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Evaluation of $CoAl_2O_4$ as ceramic pigments

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Abstract

$CoAl_2O_4$ powder was obtained from a mixture of Co and Al oxalates at a ratio of 1:8 (Co:Al). The material was calcinated at different temperatures, established from TG data, and characterized using FTIR spectroscopy, X-ray diffraction, BET surface area, and thermal analysis. The dyeing characteristics of $CoAl_2O_4$ were established by coating ceramic substrates with different concentrations of the powder.

Keywords: A. Ceramics; A. Oxide; D. Color centers

1. Introduction

A large number of substances can be used in the production of ceramic dyes. These materials must produce a uniform effect on the ceramic and should not react either with the ceramic itself or glassy coatings. Most of the ceramic dyeing materials possess the spinel structure. The main aspect of spinels is the presence of two metallic cations, A^{2+} and B^{3+}, in tetrahedral and octahedral positions, respectively. The manner in which such sites are occupied depend on the calcining temperature [1,2]. $CoAl_2O_4$ is a double oxide with a normal spinel structure. It is well known as Thenard's blue for its impressive optical effect and widely used in ceramics, glasses, paint industry, and color TV tubes as contrast-enhancing luminescent pigment [3]. Recently, some chemical routes have been used to prepare this pigment. Among them, hydrothermal synthesis [4], sol–gel [5], and organic precursors [6]. The most general method to prepare oxide spinel involves solid state reaction at 1300 K for complete reaction [7,8]. In the present investigation, $CoAl_2O_4$ was prepared and calcinated at different

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temperatures aiming at obtaining a cost-effective and thermally stable compound useful to ceramic tile dyeing.

2. Experimental procedure

Cobalt oxalate ($CoC_2O_4{\cdot}4H_2O$) was prepared from cobalt chloride ($CoCl_2{\cdot}6H_2O$—Aldrich) and acetic acid (1 M—Aldrich) and characterized by atomic absorption using acetylene flame. The resulting material was mixed to alumina (Aldrich) at a molar ratio of 1:8 (Co:Al) and ball milled for 15 min at 400 rpm in a Fritsch Micro Mill. The material was then heated at 10 °C min^{-1} and calcinated in an EDG furnace for 4 h. The calcining temperatures were determined from thermogravimetric experiments carried out under air in a Perkin Elmer thermal balance.

The eventual presence of remaining organic matter was evaluated by infrared spectroscopy using a Perkin Elmer FTIR-16 PC set-up. To that end, KBr pellets having 1 wt.% of the sample material were pressed under 5 t during 3 min. The range between 4000 and 400 cm^{-1} was studied. The surface area of the calcinated material was determined by BET using a NOVA 2000 ACIL-WEBER analyzer. The crystallographic structures present were determined from a Shimadzu diffraction equipment, model XRD-6000, using Cu Kα radiation. Powder morphology was investigated by secondary electron images obtained in a Philips XL 30 ESEM equipment.

Frits were prepared adding the dye to a 1:1 mixture of a glassy compound and a melting agent. The material was ball milled at 400 rpm for 15 min and calcinated at different temperatures, i.e. 500, 800, 1000, or 1200 °C. The diffuse reflectance of fired pigments and enameled samples was measured in a Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, in the 300–800 nm range, using standard D65 illumination. The CIE-$L^*a^*b^*$ colorimetric method, recommended by the Commission Internationale de l'Eclairage (CIE) was followed. In this method, L^* is the lightness axis [black (0) → white (100)], b^* is the blue (−) → yellow (+) axis, a^* is the green (−) → red (+) axis, and ΔE is the hue variation.

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

3. Results and discussion

The thermogravimetric plot of the mixture between cobalt oxalate and alumina (Fig. 1) was used to select the calcining temperatures. Calcination was carried out to obtain $CoAl_2O_4$. The compound became thermally stable above 650 °C. The results from infrared analyses (Fig. 2) revealed the formation of two asymmetric and wide bands between 800 and 450 cm^{-1}, typical of the spinel structure [4]. X-ray diffraction and DTA analysis (Figs. 3 and 4) showed the formation of the spinel phase. The presence of a monophase crystalline powder, having the spinel structure with lattice parameter 0.895 nm, was detected along with small contents of alumina. Both results confirmed findings reported elsewhere [5,6].

