TMS2014 Annual Meeting Supplemental Proceedings
TMS (The Minerals, Metals & Materials Society), 2014

OPTICAL AND MAGNETICAL PROPERTIES OF $FeCr_2O_4$ NANOPIGMENTS WITH SPINEL TYPE STRUCTURE

Oscar Restrepo, Juan Montoya, Edgar Chavarriaga

Universidad Nacional de Colombia, School of Mines, Medellin
ojrestre@unal.edu.co

Keywords: Nanopigments, spinel structure, Combustion solution synthesis

Abstract

Through solid state reactions at high temperatures, using iron and chromium oxides (Cr_2O_3 and Fe_3O_4) in fixed proportions as precursors, was synthesized the nanopigment $FeCr_2O_4$ with spinel type structure. For different temperatures synthesis was conducted a characterization of the material obtained through.

X-ray diffraction (XRD), spectroscopy UV-VIS-NIR, thermal analysis (DTA/TGA), scanning electron microscopy (SEM), UV-VIS spectrophotometry and colorimetry CIEL*a*b* and magnetic susceptibility. Particle size of the nanoparticles obtained by the spinel structures was less 100nm.The changes in the reflectance spectra are related to the identified phase, the crystallinity degree, the spatial planning of cations and the magnetic behavior obtained.

Introduction

Spinels containing transition metal ions have a lot of commercial importance due to their interesting structural, electrical and magnetic properties. Ferrites at the nanoscale has been intensively investigated in recent years due to their unique physical and chemical properties, as well as various technological applications such as transformers, inductors and magnetic heads for high frequency because their electrical resistivity is higher than those of the soft magnetic alloys.

The spinel crystal structure is packed face-centered cubic array of anions with holes partly filled by the cations. The oxide spinel can generally be described by the formula $(A)[B_2]O_4$, where A and B denote divalent and trivalent cations, respectively. Generally the A atoms are tetrahedraly coordinated while the B atom sare octahedrally coordinated by oxygen atoms. In the case of an inverse spinel structure, the A atoms occupy half of the B sites.

In the ceramic industry, the decoration of the parts or the manufacture of enamels with functional features require the use of ceramic pigments that meet very specific characteristics, such as structural stability in aggressive environments, Color impart efficiently and have forms and sizes particle that does not affect the properties of the enamel.

The ceramic pigments are produced industrially by thermal methods of heating at high temperatures, making mixed oxides and salts as precursors of oxides, carbonates and hydroxides. The process temperatures are usually between 800 and 1350 ˚C, at low temperatures form oxides precursors base and high temperatures become reactive mixtures and the increase in the spread of the species form solid solutions with homogeneous crystal structures very stable. After heat treatment, the products are milled to achieve certain sizes required for implementation, washed to remove residual salts that are used as mineralizes and finally dried. The black pigments used in the ceramic industry are basically ferrites and chromites with additions of cobalt, nickel or copper to improve the resistance of the compound at high temperatures accentuate the tone or black. In the ceramic industry consumption of this pigment is high, due to the possibility of obtaining more opaque shades and adjusts colors of other pigments that may not be very stable between batch and lot.

Experimental Procedure

In the present investigation, the compositions of the system $CrFe_2O_4$ were synthesized auto-combustion technique which involves citrate precursors of the concerned metals mixing them in solution state [8,9]. The stoichiometric composition of the combustion mixture for the preparation of $CrFe_2O_4$ contains $Cr(NO_3)_3$*$9H_2O$, $Fe(NO_3)_3$ *$9H_2O$ and glycine. In a typical experiment $Fe(NO_3)_3$ *$9H_2O$ (Panreac, 98% purity), $Cr(NO_3)_3$*$9H_2O$ (Panreac, 98% purity), and glycine (Panreac, 99% purity) are dissolved in deionized water in a glass beaker of 1000 cm^3 capacity, the pH is 5. The dish containing the solution is slowly heated until the formation of a gel. Then, the gel is heated up occurs self combustion of the fuel generating a flame. The dried citrate precursors were calcinated separately in a box type furnace for 2 hat 150°C at the rate of 50°C/h in order to breakdown the citrate gel complex to obtain oxide powder. The powders were crushed and ground finally.

