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Zirconium Titanate Ceramic Pigments: Crystal Structure, Optical Spectroscopy and Technological Properties

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Abstract

Srilankite-type zirconium titanate, a promising structure for ceramic pigments, was synthesized at 1400°C following three main doping strategies: a) $ZrTi_{1-x}A_xO_4$, b) $ZrTi_{1-x-y}A_xB_yO_4$ and c) $Zr_{1-x}C_xTiO_4$ where A = Co, Cr, Fe, Mn, Ni or V (chromophores), B = Sb or W (counterions) and C = Pr (chromophore); $x=y=0.05$. Powders were characterized by XRD with Rietveld refinements and DRS in the UV-Vis-NIR range; technological properties were appraised in several ceramic matrices (frits, glazes and body). Zirconium titanate can be usefully coloured with first row transition elements, giving green and greenish yellow (Co and Ni); orange-buff (Cr and V); tan-brown hues (Mn and Fe). In industrial-like synthesis conditions, a disordered structure as $(Zr,Ti)O_2$, with both Zr and Ti randomly distributed in the octahedral site, is achieved. Doping with chromophores and counterions induces unit cell dimensions variation and causes an oversaturation in zirconium oxide. Optical spectroscopy reveals the occurrence of Co^{2+} , Cr^{3+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , Ni^{2+} , V^{3+} and V^{4+} . The zirconium titanate pigments fulfil current technological requirements for low temperature applications, but exhibit a limited chemico-physical stability for higher firing temperature and in chemically aggressive media.

Key-words: ceramic pigments, crystal structure, order-disorder, optical spectroscopy, zirconium titanate, srilankite

1. Introduction

The zirconium titanate solid solution with Zr:Ti molar ratio ranging from 1:1 to 1:2 is the only stable binary compound in the Zr-Ti-O system [1]. Two structural modifications are known: high temperature disordered $Zr_{1-x}Ti_xO_4$ and low temperature ordered $ZrTiO_4$ [2-4]. The high T disordered phase crystallizes in the orthorhombic α - PbO_2 structure (space group $Pbcn$; setting of the unit cell: $a \cdot b \cdot c=4.7 \cdot 5.5 \cdot 5.0$ Å; Zr and Ti randomly distributed in the octahedral site with $0.41 < X_{Ti} < 0.53$ at 1400°C [3-4]), is stable above 1100°C and persists metastably at lower temperature because the ordering process is sluggish, being associated with a reconstructive transformation and driven by the respective preferences of the Zr and Ti ions for 8(7)-fold and 6-fold coordination respectively [3-4]. There are two types of ordered structures with different stoichiometries both stable below 1200°C [5-6]:

- a) stacking of two layers of distorted Zr sites plus two layers of octahedral Ti sites alternated along the axis a , giving rise to a doubling of the parameter a (cell setting: $a \cdot b \cdot c=9.6 \cdot 5.3 \cdot 5.0$ Å) with respect to the disordered phase; this ordering scheme is consistent with the formula $ZrTiO_4$ (Zr:Ti ratio = 1:1; $X_{Ti} = 0.5$);
- b) Zr is hosted onto one every three cation layer (Zr site approaches 8-fold coordination), so that the parameter a is threefold (cell setting: $a \cdot b \cdot c=14.4 \cdot 5.3 \cdot 5.0$ Å) as consistent with the fersmite-type structure AB_2O_6 ; in this case the formula is close to $ZrTi_2O_6$ (Zr:Ti = 1:2; $X_{Ti} = 0.67$) [3] but the same structure also occurs in $Zr_5Ti_7O_{24}$ (Zr:Ti ratio = 1:1.4) [7].

The mineral srilankite has a composition close to $ZrTi_2O_6$ of the low T ordered compound but both its natural and synthetic forms were reported to possess the orthorhombic α - PbO_2 structure, being thus isostructural with the high T disordered polymorph of $(Zr,Ti)_2O_4$ [8-9].

Zirconium titanate exhibits promising characteristics for an application as a ceramic pigment due to its high melting point ($\sim 1840^\circ\text{C}$), very high refractive indices ($n_x=2.33$, $n_y=2.38$, $n_z=2.41$) and capacity to host into its lattice a large part of the periodic table of elements [10]. Moreover, the presence of a distorted octahedral site with a low point symmetry is favourable to develop intense chromatic effects according to the crystal field theory [11-12]. However, the variable order/disorder of the structure as well as the

changing coordination of zirconium, from an octahedral to a distorted cubic site, are factors whose effects on colouring are unknown.

