as a result of the clearance of pores caused by carbon output in the forms of CO and CO₂ [37]. Evaluating the results obtained by thermogravimetric analysis (Fig. 2), it is verified that the mass loss at approximately 500 °C corresponded to the loss of residual carbon from the synthesis process; thus, calcination at 600 °C promotes mass loss and consequently cleans the surface via combustion, as previously observed. SEM images of the materials calcined at 1000 °C (Fig. 3c) show the structural differences between the not calcined and calcined at 600 °C samples, Fig. 3a-b, respectively; the disappearance of small pores followed by increases in the number and size of macropores is noted. In addition, some breaking points are observed in the structure resulting from the high-temperature synthesis. The main consequences of this are a low pore volume and low surface area, which affect the dispersion of pigments in the matrix.

3.4. Crystallographic phase formation

The diffractograms used to identify the crystalline phases formed through synthesis and the subsequent thermal treatment of nickel-zinc pigments are shown in two forms: as a function of temperature for each composition (Fig. 4) and as a function of composition for each temperature (Fig. 5).

3.4.1. Effects of the calcination temperature

The diffractograms presented in Fig. 4 confirm the development of the cubic spinel structure at all of the study temperatures (ICSD-9559, ICSD-69520 and AMCSD-000147 for $ZnAl_2O_4$, $Ni_{0.4}Zn_{0.6}Al_2O_4$ and $NiAl_2O_4$, respectively), including the not-calcined samples, which indicates that the combustion method is appropriate to produce aluminates with nickel and zinc. In the samples without nickel in their compositions (Fig. 4a), not-calcined (Ni0ZnSC) and calcined at 600 °C (Ni0Zn600) displayed a segregated ZnO (ICSD-26170) phase, indicating that the energy of the synthesis reaction (combustion energy) and a calcination process up to 600 °C are insufficient to complete the incorporation of Zn^{2+} ions into the spinel structure. As the maximum flame temperature reached approximately 900 °C, it was expected that the pure structure



Fig. 3. SEM of the Ni0.4Zn samples: a) not-calcined; b) calcined at 600 °C; c) calcined at 1000 °C.

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Fig. 4. X-ray diffractograms with varying calcination temperatures: a) Ni0Zn; b) Ni0.2Zn; c) Ni0.4Zn; d) Ni1Zn.



Fig. 5. X-ray diffractograms with varying compositions: a) not-calcined; b) 600 °C; c) 800 °C; d) 1000 °C.

would be obtained; however, the temperature only remained that high for a few seconds, which was insufficient to promote the complete incorporation of Zn^{2+} ions and obtain the pure spinel phase. As seen in the literature, the ZnO and ZnAl₂O₄ phases are

obtained with thermal treatments of the precursor powder at temperatures of up to $700 \degree C$ [11].

The sample results for Ni0.1Zn (supplementary material) and Ni0.2Zn (Fig. 4b) show similar diffractograms with the presence of

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the pure spinel phase at all of the temperatures studied. The nonappearance of segregated zinc oxide may be caused by the decrease of the zinc content in the material with the addition of a small amount of nickel in the structure, as a smaller ionic radius is advantageous for the formation of the pure spinel phase. Another explanation may be that the amount of ZnO may have been too small to be observed by the XRD technique.

In the samples with an increased nickel content at x = 0.4(Fig. 4c) and x = 1(Fig. 4d), the pure spinel phase was obtained for samples calcined at 800 °C and 1000 °C. In the samples Ni0.4ZnSC and Ni0.4Zn600, along with all materials where x = 1 (Fig. 4c and d), a nickel oxide phase (ICSD-9866) was identified, indicating the segregation of ions in the surface of the material. Specifically, for samples Ni1ZnSC and Ni1Zn600, there was also segregated metallic nickel (AMCSD-0011153). Therefore, it was revealed that adding nickel ions into the spinel structure requires more energy to complete, a fact which is adequately explained by the affinity of the divalent nickel for the octahedral sites, causing an inversion of cations (Al³⁺ and Ni²⁺) in the sites. In normal spinel, the octahedral sites are only occupied by trivalent cations while the tetrahedral sites contain bivalent cations. Octahedral sites occupied by Ni²⁺ have been described by Lorenzi et al. [5] and Gaudon et al. [17], and network enthalpy calculations involving simple ionic methods indicate that the normal spinel structure is most stable [7], and thus, the inverse spinel requires more energy.

