

Pechini Synthesis and Microstructure of Nickel-Doped Copper Chromites

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Spinel-type solid solutions were synthesized by the Pechini method and calcined between 500 and 900 °C for 4 hours and at 900 °C for 8 hours to produce ceramic pigments. The resulting powders were characterized by thermogravimetric analysis, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), particle size analysis and BET surface area measurements. The formation of spinel took place upon calcination at 700 °C. IR spectroscopy revealed the presence of ν_1 and ν_2 bands, typical of spinel structures, broadened by the presence of more than one cationic species in the structure. The specific area of the resulting powder decreased from 24.7 to 1.4 m² g⁻¹ as the calcination temperature increased from 700 to 900 °C. Microstructural analyses revealed the presence of crystalline spinel as the only phase present in powders calcined at 900 °C. Colorimetric analyses using L*a*b* coordinates and UV-visible spectroscopy revealed that the pigment was predominantly black.

Keywords: *spinel, chromites, Pechini method, ceramic pigments*

1. Introduction

Spinel are ternary oxides with the general formula AB₂O₄, where A and B are cations occupying tetrahedral and octahedral sites respectively. These oxides exhibit interesting electric, magnetic and catalytic properties¹⁻⁴, depending on their nature, charge, and distribution of ions at interstices⁵. CuCr₂O₄ crystallizes as a tetragonally distorted spinel structure. Its distortion is related to the cooperative Jahn-Teller effect of Cu²⁺ at the tetrahedral sites⁶. The substitution of tetrahedral Cu²⁺ ions by any bivalent cation does not affect the distribution of cations in the substituted spinel oxides^{7,8}. Site preference energies for oxide spinels indicate that Ni²⁺ and Cr³⁺ occupy octahedral sites, although Cr³⁺ is also capable of forcing Ni²⁺ into tetrahedral positions⁷.

The most widely used method for the preparation of spinels involves solid-state reaction of mechanically mixed metal oxides at high temperatures^{9,10}. The Pechini method^{11,12}, based on polymeric precursors, can be used to prepare spinels and it does not require high temperature calcinations and permits good stoichiometric control as well as reproducibility. This method consists of the formation of a polymeric resin between a metallic acid chelate and polyhydroxide alcohol by polyesterification.

This study is focused on the preparation of solid solutions of copper chromites doped with nickel by the Pechini method, and the investigation of the effect of heat treatment on particle size and morphology. X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) patterns were used to reveal the structural properties of the materials formed.

2. Experimental

2.1. Synthesis

Nickel-doped copper chromite powders were prepared from polymeric precursors by the Pechini method. The metal nitrate solution was mixed with a stoichiometric amount of citric acid. The resulting solution was stirred for about 1 hour on a hot plate and the temperature was stabilized at 70 °C. The mixture was heated to 90 °C, at which point ethylene glycol was added at a mass ratio of 40:60 with respect

to citric acid. The temperature was maintained constant up to resin formation, which polymerized at 300 °C. The precursor powders were then calcined for 4 hours at various temperatures, ranging from 500 to 900 °C, or at 900 °C for 8 hours.

2.2. Characterization

Chemical analyses of the metallic constituents were carried out by atomic absorption spectroscopy and a Spectra 110 Varian setup was used. Thermogravimetric analyses of the polymeric precursors were carried out in a TGA-7 Perkin Elmer balance by heating samples of 2.15 mg at 5 °C min⁻¹ in flowing air (50 mL min⁻¹). Particle size distributions were obtained in a CILAS 1064 laser analyzer. Infrared spectra (FTIR) were recorded using KBr pellets in a Perkin-Elmer 16 PC instrument. X-ray diffraction patterns (XRD) were obtained from a Shimadzu XRD-6000 X-ray diffractometer using CuK α radiation ($\lambda = 1.5418$ Å). The specific surface area of the powders was measured by nitrogen adsorption on a NOVA 2000 BET system. The microstructure of the powders was observed by examining Au-coated samples in a Philips ESEM-XL30 scanning electron microscope that was set in the high-vacuum mode. The diffuse reflectance of the powders was measured in the 300-800 nm range using a Gretac Macbeth 2180-2180 UV spectrophotometer (D-65 light). The color of the pigment was evaluated from L*a*b* colorimetric coordinates according to CIE (Commission Internationale l'Eclairage) standards using

$$\Delta E^2 = L^2 + a^2 + b^2 \quad (1)$$

where L* varies from black (0) to white (100), a* from green (-) to red (+), and b* from blue (-) to yellow (+).

