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Synthesis of magnetic nanometer pigment Fe_3O_4 by co-precipitation and gaseous reduction

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ABSTRACT

Nanocrystalline magnetite (Fe_3O_4) powders have been successfully synthesized using both co-precipitation and isothermal gaseous reduction of hematite (Fe_2O_3). In the co-precipitation route, the ferrite precursors were obtained from aqueous mixtures of ferrous chloride and ferric chloride with Fe^{3+}/Fe^{2+} mole ratio equals 2. The precipitation of ferrous ions and ferric ions was carried by using 5 M sodium hydroxide solution. In the isothermal gaseous reduction route, gas composition 20%CO-80%CO_2 and reduction temperature 1000°C for 2 hours were used in this study. The effects of synthesis conditions on the formation, crystal phase analysis, morphology analysis, Color characteristics of pigment were investigated. Moreover, the effects of CoO doping (0, 1, 2, 4 and 7%) on the physicochemical properties of magnetite produced via isothermal reduction were also investigated. The powders formed were investigated using X-ray diffraction (XRD), and scanning electron microscope (SEM) while colour properties were measurement according to the ASTM-C 609-71 by using a colorimeter instrument type Hunter Lab. The results obtained showed that the single-phase Fe_3O_4 powders were achieved at Fe^{3+}/Fe^{2+} mole ratio value 2 via co-precipitation route with nanocrystalline size for the most intense peak (311) of Fe_3O_4 phase was in the range of 13.7 nm. In the gaseous reduction route, the single-phase Fe_3O_4 powders were achieved at 20%CO-80%CO_2 gas composition and reduction temperature 1000°C. The crystallite size of the most intense peak of Fe_3O_4 phase was in the range between 133.9 and 180 nm. The addition of CoO oxide up to 2% to the hematite before reduction enhancing the colouring properties of the magnetite and beyond which a decreasing in the colouring properties were observed. The synthesized pigments were tested in typical ceramic glazes and ceramic bodies. The colouring properties of CIE- $L^*a^*b^*$ and X, Y, Z color-measurements were near a commercial black pigment. The results demonstrate the viability of using these powders at 2% CoO in Fe_3O_4 spinel as black ceramic pigments.

KEYWORDS

Pigment;
Magnetite;
Co-precipitation;
Reduction;
Isothermal.

INTRODUCTION

Composite oxides with spinel structures (AB_2O_4) and space group Fd_3m are important inorganic metalloid materials and are widely used in different fields[1]. They are used not only as heat-resistant pigments, which can be applied to porcelain and ceramics, but also as gas-sensitive materials, catalytic materials, magnetic materials and wave absorption materials. Different studies show that certain compounds with spinel structure present possible applications of great technological interest, such as pigments ($CoAl_2O_4$)[2, 3], refractories ($MgAl_2O_4$)[4, 5], catalysts ($ZnCo_2O_4$)[6, 7], electrodes ($LiMn_2O_4$)[8, 9], superconductors ($LiTi_2O_4$)[10, 11] and varistors ($Zn_7Sb_2O_{12}$)[12]. In relation to pigments, $MgFe_2O_4$ is commercially used as oil paint and $ZnFe_2O_4$ was already evaluated, with brown color and good properties[13, 14].

Pigments are finely ground solids dispersed in a liquid for application as coatings, such as paints and inks, or for blending with other materials such as ceramics, glaze, cosmetics, and plastics. On the other hand, aqueous solutions of dyes are used for coloring paper, leather, textiles and other materials. In the ceramic industry; many natural and synthetic pigments find practical application as coloring agents in glasses, enamels and unglazed bodies. Black pigment Fe_3O_4[15-17] is a compound oxide with a non-normal spinel structure which is not only used in the coating industry for qualified covering, colouration and light-resistance, but also widely in the construction industry due to its excellent alkali resistance. Fe_3O_4, as magnetic pigment, also is one of the main materials used to produce copy black powder. Nowadays, Fe_3O_4 is used in more aspects due to the development of preparation technology of nanometer powders. At present, there are many applied reports about nanometer- sized Fe_3O_4 in many different fields such as magnetic absorbing materials[18] and catalysis[19]. Nowadays, Magnetite (Fe_3O_4) nanoparticles (MNPs) have been used as magnetic carriers for a variety of biomedical applications[20]. However, the synthesis of nanometer powders with fine granularity, good dispersion and unified size and shapes is critical in the fabrication of nanometer materials. Therefore, the preparation of nanometer materials has attracted great attention and is being extensively studied.