BET data (Table 1) suggested that the surface area and porosity of the material decreased with increasing calcining temperature. Nevertheless, the values obtained exceeded those reported in the literature [5]. Results from UV-Vis analyses (Fig. 5) showed that powders calcinated below 1000 °C did not show characteristic spectroscopic features. On the other hand, as the calcining temperature

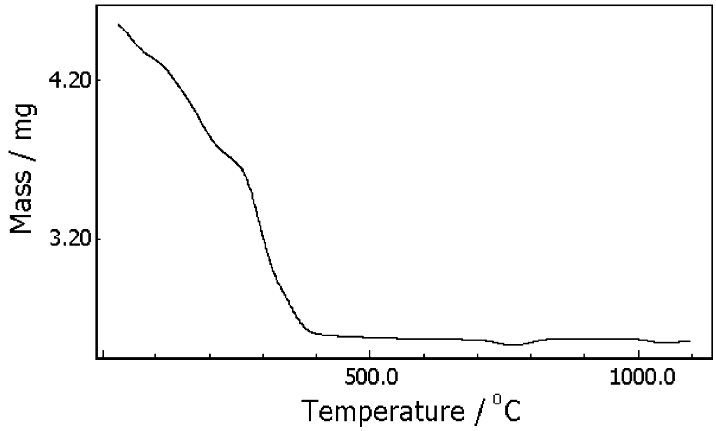

Fig. 1. Thermogravimetric curve of the mixture between cobalt oxalate and alumina.

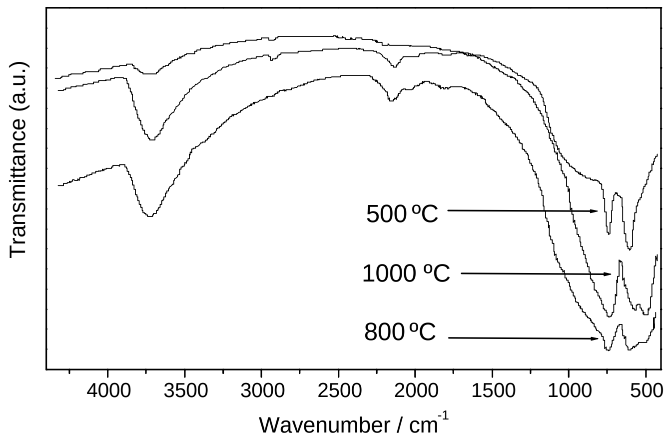

Fig. 2. Infrared spectroscopy of powder calcinated at 500, 800, or 1000 °C.

increased over 1000 °C, the material was characterized by a wavelength around 600 nm but different reflectances were observed, resulting in distinct colors.

UV-Vis analyses of the frits (Fig. 6) did not indicate any significant change in the wavelength of the material, suggesting no reaction with the glassy component of the ceramic. Samples calcinated at 1000

Table 1
Effect of temperature on the surface area of dyes calcinated at 500, 800, 1000, or 1200 °C

Sample (°C)	Co:Al (ratio)	S_{BET} ($m^2\ g^{-1}$)	Average diameter (μm)	Porosity ($cm^3\ g^{-1}$)
$CoAl_2O_4$ (500)	1:8	76.5	1.24	0.18
$CoAl_2O_4$ (800)	1:8	54.4	1.42	0.17
$CoAl_2O_4$ (1000)	1:8	19.2	2.12	0.03
$CoAl_2O_4$ (1200)	1:8	10.8	2.31	0.01

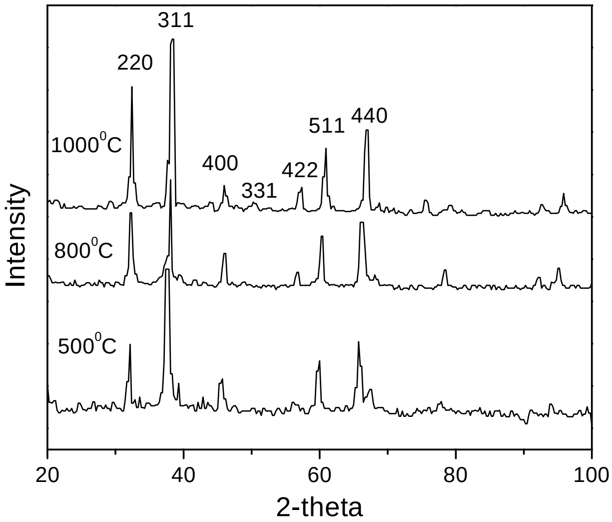

Fig. 3. X-ray diffraction pattern of powder calcinated at 500, 800, or 1000 °C.