Zirconium titanate was firstly proposed as ceramic pigment by Hund [10] who designed a huge series of chromophore (*i.e.* transition elements) + counterion (*i.e.* ion added to counterbalance the valence mismatch between chromophore and Ti^{4+}) combinations in order to test their colouring ability. There have been several reports on the effect of chemical substitutions on the properties of the zirconium titanates [13], but no structural or technological studies are available on these materials, apart a contribution on the isostructural compound $Zr(Ti,Sn)O_4$ [14] and another about a new synthesis route of zirconium titanate pigments [15].

The present study is aimed at synthesizing new ceramic pigments, performing their structural, spectroscopic and technological characterisation in order to assess their colourimetric and industrial potentialities.

The design criteria involved the selection of chromophores and counterions utilisable by the ceramic industry for their chemical and technological features (and cost). The chromophores are those currently used to impart colour to Zr- or Ti-bearing pigments, such as rutile (*i.e.* Cr, Mn, Ni, V) or zircon and baddeleyite (*i.e.* Fe, Pr, V). Furthermore, Co was chosen for its well-known colouring capacity [16-17].

2. Experimental

Along with undoped zirconium titanate, the following formulations were designed according to three different strategies:

- addition of chromophore A in substitution of titanium: $ZrTi_{1-x}A_xO_4$, where A is Co, Cr, Fe, Mn, Ni or V and $x=0.05$;
- $ZrTi_{1-x-y}A_xB_yO_4$, chromophore A (*i.e.* Co, Cr, Fe, Mn, Ni, or V) is introduced together with a counterion B (Sb or W) in the same amount ($x=y=0.05$) in replacement of titanium, in order to promote a charge balance of the structure;
- $Zr_{1-x}Pr_xTiO_4$, by replacing Pr after zirconium ($x=0.05$).

These samples are named hereafter with symbols of the chromophore and counterion added. Therefore the series doped with the chromophore only and with the chromophore plus counterion are named with C and C+C, respectively. The undoped zirconium titanate is called 'ZT'.

Reagent-grade oxides of anatase (TiO_2), baddeleyite (ZrO_2), chromophores (Co_3O_4 , Cr_2O_3 , Fe_2O_3 , Mn_2O_3 , NiO, Pr_6O_{11} , V_2O_5) and counterions (Sb_2O_3 , WO_3) were used as raw materials. No mineraliser was added.

The pigments were synthesised by the conventional ceramic process: wet mixing of raw materials in porcelain jar with alumina grinding media, drying in oven at $105^\circ C$, pulverisation in agate mortar, then calcination in alumina crucibles in an electric kiln in static air at maximum temperature of $1400^\circ C$, with thermal rate of $200^\circ C/min$, annealing time (permanence at the maximum temperature) of 1 hour and natural cooling to room temperature.

The calcined samples, previously dry ground in an agate mortar and sieved below $50\ \mu m$, were characterised by structural, spectroscopic and technological viewpoints.

X-ray powder diffraction was performed by a Philips PW1820/00 goniometer using graphite-monochromated $Cu\ K\alpha_{1,2}$ radiation, $15-130^\circ 2\theta$ measuring range, scan rate $0.02^\circ 2\theta$, 10 s per step. The structural refinements were performed by the Rietveld method with the GSAS-EXPGUI software package [18,19]. Starting atomic parameters in the *Pbcn* space group for the disordered polymorph of zirconium titanate were taken from Siggel and Jansen [14] and used for all refinements. Modal fractions of the zirconium titanate and impurity phases detected in the synthesis products were also refined.

Depending upon the number of impurities, the refined variables ranged up to 52 independent variables including: scale-factors, zero-point, 15-21 coefficients of the shifted Chebyshev function to fit the background, zirconium titanate cell dimensions, atomic positions, isotropic displacement parameters and profile coefficients: 1 gaussian (G_W) and 2 lorentzian terms (L_x, L_y). The number of variables and observations as well as the figures-of-merit of all refinements are summarised in Table 1 and an example of a Rietveld refinement plot is showed in Figure 1.