Various methods of preparing Fe_3O_4 nanoparticles have been carried out by several techniques, including co-precipitation[21], spray pyrolysis[22], microwave irradiation of ferrous hydroxide[23], microemulsion technique[24, 25], hydrothermal preparation technique[26], etc. In this context, the goal of this work is to prepare nanometric black pigments with spinel Fe_3O_4 structures by co-precipitation method. On the other hand, it is of great interest to study alternative methods of synthesis to reduce costs of preparation and improve the rate and quality (purity, stoichiometry and crystallinity) of the final products. The direct reduction of ferric oxide by gaseous reductants is an industrially important reaction. The reaction proceeds through the formation of Fe_3O_4 if the temperature is below and gas composition is controlled[27]. Many researchers have studied the gaseous reduction of iron oxide[27-29]. The data reported can be summarized by stating that the consecutive reduction of iron oxides should be viewed as a complex series of heterogeneous reactions whose rates are influenced both by chemical kinetics factors and mass (and/or heat) transfer factors[30]. Studied the dynamics of transformation from hematite to magnetite by following two solid-state methods. One of the procedures consisted of a thermal treatment under a 20% H_2 and 80% N_2 atmosphere at 375°C, whereas the second method involved a planetary ball mill to induce the transformation. The results of the first procedure evidenced a well-behaved structural transformation for which highly stoichiometric Fe_3O_4 as a single phase was obtained for treatment above 12.5 min. In contrast, a less stoichiometric magnetite in the case of the ball milled samples was obtained. The hematite/magnetite reduction as one of the iron oxides reduction stages reflects very significant morphological changes due to various crystal lattice reconstructions. The crystal structure of hematite is close-packed hexagonal while for the magnetite is an inverse spinal structure.

This paper aimed to develop a practical methodology for the synthesis and characterization of magnetite nanomaterials as magnetic materials for industrial and magnetic fluid and copy black powder pigment through co-precipitation and isothermal gaseous reduction routes. The effects of CoO doping (0, 1, 2, 4 and 7%) on the physicochemical properties of magnetite will also investigated. Moreover, the paper studied the effect of synthesis conditions on the formation, Crystal phase analysis, morphology analysis, magnetic properties and color characteristics of pigment.

EXPERIMENTAL

Two routs were applied the preparation of nanocrystalline black magnetite (Fe_3O_4). The first one was the co-precipitation while the second was the isothermal gaseous reduction.

Magnetite via co-precipitation

Chemically grade ferric chloride anhydrous ($FeCl_3$), ferrous chloride ($FeCl_2.4H_2O$) and sodium hydroxide (NaOH) were used as starting materials. The magnetite powders was prepared using a solutions of ferric chloride and ferrous chloride with Fe^{3+}/Fe^{2+} molar ratios 2. The magnetite precursors were precipitated from theses mixtures by adding gradually sodium hydroxide (5 M) solution at room temperature at d pH 10 under a gentle magnetic stirring. The aqueous suspensions were stirred gently for 15 min to achieve good homogeneity and to attain a stable pH conditions. The black magnetite co-precipitate were filtered off, washed with deionized water and dried at 60°C overnight.

Magnetite doped with CoO via isothermal gaseous reduction

Chemically grade ferric oxide (Fe_2O_3) and cobalt oxide (CoO) were used as starting materials. A series of 50g ferric oxide (Fe_2O_3) doped with 0, 1, 2, 4 and 7% CoO were mixed in a ball mill for 6 h. After that, each sample, separately, as isothermally reduced in a 20%CO–80%CO_2 gas mixture at 1000°C for reduction time 2h in a horizontal tube furnace. The samples were kept in the reduction furnace under the same reducing gas during cooling to the room temperature.

Characterization

The crystalline phases present in the different samples were identified by X-ray diffraction (XRD) on a Brucker axis D8 diffractometer using Cu-K_α (λ =1.5406) radiation and secondary monochromator in the range 2θ from 10° to 80°. The crystallite size of magnetite present in the investigated was based on X-ray diffraction line broadening and calculated using Scherrer equation. The magnetite particles morphologies were observed by scanning electron microscope.

Colour measurement

The calcite powder pigment were investigation by color measurement according to the ASTM-C 609-71 by using a colorimeter instrument type Hunter Lab. in the 300–800 nm range, with attached standard colors. From these measurements, the tristimulus values of reflection X, Y, and Z were deduced. These data were then converted to the values of color values and chromaticity dimension by means of L*, a* and b* factors. The CIE- L* a* b* colorimetric method was used, as recommended by the Commission International de I, Eclairage (CIE)[31, 32]. In this method, L* is the lightness axis [black (0) — white (100)], b* is the blue (-) —— yellow (+) axis, a* is the green (-) — red (+) axis describe the color hue. Thorough description of color is done by recalculation of chroma extent C, according the formula $C = (a2 + b^2)^{1/2}$.

