

Monoferrite BaFe_2O_4 applied as ceramic pigment

R.A. Candeia^{a,*}, M.A.F. Souza^a, M.I.B. Bernardi^b, S.C. Maestrelli^d,
I.M.G. Santos^a, A.G. Souza^a, E. Longo^c

^a LTM, Department of Chemistry, CCEN, UFPB, Campus I, Cidade Universitária, 58059-900 João Pessoa, Paraíba, Brazil

^b Crystal Growth and Ceramic Materials Group, CMDMC, USP, 13560-970 São Carlos, São Paulo, Brazil

^c CMDMC, Department Of Chemistry, CCT, UFSCar, Rod. Washington Luís, Km 235, São Carlos, SP, CP 676, 13565-905, Brazil

^d Department of Materials Engineering, UFSCar, Rod. Washington Luís, Km 235, São Carlos, SP, CP 676, 13565-905, Brazil

Received 30 May 2005; received in revised form 8 August 2005; accepted 10 October 2005

Available online 25 January 2006

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.

© 2006 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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, $\text{Ba}_2\text{Fe}_2\text{O}_5$, BaFe_2O_4 and the hexagonal $\text{BaFe}_{12}\text{O}_{19}$ [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 $\text{BaFe}_{12}\text{O}_{19}$ and Fe_2O_3 , along with other metastable phases. $\text{BaFe}_{12}\text{O}_{19}$ and $\alpha\text{-BaFe}_2\text{O}_4$ are mutually insoluble in each other as solids, and both coexist up to 1000 °C, after which point a third phase, the metastable hexagonal $\text{Ba}_2\text{Fe}_6\text{O}_{11}$, can also develop until the ternary mixture reaches its liquid point at 1175 °C, reverting to $\text{BaFe}_{12}\text{O}_{19}$ and $\alpha\text{-BaFe}_2\text{O}_4$ 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 $\text{BaFe}_{12}\text{O}_{19}$ are magnetic materials of great scientific and technological interest

* Corresponding author. Tel.: +55 83 32167441; fax: +55 83 32167441.

E-mail address: roberlucia@yahoo.com.br (R.A. Candeia).

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 K α radiation ($\lambda = 1.5406 \text{ \AA}$ and $2\theta = 20^\circ\text{--}70^\circ$),

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.

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 N₂ 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. Then, 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.

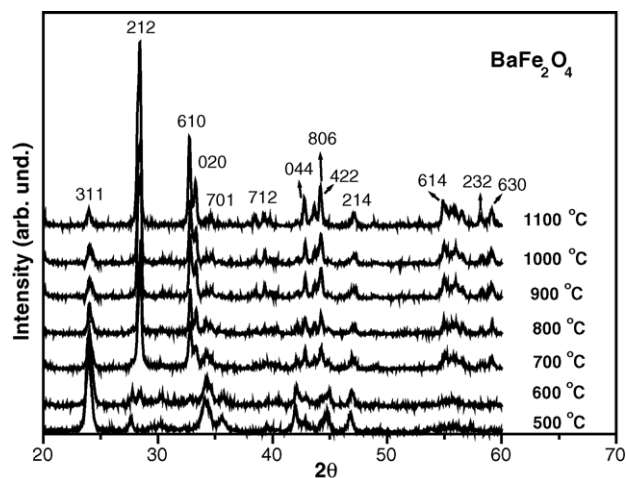


Fig. 2. X-ray diffraction patterns for the BaFe_2O_4 powder as a function of calcination temperature.