For all samples, the post-synthesis thermal treatment led to an elongation and definition of the characteristic peaks of spinel, revealing increased crystallinity; the increase of temperature caused a decrease of the peaks of the unwanted phases until they disappeared. This behaviour suggests that the crystallization process eliminates oxygen and that metal ions in segregated oxides are incorporated into the spinel structure at high temperatures, proving the essential nature of calcination to the crystallization of the material.

3.4.2. Effects of load of nickel

Fig. 5 shows diffractograms of the samples at each temperature with varied contents of chromophore ions. To improve visualization, the most intense peak at the Miller index position (I_{311}) was highlighted. At all temperatures, a similar behaviour was observed: at increased nickel concentrations, peaks were displaced to the

right. This displacement results from the ion exchange from Zn^{2+} to Ni²⁺ since they have different ionic radii. The nickel radius (0.69 Å) is lower than that of zinc (0.74 Å), so it causes a shift to the right [38]. Similar results were observed by Pandit et al. [39] in studies of the substitution of Fe³⁺ (0.645 Å) to Al³⁺ (0.535 Å).

The different occupations of the sites between the cations in nickel-zinc aluminates can cause changes in the planar densities and thus changes the planar directions, causing the appearance and disappearance of certain peaks. In the diffractograms shown in Fig. 5, a crystalline peak at the $2\theta = 19^{\circ}$ position appeared for the samples where x = 1, indexed according to Miller (I₁₁₁). For samples starting with x = 0.4, peaks at the position of $2\theta = 49^{\circ}$, referenced to Miller indices (I₃₃₁), disappeared. gahnite (NiOZn) is a normal spinel with Zn2+ cations located at the tetrahedral sites, and it has an energetically unaffordable inversion between zinc and aluminium cations [30]. The peak intensity I₍₃₁₁₎ may be assumed to originate from the contributions of Al³⁺ located at octahedral positions, and thus, the greater its intensity, the smaller the degree of inversion of its structure. Conversely, I₍₁₁₁₎ is related to the presence of nickel, which promotes the inversion process.

Quantitative phase analysis and cation inversion rate was conducted using the Rietveld method, and the results are shown in Table 4. The reliability factors of refinement varied of $C_{Rp} = 5-9\%$, $C_{Rwp} = 7-9\%$ and $R_{bragg} = 1.0-2.1$. By evaluating the effect of the calcination temperature on the quantification of phases for samples in which the nickel content x = 1 (Table 4), it can be seen that incorporation of metal nickel into the structure does not direct occur. First, metal nickel is transformed into nickel oxide and then incorporated in the spinel structure. This process is confirmed by the quantification of phases between the Ni1Zn series samples. When the calcination temperature increased to 800 °C, an increasing amount of NiO and a decreasing amount of Ni⁰ were found. Combined with the small variation in the amount of the spinel phase, it is found that metallic nickel transforms in nickel oxide before incorporation into the spinel structure. Otherwise, consider the sample Ni1Zn1000: all nickel oxide was inserted into the structure, with a proportional decrease of the amount of NiO. The work of Visinescu et al. [30] explains that the carbon residue oxidation in the burning powder process of the precursor implies the reduction of nickel oxide and degradation under an air atmosphere. The redox sequence $Ni^{2+} \rightarrow Ni^{0} \rightarrow Ni^{2+}$ implies

Table 4

Phase quantification, lattice parameter and crystallite size.