3. Results and Discussion

The stages of decomposition of the polymeric precursor to form Cu_{0.8}Ni_{0.2}Cr₂O₄ spinel were revealed in the thermogravimetric analysis (Figure 1). Initially, thermal decomposition of the mixture took place at about 30 °C with onset of decomposition of citric acid present in the polymerized solution. Following elimination of residual water,

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the material lost 2% of its mass upon heating to 500 °C, due to decomposition of organic compounds. Samples calcined from 500 to 900 °C revealed no additional mass loss.

X-ray diffraction patterns of the calcined powders are shown in Figure 2. The presence of a distorted tetragonal spinel phase along with other crystalline phases, such as CuO and Cr₂O₄, could be observed. Although spinel was formed even at relatively low calcining temperatures, it is possible to observe the steady increase in the

relative peak intensity of spinel with respect to CuO and Cr₂O₄, with increasing synthesis temperature. This indicated ongoing crystallization of spinel from its precursors. The synthesis of spinel also affected particle size distribution in the resulting powder (Figure 3). Although slight, it is possible to notice that the average particle size (D50) of the powder, representative of powder agglomerates, steadily decreased from ~10 μm to ~6 μm as the calcining temperature increased from 500 to 900 °C and time from 4 to 8 hours at 900 °C. In addition, the

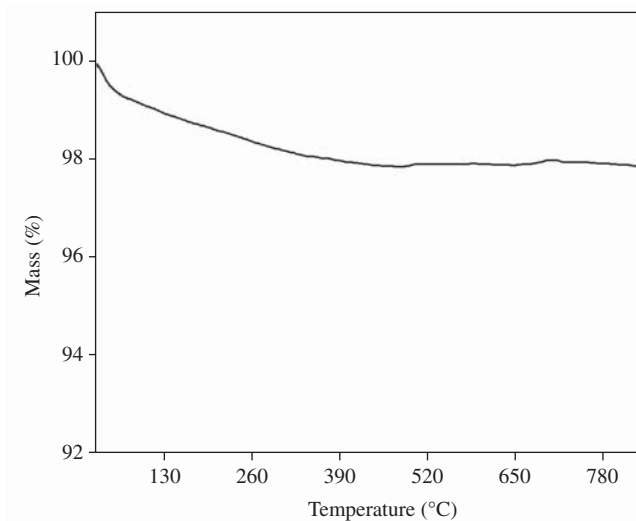


Figure 1. Thermogravimetric plot of the spinel polymeric precursor.

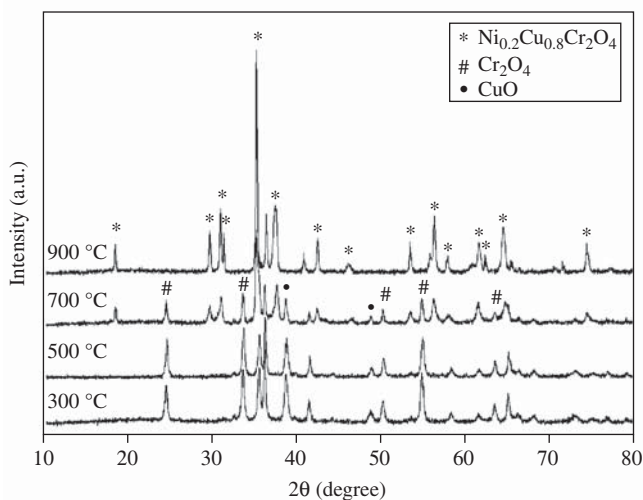


Figure 2. X-ray diffraction patterns of the polymeric precursor and powders calcined at 500 °C, 700 °C, and 900 °C for 4 hours.