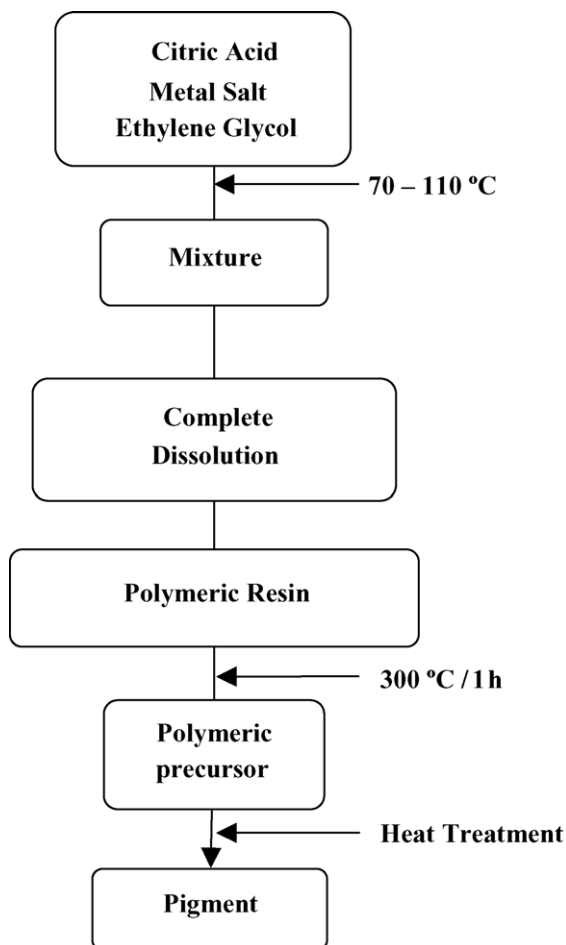


Fig. 1. Synthesis route for the powder obtained by the Pechini method.

Table 1

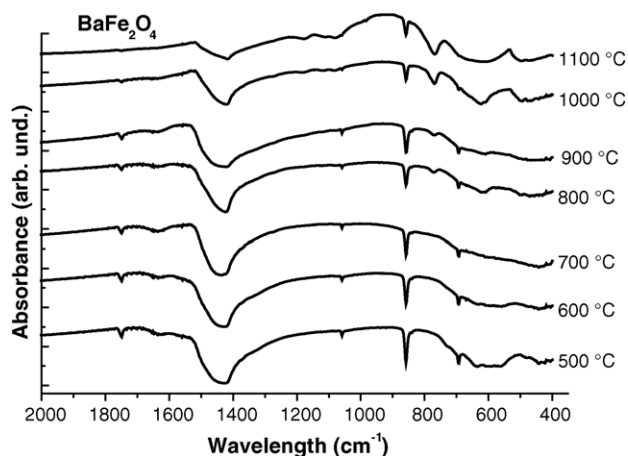
Lattice parameters, volume cell, crystallite size (T_c) and particle diameter (d_{BET}) of the system $BaFe_2O_4$ as a function of the calcination temperature

Temperature (°C)	d_c (nm)	d_{BET} (nm)	d_{BET}/d_c	Unit cell volume (Å ³)	Lattice parameters (Å)		
					a	b	c
PDF 46-0113	–	–	–	865.72	19.042	5.3838	8.4445
700	40	192	4.8	821	18.11	5.38	8.43
800	50	320	6.4	859	18.93	5.38	8.43
900	64	–	–	864	18.99	5.38	8.46
1000	68	892	13.1	865	19.00	5.38	8.46
1100	69	1002	14.5	867	19.02	5.38	8.47

The samples present a single phase above 700 °C, identified as an orthorhombic spinel like phase space group-Bb2₁m (36), according to the index card JCPDS 46–0113, whose lattice parameters are: $a = 19.042$ Å, $b = 5.3838$ Å and $c = 8.4445$ Å. At 500 °C, a non-identified intermediate phase is also observed, which disappears at 700 °C.

Castro et al. synthesized barium monoferrite, using the combustion method. Fe_3O_4 , $Ba(NO_3)_2$ and $BaCO_3$ were found as intermediate phases. After calcination at 700 °C, Fe_3O_4 and $BaCO_3$ can still be found [5].

$BaFe_2O_4$ shows a tunnel structure with iron having a tetrahedral coordination. Corners of the FeO_4 -tetrahedra change their directions blockwise in one layer parallel to the ab -plane. As a result, large and long tunnels are created by 12 FeO_4 -tetrahedra in the tetrahedra network of orthorhombic- $BaFe_2O_4$. Each of the large tunnels contains two Ba^{2+} ($Ba(1)$) atoms (double tunnels). In addition, smaller compressed quadrangular tunnels exist containing exclusively Ba^{2+} ($Ba(2)$) (single tunnels) and those tunnels which are too small for an intercalation of Ba^{2+} (vacant tunnels). The sequence double tunnel–single tunnel–vacant tunnel–single tunnel repeats along the a -axis. $Ba(1)$ shows a monocapped trigonal prismatic oxygen surrounding in the large tunnels. Along the tunnel direction there are no connections between these BaO -polyhedra. The surrounding of $Ba(2)$ is different, as soon as it shows edge-sharing BaO -polyhedra resulting in $[BaO]$ -chains along the tunnels [20].