Sample Phases (%)					Lattice Parameter (Å)	Crystal Size (nm)	γ ^a
	Spinel	ZnO	NiO	Ni ^o			
Ni0ZnSC	97.07	2.93	_	_	8.087	22.808	_
Ni0Zn600	97.27	2.73	-	-	8.087	23.197	_
Ni0Zn800	100	-	-	-	8.087	28.535	_
Ni0Zn1000	100	-	_	-	8.085	45.278	_
Ni0.1ZnSC	100	-	-	-	8.082	23.770	0.280
Ni0.1Zn600	100	-	_	-	8.077	24.029	0.271
Ni0.1Zn800	100	-	_	-	8.081	22.874	0.289
Ni0.1Zn1000	100	-	_	-	8.077	28.906	0.285
Ni0.2ZnSC	100	-	_	-	8.083	27.202	0.695
Ni0.2Zn600	100	-	_	-	8.074	25.114	0.691
Ni0.2Zn800	100	-	_	-	8.079	27.865	0.702
Ni0.2Zn1000	100	-	-	-	8.076	31.332	0.708
Ni0.4ZnSC	100	-	-	-	8.064	30.466	0.721
Ni0.4Zn600	98.14	-	1.86	-	8.061	26.109	0.720
Ni0.4Zn800	100	-	_	-	8.068	31.612	0.725
Ni0.4Zn1000	100	-	_	-	8.065	35.239	0.723
Ni1ZnSC	86.76	_	8.33	4.91	8.045	34.607	0.841
Ni1Zn600	87.44	-	10.57	1.99	8.041	42.989	0.845
Ni1Zn800	88.07	-	11.93	-	8.041	32.035	0.840
Ni1Zn1000	98.87	-	1.13	_	8.051	43.254	0.844

^a Fraction of Ni²⁺ ions in octahedral sites.

 $NiO \rightarrow Ni^{0} \rightarrow NiO$; the reaction is continuous with the elimination of oxygen and nickel accommodation in the aluminate structure.

The temperature effects on the crystallite size and the unit cell parameters were investigated. Fig. 6a-c shows these values, respectively. There was no significant change in the crystallite size between the not-calcined and calcined samples at 600 °C (Fig. 6a). again indicating that the power generated from the lower temperature is not enough to change the material structure. Analysing both together with the theoretical adiabatic flame temperature (Table 3) indicates that synthesis, even for a few seconds, reaches temperatures above 900 °C, but the large volume of gas released during the fast expansion of the synthesis reaction dissipates the heat and limits the temperature increase, which affects crystal nucleation, substantially reducing growth and stabilizing the structure. The samples calcined at 800° and 1000°C (Fig. 6a) showed crystallite growth due to the sintering of the material. The lattice parameter as a function of temperature (Fig. 6c) had little variation, suggesting the stabilization of the structures formed. All of the lattice parameters calculated by XRD are solid, with a cubic spinel structure of value 8.088 [19].

Fig. 6b–d shows the chromophore ion content effects on the crystallite size and the lattice parameter, respectively. In relation with the crystallite size (Fig. 6b), the not calcined and calcined samples at 600 °C have a similar behaviour: increases in the crystallite size are caused by the increased nickel content in the chemical composition of the synthesis materials, implying that the power generated in the synthesis and calcination at 600 °C is not enough to change or order the material structures. A different behaviour was seen for the other samples calcined at 800 °C and 1000 °C: between 0 < x < 0.1, there is a reduction in the particle size. From x = 0.1 onwards, growth occurs with the increasing nickel content. This decrease may be a result of the rearrangement of atoms in the crystalline structure, which reduces the effects and, consequently, reduces the entropy of the system by changing the particle size. The nickel content increase promotes the inversion of

the structure, which makes the system unstable, causing crystal growth from x = 0.1. This result is corroborated by analysing the results of the series calcined at 1000 °C, which had greater energy provided by the system and, consequently, a greater stabilization and percentage decrease in the particle size of the sample Ni0Zn compared with the sample Ni0.1Zn.