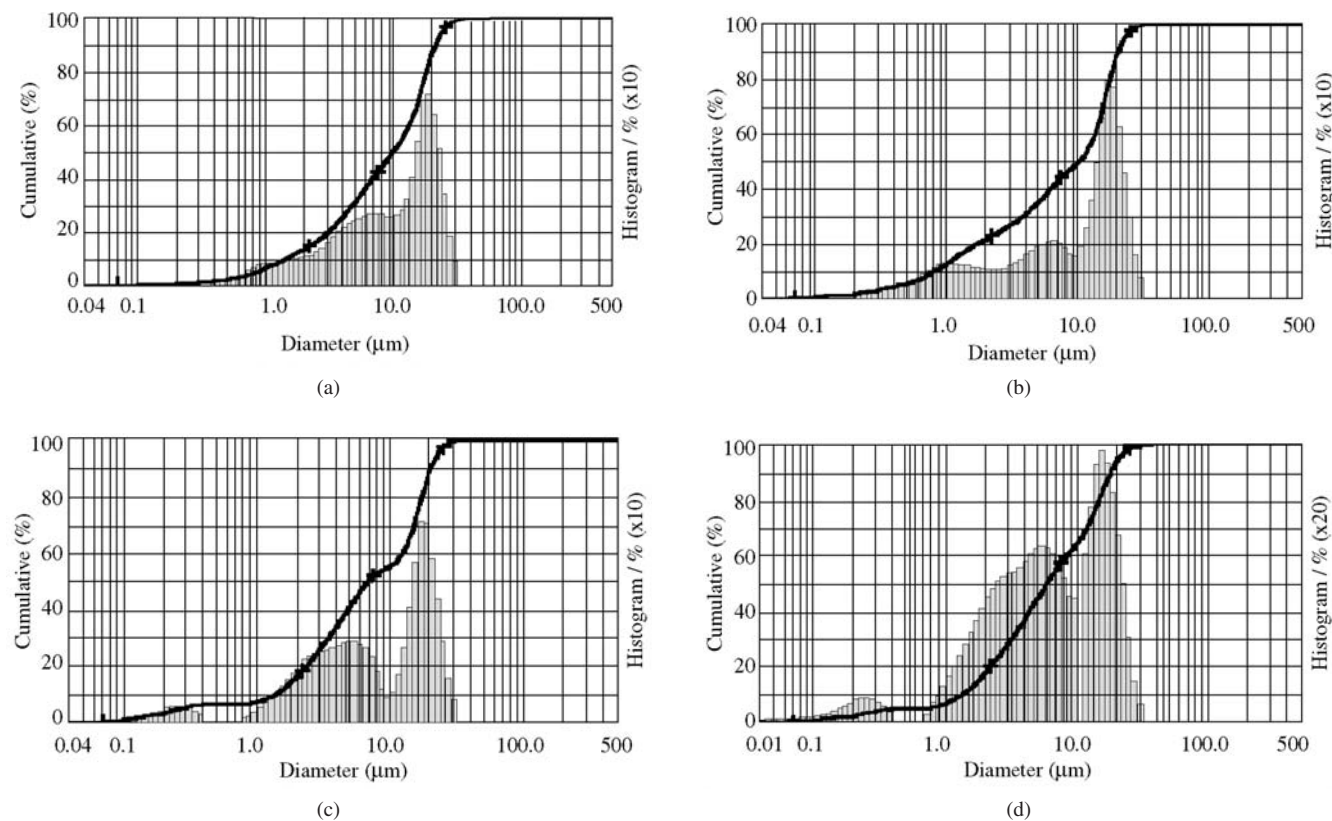


Figure 3. Particle size distribution of powders calcined at: a) 500 °C; b) 700 °C; c) 900 °C for 4 hours; d) 900 °C for 8 hours.

fraction of fine loose particles (equivalent diameter $< 1 \mu\text{m}$) also increased with crystallization of spinel. This can be confirmed from the SEM images shown in Figure 4. Along with changes in particle morphology as a function of calcining temperature, heat treatment at $500 \text{ }^\circ\text{C}$ (Figure 4a) resulted in substantial agglomeration of the powder, which is typical of the presence of unreacted CuO and Cr_2O_3 . Calcining at higher temperatures (700 or $900 \text{ }^\circ\text{C}$) or longer times (8 hours) resulted in loose and fine octahedron-shaped crystals characteristic of spinel and agglomerates. The values summarized in Table 1 reveal that the formation of spinel was accompanied by a steady decrease in specific surface area, a consequence of consumption of $\text{CuO} - \text{Cr}_2\text{O}_3$ irregular agglomerates to form regular-shaped spinel nanocrystals. The relatively low values encountered are typical of Pechini synthesis, and can be attributed to the M:AC (M = Metal; AC = citric acid) molar ratio used in the synthesis, and consequently, to the chain polymer size used in pigment preparation.

According to group theory, spinel type oxides should exhibit four IR bands $\nu_1 - \nu_4$ ¹³⁻¹⁴. In this investigation measurements were carried out up to 500 cm^{-1} , thus limiting the study to the high frequency bands (ν_1 and ν_2) of the IR spectrum. Since these bands are nearly insensitive to changes in the bivalent cation⁹, they should not be significantly affected when Cu^{2+} from CuCr_2O_4 is substituted by another bivalent cation. The infrared spectra are shown in Figure 5. Both, ν_1 at 665 cm^{-1} , and ν_2 at 580 cm^{-1} are related to bonds of the internal tetrahedra and octahedra

of the structure of $\text{Cu}_{0.8}\text{Ni}_{0.2}\text{Cr}_2\text{O}_4$. The broadening of these bands is probably due to the presence of more than one type of cation¹⁴.

