Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 26 (2006) 2301–2305

www.elsevier.com/locate/jeurceramsoc

HF^2EPR spectroscopy of Fe(III) impurities in a blue hercynite-based pigment

F. Di Benedetto[a,*], G. Andreozzi[b], G. Baldi[c], A. Barzanti[c], G.P. Bernardini[d], V. Faso[c], L.A. Pardi[e], M. Romanelli[f]

[a] *Museo di Storia Naturale, Università di Firenze, via G. La Pira, 4, I-50121, Firenze, Italy*
[b] *Dip. di Scienze della Terra, Università di Roma, "La Sapienza", P.le A. Moro, 5, I-00185, Roma, Italy*
[c] *Lab. Ricerca Avanzata, Gruppo Colorobbia, Via Pietramarina, 123, I-50053, Sovigliana, Italy*
[d] *Dip. di Scienze della Terra, Università di Firenze, via G. La Pira, 4, I-50121, Firenze, Italy*
[e] *IPCF, CNR, via G. Moruzzi, 1, I-56124, Pisa, Italy*
[f] *Dip. di Chimica, Università di Firenze, via della Lastruccia, 3, I-50019, Sesto Fiorentino, Italy*

Received 1 December 2004; received in revised form 10 March 2005; accepted 9 April 2005

Abstract

The nature and the behavior of a paramagnetic Fe(III) impurity, occurring in a new charge-transfer hercynite-based blue pigment and determined through conventional electron paramagnetic resonance (EPR) and Mössbauer spectroscopy, was investigated and ascertained through high-field high-frequency EPR (HF^2EPR) spectroscopy. The blue hercynite-based pigment is biphasic, containing both hercynite and corundum. The HF^2EPR spectral features, together with their temperature dependence allowed to assess the intensity and the symmetry of the Fe(III) crystal field interactions. Numerical simulations were used to determine the relevant hamiltonian parameters. The final attribution of Fe(III) to the octahedral sites in corundum was achieved.

The presence of corundum was found to remove ferric iron, eventually formed during the synthesis, from hercynite. The dilution of Fe(III) in the Al_2O_3 phase results in a quenching of its coloring effects. As a consequence, corundum acts as a buffer during the synthesis, stabilizing the pigment chromatic yield.

Keyword: Impurities; Spectroscopy; Colour; Spinels; Pigments

1. Introduction

Understanding the nature of the color of inorganic pigments is a relevant topic to support the research for new colored materials for the ceramic industry. High thermal stability and high chemical resistance, together with a good chromaticity, are the most required properties of such materials. Only a limited number of crystalline materials with particular structures (zirconium silicate, $ZrSiO_4$, spinels, $M^{II}M^{III}{}_2O_4$, corundum, Al_2O_3, and rutile, TiO_2) allows good-quality high temperature pigments. These crystalline colored products, in fact, must remain unaltered during industrial treatments with application temperatures over 1220 °C. The color in these structures is reached by tuning the crystalline field (CF) effects around a chromophore, usually a transition metal ion. Recently, the research applied to this topic explored different approaches to obtain colored substances for high temperature applications based on different chromogenic mechanisms, i.e. semiconductors with a visible-range tunable band gap[1] and charge-transfer (CT) pigments.[2] This latter mechanism has been recently object of interest, being able to induce very intense colors, through particularly high absorptivity. However, only few CT ceramic pigments have been proposed in literature.[2–4] The main difficulty in the synthetic strategy deals not only with the incorporation of the chromophores, as

---

* Corresponding author. Fax: +39 055 284571.
E-mail address: dibenefr@geo.unifi.it (F. Di Benedetto).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.04.007