Fig. 3. Infrared spectra of $BaFe_2O_4$, as a function of the heat treatment.

The $BaFe_2O_4$ structure leads to a different ligand field for iron, when compared to usual hematite pigments. For hematite, iron is surrounded by six oxygens in octahedral coordination. In barium monoferrite, iron is in tetrahedral coordination. As a consequence a different splitting of the five d orbitals is observed, leading to different colors [21].

Table 1 presents the values of the lattice parameters and the unit cell volume of the system in study. It is observed that the unit cell volume increases with temperature in a more effective way from 700 to 800 °C, getting almost constant above this temperature.

The absorption vibrations of the system $BaFe_2O_4$, Fig. 3, consist of well-defined bands, as follows:

- Bands at 1460 and 850 cm^{-1} , which decrease their intensity with temperature increase, while bands at 1753, 1060 and 700 cm^{-1} disappear at 1000 °C. According to literature results, $BaCO_3$ presents bands at 1750, 1460, 1060, 860 and 700 cm^{-1} [22], while $FeCO_3$ presents bands at 1523, 876 and 736 cm^{-1} [23,24]. These results indicate the presence of carbonates in the present material. These carbonate bands were not observed in XRD patterns, due to their low resolution.
- Bands at 600 and 450 cm^{-1} get well defined at higher temperatures. These bands are assigned to ν_1 and ν_2 vibrations of spinels [25–27], which belong to the same T_{1u} representation [28,29]. Similar results were obtained by González-Carreño et al. [14], which found bands at 586 and 434 cm^{-1} , for hexaferrite $BaFe_{12}O_{19}$.

Results of crystallite size and particle diameter (BET), as a function of temperature, are also presented in Table 1. An increase of both parameters with temperature is observed, but while crystallite size increases 70%, particle size increases 400%. This result is evidenced by the number of crystallites in each particle, which increases from 4.8 to 14.5, indicating the particle sintering. This is confirmed by SEM analysis (Fig. 4), whose photomicrographs indicate the presence of aggregates, with particle coalescence.

The color analysis of $BaFe_2O_4$, calcined at different temperatures, was obtained correlating the results of reflectance in the visible region (reflected wavelength) with colorimetric coordinates (tonality variation, brightness and saturation).

Fig. 5 illustrates the diffuse reflectance of the pigments before and after laboratory test. All curves present higher

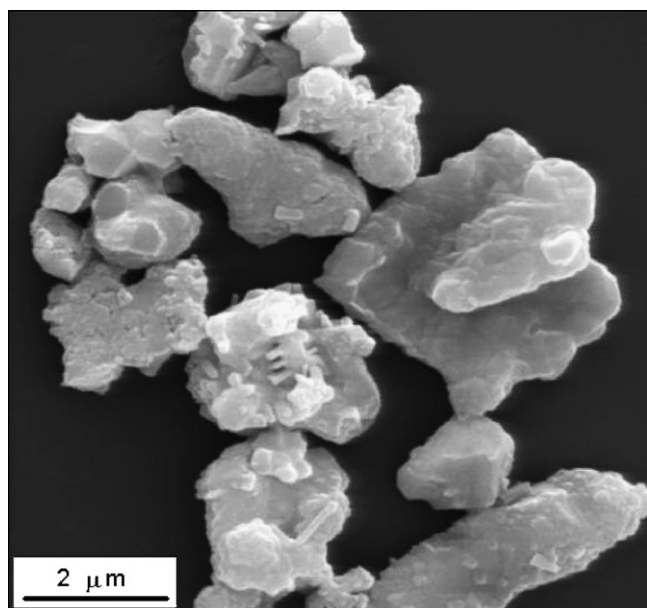


Fig. 4. SEM micrographs of BaFe₂O₄ system, calcined at 1000 °C.

reflection from 650 to 750 nm. It may be observed that reflectance increases from 600 to 800 °C, probably due to carbonate amount decrease, as observed by infrared spectroscopy (Fig. 3). The decrease in reflectance observed at higher temperatures is probably due to the sintering among particles, observed in BET (Table 1) and SEM (Fig. 4) results.