In order to identify structural changes, chemical, color and magnetic properties, it was realized a study of temperatures by subjecting the samples to 900˚C, 1,000˚C, 1,100˚C, 1,200˚C and 1,300˚C. The thermal cycle lasted 8 hours, using 2 hours to reach the desired temperature from room temperature and sustain for two hours. We used an electric oven with a power of 800 W, voltage of 220 V and resistance wire Kantal A-F.

The characterization was made by XRD (CuKα, 0-75°, 0.02°/ min and 400 cps), DTA/TGA (reference alumina, 50˚C / min, atmospheric air flow of 50 ml/min) and tablets were prepared for spectrophotometry UV-VIS-NIR (300-900 nm, CIE illuminant D65) and SEM (18 kV, BSE, SE) analyzer with energy dispersed X-ray (EDX), magnetic susceptibility (high vacuum and helium bath, 2˚C/min, 50 kHz)

Analysis of results

X-Ray Diffraction

The information obtained by XRD indicates that between 900 and 1,000 ˚ C begins to form a compound of iron and chromium. The intensity of diffraction peaks typical of this compound increases with temperature, indicating a better management structure (Figure 1).

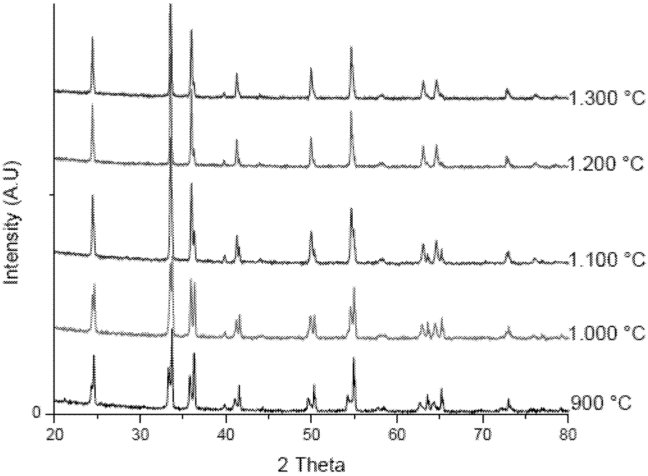

Figure 1. Relative intensity (%) vs. Temperature (° C) from some angles of diffraction

Spectroscopy

The spectrophotometric analysis shows that the mixture is subjected to higher temperatures takes on a darker brown color. This is because as they form the compound, the atoms of chromium assume an octahedral coordination with the atoms of oxygen, limiting the availability of electrons in orbit d that are responsible for the color. Then, the energy provided by radiation is not visible enough to cause energy transitions, and this absorbed energy is released in the infrared, making the material more and more opaque and its links stronger and more stable at high temperatures.

Valence electrons from atoms to form pairs of valence electrons from neighboring atoms. As a result the absorption bands of the valence electrons moving up the ultraviolet wavelengths and are no longer suitable for the production of color.

It is observed greater emissivity wavelengths between 650 and 700 nm, taking the sample at room temperature orange and brown in high temperatures. The presence of other metals such as cobalt or nickel favors the formation of a more intense black color, because the distribution is more uniform reflectance in the visible range.

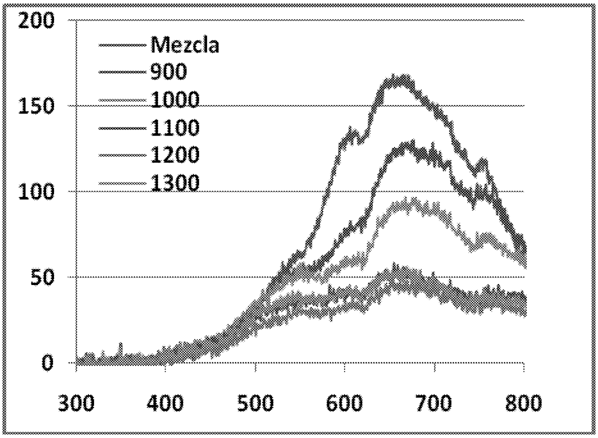

Figure 2. Emissivity spectrum (cps) vs. Wavelength (nm). Mixed oxide of iron and chromium, Fe_2O_3 and Cr_2O_3.