UV-visible-NIR spectroscopy was performed by diffuse reflectance with integrating sphere (Perkin Elmer λ 35) in the 300-1100 nm range, step 0.3 nm, using BaSO₄ as a reference. The positions of the main absorbance peaks in the optical spectra were determined through a deconvolution procedure (PFM, OriginLab), that allowed to obtain averaged values of crystal field strength (Dq_{cub}), peak splitting (δ), crystal field stabilization energy (CFSE), Racah B_{35} parameter and nephelauxenic ratio β_{35} (i.e. B_{35}/B_0 , where B_{35} is experimental and B_0 is the value of the free ion [20]). Dq was estimated by the Tanabe-Sugano diagrams and fitting spin-allowed transitions; B_{35} was calculated by spin-allowed transitions [20-22]; δ was measured as FWHM on some peaks of optical spectra; the crystal field stabilization energy (CFSE) was calculated by Dq values [11].

Technological behaviour was assessed by adding the pigment into different ceramic matrices: porcelain stoneware body (PS); ceramic glazes for floor tiles: porcelain stoneware (S1) and stoneware (S2); ceramic glaze (S3) and frit (F1) for wall tiles. The pigment addition into the body (3% wt) was carried out by wet mixing, slip drying, powder deagglomeration in agate mortar, hand pelletisation (8% wt moisture), uniaxial pressing (40 MPa) of 25 mm-diameter disks, drying in oven (105°C) and firing in an electric kiln in static air. In the case of glazes and frit, the pigment (5% wt) was wet mixed and the slip was sprinkled on porous ceramic tiles, then dried in oven and fired in an electric kiln in static air. The chemical and physical characteristics of ceramic matrices are reported in [23]. Both chromatic appearance and colour stability were evaluated by measuring the CIELab parameters L^* , a^* , b^* , and $\Delta E^*=(\Delta L^* + \Delta a^* + \Delta b^*)^{0.5}$ by diffuse reflectance spectroscopy in the visible range (HunterLab Miniscan MSXP4000, 400-700 nm, white glazed tile reference $x=31.5$, $y=33.3$). ΔE^* expresses the total chromatic change with respect to a reference: the lower ΔE^* , the more stable the pigment.

3. Results

3.1. X-ray powder diffraction

The undoped zirconium titanate (ZT), as formed in our synthesis conditions, has crystallographic features similar to those of the disordered structure of the high T polymorph of ZrTiO₄, in which Zr and Ti (ratio 1:1) are expected to be randomly distributed in one crystallographically independent octahedral site. Disorder is first indicated by the absence in the XRD patterns of the superstructure reflections which have been observed in the ordered low T polymorph of ZrTiO₄ [3,5]. The b dimension of the ZrTiO₄ unit cell has been reported to vary from about 5.33 Å to 5.53 Å as a function of the ordering degree, the largest value being for the more disordered phase [6]. The b -axis length refined in our undoped ZrTiO₄ sample (5.467 Å) is consistent with an essentially disordered state. The large cooling rate ($> 100^\circ\text{C}/\text{h}$), as inferred from the b -axis [6], agrees with the evidences that natural cooling (as applied in our process) usually preserves the disordered structure [24,25]. Furthermore, the absence of any ZrO₂ phase in the undoped (Zr,Ti)₂O₄ sample and the refined occupancy of the octahedral site both indicate a Zr:Ti ratio close to 1:1. On the contrary, all the doped and co-doped samples, except CrW, are not monophasic but present secondary phases such as baddeleyite (ZrO₂), rutile (TiO₂) and tialite (Al₂TiO₅). The latter impurity phase, unexpected from the starting batch composition, is explained by the reaction of Al₂O₃, deriving from contamination by alumina grinding media, with TiO₂

