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HF^{2}EPR investigation of a Cr-bearing gahnite pigment

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Abstract

A pink gahnite pigment, containing the chromophore ion Cr^{3+}, has been synthesised under industrial conditions and characterised by X-ray powder diffraction (XRPD), electronic spectroscopy, electron paramagnetic resonance spectroscopy (EPR) and HF^{2}EPR. The paramagnetic resonance techniques, in particular, have been applied to determine the incorporation of the chromophore in the spinel structure and to study its distribution. The pigment was found to be formed by aluminium borate and, mainly, gahnite ($ZnAl_2O_4$). The Cr^{3+} ion was revealed to be incorporated only in the octahedral site of this latter phase. The chromophore is subjected to a strong crystal field ($\Delta_0 = 18800\,cm^{-1}$), which determines its colouring properties. A large zero field splitting interaction was observed in the X-band EPR spectra and interpreted by comparison with the high-frequency W-band spectra. The axial symmetry of the crystal field surrounding Cr^{3+} was ascertained by both the techniques. The observed spectroscopic features are due to the single ion properties of Cr^{3+} in a strong field, thus ruling out any possible clustering of the chromophore within the structure.
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1. Introduction

In the last years an extensive research has been dedicated to characterise traditional and glass ceramic pigments, with the aim of increasing the number of coloured materials useful for industrial applications and refining of their colouring properties. In this field, several studies have been focused to the investigation of pink-red Cr^{3+}-doped spinels, due to their chromatic and technological properties. The chromophore Cr^{3+}, in fact, may be responsible of green colours, when subjected to low crystal field, whereas in high field it induces a red-pink colour.[1] On the other hand, spinels ($Me^{2+}Me^{3+}{}_2O_4$) belong to one of the most refractory class of materials. They are stable even in drastic thermal and redox industrial treatments,[2] therefore, the pigment can be used in ceramic applications as fast firing and in high temperature glazes. The insertion of this efficient chromophore into a very stable structure has been studied, not only to improve and control the relative synthesis, but also to exploit the possible advanced application of the new material, in particular in the field of glass ceramics and of optoelectronics.[1,3–5]

Different spectroscopic techniques have been applied to the characterisation of the colouring properties of several Cr-doped spinels, via the determination of the relative energy level distribution. In particular, the electronic transition of Cr^{3+} in the similar octahedral sites of spinel, gahnite and ruby have been interpreted by several authors,[1,3,5–7] reaching both a complete attribution of the bands in the UV and vis ranges, and the determination of the crystal field parameters. Electron paramagnetic resonance spectroscopy (EPR) techniques represent a specific tool to investigate the crystal

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field surrounding the paramagnetic Cr^{3+} ion.[8–10] Nevertheless, only few EPR investigations have been performed on these materials.[11,12] EPR spectroscopy has revealed a great capability to investigate not only the Cr distribution within the spinel, but also the partition of this ion between the spinel and the glass, during the glass ceramic formation.[12] A further characterisation arises from the use of high-field high-frequency EPR (HF^2EPR) investigation, which discriminate the single ion properties via the better resolution of the spectrum and the characterisation of the field dependent spectral parameters.

A EPR and HF^2EPR study of a traditional Cr-bearing gahnite pigment, obtained by an industrial synthetic approach, has been undertaken, in order to fully characterise the doping process and the colouring properties of this material. The characterisation of the pigment has been integrated with X-ray powder diffraction (XRPD) Rietveld phase and structural analysis and with electronic spectroscopy, performed in the UV and vis range.

