THE NATURE OF THE CHROMOPHORE CENTRE IN AN IRON ZIRCON PIGMENT PREPARED BY CONVENTIONAL AND SOL-GEL ROUTES.

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ABSTRACT

A combination of X-ray Absorption Spectroscopy, X-ray, Diffraction, X-ray Fluorescence, Scanning Electron Microscopy, and Colour Measurements has been used to determine the nature and extent of iron incorporation into an iron zircon ceramic pigment. It is shown that the iron exists in two forms as trapped Fe_2O_3 *(Haematite) and as a lattice dopant species in the zircon host pigments. Furthermore the lattice dopant replaces silicon at a tetrahedrally co-ordinated site. It is possible by sol-gel routes to incorporate a higher proportion of the iron as a lattice dopant. Colour measurements reveal that lattice substitution produces a cream colour but a coral red is produced only when haematite is present.*

INTRODUCTION

The majority of pigments used by the ceramics industry are produced by traditional routes involving the mixing of the precursor materials and co-firing at high temperature (1400 -1700 °C). This current process is inefficient in that optimal mixing and firing conditions are rarely if ever achieved resulting in the incomplete reaction of the precursors and the likelihood of reduced colour intensities. The development of potentially more efficient alternative wet chemical routes (e.g. sol-gel) has attracted much attention over the years. Similarly extensive work has been conducted in the development of zircon based pigment systems since the discovery of vanadium blue in the late 1940's.[4] This has led to the production of many pigments, notable examples being praseodymium yellow iron coral zircon and cadmium based reds . Today, zircon based pigments are used extensively in the ceramic industries due to their performance at high temperatures. Despite this there has been and continues to be much controversy as to the location, role, oxidation state and nature of the chromophore species within the zircon host structure. Early studies of the vanadium zircon system suggested that vanadium was present in the +4 state and on the basis of the ionic radii that vanadium substituted either directly for Zr or Si or less likely in an interstitial site. Various techniques that have been utilised to obtain accurate measurements of the lattice parameters of the zircon pigment including Single Crystal X-ray Diffraction, coupled with Atomistic and Theoretical Simulations 11 and finally X-ray Absorption Spectroscopic analysis. These studies indicate that vanadium tends to replace both zirconium and silicon by a direct lattice substitution mechanism.

By contrast much less work has been directed towards the synthesis of iron zircon pigments other than by conventional ceramic routes. Recently it has been reported than iron zircons can be produced by the pyrolysis of Aerosols and by sol-gel routes. However less work has been devoted to understanding the nature of the chromophore centre. Research on conventionally prepared samples suggest that haematite is present as trapped occlusions in the zircon host. Furthermore, advantage has been taken of the fact that Fe has a Mossbauer active nucleus. Early studies indicated that the iron was present as Fe(IV), but more recent work indicates that the iron is present as Fe(III) and is present as both Fe_2O_3 and in a rhombic substituted site. In the sample prepared by pyrolysis of an aerosol, Mossbauer spectroscopy revealed only the presence of Fe_2O_3.

In this paper by using a combination of X-ray Absorption Spectroscopy (XAS), X-ray Powder Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Colour Measurements have been used to determine the nature and extent of iron incorporation into an iron zircon ceramic pigment. From these results we can assign which features are crucial in producing a given colour in the iron zircon system.

CONCLUSION.

1. The intimate reaction conditions afforded by the sol-gel route enable us to introduce a higher percentage of the iron dopant into the zircon lattice compared to conventional ceramic routes.

2. The iron that is incorporated into the zircon host lattice is 4 co-ordinated and replaces silicon.

3. The lattice-incorporated iron produces a weak cream coloured pigment but an intense coral pigment is only formed when hematite is present in the form of discrete particles physically entrapped within a zircon crystalline matrix.

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