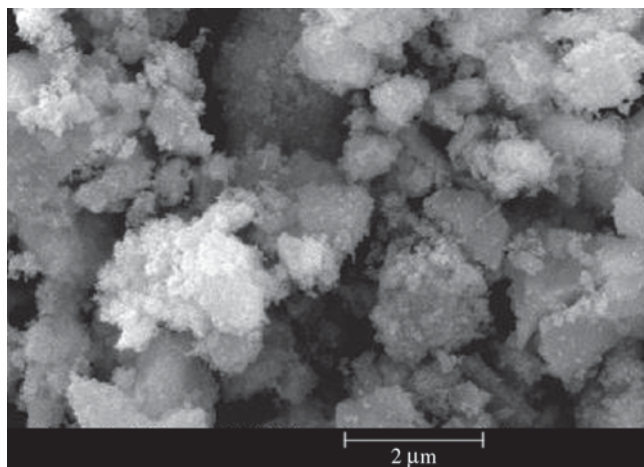
Results from UV- visible spectroscopy (Figure 6) revealed an absorption band in the $400\text{-}700 \text{ nm}$ range as a result of complete light absorption, typical of highly reflective systems. This was further confirmed by the colorimetric coordinates (Table 2). The relatively high values of L^* (31.81) along with low a^* and b^* , 0.10 and 1.07 respectively, suggested full light absorption, and consequently a black pigment. When applied to ceramic frits the pigment remained

Table 1. Specific surface area of calcined powders.

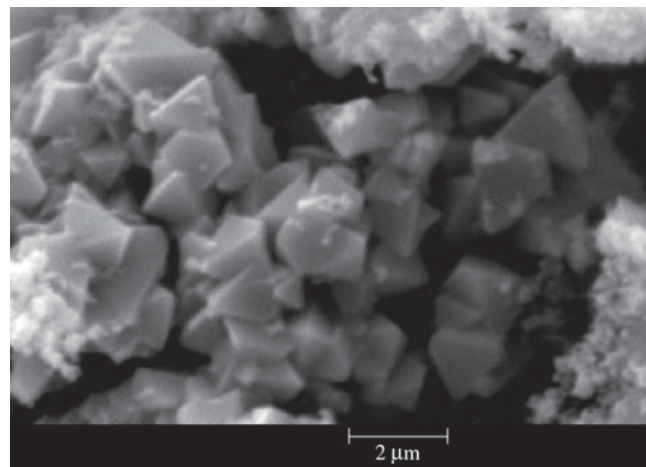
	Calcination profile			
	500 °C/4 h	700 °C/4 h	900 °C/4 h	900 °C/8 h
Specific surface area ($\text{m}^2 \text{ g}^{-1}$)	24.7	7.2	2.0	1.4

Table 2. Colorimetric coordinates of powder calcined at $900 \text{ }^\circ\text{C}$ for 8 hours.

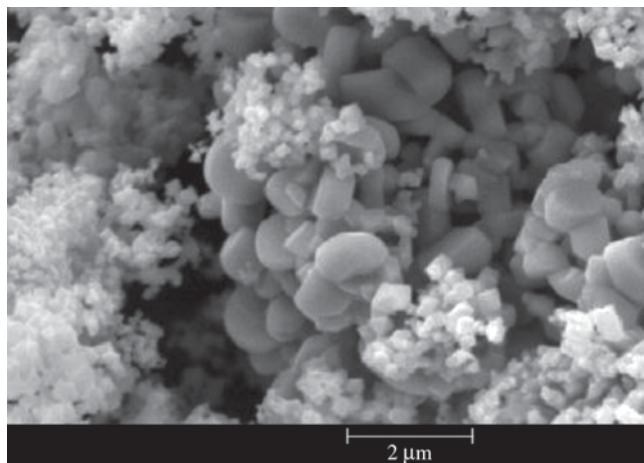
	L^*	a^*	b^*
Powder	31.81	0.10	1.07
Frit	0.00	0.00	0.00