It should be observed that curve profile is different from other ferrite results. Ferrite reflectance usually presents a band between 650 and 780 nm [3,30]. For BaFe₂O₄, there is no high reflectance plateau. Otherwise, reflectance increases continuously up to 750 nm. This may be due to the iron ligand field. For the other ferrites, Fe²⁺ and Fe³⁺ are present in octahedral and tetrahedral coordination, while, in barium ferrite, iron is only in tetrahedral coordination. It should be emphasized that octahedral ligand field leads to a higher splitting of d orbitals than tetrahedral one. Consequently, electron transition occurs with a higher energy absorption (or a smaller wavelength) [21].

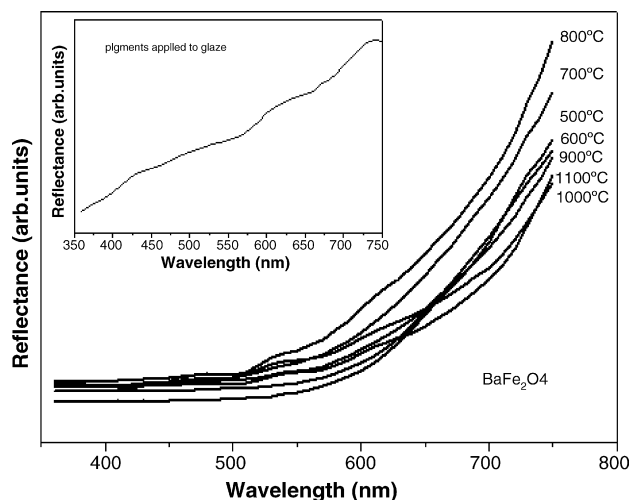


Fig. 5. Diffuse reflectance of BaFe₂O₄ system, as a function of the heat treatment.

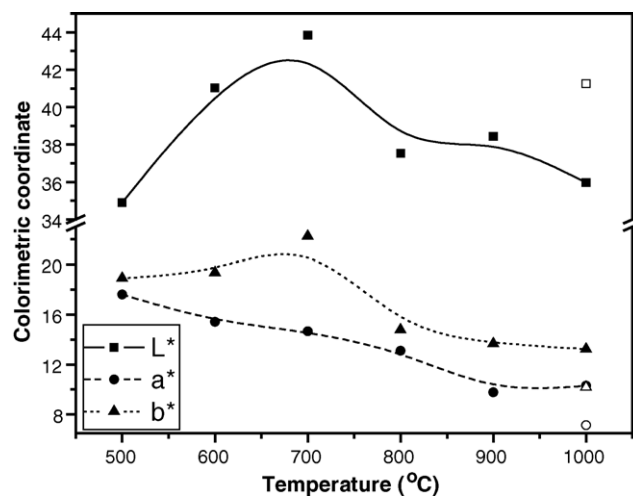


Fig. 6. Colorimetric coordinates, as a function of heat treatment. Open symbols indicate results of pigment calcined at 1000 °C and applied to a ceramic piece.

As a consequence, the resulting color is a direct evidence of Fe³⁺ or Fe²⁺ ions coordinated by oxygen [31,32]. This result may also be observed in Fig. 6, which presents the colorimetric coordinates of pigments before and after laboratory test. After laboratory test, the ceramic pieces presented a good aesthetic aspect, without defects as bubbles, superficial texture, among others.

Results presented in Fig. 6 indicate that L^* and b^* coordinates increase up to 700 °C, decreasing at higher temperatures. As stated before, for diffuse reflectance results, the increase may be due to carbonate elimination, while the decrease may be due to sintering among particles. A continuous decrease with temperature was observed for a^* parameter. According to García et al. [33], the iron (III) oxides suffer a reduction to Fe²⁺ ion, promoted by the emission of molecular oxygen according to Eq. (1), when fired at high temperature or when in the presence of unoxidized organic material. In the present case, this unoxidized organic material is in the form of carbonate and may lead to Fe³⁺ reduction, changing the pigment color.



