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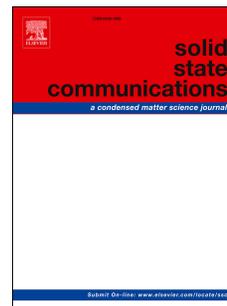
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CRediT author statement

Y. El Jabbar: Conceptualization, Writing-Original Draft, Data curation. **H. Lakhli** : Software, Formal analysis. **R. El Ouatib:** Supervision, Project administration, Validation. **L. Er-Rakho:** Supervision, Project administration, Validation **S. Guillemet-Fritsch:** Resources, Investigation, Visualization. **B. Durand:** Resources, Investigation, Visualization

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Preparation and characterisation of green nano-sized ceramic pigments with the spinel structure AB_2O_4 (A = Co, Ni and B = Cr, Al)

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Preparation and characterisation of green nano-sized ceramic pigments with the spinel structure AB_2O_4 (A = Co, Ni and B = Cr, Al)

Abstract

Inorganic pigments based on AB_2O_4 (A = Co, Ni; B = Cr, Al) spinel structures with green colour were successfully synthesised by the polymeric route. The effect of the substitution of trivalent and divalent cations on the structural, optical and morphological properties of the pigments was investigated. The synthesised nanopowders were examined using thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller analysis (BET), UV–vis diffuse reflectance measurements, and CIEL*a*b* colorimetric analyses. The results show that the $CoCr_2O_4$ spinel and the spinels substituted by nickel and aluminium cations were obtained with a single phase after heat treatment at 900°C . The produced powders present shades of the green colour with improvement in morphology for the substituted samples. The $Ni_{0.5}Co_{0.5}CrAlO_4$ nanoparticles consisted of grains of quasi-spherical shape with sizes between 50 and 75 nm. This powder was used in small quantities with glazes for coloring tests on the surfaces of ceramic substrates.

Keywords: Inorganic pigment; Substitution; Shades; Morphology.

1 .Introduction

The visual appearance of an object can play an important role in the industrial and artistic sectors. Colour and shine have become criteria for appreciating many products and evaluating the purchase decision. In the fields of surface engineering and ceramic industries, the use of inorganic pigments improves certain physical properties such as hardness, impermeability and corrosion resistance. Pigments are thus judged for both their tinting strength and for their heat stability and light from the external environment, as well as attacks from chemical agents in additives such as the mixtures, like binders and varnishes, used during coating operations [1–6].

The granulometry of the pigments is also of particular interest. In fact, powders with fine particle sizes and high specific surfaces offer high tinting strength [7,8]. In general, inorganic pigments are prepared by traditional methods based on mixtures of oxides, hydroxides or carbonates. These methods have the advantage of being inexpensive and simple to implement. However, they require high temperatures and long heat treatments to obtain the homogenous phase; in addition, the materials produced by this process exhibit heterogeneous particle size distribution and low specific surface area [9–13]. Recently, other synthetic routes using a wet process based on soft chemistry have been developed to avoid these disadvantages. Indeed, several works based on sol-gel synthesis, coprecipitation methods, hydrothermal techniques and others make it possible to produce fine powders with high chemical and morphological homogeneities [14–17].

For industrial needs, ongoing research work in this area has focused on the development of inorganic materials that meet demand criteria. Among the most preferred materials to be used as pigment are the oxides of spinel structure with the general formula AB_2O_4 due to their many advantageous properties, including high chemical and thermal stability, and their interesting optical properties. In these oxides, (A) represents the divalent metal ions, while (B)

represents trivalent metal ions. The addition of various chromophores (mainly transition elements) provides a wide variety of colours [18–20].

The present paper focuses on green pigments-based on spinel oxides. Various shades of green pigment are used in ceramic manufacturing. Uvarovite ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$) is a green pigment obtained from potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), calcium carbonate (CaCO_3) and quartz (SiO_2)[21]. Eskolaite (Cr_2O_3) is the most heavily used oxide in ceramic manufacturing and doping with other elements such as ZnO and MgAl_2O_4 and the silicates $\text{MgAl}_2\text{Si}_3\text{O}_{12}$ can lead to various shades of green pigments[22]. Other types of inorganic green pigments have been studied based on phosphates such as xenophyllite ($\text{Na}_4\text{Fe}_7(\text{PO}_4)_6$) and vivianite ($\text{Fe}_3(\text{PO}_4)_2$) [23]. In this work we report on the synthesis of CoCr_2O_4 ultrafine powders doped with nickel and aluminium. The effect of the metal substitution on the structural, optical and morphological properties is discussed.

