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HF²EPR 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 HF²EPR. 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.

Keywords: Cr; Gahnite; EPR; Crystal chemistry; Pigments

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-

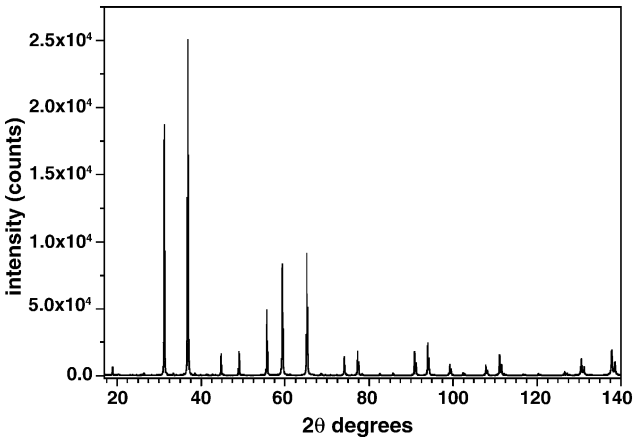

Fig. 1. XRPD pattern of PG Cr pigment.