The laboratory test, done with pigment calcined at 1000 °C (Figs. 5 and 6), indicates that the pigment is chemically and thermally stable, as no surface defects were observed. Comparing the colorimetric coordinates of the pigment calcined at 1000 °C before and after laboratory test, a small change in tonality may be observed ($\Delta H^* = 2.8$) while the saturation decrease ($\Delta C^* = -4.4$) and the lightness increase ($\Delta L^* = 5.3$) are more important.

4. Conclusion

The pigment BaFe₂O₄ was obtained by the polymeric precursor method, with single phase and brown color. Diffuse reflectance and chromatic coordinates results indicate that

carbonate presence as well as sintering among particles change the color, leading to its variation as a function of the heat treatment of the pigment precursor. Differences between UV–vis spectra of BaFe_2O_4 and other ferrites are probably due to the iron ligand field—while the former presents iron in tetrahedral sites, the latter present iron in octahedral and tetrahedral sites. The pigment presents a suitable technological behavior without reactions between glaze and pigment, indicating that powders are chemically and thermally inert up to 1000 °C.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian financing agencies CNPq, FAPESP/CEPID.

References

- [1] F. Bondioli, T. Manfredini, A.P.N. Oliveira, Pigmentos Inorgânicos: Projeto, produção e aplicação industrial, *Cerâmica Industrial* 3 (4–6) (1998) 13–17.
- [2] R.A. Eppler, Selecting ceramic pigments, *J. Am. Ceram. Soc. Bull.* 66 (11) (1987) 1600–1610.
- [3] R.A. Candeia, M.I.B. Bernardi, E. Longo, I.M.G. Santos, A.G. Souza, Synthesis and characterization of spinel pigment CaFe_2O_4 obtained by the polymeric precursor method, *Mater. Lett.* 58 (2004) 569–572.
- [4] G. Yang, B. Han, Z. Sun, L. Yan, X. Wang, Preparation and characterization of brown nanometer pigment with spinel structure, *Dyes Pigments* 55 (2002) 9–16.
- [5] S. Castro, M. Gayoso, A.C. Rodriguez, Study of the combustion method to prepare fine ferrite particles, *J. Solid State Chem.* 134 (1997) 227–231.
- [6] S.K. Rakshit, S.C. Parida, Z. Singh, R. Prasad, V. Venugopal, Thermodynamic properties of ternary oxides in the system Ba–Fe–O using solid-state electrochemical cells with oxide and fluoride ion conducting electrolytes, *J. Solid State Chem.* 177 (2004) 1146–1156.
- [7] R.C. Pullar, A.K. Bhattacharya, Crystallisation of hexagonal M ferrites from a stoichiometric sol–gel precursor, without formation of the α - BaFe_2O_4 intermediate phase, *Mater. Lett.* 57 (2002) 537–542.
- [8] Y.A. Koksharov, D.A. Pankratov, S.P. Gubin, I.D. Kosobudsky, M. Beltran, Y. Khodorkovsky, A.M. Tishin, Electron paramagnetic resonance of ferrite nanoparticles, *J. Appl. Phys.* 89 (4) (2001) 2293–2298.
- [9] T. Fujiwara, Magnetic-properties and recording characteristics of barium ferrite media, *IEEE Trans. Magn.* 23 (1987) 3125.
- [10] V. Berbenni, A. Marini, N.J. Welham, P. Galinetto, M.C. Mozzati, The effect of mechanical milling on the solid state reactions in the barium oxalate–iron(III) oxide system, *J. Eur. Ceram. Soc.* 23 (2003) 179–187.
- [11] K. Haneda, A.H. Morrish, Magnetic properties of small particles for possible magneto-optical pigments, *IEEE Trans. Magn.* 35 (1999) 3490–3495.