The lattice parameter relation (Fig. 6d) was observed to linearly decrease with nickel incorporation into the spinel, indicating the formation of a solid solution, implying isomorphic substitutions of Zn^{2+} by Ni²⁺ ions. The decrease is attributed to the nickel radius (0.69 Å) being smaller than that of zinc (0.74 Å), confirming the diffractogram analysis results (Fig. 5), which show a right shift of the peaks.

3.5. Infrared spectroscopy

The infrared spectra of the synthesized pigments were obtained and are shown in Fig. 7. Analysing all of the sample results, no significant variations with the increasing calcination temperature were observed; only a small displacement of the bands was noted, which was caused by the better accommodation of ions at their preferred sites. All of the spectra present bands in the range of $500-900 \text{ cm}^{-1}$, which are associated with the vibrations of M – O, Al–O and M-O-Al and are characteristic of the spinel structure [28], confirming the XRD analysis results that identified the major phase of all samples.

The FT-IR results of all the Ni0Zn and Ni0.1Zn samples (Fig. 7a and b) present absorption bands close to 497, 553 and 661 cm⁻¹, which are attributed to the stretching vibrations of aluminium located in the octahedral sites (AlO6) [6] and zinc located in tetrahedral sites [3]. The default band is around 720 cm⁻¹ and is associated with the vibration of aluminium at tetrahedral sites (AlO4), showing that the ZnAl₂O₄ spinel is normal (bivalent metallic ions in tetrahedral sites and trivalent metallic ions in octahedral sites of the crystalline structure). This zinc aluminate



Fig. 6. a) Particle size as a function of the calcination temperature; b) particle size as a function of the nickel content; c) lattice parameter as a function of the calcination temperature; d) lattice parameter as a function of the nickel content.

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Fig. 7. FT-IR with varying temperatures: a) Ni0Zn; b) Ni0.1Zn; c) Ni0.4Zn; d) Ni1Zn.

behaviour is most common [30].

For Ni0.2Zn, a decreasing low shift at 500 cm^{-1} was observed, which may have been caused by the decrease in the amount of zinc. The tendency of the displacement of the peaks to the right was confirmed with the samples of Ni0.4Zn and Ni1Zn (Fig. 7c and d). The bands near $500-524 \text{ cm}^{-1}$ are assigned to the stretching of nickel in the octahedral sites (NiO6) [40], and those near $602-610 \text{ cm}^{-1}$ (least intense) are attributed to nickel in the tetrahedral

sites (NiO4) at low amounts. The band absorption at 449 cm⁻¹ represents NiO [11], confirming its identity in the diffractograms (Fig. 4d).

By maintaining the same temperature and varying the nickel content (Fig. 8), it is easier to observe the displacement of the absorption band from AlO6 to AlO4, which indicates the inversion of the structure with the increase in the amount of nickel. This inversion results from nickel entering the octahedral sites, forcing



Fig. 8. FT-IR with varying nickel contents: a) not-calcined; b) 600 °C; c) 800 °C; d) 1000 °C.

aluminate to the tetrahedral sites. The change in ion position promotes the final spinel properties with the more perceptible colouring.

3.6. Colourimetry

Table 5 shows the visual aspects and average values of the colorimetric variables (CIELab) for all of the pigments produced and dispersed in a colourless varnish, along with the quantitative difference of the colour between them. Each variable was measured in triplicate, and the average values were subjected to the Tukey test at the 5% level of probability to evaluate whether the colours obtained were significantly different—that is, if changes in the chromophore ion content and the calcination temperature significantly influenced the colours formed. The test was conducted on a set of samples with the same chromophore content and a variable calcination temperature and on a set of samples with a constant

Table 5

Colorimetric properties of powdered pigments - Ni_xZn_{1-x}Al₂O₄.

calcination temperature but a variable chromophore ion content.

Observing the visual pigments presented in Table 5, it is noted that the samples Ni0Zn800 and Ni0Zn1000 tend to be white. White was expected because zinc has all of its d orbitals filled and thus was not colourful. The samples of x > 0 have cyan tones. With the increasing temperature, the tonality becomes easier to visually identify, and with the increase of the nickel content, the samples become darker.