during calcination. Compared to the undoped sample, both the series C and C+C, show a strong regular decrease of the *b* cell parameter (Fig. 2b), which is responsible for the overall contraction of the unit cell volume (see also Tab. 3). At the same time a moderate and slight increase is observed for the *a* (Fig. 2a) and *c* (Fig. 2c) cell parameters, respectively, the variation of the latter being more regular. Samples V and VW are the only ones showing the *c*-axis smaller than ZT. Despite their regularity, these trends cannot be simply explained on the basis of different ionic size of atoms involved in isomorphous substitutions. As previously discussed, the *b*-axis shortening might be explained by an increased degree of ordering brought about by doping. In fact it is known that little uncoupled substitutions of trivalent ions (e.g. Y³⁺) for Zr⁴⁺ are able to enhance the ordering kinetics, presumably through the introduction of oxygen vacancies [13]. Figure 2b shows that the *b* contraction is actually larger for C series compared to the C+C one. A clear inverse relationship is observed between the *b*-axis length and the amount of baddeleyite (ZrO₂) refined in doped and co-doped samples (Fig. 3). This behaviour reveals an increasing departure from the designed Zr:Ti=1:1 stoichiometry towards the Zr:Ti=1:1.4 or Zr:Ti=1:2 molar ratios of the zirconium titanate phase present in the mixture as related to the shortening of the *b*-axis. The presence of small amounts of exsolved ZrO₂ was previously reported upon formation of the ordered polymorph of undoped zirconium titanate [2]. Therefore, the increasing excess of ZrO₂ can be taken as an additional evidence for the increased degree of ordering of doped and co-doped samples. It should be noted, however, that the presence of the Al₂TiO₅ phase in many samples may be also responsible for an excess in ZrO₂ likely to crystallize as baddeleyite (Fig. 14). The refined occupancies in the octahedral site (Table 3) are consistent with the Ti-enrichment of the zirconium titanate pigments. Hence, a compositional variability (0.47<*x*<0.64) can be inferred for the synthesized Ti_{1-x}Zr_xO₄ compounds corresponding to the compositions expected for the disordered phase [3-4] or even with a slight Ti excess, in the midway to the srilankite field.

The above results are somehow in contrast since, on one side, the shortening of the *b*-axis and the presence of exsolved ZrO₂ might be both regarded as indications of cation ordering within the Zr-Ti layers of doped and co-doped samples, while, on the other side, the absence of superstructure peaks in all zirconium titanate pigments and the satisfactory quality of structure refinements performed with the disordered structure model (space group *Pbcn*; setting of the unit cell: *a* · *b* · *c*=4.7 · 5.5 · 5.0 Å) clearly show that all samples retained a mainly disordered state. This situation is very similar to what reported by Sham et al. [26] for zirconium titanate samples synthesized by sol-gel and treated at 1000°C. The authors successfully performed crystal structure refinements based on the disordered model (no superstructure peaks were reported) while the occupancy refinements of Zr/Ti ratio and the coexistence of a ZrO₂ phase, showed that the stoichiometry of samples was close to Zr₅Ti₇O₂₄, as for the ordered structure. From the above considerations, our zirconium titanate pigments are consistent with the srilankite-type structure in which the Zr/Ti disordered state coexists with a Ti-enriched stoichiometry.

3.2. Optical spectroscopy

The sample ZT exhibits a weak light absorption in the violet region, probably connected with a metal-ligand charge transfer (CT) analogue to the well-known Ti⁴⁺-O²⁻ CT in rutile [12]. However, comparing the two spectra (Fig. 5), it is clear that the position of the CT band of zirconium titanate is shifted to higher energies as well as the band slope is much less inclined, so playing minor effects on the visible range. At all events, some overlappings of CT and crystal field (CF) effects may occur, making more difficult the quantitative interpretation of optical spectra with measurement of CF strength (*Dq*) as well as interelectronic repulsion Racah B parameter. In order to enhance the resolution of CF

peaks in the blue to UV range, the CT contribution was removed by systematic subtraction of the spectrum of undoped zirconium titanate.

The wavenumbers of CF peaks and band width (δ), the inferred values of average (cubic) Dq and Racah B_{35} as well as the calculated crystal field stabilization energy (CFSE) and nephelauxenic ratio (β_{35}) are listed in Table 5. For simplicity safe, CF peaks are described as the symmetry of octahedral site would be cubic, despite the point symmetry of the $(Zr,Ti)O_6$ is C_2 . Just in case of a conspicuous peak splitting the terminology is referred to a lower symmetry group.

