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Monoferrite $BaFe_2O_4$ applied as ceramic pigment

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Abstract

This work had the objective of studying the ceramic pigment $BaFe_2O_4$, which presents iron as the chromophore ion, and barium as net modifier. Synthesis was done by the polymeric precursor method. After calcination at different temperatures, characterizations were done by X-ray diffraction, infrared spectroscopy, surface area by BET, scanning electron microscopy, UV–vis spectroscopy and colorimetric analysis, using CIELab system. The soft chemical synthesis method leads to a high crystallinity material after calcination at 700 °C, while usual methods require higher temperatures (above 850 °C) or lead to secondary phases. The powders were applied on ceramic pieces in order to evaluate the behavior of the system when added to a glaze. Pigments presented dark brown color, with homogeneous surfaces of the glaze.

Keywords: **C**. Colour; **D.** Ferrites; Method Pechini; Pigments

1. Introduction

In the last years, the development of pigments for the production of tiles, ceramic coatings or cosmetics has become a need, because the aesthetic aspect and the color frequently represent the parameters of interest [1].

Color is an optical property that takes to countless applications. A good ceramic pigment has indispensable requirements, such as high temperature stability, reproducibility and chemical inertia [2]. The final color of each pigment is due to the addition of a chromophore ion (usually transition metals) into an inert matrix, or this ion may be part of the own matrix, as in the case of ferrite [3].

Among the pigment classes, one of the most important is the spinel group, AB_2O_4, due to its capacity of accommodating different cations, leading to a variety of colors and tonalities. Among spinels, this work evaluated the behavior of barium monoferrite, $BaFe_2O_4$. Spinel ferrites combine interesting soft magnetic properties with rather high electrical resistivities. Some ferrites have also been applied as brown pigments, as catalytic materials, magnetic materials and wave absorption materials [4].

Numerous studies have been done on the phase relations in Ba–Fe–O ternary system. Three stable phases were reported, namely, $Ba_2Fe_2O_5$, $BaFe_2O_4$ and the hexagonal $BaFe_{12}O_{19}$ [5,6].

In spite of this, many apparently contradictory results have been found, with the hexagonal $BaFe_2O_4$ phase usually being reported as coexisting with $BaFe_{12}O_{19}$ and Fe_2O_3, along with other metastable phases. $BaFe_{12}O_{19}$ and α-$BaFe_2O_4$ are mutually insoluble in each other as solids, and both coexist up to 1000 °C, after which point a third phase, the metastable hexagonal $Ba_2Fe_6O_{11}$, can also develop until the ternary mixture reaches its liquid point at 1175 °C, reverting to $BaFe_{12}O_{19}$ and α-$BaFe_2O_4$ on cooling [7].

Fine-particle spinel ferrites, such as $BaFe_2O_4$, are useful for the low temperature preparation of high-density ferrites and as suspension materials for ferromagnetic liquids. Nanoparticles of $BaFe_2O_4$ demonstrate a resonance anomaly near 125 K that could indicate the presence of a magnetic phase. On the other hand, hexagonal magnetic hard ferrites such as $BaFe_{12}O_{19}$ are magnetic materials of great scientific and technological interest

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due to their relatively strong anisotropy and moderate, but still interesting magnetization. They are applied as permanent magnets, in microwave devices or in perpendicular magnetic recording. Another application is in catalysis area [4,8–11].

Different synthesis methods have been evaluated, such as coprecipitation [12,13], aerosol [14,15] or sol–gel [16,17]. In this work, the polymeric precursor method (Pechini) [17] was used in $BaFe_2O_4$ synthesis, for application as ceramic pigment.

2. Experimental procedure

The polymeric precursor was prepared by the Pechini method, which has been used to synthesize polycationic powders. Precursors used were citric acid (Vetec), iron III nitrate (Vetec) and barium acetate (Reagen), to synthesize the metallic citrate, which was polymerized using ethylene glycol (Synth).

Fig. 1 schematically presents the $BaFe_2O_4$ synthesis. After the primary calcination, the polymeric precursor was obtained, which was calcined between 500 and 1100 °C, with a heating rate of 10 °C min^{-1} in air atmosphere.

The determination of the crystalline phases was carried out by X-ray diffraction (XRD) with Siemens D-5000 Diffractometer with Cu Kα radiation (λ = 1.5406 Å and $2\theta = 20°–70°$), at room temperature. Cell volume was calculated using the Rede 93 program, based on the least square method, developed at the Chemistry Institute of Unesp, at Araraquara, SP, Brazil [18]. Quartz was used as an external standard.