2. Experimental procedure

All the chemicals used to begin this work were of pure grade: nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, Sigma Aldrich), cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, Sigma Aldrich), aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.0%, Sigma Aldrich) and chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.0%, Sigma Aldrich). The reagents were dissolved in distilled water with a molar ratio of the cations metal $\text{A}^{2+}/\text{B}^{3+}$ of 1: 2, then poured into a solution of polyacrylic acid (10% by weight) as a chelating and gelling agent. The pH of the mixture was adjusted to 7 by using ammonium hydroxide solution under constant stirring. The initial synthesis was based on the preparation of CoCr_2O_4 spinel oxide, after which the synthesis was based on a substitution of 50% of the tetrahedral and octahedral sites by nickel and aluminium, respectively. The experimental protocol is summarized in Fig. 1. Thermal analysis was carried out by thermogravimetric/differential thermal analyzer (APPARTUS SHIMADZU). XRD patterns

were obtained at room temperature using a Bruker D8 employing CuK α radiation as the X-ray source. The surface morphology of the samples was examined by JEOL JSM 6700F scanning electron microscopy (SEM) using a 30 kV voltage. Diffuse reflectance was measured with a Perkin Elmer Lambda 35 UV-Vis spectrophotometer. The specific surface area of the powder was measured using Brunauer-Emmet-Teller (BET) method by Micrometrics Flowsorb II 2300 instrument. The colorimetric measurements were performed in the CIE L*a*b* (L*a*b* colorimetric system of the Commission Internationale de l'Eclairage) using a CHROMA METER CR-400/410 colorimeter (KONICA MINOLTA).

3. Results and discussion

3.1. Thermal analysis

Thermogravimetry-differential thermal analysis (TG-DTA) was performed to monitor the thermal decomposition process under an air atmosphere of the precursors obtained after pyrolysis (300 °C/12h) up to 1000 °C with a temperature rise rate of 10°C/min and sample sizes between 15–25 mg in open Pt crucible were used. Fig. 2 represents the TGA and DTA curves of the precursor produced from the initial synthesis based on the preparation of the cobalt chromite (CoCr₂O₄). The TG-DTA curves for the substituted compositions show similar thermal behaviours. The TGA thermogram shows a total weight loss of around 16%. This is due to the elimination of water adsorbed on the surface of the powder and the removal of organic residues. After 900°C, no discernible mass loss was observed on the TGA curves. DTA curves showed slight endothermic inflections at around 925 °C, which can be attributed to the reduction of Co³⁺ to Co²⁺ [24].

3.2. X- ray diffraction

Based on the TG-DTA results, the precursors obtained by pyrolysis were calcined in a muffle furnace under air atmosphere and the heat treatment temperature was adjusted to 900 ° C for 5 hours. The produced powders were analysed by X-ray diffraction. The XRD patterns of the obtained samples demonstrated a single phase of spinel (see, Fig. 3). The characteristic peaks of sample (a) are indexed to the crystallographic planes of CoCr_2O_4 (JCPDS files no. 080–1668). Samples (b) and (c) have a similar system of lines with a slight shift. This confirms that the Ni and Al cations have been successfully inserted into the spinel oxides without forming any other phase. Rietveld refinement of the XRD patterns was performed using FullProf suite software in order to obtain more structural information. The refined parameters include the scale factor, sample displacement, background, peak shape, lattice constants, atomic positions for the oxygen atoms and the isotropic thermal parameters for each atom. The quality of the refined structural models was checked using the reliability index parameters. The refinements were carried out in the $Fd-3m$ space group. The refined parameters obtained and the graphical illustration (experimental, calculated and difference signals) for the substituted sample $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ are depicted in Fig. 4. The refinement of cations occupancy at 8a sites and 16d sites confirms the direct spinel-type structure of the sample with negligible inversion.