The Tukey analysis at 5% of the colorimetric CIELab variables identified the same statistical values to a* for x = 0 at 600 °C and 800 °C. However, in all samples, at least one of the variables presented average values that were different from the others, and as the pigment colour is characterized by three variables in CIELab, only one pigment being different is enough to distinguish different colours between pigments. Therefore, changes of both the ion content and calcination temperature caused significant changes in the nickel-zinc pigment colour. The Tukey analysis at 5% confirms

Sample	Powder dry	Powder dry				Powder dispersed in varnish colorless			
	Visual Aspect	L*	a*	b*	Visual Aspect	L*	a*	b*	$\Delta \mathbf{E}$
Ni ₀ Zn		28.83 ^{aa}	1.07 ^{aa}	7.17 ^{aa}		23.23	1.10	5.80	5.76
Ni ₀ Zn		43.70 ^{ba}	0.77 ^{aa}	5.50 ^{ba}		42.03	-1.00	4.10	2.80
Ni ₀ Zn	Ø	46.23 ^{ca}	-0.83 ^{ca}	5.77 ^{ca}		37.33	-1.23	4.93	8.93
Ni _{0.1} Zn600		34.90 ^{ab}	-1.23 ^{ab}	4.80 ^{ab}		23.23	1.10	5.80	4.65
Ni _{0.1} Zn800		38.43 ^{bb}	-2.67 ^{bb}	2.97 ^{bb}		42.03	-1.00	4.10	6.91
Ni _{0.1} Zn1000		45.43 ^{ca}	-3.17 ^{bb}	1.20 ^{cb}		37.33	-1.23	4.93	1.98
Ni _{0.2} Zn600		25.37 ^{ac}	-0.40 ^{ac}	4.93 ^{ab}		30.57	-0.13	3.53	6.24
Ni _{0.2} Zn800		36.37 ^{bc}	-3.73 ^{bc}	2.90 ^{bb}		32.63	-5.57	0.57	6.13
Ni _{0.2} Zn1000		40.57 ^{cc}	-4.17 ^{cc}	0.67 ^{cc}		45.20	-2.47	-0.63	7.00
Ni _{0.4} Zn600		33.07 ^{ad}	-1.07 ^{ab}	3.13 ^{ad}		19.27	-0.77	3.67	10.43
Ni _{0.4} Zn800		33.63 ^{ad}	-3.73 ^{bc}	4.40 ^{bd}		30.47	-5.00	1.83	2.57
Ni _{0.4} Zn1000		35.17 ^{cd}	-3.73 ^{bc}	4.40 ^{bd}		33.67	-4.73	-0.40	7.79
Ni ₁ Zn600		21.40 ^{ae}	-3.73 ^{ae}	0.87 ^{ae}		22.87	-2.17	1.27	1.41
Ni ₁ Zn800		29.40 ^{be}	-5.23 ^{be}	5.27 ^{be}		31.20	-4.57	4.40	1.78
Ni ₁ Zn1000		28.43 ^{ce}	-6.00 ^{ce}	3.33 ^{ce}		27.53	-4.30	2.97	10.94

a, b, c, d, e mean values following the same set of letters and same column no differ from each other by Tukey 5% test.

the visual analysis of differences in pigments, as shown in Table 5. Furthermore, Table 5 clearly displays that the colours are visually different between the dry powder and that dispersed in varnish, although the dispersed colours continue to give the same cyan tones. The values of ΔE (Equation (4)) shows no trend. Only Ni1Zn600 exhibited a colour difference between 0 and 1.5, meaning the materials compared exhibited a similar colour. Some samples had ΔE in the range of 1.5–5, which indicates that different colours were observed. The majority of samples had ΔE values above 5, implying a clearly observed difference in colour [41].