2. Experimental procedures

A Cr-bearing gahnite pink pigment was prepared by mixing commercial reagents: 42.1 wt.% ZnO, 54.3 Al_2O_3, 1.6 Cr_2O_3 as precursor containing the colouring element, and adding 2.0 wt.% H_3BO_3 as mineraliser. The mixture was homogenised and dry milled, to improve the powder reactivity during the thermal treatment. The charges were heated in a high temperature furnace (Lenton EHF 1700) in alumina crucibles. The thermal treatment consisted in a temperature increase from room temperature up to 1400 °C in 6 h, and a plateau of 4 h at 1400 °C. Owing to the fact that the eutectic point of the ZnO–Al_2O_3 system occurs at ∼1700 °C (82.5 mol% ZnO), the boric acid improved the synthetic process allowing a faster crystallisation and a closer reaction among the starting powders. At the end of the thermal treatment, pink-coloured homogeneous powders were obtained after cooling in air and crumbling. The sample was successively powdered in a ball mill, and checked by means of X-ray powder diffraction, using a Philips PW 3710 diffractometer with Cu anode and graphite monochromator, equipped with PC-X'Pert Pro software for data acquisition and handling. Experimental conditions were: 20 mA, 40 KV, 10°–140° 2θ, step size 0.02° 2θ, 2 s/step, plexiglas support. The phase composition and the crystal chemistry of the obtained data were refined through the Rietveld algorithm, by using the Rietquan software.[13]

Electron paramagnetic resonance spectroscopy measurements were performed on powdered samples, dispersed in paraffin wax to avoid spurious effects from magnetic alignment phenomena, and kept into amorphous silica capillaries. Data were collected at room temperature using a Bruker ER 200D-SRC spectrometer operating at X-Band (about 9.5 GHz) interfaced with DS/EPR software to a PC for data acquisition and handling. The g-values were determined using DPPH radical [2,2-di(4-tert-octyl-phenyl)-1-picrylhydrazyl, $g = 2.0037$] as an external standard. EPR parameters have been refined by means of spectral simulations.

The HF^2EPR experiments were performed using the single pass technique,[14] using a probe adapted for ultra-wide band measurements. The source consists of 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).

UV–vis investigations were performed by means of a Perkin-Elmer Lambda 800 UV–vis spectrometer equipped with an integration sphere. Spectra were acquired from 300 to 800 nm with a step size of 1 nm. The diffuse reflectance spectra were automatically converted to absorbance spectra by using the Kubelka Munk function. Spectral absorption were fitted assuming gaussian line shapes by means of Microcal Origin 6.0 package.

3. Results

3.1. XRPD characterisation

The XRPD pattern shows the Cr-bearing pigment (PG Cr) to be polyphasic containing mainly gahnite, $ZnAl_2O_4$, and aluminium borate, $Al_{18}B_4O_{33}$, as a minor phase (Fig. 1). This latter phase is a common reaction product, when B is added to the reactants, because of the limited solubility of this ion in the spinel structure.[2] No traces of other phases, in particular the reactant Cr_2O_3 or oxidised Cr products are observed but gahnite. The Rietveld quantitative analysis of the phase composition of the pigment indicates gahnite to represent the 98(2) wt.% of the total charge, the aluminium borate being the remaining 2(2) wt.%. Considering the initial composition of the charge, all the boric acid reacted to form the aluminium borate. The minimum detection limit of the present experimental spectrum is <1 wt.%. The absence of oxidation products of Cr, the presence of whose is rele-

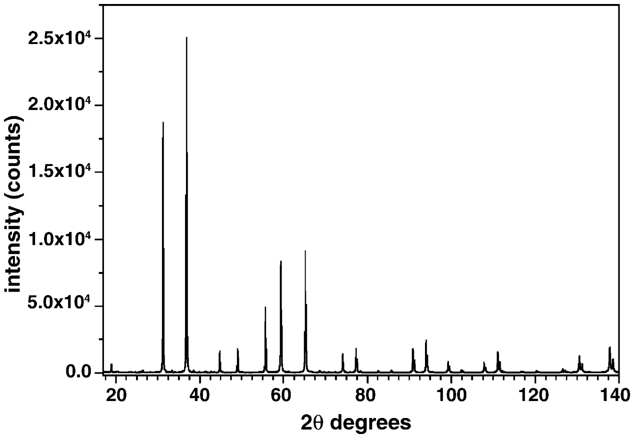

Fig. 1. XRPD pattern of PG Cr pigment.