Table 1
Phase and chemical composition of the pigment and CIELab coordinates

Phase	wt%	Formula
Corundum	90	Al_2O_3
Hercynite	10	$Fe_{0.97}Ti_{0.06}Al_{1.94}O_4$
CIELab coordinates	L*	54.13
	a*	−0.15
	b*	−8.33

in CF pigments, but also with the control of their distribution in the crystalline structure. An accurate spectroscopic study is therefore necessary to fully understand the complex origin of the color for crystalline materials, locally characterized by differences in chemical composition, site occupancy and metal distribution. Moreover, not only the chromophore, but also some impurities may strongly affect the overall chromaticity of the final product. In order to discriminate among different superimposed effects, electron paramagnetic resonance (EPR) investigations, performed in multifrequency (from 9.5, EPR, up to 300 GHz, HF^2EPR) have proved to be a powerful tool to discriminate single-ion properties, due to the extreme specificity of this spectroscopy for valence state.[5]

A new deep blue pigment based on hercynite ($FeAl_2O_4$) spinel structure was obtained by Baldi et al.[6], through an high temperature treatment in reducing atmosphere. Previous studies[2,6], performed using different spectroscopic techniques, Mössbauer, DRS, EPR, evidenced the polyphasic nature of the pigment and they ascertained the presence of at least two coloring centers, namely a Fe(III) chromophore and a Fe(II)–Ti(IV) charge-transfer pair. The crystal chemistry of this latter chromophore, inferred by the comparison of the different results, led to its attribution to the hercynite fraction. On the contrary, a final assessment of the Fe(III) impurity in the sample was not achieved and only a tentative attribution of this species to corundum, the other phase constituent of the pigment, was formulated.[2] The major difficulties in studying the crystal chemistry of Fe(III) in this pigment arose from its subordinate contribution in the Mössbauer spectrum[2] and, in particular, in the very complex X-band EPR spectrum.[6] A high-frequency HF^2EPR study was, therefore, undertaken, in order to finally assess the crystal chemistry of Fe(III) and to better understand the contribution of this dopant to the color of the pigment.

2. Sample characterization and experimental procedures

The details of the synthesis of the studied pigment are reported elsewhere.[2] The minero-chemical characterization, performed by means of XRD and EPMA, evidenced the pigment to be biphasic, corundum and Ti-bearing hercynite being the only constituents of the mixture. The percent amount and the mean chemical composition of both phases are listed in Table 1. The pigment results mainly constituted by corundum, whereas hercynite represent only a minor associated phase. On the other hand, as evident from the chemical compositions, the color information is introduced namely by this latter phase. No evidence of Fe(III) in corundum was observed by EPMA analyses, thus suggesting this species to be present as a minor valence state in hercynite or a very diluted substituent of Al in corundum.

The powdered pigment was pressed together with a small amount of *n*-eicosane, inert in the EPR techniques, to obtain a platelet suitable for the investigation. The HF^2EPR experiments reported in this study were performed from room down to liquid helium temperature using the single pass technique with a probe adapted for ultra-wide band measurements.[7] The source was a Gunn effect diode emitting at 95 GHz. The magnet is a superconducting magnet (Oxford Instruments) operating at a maximum field of 12 T. The detector is a hot electron bolometer (QMC Instruments).

Simulations of the experimental spectra were performed with Weihe simulation software.[8,9] The SIM program has been specifically designed in order to leave the maximum freedom in the choice of the model for the spin system under investigation. The number of interactions that can be introduced and the orientation of the relative tensors, in fact, may be independently chosen. The flow of the program implies numerical diagonalization of the spin hamiltonian matrix, the retrieval of the transitions fields, probabilities and intensities and, if requested, a powder integration with a standard algorithm. Although fairly simple the SIM program proved to be quite efficient for the simulation of very high-field spectra due to the lack of any restraint in the allowed range not only for the spin hamiltonian interactions, but also for the experimental parameters, in particular magnetic field and frequency.