3.3. Optical properties

The shades of the colour green of the synthesised powders CoCr_2O_4 , CoCrAlO_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ are shown in the images presented in Fig. 5. The diffuse reflectance spectra obtained by UV-Visible analysis show the presence of broad bands located in the visible region (530–670 nm) (Fig. 5). These absorptions can be attributed to the allowed transitions ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ and ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$, respectively, of the Co^{2+} and Ni^{2+} ions in the

tetrahedral sites and to the transitions ${}^4A_{2g} \rightarrow {}^2T_{2g}$, ${}^4A_{2g} \rightarrow {}^2T_{1g}$ and ${}^4A_{2g} \rightarrow {}^2E_g$ of chromium in the octahedral site [25–28]. The colorimetric coordinates (L^* , a^* and b^*) obtained by colorimetric analysis make it possible to quantify the colour of the pigments (see Table 1). For the composition doped with 50% of Al (sample 2), it was found that component ($-a^*$), which is responsible for the green colour, was reduced by almost half and component ($-b^*$), which is responsible for the blue colour, was slightly decreased. The ratio between these components (a^*/b^*), which indicates the saturation of the green hue, was reduced from 1.21 to 0.71. The additional substitution by 50% of Ni allows this ratio to 1.41. This is due to the decrease in the $-b^*$ component, a characteristic of the blue coloration, which depends on the cobalt concentration.

3.4. Morphological properties

The morphology of the synthesised green powders was examined using SEM analysis. As shown in Fig. 6, the micrograph of the CoCr_2O_4 powder (Fig. 6 (a)) shows grains of different shapes and an agglomerated state. The grain size was estimated to be 75–200 nm. The CoCrAlO_4 powder (Fig. 6 (b)) is formed of grains with a quasi-spherical shape more or less agglomerated with sizes estimated to range between 35 nm and 100 nm. The image of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ (Fig. 6 (c)) shows a fine powder with zones of agglomeration and consisting of quasi-spherical grains whose sizes were estimated to range between 50 nm and 75 nm. Measurement of the specific surface area by the BET method shows that the substitution of 50% of Al in the CoCr_2O_4 spinel makes it possible to increase the surface area from $6 \text{ m}^2/\text{g}$ to $12.4 \text{ m}^2/\text{g}$. The second substitution by 50% of Ni resulted in a surface area of about $18 \text{ m}^2/\text{g}$. The grain sizes determined from the values of the specific surface areas were estimated by considering the hypothesis that the grains are monodispersed and spherical [29]. The obtained values were in the same order of size as those observed in the SEM micrographs.

3.5. Ceramic colouring efficiency tests

Ceramic colouring efficiency tests were used to evaluate the efficiency of the green colour coverage of the synthesised pigments on the ceramic substrates. The $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ nanoparticles were mixed in different amounts with transparent glaze powders, the chemical composition of which is given in Table 2. The mixtures were homogenised and deposited on to the ceramic substrates and then fired at 920°C for 30 minutes with a heating rate of $10^\circ\text{C}/\text{min}$. Fig. 7 shows the images of the coloured surfaces of the substrates obtained after firing. It was observed that mixing the glaze with a small amount of the nanoparticle pigment results in green colour coverage. The $L^*a^*b^*$ colorimetric parameters measured on the coloured surface are given in Table 3. The hue variation between the two samples can be calculated by using CIE ΔE_{2000} color-difference formula (ΔE_{00}) [30] and by the following equation $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [31]. We noted that a quantity of 4% of the pigment mixed with the glaze is sufficient for obtaining a contrast of less than 2, which can be difficult to distinguish with the human eye.

4. Conclusion

Green pigments based on the spinel structure were successfully synthesised using the polymeric route. The substitution of 50% of Al and Ni in the spinel CoCr_2O_4 leads to improving the morphology of the powders with different shades of the colour green. The obtained nanoparticles consist of grains of almost spherical shapes. The specific surface area increases after the substitution from $7\text{ m}^2/\text{g}$ to $18\text{ m}^2/\text{g}$. Ceramic colouring efficiency tests show that an amount of less than 4% wt of the prepared pigment was sufficient for good coverage of the green colour.