Application of pigment in glaze coating and ceramic body

The materials used in this application from glaze and bodies in perima ceramic company in Egypt. To evaluate the colour development in common products, the pigment was added (5%) to commercial glazes and (10%) to ceramic bodies:

1- A transparent and lustrous, lead-free glaze, referred to as Perima ceramic company and fired at 1150 °C.

2- A ceramic body, referred to as perima ceramic company, also fired at 1150 °C.

For comparison purposes, a commercial, black Fe_3O_4 spinel pigment was also evaluated. The mixtures were prepared by wet ball-milling for 30 min and then dried at 110 °C. As in the preparation of the pigments, the use of ethanol accelerated the drying process.

RESULTS AND DISCUSSIONS

Investigation and characterization of phases

The XRD patterns of magnetite nanostructures obtained from the co-precipitation of ferric and ferrous ions at pH 10 (5 M NaOH) at room temperature are shown in Figure 1. The Figure shows only peaks for magnetite as that in ASTM standard of XRD. This indi-

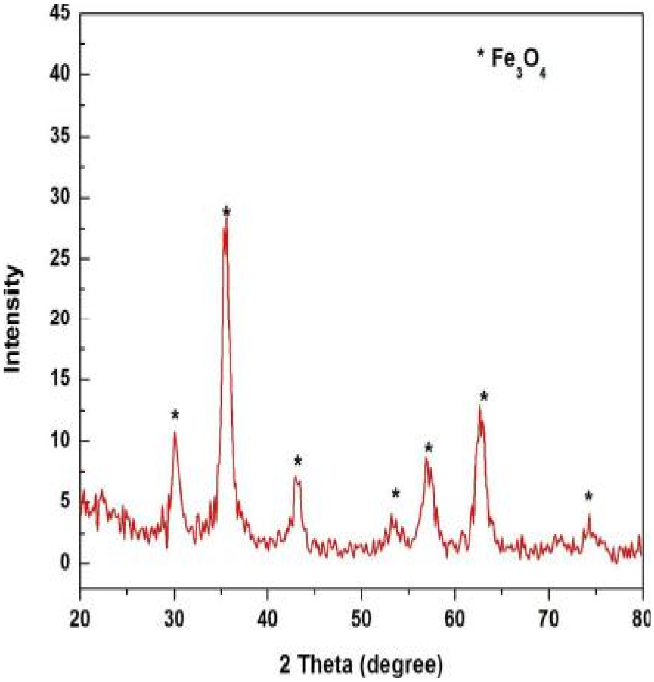

Figure 1 : XRD patterns of the produced nanocrystalline magnetite powders from the precursors precipitated at pH 10 and Fe^{3+}/Fe^{2+} mole ratios 2.

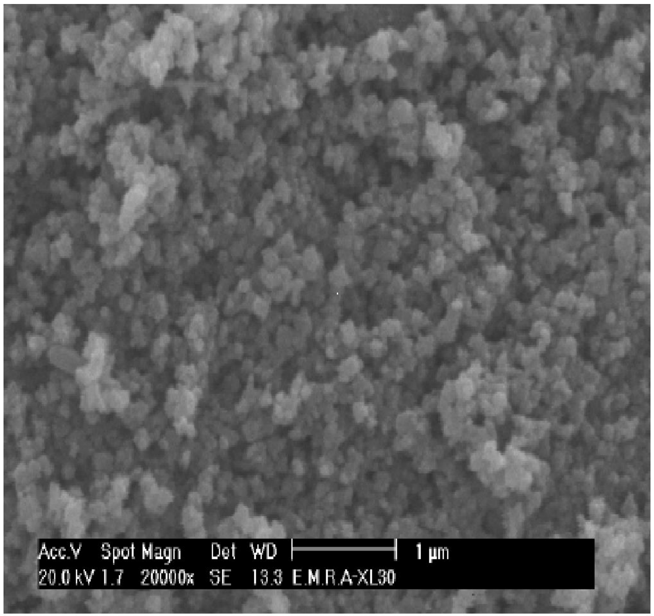

Figure 2 : SEM micrograph of the produced nanocrystalline magnetite powders from the precursors precipitated at pH 10 and Fe^{3+}/Fe^{2+} mole ratios 2.