3. Results

The HF^2EPR spectra of the pigment sample registered at different temperatures are shown in Fig. 1, as a first derivative of radiation absorption versus the applied magnetic field (in T). The room-temperature spectrum consists of a central intense doublet, centered at ∼3.38 T, corresponding to the resonant field for a spin-only Fe(III) in cubic symmetry.[10] The central doublet is surrounded by two weaker broad lines, at 3.22 and 3.50 T, respectively, and by two outer doublets, at 3.03 and 3.76 T, respectively. Considering the half-filled d-configuration typical for Fe(III) (d^5, $S = 5/2$), possible anisotropies of the Zeeman interaction may be considered small or negligible, due to the large gap between the ground state and the first excited states. Moreover, no hyperfine interactions are expected, since Fe nucleus is non-magnetic.[11] As a consequence, the spectrum can be explained in terms of a Fe(III) line, structured by the zero-field interaction: five lines, with intensity decreasing from the center to the sides of the spectrum, are observed for $S = 5/2$ systems[10], because the ±1/2, ±3/2 and ±5/2 states are separated in energy by spin–spin and crystal field interactions.

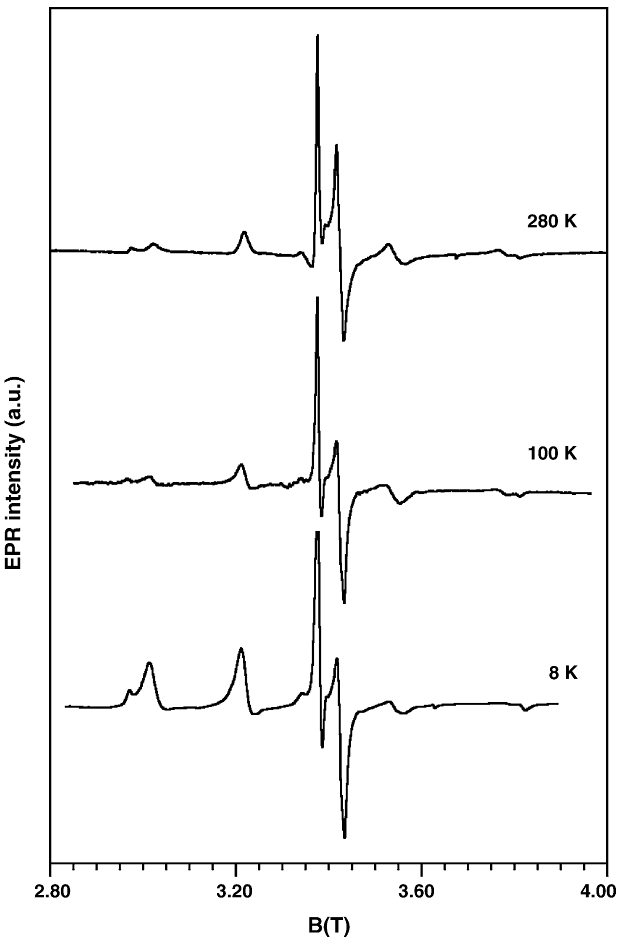

Fig. 1. Experimental HF^{2}EPR spectra registered at W-band (95 GHz) at different temperatures. The ordinate values are reported as first derivative of the absorbed intensity. Spectra are normalized.