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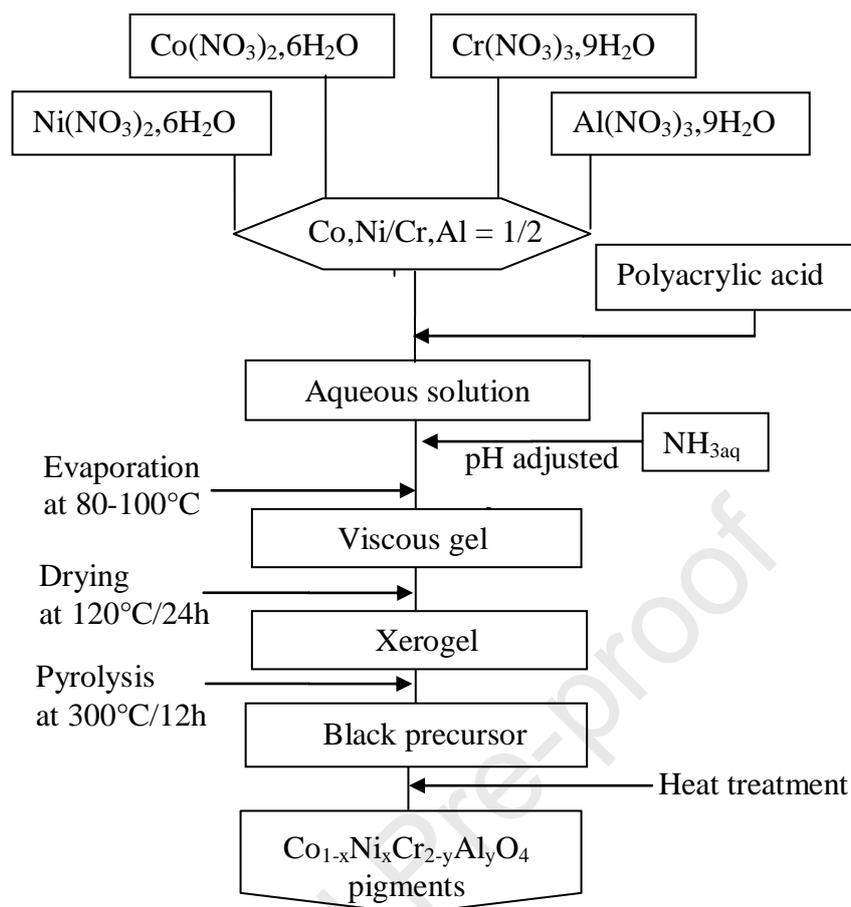


Fig. 1. Flowchart for the preparation of $\text{Co}_{1-x}\text{Ni}_x\text{Cr}_{2-y}\text{Al}_y\text{O}_4$ ($0 \leq x \leq 1$, $0 \leq y \leq 2$) powdered pigments.

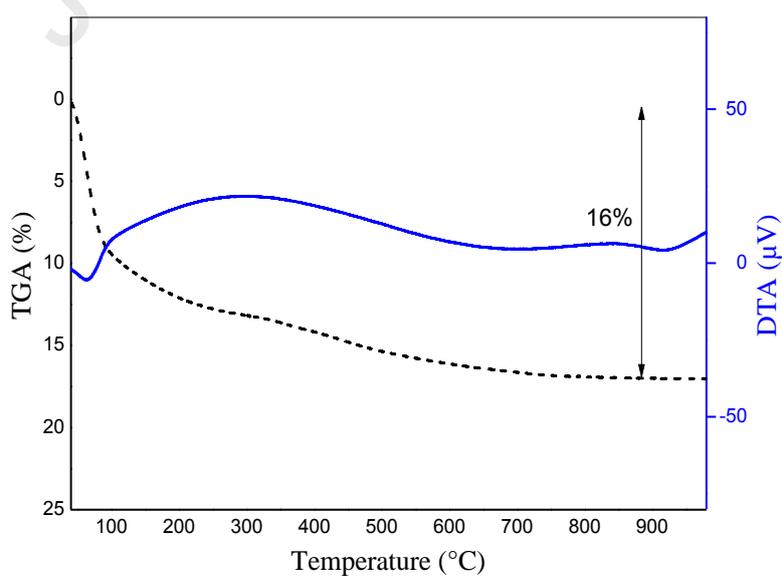


Fig. 2. TG-DTA analysis of dried gel of CoCr_2O_4 precursor.