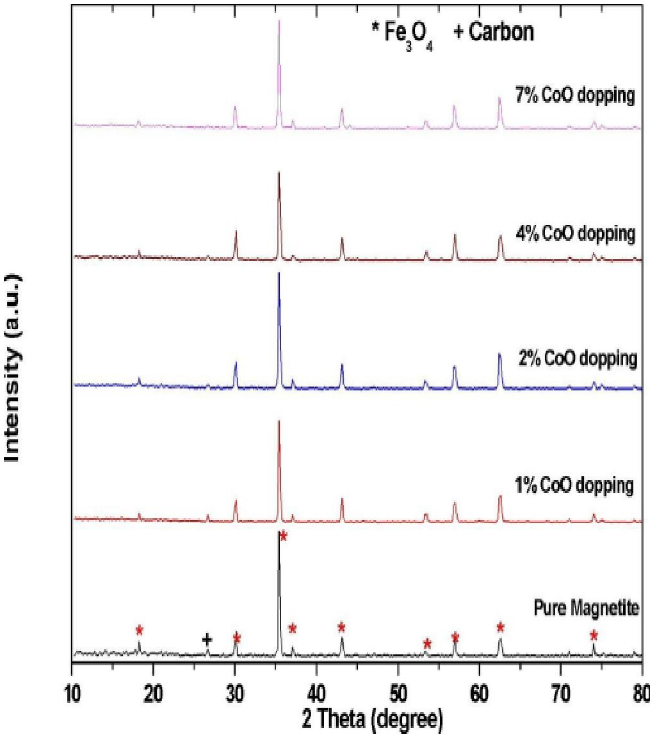

Figure 3 : Effect of CoO doping on the XRD patterns of the nanocrystalline magnetite powders produced via isothermal gaseous reduction using 20%CO-80%CO_2 gas mixture at 1000°C.

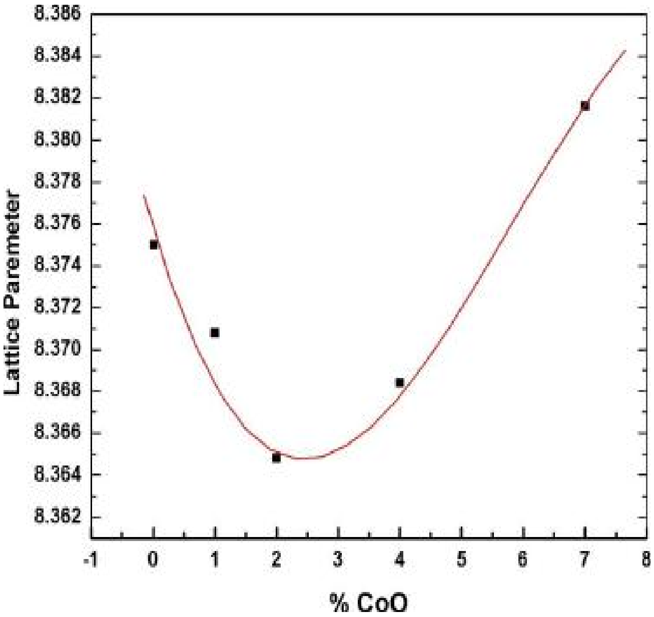

Figure 4 : Effect of % CoO additions on the lattice parameters of magnetite powders synthesized by isothermal gaseous reduction of hematite.

cated that a single- phase of nanocrystalline magnetite (Fe_3O_4) powders have been synthesized using the co-precipitation route in room temperature without the presence of impurities. As can be seen, low crystalline magnetite phase is formed as observed from the low intensity and broad peaks. The nanocrystalline size of the most intense peak (311) of Fe_3O_4 phase calculated using Scherrer equation was in the range of 17nm.

The microstructures of the prepared nanocrystalline size sample had to be thoroughly examined to be able