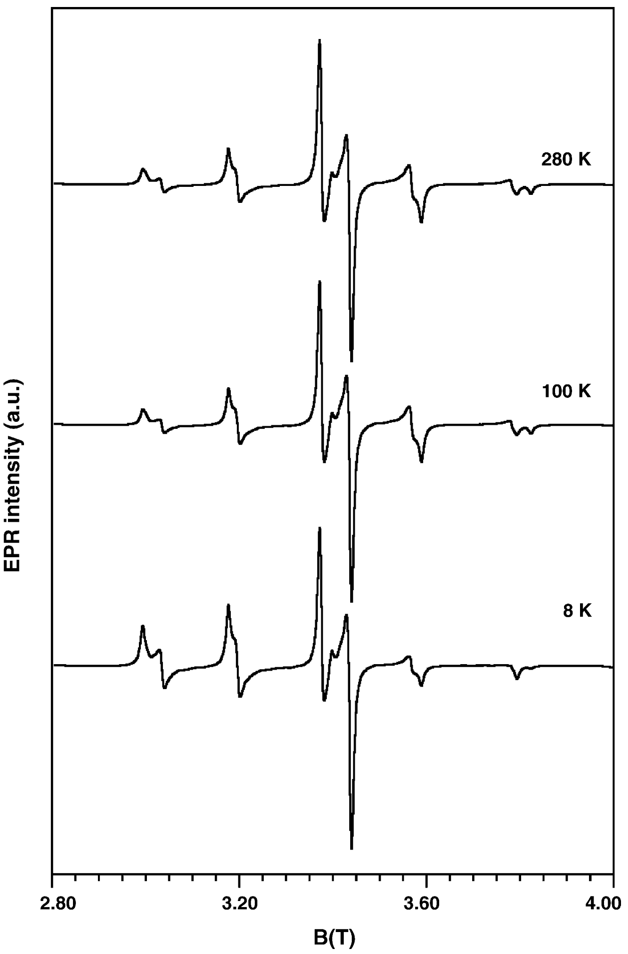

Fig. 2. Simulation of the HF^{2}EPR spectra of Fig. 1.

At lower temperatures, the overall spectrum results unchanged as concerns the number of the lines and their resonant fields. However, a relevant increase of the intensity of the low-field lines (i.e., 3.03 and 3.22 T) is evident, in particular at 8 K, whereas the high-field lines (3.50 and 3.76 T) result less intense. The temperature dependence of the relative intensity of the transitions within the $2S+1$ states of the ground multiplet are determined by depopulation effects: the lower the energy of a state, the larger its population. The variations of the line intensity, therefore, allow an unambiguous determination of the sign of the zero field splitting.

The interpretation of the spectra in the frame of the spin Hamiltonian theory can be only made through simulation of the temperature-dependent spectra. Nevertheless, some reasonable prediction concerning the relevant spin Hamiltonian parameters can be made from the distance of the observed external doublets. Assuming an axial symmetry of the interaction, the ZFS splits the Zeeman line into 2S lines.[10] The difference, Δ, between the reported high- and low-field resonance values, i.e. the total splitting of the spectrum, is related to the value of the axial component, D, of the ZFS tensor by: $D' = \Delta/(2S-1)$. In the present case thus $D \sim 185$ mT. Moreover, a splitting (~50 mT) of the high and low-field lines is evident, thus providing a clear fingerprint of rhombic distortion of the crystal field. The quantitative simulation of the spectra were performed, taking into account both the axial, D, and rhombic, E, ZFS parameters. The best-fit simulated spectra are shown in Fig. 2 and the relative Hamiltonian parameters in Table 2. No asymmetry of the Zeeman tensor was necessary to reproduce all the experimental line position.[11] The best-fit D and E values, the former slightly differing from its estimation on the basis of the spectral features, allow to fit quite well all the spectral features. Nevertheless, different values of the distance between two consecutive ZF lines suggest that a small fine cubic interaction, a, is present.[11] In the

Table 2
Best-fit spin Hamiltonian parameters used in the simulations

Parameter		Value
$g_x = g_y = g_z$		2.0020
ΔH (mT)		6
ZFS parameter	(mT)	(cm^{-1})
D	198	0.1850
E	1.7	15.9×10^{-4}

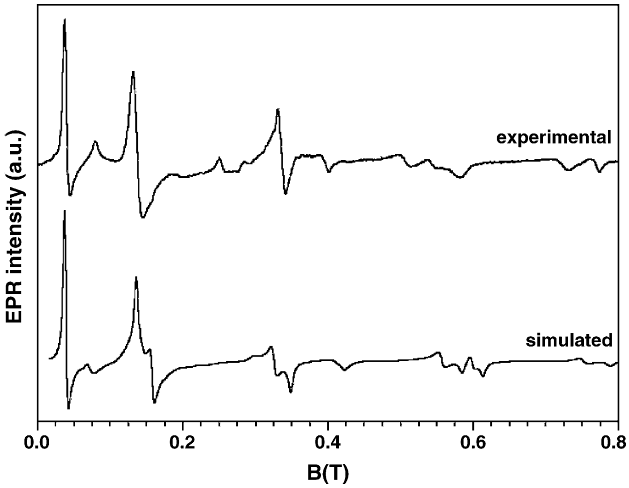

Fig. 3. Comparison between the X-band (9.5 GHz) experimental spectrum (modified from Ref. [1]) and the simulation obtained using the W-band set of Hamiltonian parameters (see Table 1).