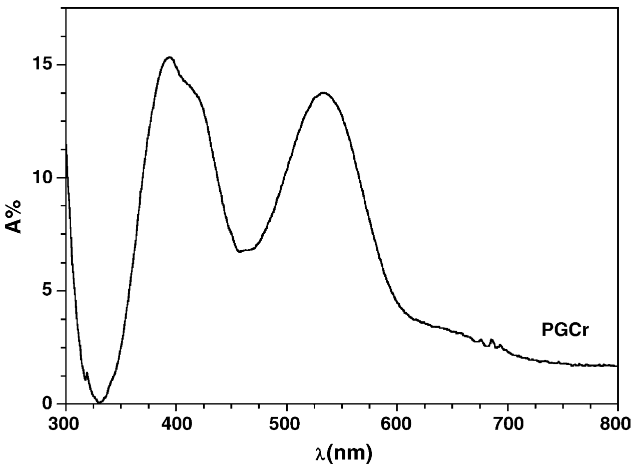

Fig. 2. UV–vis absorbance (*A*%) vs. wavelength (nm) spectrum of PG Cr.

vant from the health and environmental point of view, is to be assumed below to this limit.

As concerns the fate of Cr during the firing treatment, the phase composition of the products suggests a full incorporation in the gahnite fraction. To verify the liability of this assumption, a Rietveld crystal chemical refinement has been performed on the X-ray data in the range 17°–140° 2θ (Fig. 1). The best refinement of the PG Cr powder pattern ($r = 1.80\%$) indicates 0.05(2) atoms per formula unit of Cr^{3+} in the octahedral (O) site in gahnite, leading to the crystal chemical formula $Zn[Cr_{0.05}Al_{1.95}]O_4$.

3.2. Spectroscopic investigation

The UV–vis experimental spectrum *A*% (absorption %) versus λ (wavelength) of PG Cr is shown in Fig. 2, in the range 300–800 nm. Two main absorption bands, the second of which exhibits a structured feature, are present in the visible range, centred at 532 and 400 nm, respectively. The wavelength of each band component was refined, by means of a Gaussian decomposition, to 532(2), 425(2) and 388(2) nm (corresponding to 18,800; 23,500 and 25,800 cm^{-1}, respectively). The intensity and position suggest these bands to be related to d–d electronic transition. On the contrary, a fourth intense band, visible at $\lambda < 330$ nm, has been attributed to a metal-oxygen charge transfer.

The room temperature X-band paramagnetic resonance spectrum of PG Cr (Fig. 3) consists of two signals at about 1800 G and 3400 G, corresponding at *g*-values of 3.87 and 2.05, respectively. The spectral features resemble those determined for a paramagnetic ion in axial symmetry, with a strong distortion. However, in literature[11] a similar spectrum of a Cr-bearing spinel ($MgAl_2O_4$) has been differently interpreted, considering a large zero field interaction acting on a ground state with a small spin orbit mixing of the excited levels. According to these authors, the X-band spectrum allows to reveal only a part of the zero field transitions, which "mimic" an axially distorted coordination. To discriminate between the two interpretations, the correspondent W-band EPR spectrum, shown in Fig. 4, has been acquired: as predicted by Stahl Brada and Low,[11] the full spectrum appears evident, with four intense lines at 22,500; 30,000; 35,000 and 42,250 G, which cannot be explained in terms of an axially distorted coordination for Cr^{3+}.

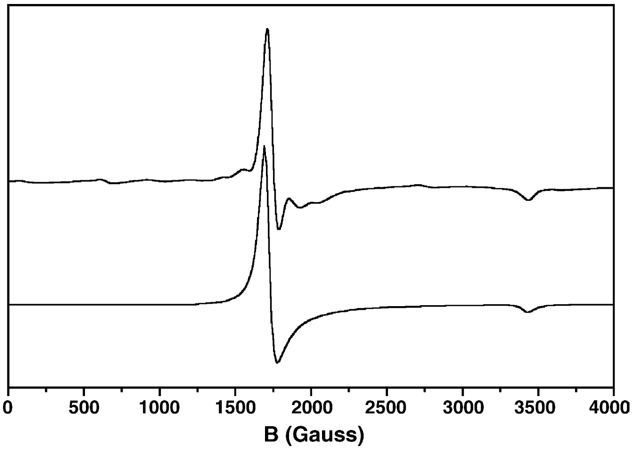

Fig. 3. Experimental (upper curve) and simulated (lower curve) X-band (9.5 GHz) EPR spectra, magnetic field values in gauss (G).