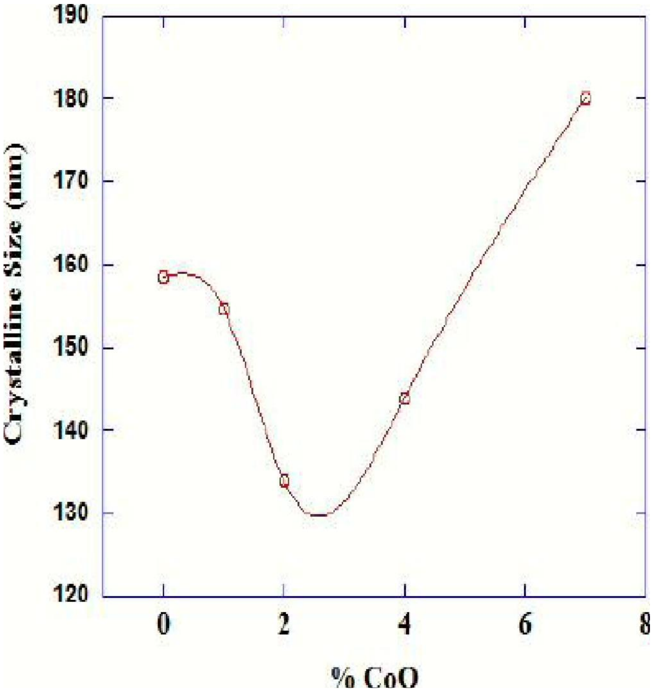

Figure 5 : Effect of % CoO additions on the crystalline size of magnetite powders synthesized by isothermal gaseous reduction of hematite.

to determine the most common structure that characterized the examined magnetite and shown in Figure 2. It can be observed that the magnetite powders possessed a uniform fine structure with a unclear crystalline microstructure. The SEM microstructure indicates that magnetite particles were quasi-spherical particles with a quite uniform size distribution.

The effect of cobalt oxide doping on the crystal structure of the magnetite prepared from hematite through isothermal gaseous reduction at 20%CO-80%CO_2 and 1000°C is given by the XRD patterns in Figures 3. The percent of cobalt oxide addition were 0, 1, 2, 4 and 7% and the sample named M, MC1, MC2, MC4 and MC7 respectively. The powder XRD patterns of all systems showed sharp and intensive peaks characteristic of the single phase of cubic structure of Fe_3O_4 with traces of precipitated carbon. The diffraction peaks corresponding to (2 2 0), (3 1 1), (2 2 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of magnetite were observed with a traces of precipitated carbon. The absence of extra lines for hematite (Fe_2O_3) in the diffraction patterns ensures phase purity. This means that the isothermal reduction of hematite at 1000°C and 20%CO-80%CO_2 resulted in a complete conversion of Fe_2O_3 to yield Fe_3O_4 as a single phase. However, the doping with either 4wt% CoO followed by isothermal gaseous reduction at 1000 °C resulted in a decrease in the peak height of magnetite phase. This means that the CoO may be had a different behavior than that at lower content of of CoO. The lattice parameter for the cubic Fe_3O_4 samples with cobalt oxide varying from 0.0 to 7% by weight as a function of Co ions were calculated for the (3 1 1) plane and the results are shown in Figure 4. The results indicate that introducing differ-

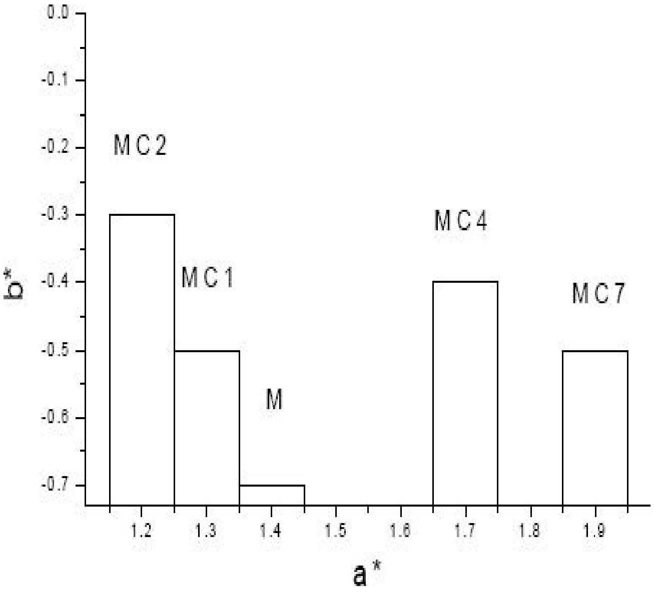

Figure 6 : Colorimetric parameters in the plan *a*×*b* of the magnetite pigments Fe_3O_4 synthesized by isothermal gaseous reduction of hematite doped with different percent of CoO.

TABLE 1 : The color properties of the sintered magnetite pigment powder.