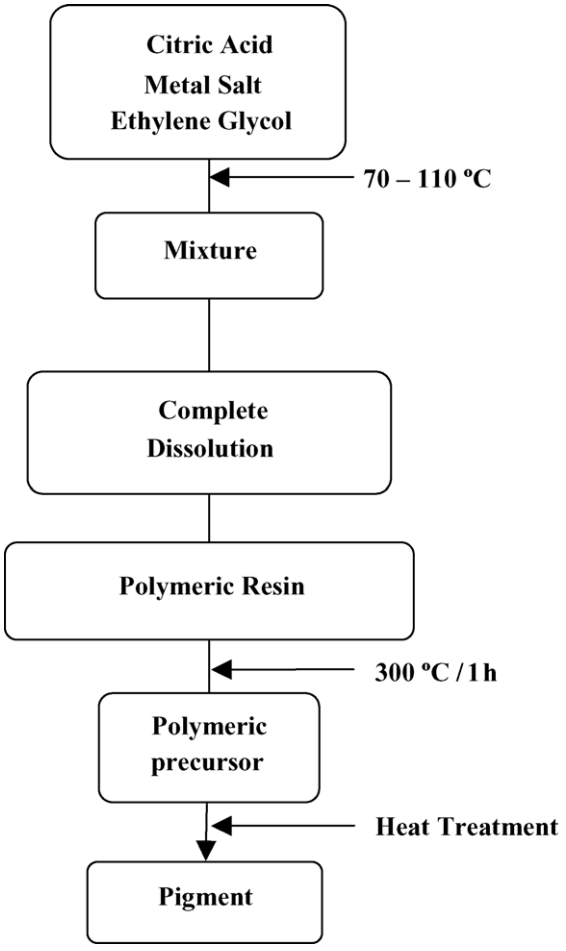

Fig. 1. Synthesis route for the powder obtained by the Pechini method.

Infrared spectra were obtained using KBr pellets, in the range of 2000 to 400 cm^{-1} (spectrophotometer BOMEM, model MB–102).

The surface area measurements of the pigments were accomplished by a Micromeritics ASAP 2000 equipment, using N_2 as the adsorption/desorption gas. The particle average diameter was calculated using the BET method, d_{BET}.

Scanning electron microscopy (ZEISS DSM, 940) was used to characterize the pigment morphology.

In the laboratory test, pigments were applied on ceramic pieces. A mixture of glaze (commercial glaze—GERBI, Brazil) and 3% of sieved pigment was used (mass ratio). The mixture was homogenized in a ball mill during 10 min. The slip was poured on the ceramic biscuits obtaining an uniform glaze layer, which was then heat treated up to 500 °C with heating rate of 10 °C min^{-1}, which was then increased to 15 °C min^{-1} up to 1000 °C for 1 h. Than, the furnace was cooled back to room temperature at 10 °C min^{-1}.

Colorimetric parameters (L^*, a^* and b^*) and diffuse reflectance of powders and glazed samples were measured with the Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, from 300 to 800 nm, using the D65 illuminant with measurement at 8°. The CIE-$L^*a^*b^*$ colorimetric system, recommended by the CIE (Commission Internationale de l'Eclairage) [19] was followed. In this system, L^* is the lightness axis (where black is equal to 0 and white to 100), b^* represents the color varying from blue (negative axis) to yellow (positive axis), a^* represents the color varying from green (negative axis) to red (positive axis).

3. Results and discussion

Fig. 2 illustrates the XRD patterns of the materials synthesized by the Pechini method, calcined at different temperatures.

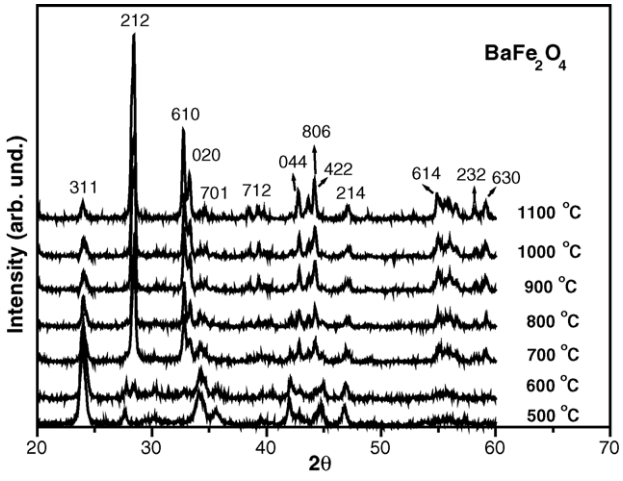

Fig. 2. X-ray diffraction patterns for the $BaFe_2O_4$ powder as a function of calcination temperature.