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Original Article

New spectroscopic and diffraction data to solve the vanadium-doped zircon pigment conundrum

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ABSTRACT

The literature on V-doped zircon pigments offers a puzzling situation with unanswered questions about the origin of turquoise colour. In this study, new diffraction (XRPD) and spectroscopic (EPR, EAS) data were obtained on four industrial pigments, whose vanadium content is much higher than samples from previous investigations. Both EPR features and XRPD results indicate the occurrence of tetrahedrally-coordinated V⁴⁺ at the zircon interstitial site 16g. EPR spectra at 5 K exhibit a structured multiplet attributed to isolated V⁴⁺ ions and an exchange-narrowed line resulting by clustering of V⁴⁺ ions. The intensity of optical bands is stronger in samples affected by V⁴⁺ clusters. However, the turquoise colour stems from the window of transmitted green-blue light, which depends on both the tail of the main optical band (²B ← ²A) and the onset of charge transfer phenomena. Small variations in these two bands readily turn into a chromatic shift from light blue to green.

1. Introduction

The ceramic industry is currently utilizing only one pigment with colour between green and blue, namely in the turquoise-cyan range, that is vanadium-doped zirconium silicate [1,2]. Nickel-doped hibonite or Mn³⁺-doped oxides were also proposed as turquoise pigment [3–5], but they never entered in the industrial use because of technological limits in ceramic processing.

Seabright [6] patented the V-doped zircon as ceramic pigment in 1948. Its peculiar turquoise colour soon attracted the academic interest and early attempts to explain the origin of colour go back to the 1960s [7–10]. Since the 1970s, the V-doped zircon has been a milestone of the “ceramic palette”, being able to cover the wide colour space from light blue to green and, by mixing with Pr-doped zircon, to yellowish green [1,11]. However, the advent of inkjet printing, that since 2009 has almost completely replaced previous decoration techniques, changed drastically both technological requirements and colour demand for ceramic pigments [12].

On one side, inkjet printheads work properly only with submicronic pigments, a constraint which has imposed the colorant industry to a further process of micronization [13]. This makes conventional pigments more reactive (due to higher specific surface area), but it damages their crystal structure, leading eventually to amorphisation [14].

These drawbacks can be somewhat overcome by increasing the solid load of inks, but this has repercussions on ink viscosity and surface tension, which must be within the window acceptable by inkjet printers [15]. On the other side, digital decoration is managed by quadrichromy (four basic colours: Cyan, Magenta, Yellow and Black). This circumstance brought about a dramatic reduction of the potential candidates as pigments in digital inks [1,12]. In principle, V-zircon should be the best candidate for the Cyan ink, but strong limitations arise when the pigment is micronized and then applied on glazes for ceramic tiles [13,14].

The ceramic pigment manufacturers faced the “digital era” by reformulating their recipes in order to get better performances. This improvement was successful for various pigments, including blue and black spinels, magenta malayaite, and particularly yellow zircon obtained by praseodymium doping [16–19]. Noteworthy the reason why V-doped zircon is unreliable for inkjet printing, while Pr-doped zircon is widely utilized, is not fully understood yet. A deeper comprehension of this different behaviour would pave the way to an actual engineering of micronized pigments, starting from a proper design of crystal structural features.

Vanadium may be in principle located at different sites of the zircon lattice, especially in the case of high V concentration, as in industrial pigments. The crystal structure of zircon (ZrSiO₄; s.g. *I*₄₁/*amd*) consists

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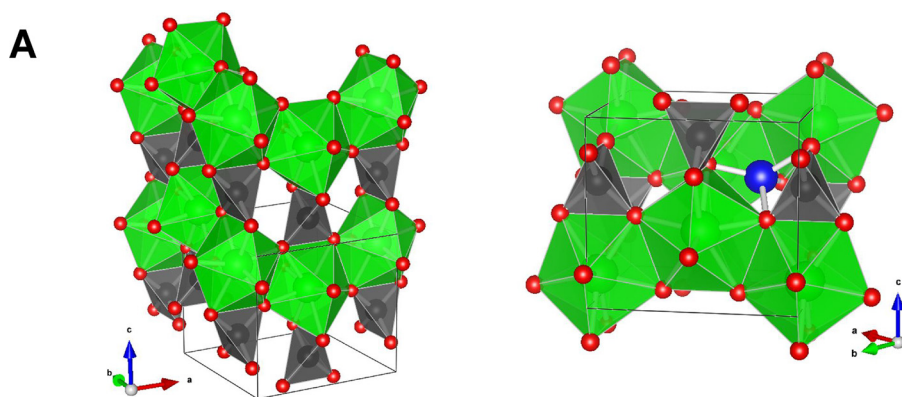


Fig. 1. Schematic representation of the ZrSiO_4 polyhedral arrangement in a perspective view along the c -axis where isolated SiO_4 tetrahedra share corners and edges with ZrO_8 dodecahedra. These latter are arranged in chains parallel to the ab plane through edge-sharing (A); polyhedral representation of the zircon tetragonal unit-cell (s.g. $I4_1/amd$) where Zr^{4+} (within dodecahedra) and Si^{4+} (within tetrahedra) occupy the $4a$ and $4b$ Wyckoff positions, respectively, whereas the $16g$ position is highlighted by means of a tetrahedrally coordinated atom within an interstitial void (B).