Fig. 9 shows the colourimetry results obtained by CIELab as functions of the calcination temperature and nickel content in the spinel structure, separately. Focusing on luminosity (L*), the same increase with the calcination temperature was observed in all of the studied samples. The addition of nickel caused a decrease of the value of L*, except for the nickel series at 600 °C, which presented an oscillation. This behaviour confirms the visual assessment result (Table 5). As $ZnAl_2O_4$ is white, when a chromophore dopant is added to it, the sample tends to present a different tone from white and darkens (L* decrease). Nickel has an incomplete d orbital, and the electronic transitions in this orbital leads to the observed colour. A similar behaviour was also found by Queiroz et al. [6].

For the other CIELab parameters, a* and b*, in general, the values decreased with the increasing temperature. An increasing nickel concentration caused a decrease in the value of a*, which indicates a propensity toward green. b* remained stable with only slight decreases, tending towards blue. In Table 5, the samples doped with nickel have a cyan colouring. Nickel aluminates belong to the class of cyan pigments, whose colour results from a mix of two colours: blue and green [29,42]. The pigments' colours confirm the diffraction analysis results of Ni0.4Zn and Ni1Zn (Fig. 4), in which nickel oxide was identified as a secondary phase. The observed bluish colouring is characteristic of Ni²⁺ ions located in tetrahedral sites, even in low amounts, while the greenish colouring results from a mix of nickel-zinc aluminate (blue) with a small amount of NiO (yellow-green) [5]. Thus, the cyan colouring of aluminates is

governed by ions present in the structure of NiO in samples, indicating the incomplete incorporation of nickel in the spinel structure. The movement of tetrahedral ions to the octahedral sites confirms the observed FT-IR results: changes in the binding field and the d orbitals also cause colouring changes. To predict the values of the CIELab parameters and, consequently, the final colour of the pigments formed under different synthetic conditions, surface maps were built from the CIELab data as functions of both the calcination temperature and nickel content. The results are shown in Fig. 10, and the functions obtained are given by equations (5)–(7). Each equation satisfactorily describes the experimental data and can be used to predict he material behaviour.

$$L = -23.655 - 0.6078LNi + 0.1286CT + 5.629LNi^{2} - 0.023LNiCT - 5.916x10^{-5}CT^{2}$$
(5)

$$a^{*} = 13.5853 - 9.6714LNi - 0.03CT + 5.329LNi^{2} - 7.384x10^{-5}LNiCT + 1.4833x10^{-5}CT^{2}$$
(6)

$$b^* = 2.1743 - 18.818LNi + 0.0155CT + 5.6357LNi^2 + 0.0144LNiCT - 1.45x10^{-5}CT^2$$
(7)

CT represents the calcination temperature, and LNi represents the nickel content in the spinel structure.

4. Conclusion

The variable tones obtained through nickel doping in zinc aluminate are advantageous to industries that use pigments, as they afford different colours to meet increasingly specific market demands, possibly replacing cobalt ions in the production of cyan pigments. The material was synthesized by combustion using glycine as a propellant at a stoichiometric ratio, and the results indicated that this route of synthesis is suitable for the production



Fig. 9. Effect of the calcination temperature and chromophore ion content on the colorimetric variables of the pigment powder.

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Fig. 10. a) Luminosity variable (L*); b) chromaticity variable a*; c) chromaticity variable b* as a function of the calcination temperature and nickel content.

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of nanometric spinel powders with high purity. The chromophore ion does not affect the morphological properties but does affect the spinel structure. Zinc spinel has a normal structure, and increasing the value of x (nickel content) causes an inversion of its structure.

Aluminates doped with nickel presented colours varying between blue and green, similar to dark cyan, and a higher nickel content led to a more intense cyan colour. The colourimetry data of ΔE indicates that the dilution of a pigment powder in a colourless matrix acrylic varnish causes significant changes to the colours of all samples, although they still have cyan tones. The model proposed to calculate L^{*}, a^{*} and b^{*} at different calcination temperatures and with varying nickel contents is sufficient to reproduce the presented experimental data.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2019.152477.

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