Sample	Color Values			Tristimulus Values			Chromaticity Values		Chroma
	L*	a*	b*	Y	X	Z	x	y	C
Pure (M)	18.4	1.4	-0.4	3.3	3.4	4.1	0.32	0.31	1.57
1% CoO(MC1)	15.8	1.3	-0.5	2.5	2.5	3.0	0.31	0.31	1.39
2% CoO (MC2)	15.2	1.2	-0.3	3.0	3.0	3.6	0.31	0.31	1.53
% CoO (MC4)	17.4	1.7	-0.4	2.3	2.4	2.8	0.32	0.31	1.77
7% CoO (MC7)	18.6	1.9	-0.5	3.4	3.4	4.1	0.31	0.31	1.97

ent amounts of Co ions gives a detectable change in the lattice parameter. With increased Co content, the value of the lattice parameter decreased from 8.375 Å for *CoO*=0.0% to 88.3648 Å for *CoO*= 7%. Beyond this doping, an increase in the lattice parameters was found. This change of lattice parameter with the change of CoO can be attributed to the progressive dissolution of Co ions into the spinel structure and this can directly influence the magnetic and colouring performance of the magnetite.

From the XRD patterns, the average crystalline sizes for the spinel phase were estimated (Figure 5) from the broadening of the strongest diffraction peak using the Debye–Scherrer formula. It was found that the average grain size decreased from 158.5 nm for the sample that prepared by the reduction of pure hematite without doping to 133.9 nm for the sample that doped with 2% CoO. After the 2% CoO doping, the crystalline size of the pure single phase magnetite produced was increased by increasing the doping percent. It increased from 143.9 nm for the magnetite powders produced containing 4% CoO to 180.1nm for the powders produced containing 7% CoO as doping.

Color characteristics of pigment

The color's tri-stimulus values(X,Y,Z) and chromaticity coordinate (x,y) of the pigment were measured using a colorimeter instrument type Hunter Lab. with attached standard colors, and then calculated the lightness value and CIE chromaticity[31]. The results are shown in TABLE 1. The TABLE showed that L* and b* values increases, while a* vary randomly. These results can be attributed to the high amount of defects (oxygen vacancies) in the structure of magnetite prepared via isothermal gaseous reduction. Defects lead to distorted tetrahedral and octahedral sites, changing the ligand-field around the chromophore, changing the observed color[32]. TABLE 1 also shows that the colorimetric coordinates in the plan $a \times b$ for the pigments were in agreement with what is illustrated in Figure 6. The L* parameter of sample MC2 is decrease and better black than other sample because the percentage of 2% CoO reduction of brightness. MC2 sample is high in a* and b* values and near to zero value or center of axis (zero black) of a*, b* values, a reasonably strong black hue. It can be also observed that there is a decrease in

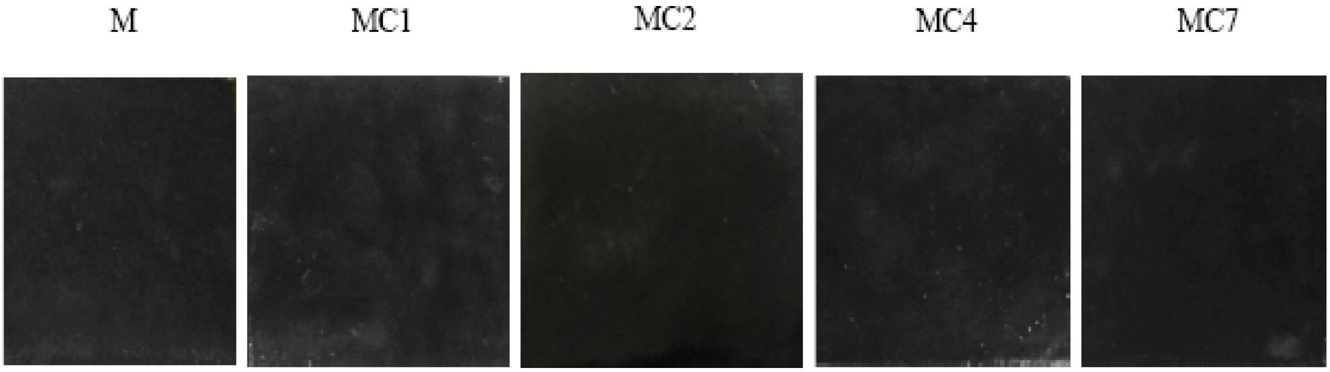

Figure 7 : Colour sample of pure Fe_3O_4 and that doped with different percent of CoO by glaze bodies containing 5% wt pigment.