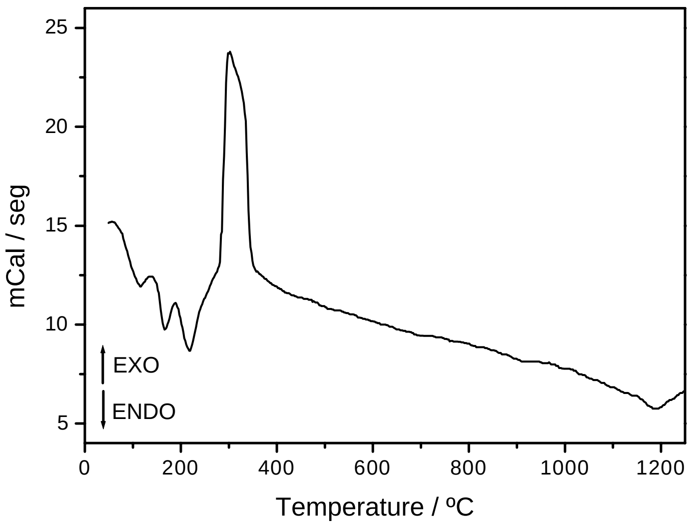

Fig. 4. DTA of mixture between cobalt oxalate and alumina.

Table 2
Colorimetric coordinates of calcined powders applied to glassy substrates

Sample	Powder pigments				Pigments applied to glaze			
	ΔE	L^*	a^*	b^*	ΔE	L^*	a^*	b^*
$CoAl_2O_4$ (1:8)[a]	53.46	50.248	−6.449	−17.094	53.98	48.132	−3.404	−24.215
$CoAl_2O_4$ (1:8)[b]	63.15	44.346	−13.554	−42.872	47.03	37.779	−5.772	−27.423

[a] Samples annealed at 1000 °C.
[b] Samples annealed at 1200 °C.

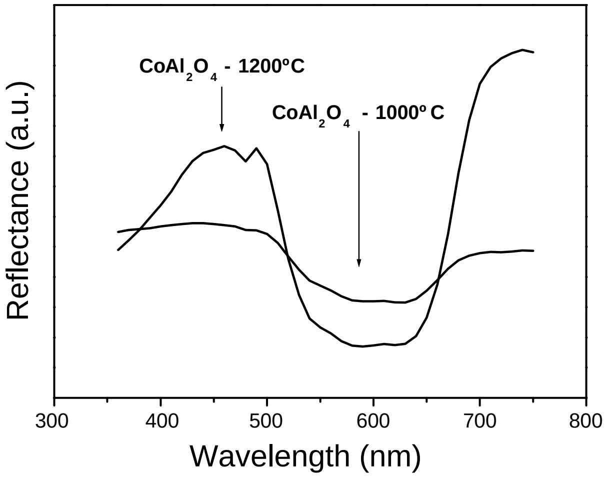

Fig. 5. UV-Vis analyses of powder calcinated at 1000 or 1200 °C.

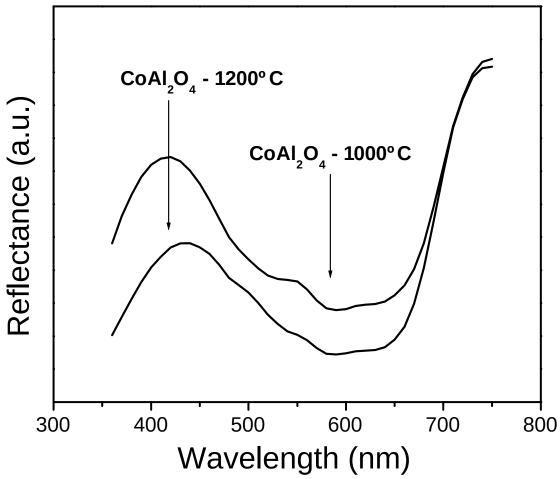

Fig. 6. UV-Vis analyses of frits produced at 1000 or 1200 °C.

or 1200 °C revealed an intense blue component (high a^* and b^*), that increased with increasing temperature. Similar observations were made for glass substrates coated with this material, which also depicted high luminosity (L^*). The reflectance of those samples, both prior to and after application onto glassy substrates, showed absorption bands in the 450–600 nm range (Table 2)

4. Conclusions

The calcining temperature affects the color of the pigments on glassy ceramic coatings. The best results were obtained calcining the spinel $CoAl_2O_4$ phase at 1000 or 1200 °C. Different temperatures also resulted in the formation of crystalline phases but with unsatisfactory coloring effects on ceramic tiles.

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