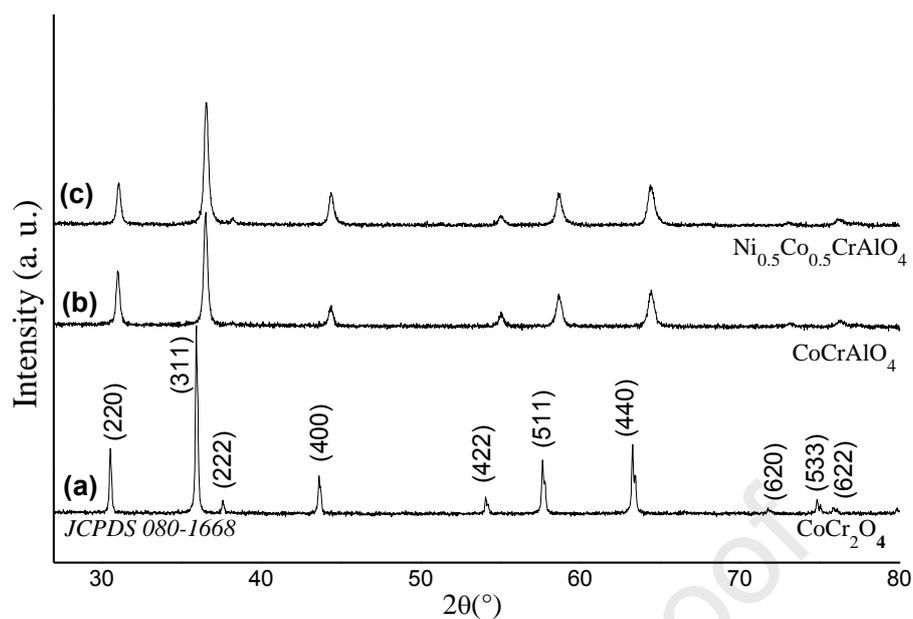


Fig. 3. X-ray diffraction patterns of CoCr_2O_4 and substituted spinels.

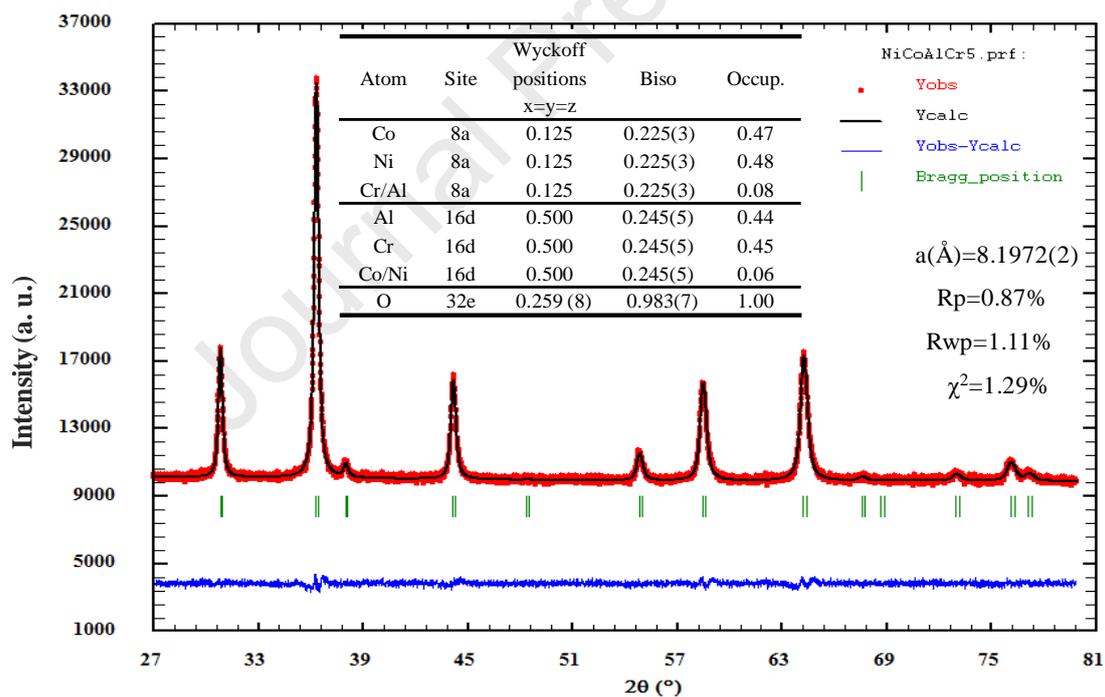


Fig. 4. Rietveld refinement of XRD pattern of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ sample.