Scanning electron microscopy

In Figures 3 and 4 is shown the image of scanning electron microscopy to spinel structure obtained by the method of self-ignition, calcined at 1000°C and 800°C respectively. Both present a spherical morphology trend with particle sizes of about 1 micron. Despite having calcined two samples at different temperatures must be the grain size is similar, therefore it is feasible to produce the spinel CrFe2O4 autocombustion method at temperatures below 1000 ° C. Agglomeration speed changes because of the self-combustion reaction is faster due to a high exothermicity of the system.

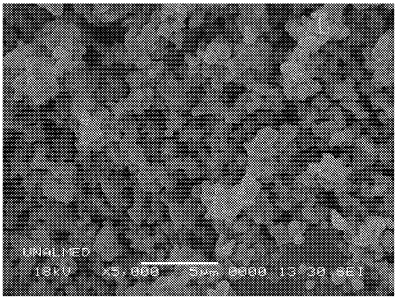

Figure 3. Scanning electron microscopy. Sample calcined at 1000˚C.

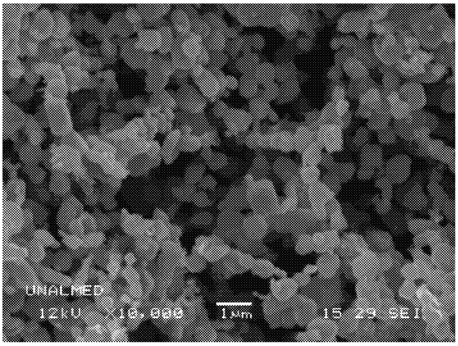

Figure 4. Scanning electron microscopy. Sample calcined at 800°C

Colorimetric measurements

In Table 1 is shown the color coordinates of samples prepared at different temperatures. It is concluded that increasing the temperature tends to darken (L-coordinate decreases), to turn green (decreases coordinate a) and blue (decreasing the coordinate b).

Table 1. Colour coordinates of samples

	Temperature (°C)				
Coordinate	**900**	**1000**	**1100**	**1200**	**1300**
a*	11.26	4.86	3.28	2.32	1.48
b*	12.84	6.37	4.45	3.04	4.65
L*	41.8	36.65	34.67	31.82	31.03

Magnetic Susceptibility

The measure of magnetic susceptibility (Figure 7) was done in a small temperature range, that is why it is not why it is not possible to identify magnetic transitions. As temperature increases the degree of magnetization in the material decreases, because the electrons gain kinetic energy, meaning that their movements tend to be more random and thus the sum of magnetic components will decrease by a lack of order.

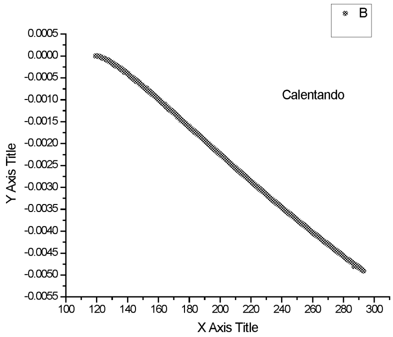

Figure 7. Magnetic susceptibility vs. X-Temperature (K).

Conclusions

Ceramic pigments were obtained with $CrFe_2O_4$ spinel structure to a temperature of 800°C and a reaction time of 6 hours, which demonstrates its advantage over the traditional method and the results show that at a temperature of 1000°C and in a time of 16 hours is not obtained pure phase, as the kinetics of solid state reaction is very slow. Nearly spherical morphology and particle size of about 1 micron obtained by alternative methods show monitoring can be done on these two parameters of importance for the final application of the enamel.

It can be concluded that as increasing the calcination temperature, the samples exposed attenuation in emissivity, whilst maintaining a constant hue. The magnetic measurements show a decrease in magnetic susceptibility as a function of temperature, which shows that at room temperature this spinel no significant magnetic behavior.