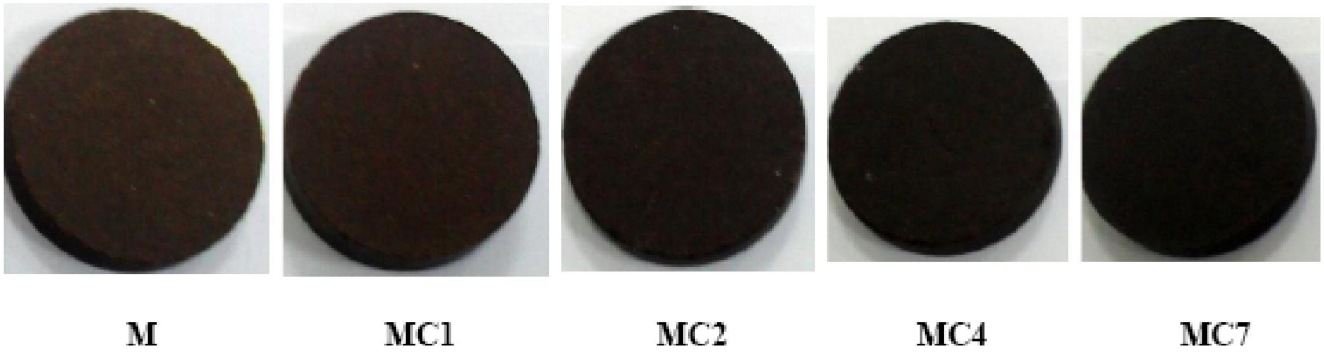

Figure 8 : Colour sample of pure Fe_3O_4 and that doped with different percent of CoO by ceramic bodies containing 10% wt pigment.

the *L**, *a** and *b** parameters with the increase of the Co^{2+} concentration at 2% which may be due to the tetrahedral coordination change (NC = 4) to the octahedral coordination (NC = 6) established by the substitution of Co^{2+} for Fe^{2+} ions. The composition MC2 shows the smallest values of colorimetric parameters resulting in darker color than the composition M, MC2, MC4, MC7.

All compositions can be application in transparent glaze and ceramic bodies. The sample MC2 in glaze is dark hue and the optimum color; however MC4 and MC7 were apparent black with some bluish spots and the samples M, MC1 are pale dark hue as seen in Figure 7. The degree of darkness black color is increase with increase of cobalt percentage in magnetite spinel powder from sample M to MC7. The sample MC7 in ceramic body is highest dark black hue and better black color. The samples M and MC1 are pale black hue (Figure 8). The MC2 in glaze and MC7 in ceramic body performed better in all matrixes as indicated by the hue in Figures 7 and 8. Result can be improved via the amount of cobalt in the pigment, by the formation of iron cobalt partial inverse spinel, $(Fe\,Co)\,(Fe)_2O_4$. This compound has been proposed by different authors[33-36] and is present in the commercial pigment.

CONCLUSION

1. A single- phase of nanocrystalline magnetite (Fe_3O_4) powders were produced using the co-precipitation route without using annealing temperature.
2. The nanocrystalline size of the prepared Fe_3O_4 phase prepared by using co-precipitation methods was in the range of 17nm while the particles were quasi-spherical particles with a quite uniform size distribution.
3. The isothermal reduction of hematite at 1000°C and 20%CO-80%CO_2 resulted in complete conversion of Fe_2O_3 to yield Fe_3O_4 as a single phase
4. The value of the lattice parameter and the crystalline size were decreased with the increase of CoO addition up to 2%CoO beyond this doping, an increases in the lattice parameters and crystalline size were observed.
5. The results demonstrate the viability of using these powders at 2% CoO in Fe_3O_4 spinel as black ceramic pigments.

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REFERENCES

[1] A.L.Lewis; “Pigment Handbook”, New York: Wiley, 758e63, **(1987)**.
[2] J.Meng, G.Yang, L.Yan, X.Wang; Dyes and Pigments, **66(2)**, 109-113 **(2005)**.
[3] Woo-Seok Cho, Masato Kakihana; J.Alloys and Compounds, **287(1-2)**, 87-90 **(1999)**.
[4] D.Mohapatra, D.Sarkar; J.Materials Processing Technology, **189(1-3)**, 279-283 **(2007)**.
[5] I.Ganesh, S.Bhattacharjee, B.P.Saha, R.Johnson, K.Rajeshwari, R.Sengupta, M.V.Ramana Rao, Y.R.Mahajan; Ceramics International, **28(3)**, 245-253 **(2002)**.
[6] Patricio A.Reyes, Jorge F.Plaza De Los Reyes; Bulletin des Societes Chimiques Belges, **93(10)**, 851-856 **(1984)**.
[7] X.Wei, D.Chen, W.Tang; Materials Chemistry and Physics, **103(1)**, 54-58 **(2007)**.
[8] J.S.Gnanaraj, V.G.Pol, A.Gedanken, D.Aurbach; Electrochemistry Communications, **5(11)**, 940-945 **(2003)**.
[9] M.M.Thackeray, M.F.Mansuetto, J.B.Bates; J.Power Sources, **68(1)**, 153-158 **(1997)**.
[10] J.P.Kartha, D.P.Tunstall, John T.S.Irvine; J.Solid State Chemistry, **152(2)**, 397-402 **(2000)**.
[11] O.Durmeyer, J.P.Kappler, A.Derory, M.Drillon, J.J.Capponi; Solid State Communications, **74(7)**, 621-624 **(1990)**.
[12] Gabrielle C.Miles, Anthony R.West; J.American Ceramic Society, **88(2)**, 396-398 **(2005)**.
[13] R.A.Candeia, M.A.F.Souza, M.I.B.Bernardi, S.C.Maestrelli, I.M.G.Santos, A.G.Souza, E.Longo; Materials Research Bulletin, **41(1)**, 183-190 **(2006)**.
[14] C.Xavier, R.Candeia, M.Bernardi, S.Lima, E.Longo, C.Paskocimas, L.Soledade, A.Souza, I.Santos; J.Thermal Analysis and Calorimetry, **87(3)**, 709-713 **(2007)**.