present simulations, this cubic interaction was not taken into account, but a comparison between the best-fit and the experimental spectra allowed to establish a value of $a \sim -12$ mT (114×10^{-4} cm^{-1}). It is noteworthy to mention that the temperature variation of the experimental spectra is consistent with a single set of parameters, i.e. no (or very small) variation of the zero-field interaction is observed with temperature.

An attempt was also done to simulate the X-band spectra,[6] using the same set of parameters. The comparison of the two spectra (Fig. 3) shows that all the main lines are well reproduced. The peculiar X-band spectrum, therefore, is caused by a relatively strong zero-field interaction, of the order of 200 mT, which is fully comparable with the magnitude of Zeeman interaction, ~330 mT at 9.5 GHz, thus preventing the recognition of all the ZF lines within the available field range (0–1 T).

4. Discussion and conclusions

The EPR results clearly indicate that Fe(III) is undergoing an axial crystal field interaction, as evidenced by the large D parameter value. The D/E ratio, greater than 100, confirms that only a minor rhombic component is acting on the paramagnetic Fe(III).

Only three cation sites are present in the mixture constituting the pigment: the tetrahedral, T_H, and octahedral, O_H, sites in hercynite, and the octahedral, O_C, site of corundum. The T_H site in gahnite has a $\bar{4}3m$ cubic point symmetry, thus ruling out the possible presence of large axial zero-field interaction. On the contrary, both the O_H and the O_C sites possess an axial point symmetry, $\bar{3}m$ and 3, respectively. The axial D parameter values for Fe(III) in similar coordination has been reported to be 0.2442 cm^{-1}, in the isostructural Fe-bearing $ZnGa_2O_4$ spinel,[12] and 0.1679 cm^{-1},[13] in corundum. These two data account for clearly different structural environment, where the distortion-induced ZFS interaction appear to be prevalent in the spinel structure. The present experimental D value, 0.185 cm^{-1}, suggests the octahedral site in corundum as the most likely attribution for the Fe(III) position. The small mismatch between the present and the literature[13] values may be ascribed to the different temperatures of annealing, which may affect the overall crystal field interaction.

A further indication may be provided by considering the next-nearest neighboring coordination shell: in the corundum structure a next-nearest Al ion is present at ~2.51 Å, in an face-sharing octahedron. The overall local symmetry of the two octahedra, by assuming a small Fe–Al interaction, is orthorhombic, thus justifying the rise of a E rhombic parameter. In the hercynite structure, the next-nearest Al ions occur only at ~2.88 Å, through edge-sharing octahedra: the intensity of the rhombic Fe–Al interaction is in this case definitely smaller.

Finally, the presence of Fe(III) in corundum is confirmed examining not only the single features of the spectrum, but the entire spectrum itself. Indeed, if contained in hercynite, Fe(III) would be immersed in a non-diluted magnetic environment, induced by the Fe(II) ions at the T_H position. The consequent EPR spectrum would present the temperature dependence and the dipolar broadening of the linewidth, usual for Fe(III) in concentrated magnetic environment[11], independently from the structural position, O_H or T_H, occupied by trivalent iron. On the contrary, the experimental spectra are clearly arising from a diluted species, as it occurs for paramagnetic substituents in corundum. Thus, all the spectroscopic features confirm Fe(III) to be in the distorted octahedral symmetry of corundum.