Simulations of both the X- and W-band spectra were performed with Weihe simulation software.[8,15] Problems were encountered in fact using simulations of the X-band spectrum with other simulation program, because the high zero field splitting effect of Cr^{3+} prevents the application of the perturbation approach. The best simulations of the spectra were achieved at both the used frequencies with a single set of parameters using the following spin hamiltonian:

$$H = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B[B_x S_x + B_y S_y] + D\left[S_Z^2 - \frac{5}{4}\right]$$

with ($S = 3/2$, $I = 0$) $g_{||} = 1.980$ and $g_{\perp} = 2.000$, and $D = 0.94\ cm^{-1}$ (∼9400 G).

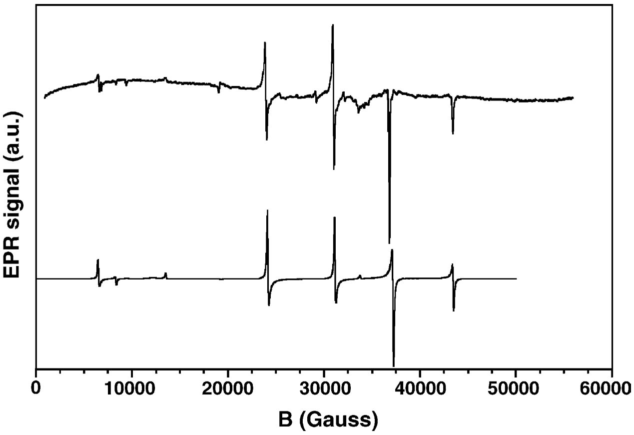

Fig. 4. Experimental (upper curve) and simulated (lower curve) W-band (95 GHz) EPR spectra; magnetic field values in gauss (G).

4. Discussion

The presence of a single phase, able to host Cr^{3+} ions, evidences the almost complete incorporation of the chromophore, due to the marked preference of this ions for the high field O sites of spinels and corundum.[7] The results of the Rietveld refinement also confirm the replacement of Al^{3+} with Cr^{3+} in the gahnite O site. The final proof of the production of Cr-bearing gahnite is provided by the diffuse reflectance data, which may be explained in terms of a Cr^{3+} ion in a distorted octahedral coordination, without evidencing spectral features related to Cr^{3+} in other phases and/or sites. The interpretation of the UV–vis absorbance spectra, in fact, has been used to identify the nature of the surrounding crystal chemical environment of trivalent Cr.[1,7]

According to the Tanabe–Sugano diagram of d^3 ion (Cr^{3+}) in O_h symmetry, three spin-allowed CF transitions, $^4A_{2g} \rightarrow {}^4T_{2g}$ (^4F) [band $\nu 1$], $^4A_{2g} \rightarrow {}^4T_{1g}$ (^4F) [band $\nu 2$] and $^4A_{2g} \rightarrow {}^4T_{1g}$ (^4P) [band $\nu 3$], occur. However, only the first two bands are generally observed in optical spectra of Cr^{3+}-bearing minerals, the third band being high energetic and usually hidden by the charge—transfer transitions. In a lower symmetric coordination, the states $^4T_{2g}$ (^4F) and $^4T_{1g}$ (^4F) of Cr^{3+} are resolved into two or three additional levels.[6]

On this basis, the components of the structured band $\nu 2$ can be interpreted as due to trigonal compression D_{3d} of the octahedral site in spinel,[6] in this case, the excited state $^4T_{1g}$ (^4F) is splitted into $^4A_{2g}$ and $^4E_{2g}$ levels.[16] Thus, the experimental bands are assigned to the electronic transition, $^4A_{2g} \rightarrow {}^4T_{2g}$ (^4F) [band $\nu 1$], $^4A_{2g} \rightarrow {}^4A_{2g}$ (^4F) and $^4A_{2g} \rightarrow {}^4E_{2g}$ (^4F) [band $\nu 2$]. The $\nu 1$ band provides directly the crystal field splitting parameters, Δ_0. The Racah parameter B was calculated by assuming a mean value for the $\nu 2$ bands, by the relationship:[6]

$$B = \frac{(2\nu 1 - \nu 2)(\nu 2 - \nu 1)}{(27\nu 1 - 15\nu 2)}$$

The calculated parameter values, reported in Table 1 together with those of the literature, evidence a very good agreement. No information were obtained about the Racah parameter C, because of the experimental absence of spin-forbidden transitions.

