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CRYSTAL CHEMISTRY OF GAHNITE-BASED PIGMENTS: A DRS, EPR AND HF²EPR STUDY

Lorenzi, G.[1], Baldi, G.[1], Di Benedetto, F.[2], Faso, V.[1], Lattanzi, P.F.[3], Pardi, L.A.[4] & Romanelli, M.[5]

[1] Laboratorio di Ricerca Avanzata, Colorobbia Group, via Pietramarina 123, I50053, Sovigliana Vinci (Italy)
[2] Museo di Storia Naturale, Università di Firenze, via G. La Pira 4, I50121, Firenze (Italy)
[3] Dipartimento di Scienze della Terra, Università di Cagliari Via Trentino, 51 - I09127 – Cagliari (Italy)
[4] Istituto per i Processi Chimico- Fisici -CNR, via G. Moruzzi 1, I56124 Pisa (Italy)
[5] Dipartimento di Chimica, Università di Firenze, via della Lastruccia 3, I50019 Sesto Fiorentino (Italy)
e-mail: dibenefr@geo.unifi.it

The exact knowledge of the phase composition and of the crystal chemistry of the inorganic pigments, in relation to their colouring properties, represents a fundamental step to improve the quality of the final product and to lower the production costs. Spinel-based pigments are widely studied because of their stability even in drastic thermal and redox industrial treatments. The insertion of metal ion chromophores into this structure allow, not only to improve and control the relative synthesis, but also to exploit their use in ceramic applications as fast firing and in high temperature glazes.

Two synthetic Cr- and Ni- bearing gahnite ($ZnAl_2O_4$) based pigments, pink and blue, respectively, representing potential candidates in the manufacturing of coloured bulk glass-ceramics, have been investigated by different spectroscopic techniques: DRS, EPR and HF²EPR. The two pigments were synthesised from industrial raw materials (Al_2O_3, ZnO and Cr_2O_3/$NiCO_3$) by firing at elevated temperatures with a short thermal cycle. The final products were investigated by X-ray powder diffraction (XRPD), thus revealing gahnite as major/unique phase. Rietveld refinements, performed on high-quality powder patterns, suggest the doping chromophore (Cr/Ni) to be quantitatively incorporated in the spinel structure. Nevertheless, the data do not allow to ascertain the crystal chemistry of the synthesised gahnite, and its relation to the observed colour.

Diffuse reflectance spectra were collected on both pigments, to identify the transitions in the UV and VIS range, whereas EPR and HF²EPR spectroscopies were applied only on the Cr-bearing material, because Ni^{2+} is undetectable in room temperature experiments. The obtained results point to an octahedral coordination for both Cr^{3+} and Ni^{2+} in gahnite; a small fraction of tetrahedral Ni was determined in the blue pigment. Both ions have been found to be isolated, the spectral evidence of pairs and/or clusters being absent. In both materials, the bulk colours arise from single ion crystal field transitions of the doping chromophore, Cr and Ni, respectively. The crystal field surrounding the chromophore has been fully interpreted. Moreover, the systematic characterisation of the products of several syntheses allowed to establish the efficiency of the doping process and dependence of the crystal chemistry on the synthesis condition, thus giving relevant information on the stability of the pigment colour.