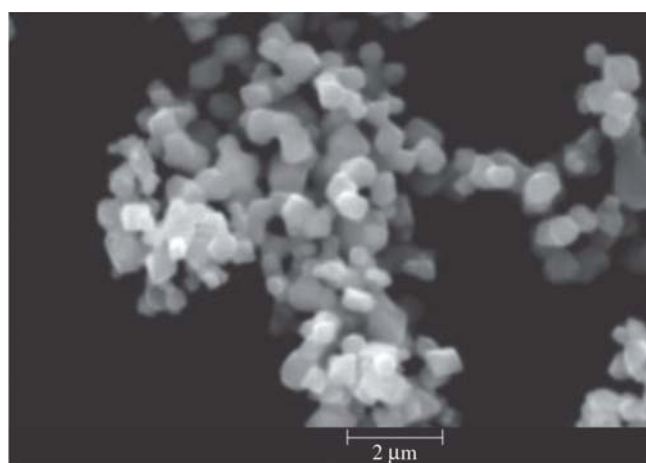
(a)



(b)



(c)



(d)

Figure 4. SEM images of powders calcined at: a) $500 \text{ }^\circ\text{C}$; b) $700 \text{ }^\circ\text{C}$; c) $900 \text{ }^\circ\text{C}$ for 4 hours; d) $900 \text{ }^\circ\text{C}$ for 8 hours.

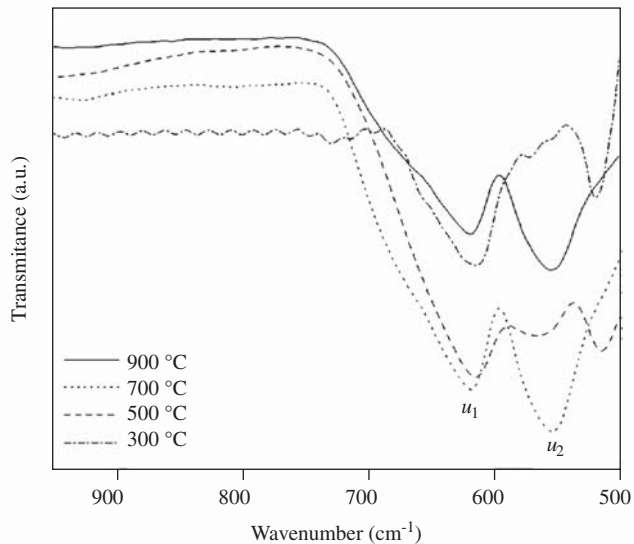


Figure 5. Infrared absorption pattern of the polymeric precursor and powders calcined at 500 °C, 700 °C, and 900 °C for 4 hours.

black although it changed its hue slightly. The values L^* , a^* and b^* changed to zero as a consequence of the interaction of the pigment with the glassy material.

4. Conclusions

$\text{Cu}_{0.8}\text{Ni}_{0.2}\text{Cr}_2\text{O}_4$ spinel was synthesized from polymeric precursors using the Pechini method. The crystallization of the spinel structure upon calcining at 700 °C. $\text{Cu}_{0.8}\text{Ni}_{0.2}\text{Cr}_2\text{O}_4$ was the only phase present upon calcination at 900 °C. Both, loose particles and agglomerates were formed. The average size of the powder was 8 μm . Black pigments were obtained from the synthesis. Despite slight variations in the colorimetric coordinates, no significant change in color was observed when the pigments were applied to ceramic frits.

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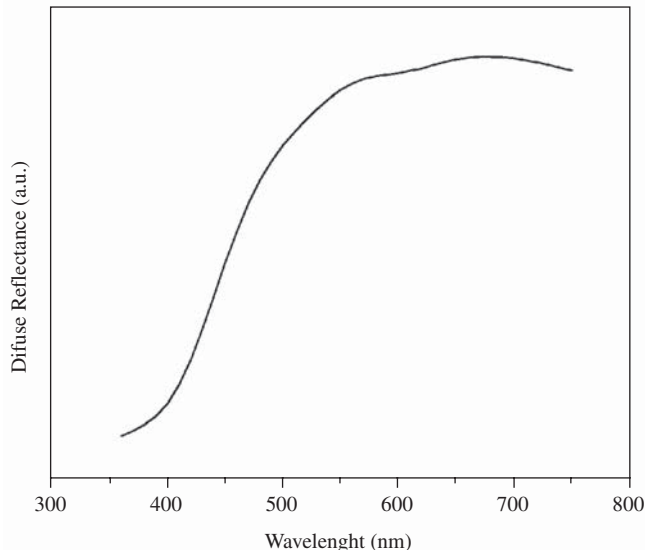


Figure 6. UV-Visible pattern of nickel-doped copper chromites calcined at 900 °C for 8 hours.

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