[15] W.Y.Qiang, L.Q.Yu, Y.U.Ding, J.X.Yang; Chin.J.Inorg.Chem., **19(4)**, 411 **(2003)**.

[16] C.R.Lin, Y.M.Chu, S.C.Wang; Materials Letters, **60**, 447-450 **(2006)**.

[17] M.A.Legodi, D.De Waal; Dyes and Pigments, **74(1)**, 161-168 **(2007)**.

[18] M.H.Liao, D.H.Chen; Biotechnol.Lett., **24**, 1913 **(2002)**.

[19] S.Takenaka, T.Kaburagi, C.Yamada, K.Nomura, K.Otsuka; J.Catal., **228**, 66 **(2004)**.

[20] Th.Leventouri, A.C.Kis, J.R.Thompson, I.M.Anderson; Biomaterials, **26**, 4924 **(2005)**.

[21] G.Visalakshi, G.Venkateswaran, S.K.Kulshreshtha, P.N.Moorthy; Mater.Res.Bull., **28**, 829 **(1993)**.

[22] T.Gonzalez-Catteno, M.P.Morales; Mater.Lett., **18**, 151 **(1993)**.

[23] D.Dong, P.Hong; Mater.Res.Bull., **30**, 537 **(1995)**.

[24] V.Chhabra, P.Ayyub; Mater.Lett., **26**, 21 **(1996)**.

[25] Y.Deng, L.Wang,W.Yang, S.Fu, A.Elaïssari; J.Magn.Magn.Mater., **194**, 254 **(1999)**.

[26] Y.Li, H.Liao, Y.Qian; Mater.Res.Bull., **33**, 841 **(1998)**.

[27] M.Bahgat; Materials Letters, **61(2)**, 339-342 **(2007)**.

[28] J.P.Gaviría, A.Bohe, A.Pasquevich, D.M.Pasquevich; Physica B: Condensed Matter, **389(1),(1)**, 198-201 **(2007)**.

[29] G.Nabi, W.K.Lu; Ind.Eng.Chem.Fundamen., **13(4)**, 311-316 **(1974)**.

[30] J.D.Betancur, J.Restrepo, C.A.Palacio, A.L.Morales, J.Mazo-Zuluaga, J.J.Fernandez, O.Perez, J.F.Valderruten, A.Bohorquez; Hyperfine Interactions, **148/149**, 163-175 **(2003)**.

[31] CIE, Recommendations on Uniform Color Spaces, Color Difference.

[32] Equations, Psychometrics Color Terms. 1971 Edition, Supplement no. 2 of Cie Publ.No. 15 (e1-1.31), Bureau Central de la CIE, Paris, **(1978)**.

[33] K.Nassau; The Physics and Chemistry of Color-The Fifteen Causes of Color, Vol. 5, Wiley-Interscience Publication, John Wiley & Sons, 79-85 **(1983)**.

[34] R.A.Eppler; Ceram.Bull., **60**, 562e5 **(1981)**.

[35] W.A.Deer, R.A.Howie, J.Zussman; An Introduction to the Rock Forming Minerals. 2nd Edition, London: Addison Wesley Longman Ltd, **(1992)**.

[36] J.M.Magalh~aes, J.E.Silva, F.P.Castro, J.A.Labrincha; J.Environ.Manage., **75**, 157-166 **(2005)**.

[37] J.Calbo, M.A.Tena, G.Monro´s, M.Llusar, R.Galindo, J.A.Badenes; Am.Ceram.Soc.Bull., **84(9)**, 201-209 **(2005)**.