- [12] D. Chen, Y. Chen, Synthesis of the barium ferrite ultrafine particles by coprecipitation in the presence of polyacrylic acid, *J. Colloid Interface Sci.* 235 (2001) 9–14.
- [13] W. Roos, Formation of chemically coprecipitated barium ferrite, *J. Am. Ceram. Soc.* 63 (1980) 601–603.
- [14] T. González-Carreño, M.P. Morales, C.J. Serna, Barium ferrite nanoparticles prepared directly by aerosol pyrolysis, *Mater. Lett.* 43 (2000) 97–101.
- [15] E. López-Navarrete, A.R. González-Elipé, M. Ocaña, Non-conventional synthesis of Cr-doped SnO_2 pigments, *Ceram. Int.* 29 (2003) 385–392.
- [16] X. Sui, M. Scherge, M.H. Kryder, J.E. Snyder, V.G. Haris, N.C. Koon, Barium ferrite thin-film recording media, *J. Magn. Magn. Mater.* 155 (1996) 132–139.
- [17] M.I.B. Bernardi, S. Cava, C.O. Paiva-Santos, E.R. Leite, C.A. Paskocimas, E. Longo, Comparison of blue pigments prepared by two different methods, *J. Eur. Ceram. Soc.* 22 (2002) 2911–2919.
- [18] C.O. Paiva-Santos, D. Garcia, Y.P. Mascarenhas, J.A. Eiras, Influência da adição de La e Sr nos parâmetros estruturais do PbTiO_3 , *Cerâmica* 35 (1989) 153.
- [19] CIE, Recommendations of Uniform Color Spaces, Color Difference Equations, Psychometrics Color Terms, Supplement no. 2 of CIE Publ. No. 15 (E1-1.31) 1971, Bureau Central de la CIE, Paris, 1978.
- [20] H.k. Müller-Buschbaum, The crystal chemistry of AM_2O_4 oxometallates, *J. Alloys Compd.* 349 (2003) 49–104.
- [21] R.J. Borg, G.J. Dienes, *The Physical Chemistry of Solids*, Academic Press, 1992.
- [22] P. Durán, D. Gutierrez, J. Tartaj, M.A. Banãres, C. Moure, On the formation of an oxycarbonate intermediate phase in the synthesis of BaTiO_3 from (Ba,Ti)—polymeric organic precursors, *J. Eur. Ceram. Soc.* 22 (2002) 797–807.
- [23] K. Nakamoto, Inorganic compounds, in: *Infrared Spectra of Inorganic and Coordination Compounds*, third ed., John Wiley and Sons, New York, 1970 (Part II).
- [24] H.I. Saleh, Reaction mechanisms of strontium ferrites synthesis, *J. Chin. Chem. Soc.* 49 (2002) 341–348.
- [25] J. Preudhomme, P. Tarte, Infrared studies of spinels-I. A critical discussion of the actual interpretations, *Spectrochimica Acta* 27 (1971) 961–968.
- [26] J. Preudhomme, P. Tarte, Infrared studies of spinels-III. The normal II–III spinels, *Spectrochimica Acta* 27 (1971) 1817–1835.
- [27] M.A. Ahmed, E. Ateia, S.I. El-Dek, Spectroscopic analysis of ferrite doped with different rare earth elements, *Vibrat. Spectrosc.* 30 (2002) 69–75.
- [28] W.B. White, B.A. De Angelis, Interpretation of the vibrational spectra of spinels, *Spectrochimica Acta* 23 (1967) 985–995.
- [29] G.C. Allen, M. Paul, Chemical characterization of transition metal spinel-type oxides by infrared spectroscopy, *Appl. Spectrosc.* 49 (1995) 451–458.
- [30] F. Bondioli, A.M. Ferrari, C. Leonelli, T. Manfredini, Syntheses of Fe_2O_3 /silica red inorganic inclusion pigments for ceramic applications, *Mater. Res. Bull.* 33 (5) (1998) 723–729.
- [31] H.L. Tuller, S.R. Rotman, *Wide-gap Luminescent Materials—Theory and Applications*, Kluwer Academic Publishers, 1997.
- [32] A. Djemai, G. Calas, J.P. Muller, Role of structural Fe(III) and iron oxide nanophases in mullite coloration, *J. Am. Ceram. Soc.* 84 (7) (2001) 1627–1631.
- [33] A. García, M. Llusar, S. Sorlí, J. Calbo, M.A. Tena, G. Monrós, Effect of the surfactant and precipitant on the synthesis of pink coral by a micro-emulsion method, *J. Eur. Ceram. Soc.* 23 (11) (2003) 1829–1838.