of chains of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra running parallel to the c -axis. As shown in Fig. 1A, those chains are joined by edge-sharing ZrO_8 dodecahedra along the ab -plane, so that each ZrO_8 polyhedron shares edges with four adjacent ZrO_8 dodecahedra [20,21]. Both Zr^{4+} and Si^{4+} are located at crystallographic sites (Wyckoff positions $4a$ and $4b$, respectively) with the same symmetry (i.e. $-4m2$ or D_{2d}), whereas O^{2-} finds place at the $16h$ position with site symmetry $.m$. or C_s . The polyhedral arrangement of the zircon structure gives rise to voids between tetrahedral and dodecahedral sites, i.e. potential interstitial sites within which impurity elements can be accommodated [21]. Among those interstitial sites, the tetrahedral site located at the $16g$ Wyckoff position (Fig. 1B) with symmetry $..2$ or C_2 has been proposed for hosting V^{4+} ions [22].

It is recognized how difficult is to keep under strict control all variables in the synthesis of V-doped zircon pigments [23–25]. Vanadium is more or less easily volatilized during calcination, that is usually carried out at temperatures between 800 and 1000 °C with various mineralizers, mostly alkaline fluorides [26–29]. Such mineralizers are necessary to get the formation of zircon, which takes place on zirconia by transportation of silicon and oxygen across the interface [8,23]. The role of fluorine is likely that of vehiculating silicon in the gaseous phase through SiF_4 complexes [26,27]. In the industrial practice, the starting batch contains the precursor (ammonium metavanadate) in excess with respect to the “optimal” doping, i.e. 3%–5% wt. as vanadium pentoxide, because some will be lost by volatilization [1,4]. Thus, pigment manufacturers cannot exactly predict the amount of vanadium actually inside the zircon structure, that is a consequence of synthesis conditions [23,27–29]. Although the vanadium concentration is the main factor controlling the intensity and stability of turquoise colour, other factors play a relevant role: amount and type of vanadium precursor, synthesis route, particle size, and so on [30–33].

In the literature, there is a long time debate about the valence, oxygen coordination, and localization of vanadium ions responsible of turquoise colour in the zircon crystal structure [8,22,34–47]. Although there is a large convergence on V^{4+} as the chromophore ion, opinions differ significantly about which site is hosting the V^{4+} ions in the zircon lattice. Such disparate viewpoints stem from a remarkably wide range of experimental techniques (Table 1) and produce a patchwork of useful observations, even though none of them individually conclusive. Interestingly, some papers relate the V^{4+} partition among the zircon sites to the amount of vanadium and/or the use of mineralizers [44,46,47]. It is worthwhile noting that most literature data refer to zircon doped with low to very low amount of vanadium, at variance with industrially manufactured pigments, which in most cases still rely on the original patent recipe [6].

The main goal of the present study is to shed light – by cross-checking literature data with new experimental results – on still unanswered questions about the valence state and location of vanadium ions inside the zircon lattice. This achievement would allow the full comprehension of colouring mechanisms in industrial pigments, with

important repercussions on their technological properties and especially the behaviour during micronization and firing.

2. Materials and methods

Materials: four samples of V-doped zircon (named **BM61**, **TZ**, **423** and **5108**, respectively) were investigated to include industrially manufactured turquoise pigments (supplied by four different colorant-makers) in order to widen the range of vanadium concentration and colour properties. No specific information is available on the industrial synthesis conditions and mineralizers employed, beyond a general description of the process [6].

2.1. Chemical and physical characterization

The chemical composition of industrial pigments was performed by X-ray Fluorescence Wavelength Dispersive Spectrometry (XRF-WDS) using a Panalytical Axios spectrometer with experimental conditions (power, voltage and current of the X-ray tube, diffracting crystal, detector window) tailored for each analyte. The sample was melted (1200 °C in platinum crucible with lithium borate-to-sample ratio 9:1) to get a glassy disc (50 mm diameter). Calibration of the counts per concentration straight lines were set up using zircon reference materials. The results obtained in this way (10 replicates) are reported in Table 2.

The morphology of pigment particles was observed under a Scanning Electron Microscope (SEM, Zeiss SUPRA 50VP). Pigment powders were scattered and glued on a copper support, then gold coated.

The particle size distribution was determined by X-ray monitoring of gravity sedimentation, using a Micromeritics SediGraph 5100 apparatus and applying the experimental conditions of ASTM C958 standard. Samples were dispersed by ultrasonic bath in a 0.5% W/W sodium hexametaphosphate aqueous solution. The median particle size (50th percentile of the cumulative curve) is reported in Table 2.

The colour was measured on pigment powders by Hunterlab Miniscan MSXP4000 spectrophotometer equipped with an integrating sphere (illuminant D65, detection angle 8°, 5 replicates). The results are expressed in CIE $L^*a^*b^*$ coordinates, where L^* is brightness (100 = white, 0 = black) while a^* and b^* are chromatic coordinates (+ a^* = red, – a^* = green, + b^* = yellow, – b^* = blue) and $C^* = (a^{*2} + b^{*2})^{0.5}$. Averaged values can be found in Table 2.

2.2. X-ray diffraction data collection and Rietveld refinements

X-ray powder diffraction measurements were performed at room temperature using a Bruker D8 Advance diffractometer on a Bragg-Brentano geometry with a X-ray tube operating at 40 kV and 40 mA. Experimental data were collected by means of a Si(Li) solid-state detector set to discriminate $\text{Cu K}\alpha_{1,2}$ radiation in the 5–130° 2θ angular

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