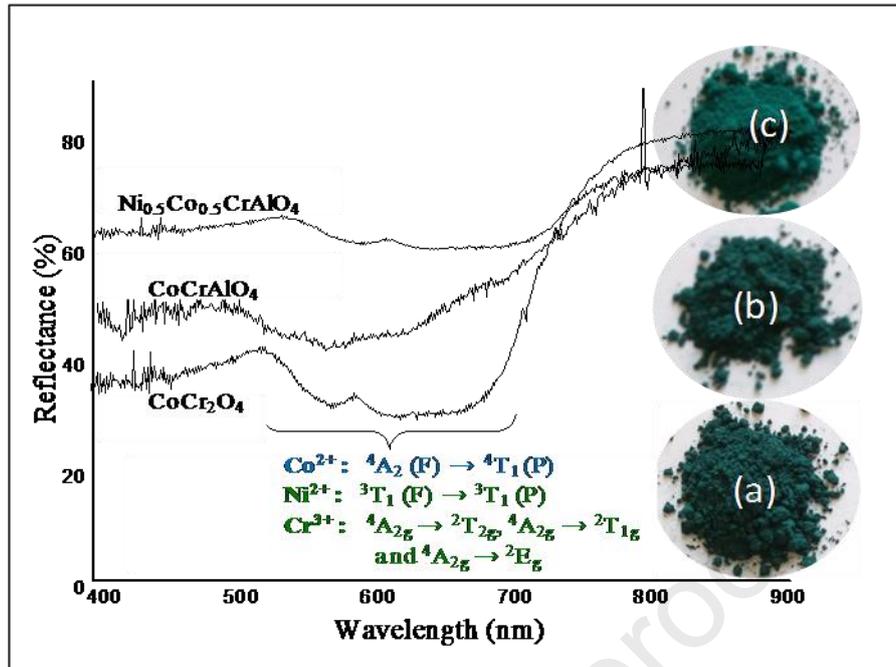


Fig. 5. Shades of the green colour and diffuse reflectance spectra of (a): CoCr_2O_4 , (b): CoCrAlO_4 and (c): $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ powders.