Taking into account the present and literature[2,6] spectroscopic results, the two chromophore were ascertained to occur in different phases: the Fe(II)–Ti(IV) pair in hercynite and Fe(III) in corundum. Accordingly, the formula unit of the latter phase, recalculated on the basis of both the pigment phase composition and of the Fe speciation derived from the Mössbauer analysis, is $Al_{1.993}Fe_{0.007}O_3$. This chemical formula accounts for all the experimental results, being Fe enough diluted to be almost undetectable under the standard conditions of the EPM analysis, and to give rise to structured, single-ion EPR spectra.

The final assessment of the crystal chemistry of the paramagnetic species in the pigment leads to some consideration about the effects of the synthetic procedure and the coloring yield:

- under a reducing environment, Fe(II) tends not to enter within the corundum structure, present as starting material for the synthesis, but it prefers to segregate in a more suitable structure, the spinel;
- on the contrary, Fe(III) even if sometimes present in hercynite in minor amounts due to the oxidizing synthesis conditions, represents an obvious vicariant of Al in the corundum structure, where it is largely stabilized;

- the blue color of the pigment is mainly due to the hercynite chromophore pair, the efficacy of which may be ascribed to the large molar extinction coefficient associated to the Fe(II)–Ti(IV) charge-transfer pair;
- the presence of Fe-bearing corundum does not represent a source of instability of the final color of the pigment: due to its crystal field nature, the d–d transition of Fe(III) do not compete with the more intense process of hercynite; on the contrary, corundum acts as a buffer for the final coloring yield, subtracting the Fe(III) formed by a non-perfect reducing environment.
- a more effective problem concerning with the presence of corundum in the final mixture consists with the overall loss of intensity of the color: the presence of a large "white" fraction in the pigment drastically decreases the saturation of the color, thus limiting its potential applications.

Acknowledgments

This work was carried out with the partial financial support of Italian CSGI and CNR. The HF^2EPR laboratory acknowledges the Interuniversitary Consortium for the Science and Technology of Materials (INSTM) and the National Research Council for financial support. The EC network SENTINEL, contract number: HPRI-CT-2000-40022 is also acknowledged for the scientific collaboration and the technological cooperation.

References

1. Guenther, E. and Jansen, M., *Mat. Res. Bull.*, 2001, **36**, 1399.
2. Andreozzi, G. B., Baldi, G., Bernardini, G. P., Di Benedetto, F. and Romanelli, M., *J. Eur. Ceram. Soc.*, 2004, **24**, 821.
3. Preda, M., Meghea, A., Melinescu, A. and Rau, I., *Rev. Roum. Materiale*, 2002, **32**(3), 163.
4. Aruna, S. T., Ghosh, S. and Patil, K. C., *Int. J. Inorg. Mater.*, 2001, **3**(4/5), 387.
5. Di Benedetto, F., Bernardini, G. P., Caneschi, A., Cipriani, C., Danti, C., Pardi, L. *et al.*, *Eur. J. Miner.*, 2002, **14**, 1053.
6. Baldi, G., Barzanti, A., Bernardini, G. P., Di Benedetto, F., Faso, V. and Romanelli, M., *Adv. Sci. Tech.*, 2003, **34**, 299.
7. Hassan, A. K., Pardi, L. A., Krzystek, J., Sienkiewicz, A., Goy, P., Rohrer, M. *et al.*, *J. Magn. Reson.*, 2000, **125**, 300.
8. Glerup, J. and Weihe, H., *Acta Chim. Scandinavica*, 1991, 444.
9. Tregenna-Piggott, P. L. W., Weihe, H., Bendix, J., Barra, A. L. and Gudel, H. U., *Inorg. Chem.*, 1999, **38**, 5928.
10. Calas, G., *Rev. Miner.*, 1988, **18**, 513.
11. Abragam, A. and Bleaney, B., *Electron Paramagnetic Resonance of Transition Ions*. Clarendon Press, Oxford, 1970.
12. Krebs, J. J., Stauss, G. H. and Milstein, J. B., *Phys. Rev. B*, 1979, **20**(7), 2586.
13. Wen-Chen, Z., *Physica B*, 1998, **245**, 119.