

UV-VISIBLE-NIR SPECTROSCOPY AND XRPD OF RUTILE PIGMENTS DOPED WITH CHROMOPHORES (Cr, Mn, Ni, V) AND COUNTERIONS (Mo, Nb, Sb, W)

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The high refractive indices and melting point of TiO₂ make it a valuable pigment for ceramic applications, where anatase is progressively converted to rutile on heating. The capacity of the rutile structure to host a number of the first row transition elements allows to get a rather wide colour palette: orange (Cr), brown (Mn), yellow (Ni) and gray (V). Together with the chromophore, a high field strength ion (so-called *counterion*) is added in the industrial practice to achieve the desired colour and improve the technological properties of pigments.

The colouring mechanisms have been not thoroughly investigated, being generally attributed to crystal field transitions, with some role played by a Ti-O charge transfer (EPPLER, 1987; ISHIDA et al., 1990; SORLÍ et al., 2004).

The aim of this work is to understand better these mechanisms on typical industrial co-doped rutile pigments having the stoichiometry Ti_{1-2x}A_xB_xO₂, where A = Cr, Mn, Ni, V (chromophore ion) and B = Mo, Nb, Sb, W (counterion), with x=0.03. Samples were prepared by conventional ceramic process (firing from 700 to 1100 °C). A combination of UV-visible-NIR spectroscopy (diffuse reflectance, Perkin Elmer λ35, 200-1100 nm, integrating sphere, BaSO₄ as reference, standard illuminant D₆₅ and observer 10°) and X-ray powder diffraction (Philips PW 1820/00, monochromated-CuK_{α1,2} radiation, 15-130°2θ, 0.02°2θ/10s) with Rietveld refinement (GSAS-EXPGUI) was used for pigment characterization.

The colour of rutile pigments is determined by both charge transfer (CT) and crystal field (CF) effects: a Ti⁴⁺-O²⁻ CT band shifts from the UV to the visible region with the anatase-to-rutile transformation, contributing to get an intense coloration. A progressive incorporation of chromophore into the rutile lattice produces CF d-d transitions, partially overlapped with the CT band, and complex spectra very difficult to be quantitatively interpreted. Moreover, there are clues that the valence of some transition elements changes during the synthesis: the cell volume is correlated with the weighed cationic radius assuming the following valence, coherent with optical spectroscopic data: Cr³⁺, Mn³⁺, Ni²⁺/Ni³⁺, V⁴⁺, Mo⁵⁺, Nb⁵⁺, Sb⁵⁺/Sb³⁺, W⁵⁺. The cell dimensions *a* and *c* are mainly affected by the ionic radii of chromophores and counterions, respectively, according to the sequences: V<Cr<Mn<Ni and Mo~W<Nb<Sb.

References

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