References

[1] J.B. Goodenough, A.L. Loab, Phys. Rev. 98 (1955) 391.
[2] V.K. Sankaranarayanan, N.S. Gajbhiye, J. Am. Ceram. Soc. 73 (1990) 1301.
[3] A. Verma, O.P. Thakur, C. Prakash, T.C. Goel, R.G. Mendiratta, Mater. Sci. Eng. B 116 (2005) 1.
[4] A.A. Goldman, Handbook of Modern Ferromagnetic Materials, Kulwer Academic Publishers, Boston, USA, 1999.
[5] Nathawan P, Darshane VS. Structural. Transport, magnetic and infraredstudies of the oxidic spinels Co2-XTi1-XFe2XO4. Journal of Physics. 1988;21(6):3191-3203.
[6] Vlasenko VM, Chernobrivets VL. Methane chlorination on spinel copperchromiumcatalyst in the presence of oxygen. Russian Journal of Applies Chemistry. 1998; 71(8):1393-1396.
[4] Erran E, Trifino F, Vaccari A, Richter M. Structure and reactivity of Zn-Cr mixed oxides Role of non-stoichiometry in the catalytic synthesis ofmethanol. Catalysis Letter. 1989; 3(1):65-72.

[8] Câmara MSC, Lisboa-Filho PN, Cabrelon MD, Gama L, Ortiz WA, Paiva- Santos CO, Leite ER, et al. Synthesis and characterization of Li2ZnTi3O8 spinel using the modified polymeric precursor method. Materials Chemistry and Physics. 2003; 82(1):68-72.

[9] McClure D. The distribution of transition metal action in spinels. Journal of Physical Chemistry Solids. 1957; 3:311-317.

[10] Preudhomme J, Tarte P. Infrared studies of spinels-III. The normal II-III spinels. Spectrochimica Acta Part A: Molecular Spectroscopy. 1971; 27(90):1817-1835.

[11]. Chokkaram S, Srinivasan R, Milbrun DR, Davis BH, Conversion of2-octanol over nickel-alumina, cobalt-alumina, and alumina catalysts.Journal of Molecular Catalysis A: Chemical. 1997; 121(2-3):157-169.

[12] L. Chen, Y. Liu, and Y. Li, J. Alloy Compd., 381, 266, (2004).

[13] Z. Lu, Y. Tang, L. Chen, and Y. Li, J. Cryst. Growth, 266, 539, (2004).

[14] R.C. Kambale, P.A. Shaikh, N.S. Harale, V.A. Bilur, Y.D. Kolekar, C.H. Bhosale, K.Y. Rajpure. Structural and magnetic properties of Co1−xMnxFe2O4 (0≤x≤0.4) spinel ferrites synthesized by combustion route. Journal of Alloys and Compounds 490 (2010) 568–571.

[15] A.C.F.M. Costa, A.M.D. Leite, H.S. Ferreira, R.H.G.A. Kiminami, S. Cava, L. Gama. Brown pigment of the nanopowder spinel ferrite prepared by combustion reaction. Journal of the European Ceramic Society 28 (2008) 2033–2037

[16] Aruna ST, Rajam KS. Mixture of fuels approach for the solution combustion synthesis of Al2O3–ZrO2 nanocomposite. Mater Res Bull 2004; 39:157–67.

[17] Câmara MSC, Lisboa-Filho PN, Cabrelon MD, Gama L, Ortiz WA, Paiva- Santos CO, Leite ER, et al. Synthesis and characterization of Li2ZnTi3O8 spinel using the modified polymeric precursor method. Materials Chemistry and Physics. 2003; 82(1):68-72.

[18] Chen L, Liu Y, y Li Y, J. Alloy Compd., 381, 266, (2004).

[19] Chick, L.A., Pederson, L.R., Maupin, G.D., Bates, J.L., Thomás, L.E and Exarhos, G.J., Materials Letters, 1990, 10.

[20] Chokkaram S, Srinivasan R, Milbrun DR, Davis BH, Conversion of2-octanol over nickel-alumina, cobalt-alumina, and alumina catalysts.Journal of Molecular Catalysis A: Chemical. 1997; 121(2-3):157-169.