The EPR spectra performed at X-band and 95 GHz and room temperature could be simulated with a single set of spin hamiltonian parameters which confirms the goodness of the model. The system shows an axial symmetry with a rather high value of D in agreement with that reported in literature,[11] extrapolated from the X-band spectrum of a single crystal Cr^{3+}-bearing $MgAl_2O_4$ spinel. These spectra are determined by isolated ions in a D_{3d} pseudo-octahedral coordination.

The comparison of all the experimental results points to the presence of the chromophore Cr^{3+} in the pseudo-octahedral D_{3d} site of the gahnite structure. In this site, the chromophore is subjected to a strong crystal field, with axial symmetry, which determines all the colouring and spectroscopic properties of the PG Cr pigment. No evidence of short range ordering and/or clustering of the solute Cr ions in the host gahnite lattice has been identified. No evidence of mineral phases containing Cr in valence states higher than 3 have been detected, within the specific detection limits, by all the characterisation techniques adopted in this study; the synthetic process, therefore, appears fast and quantitative.

Both electronic and paramagnetic resonance spectroscopies represent very powerful indicators of the incorporation of Cr^{3+} in gahnite[12] and useful tools to investigate the distribution of this ion in the spinel structure: the two spectroscopies, therefore, can be profitably used for the characterisation and control of Cr-gahnite based materials.

Table 1
Crystal field parameters for Cr^{3+} in spinels (cm^{-1}): (a) reference[6], (b)[7], (c) [1] and (d) this study

CF parameters	$MgAl_2O_4$	Ruby		Gahnite	
	(a)	(a)	(b)	(b) (c)	(d)
Δ_0	18520	18150	18200	18620	18800
B	612	636	629	629	550
C			3230	3278	

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References

1. Koepke, Cz., Wisniewski, K., Grinberg, M. and Beall, G. H., *Spectrochim. Acta A*, 1998, **54**, 1725.
2. Andreozzi, G. B., Baldi, G., Bernardini, G. P., Di Benedetto, F. and Romanelli, M., *J. Eur. Ceram. Soc.*, 2004, **24**(5), 821.
3. Fairbank Jr., W. M., Klauminzer, G. K. and Schawlow, A. L., *Phys. Rev. B*, 1975, **11**, 60.
4. Grinberg, M., Russell, D. L., Holliday, K., Wisniewski, K. and Koepke, Cz., *Opt. Commun.*, 1998, **156**, 409.
5. Grinberg, M., Wisniewski, K., Koepke, Cz., Russell, D. L. and Holliday, K., *Spectrochim. Acta A*, 1998, **54**, 1735.
6. Burns, G. R., *Mineralogical applications of crystal field theory*. Cambridge University Press, 1993.
7. Koepke, Cz., Wisniewski, K., Grinberg, M., Russell, D. L., Holliday, K. and Beall, G. H., *J. Lumin.*, 1998, **78**, 135.
8. Glerup, J. and Weihe, H., *Acta Chim. Scand.*, 1991, 444.
9. McGarvey, B. R., *Transition Met. Chem.*, 1966, **3**, 89.
10. Bencini, A. and Gatteschi, D., *Transition Met. Chem.*, 1982, **8**, 1.
11. Stahl-Brada, R. and e Low, W, *Phys. Rev.*, 1959, **116**, 561.
12. Costa, V. C., Lameiras, F. S., Pinheiro, M. V. B., Sousa, D. F., Nunes, L. A. O., Shen, Y. R. *et al.*, *J. Non-Cryst. Solids*, 2000, 209.

13. Lutterotti, L., Ceccato, R., Dal Maschio, R. and Pagani, E., *Mater. Sci. Forum.*, 1998, **278–281**, 93.
14. Hassan, A. K., Pardi, L. A., Krzystek, J., Sienkiewicz, A., Goy, P., Rohrer, M. *et al.*, *J. Magn. Reson.*, 2000, **142**, 300.
15. Tregenna-Piggott, P. L. W., Weihe, H., Bendix, J., Barra, A. L. and Gudel, H. U., *Inorg. Chem.*, 1999, **38**, 5928.
16. Rossano, S., Galoisy, L. and e Gwamnesia, G., *Eur. J. Mineral.*, 1996, **8**, 471.