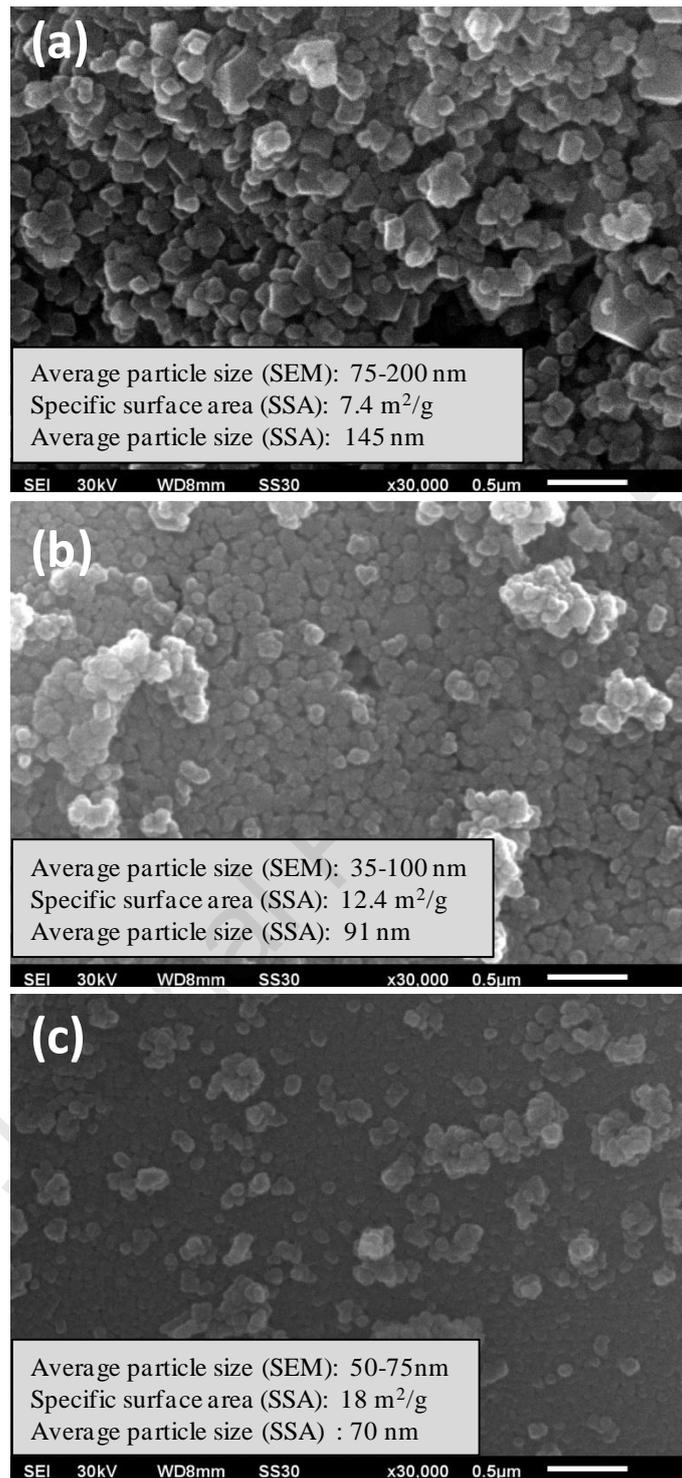


Fig. 6. SEM micrographs and estimated grain sizes of (a): CoCr_2O_4 , (b): CoCrAlO_4 (c): $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ powders.

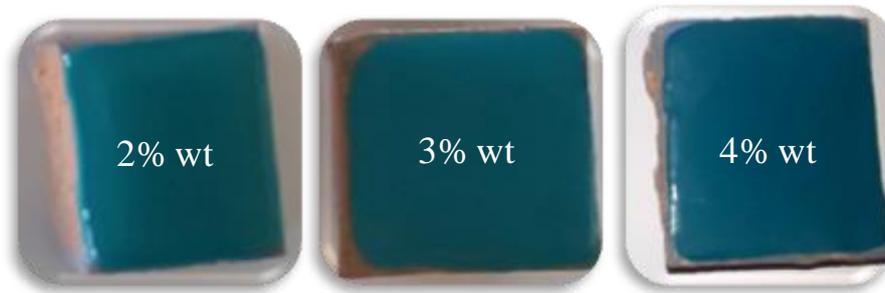


Fig. 7. Pictures of the ceramic substrates covered with a mixture of glazes and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ nanoparticles obtained after firing.

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Table 1Colorimetric coordinates of CoCr_2O_4 , CoCrAlO_4 and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{CrAlO}_4$ powders.

Sample	Colorimetric coordinates			Saturation in green hue
	L*	a*	b*	a*/b*
(1) CoCr_2O_4	49.6	-23.9	-19.7	1.21
(2) CoAlCrO_4	41.2	-11.4	-16.1	0.71
(3) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{AlCrO}_4$	41.6	-10.3	-7.3	1.41

Table 2

Chemical composition of the transparent glaze.

Oxide	K_2O	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	Na_2O
Content/%	5.77	17.08	62.68	3.90	0.32	0.29	9.93

Table 3

Colorimetric coordinates of the coloured surface of ceramic substrates measured after firing.

L*a*b* of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{AlCrO}_4$ pigment	L*	a*	b*	ΔE^*	ΔE_{00}
	41.64	-10.26	-7.32		
2%	45.64	-7.87	-5.25	5.01	4.45
3%	43.87	-8.35	-5.75	3.33	2.80
4%	42.35	-8.95	-6.11	1.92	1.49
5%	40.12	-9.42	-6.88	1.79	1.55

Highlights:

- Ultrafine powders were prepared by the polymeric route.
- CoCr_2O_4 spinel and the spinels substituted by nickel and aluminium cations are in the crystalline phase at 900°C .
- The effect of the metal substitution on the structural, optical and morphological properties was discussed.
- The substitution of 50% of Al and Ni in the spinel CoCr_2O_4 leads to improving the morphology of the powders with different shades of the colour green.
- Ceramic colouring efficiency tests show that an amount of less than 4% wt of the prepared pigment was sufficient for good coverage of the green colour.

Declaration of interests

→ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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