3.2.1. Cobalt doping

Two main effects are found in the case of cobalt doping, as broad bands around 16500 and 23000 cm^{-1} respectively, plus an absorbance increase below 10000 cm^{-1} that is likely to be the tail of a peak centred at wavenumbers just below 9000 cm^{-1} (Fig. 6). All these peaks can be attributed to Co^{2+} in octahedral coordination and particularly to the CF transitions: ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{2g}({}^4F)$ at ~ 9000 cm^{-1} (ν_1), ${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F)$ at ~ 16500 cm^{-1} (ν_2) and ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$ at ~ 23000 cm^{-1} (ν_3). These spectral features indicate a CF strength Dq around 880 cm^{-1} and B_{35} values in the 600-690 cm^{-1} range. The ν_2 transition appears to be clearly threefold splitted (${}^4A \rightarrow {}^4A$ 4B 4B) according to the low point symmetry of the $(Zr,Ti)O_6$ octahedron [11-12]. This splitting is as wide as ~ 2600 cm^{-1} in the CoSb and CoW pigments and ~ 2750 cm^{-1} in the Co sample.

3.2.2. Chromium doping

The occurrence of Cr^{3+} into the zirconium titanate lattice generates two main parity-forbidden transitions: $\nu_1 = {}^4A_{2g}({}^4F) \rightarrow {}^4T_{1g}({}^4F)$ and $\nu_2 = {}^4A_{2g}({}^4F) \rightarrow {}^4T_{2g}({}^4F)$, that are observable as broad absorbance bands centred approximately at 14000 cm^{-1} and 19000 cm^{-1} respectively (Fig. 7). The CF strength varies in the 1420-1490 cm^{-1} range, while the B_{35} values fluctuate widely from 400 to 640 cm^{-1} , due to some uncertainties in deconvolving the broad ν_2 band. The low point symmetry of the Cr^{3+} site causes a threefold splitting of the ν_1 transition, as wide as ~ 1300 cm^{-1} , with a considerable broadening of the ν_2 peak.

3.2.3. Fe-doped srilankite

The spectra of iron-doped zirconium titanate present a single absorbance peak at ~ 20500 cm^{-1} , due to the predominant ${}^6A_1({}^6S) \rightarrow {}^4E, {}^4A({}^4G)$ transition of Fe^{3+} in octahedral environment (ν_3). Further very weak bands may be deconvolved at about 13500 cm^{-1} and 15500 cm^{-1} , corresponding to the spin-forbidden transitions $\nu_1 = {}^6A_1({}^6S) \rightarrow {}^4T_1({}^4G)$ and $\nu_2 = {}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$ respectively (Fig. 8).

The DRS curves of Fe and FeW samples are very similar, while the FeSb co-doping causes an absorbance increase in the 9000-20000 cm^{-1} range, whose origin could be related to the occurrence of a significant amount of baddeleyite. In fact, this latter oxide is able to host iron (and particularly Fe^{2+}) inside its lattice, with increased light absorption in the red-orange region. The Dq values, widely ranging in between 1200 and 1400 cm^{-1} , are inferred with many uncertainties due to the low definition of the spin-forbidden peaks.

3.2.4. Mn-doped srilankite

There is a clear difference between the spectra of Mn and MnSb on one side and that of MnW on the other: the former exhibit absorbance curves regularly increasing from NIR to UV, with two weak bands around 18000 and 24000 cm^{-1} ; the latter presents a lower absorbance in the IR-visible range, with two sharper bands centred at ~ 14500 and ~ 20000 cm^{-1} respectively (Fig. 9). These features are consistent with the occurrence of both Mn^{2+} and Mn^{3+} in octahedral coordination, being the strong band at ~ 24000 cm^{-1} attributable to the ${}^6A_1({}^6S) \rightarrow {}^4E, {}^4A({}^4G)$ transition of Mn^{2+} (ν_3), while the other two peaks may be interpreted

as either the widely splitted transition ${}^5E_g({}^5D) \rightarrow {}^5T_{2g}({}^5D)$ of Mn^{3+} in a distorted environment [12] or the spin-forbidden transitions ν_1 and ν_2 of Mn^{2+} . In the hypothesis of Mn^{3+} – that is the valence of manganese precursor used in our synthesis – Dq would vary from 1470 to 1730 cm^{-1} , with a peak splitting between 4600 and 7600 cm^{-1} . Though a reduction to Mn^{2+} during calcination was already recorded in other systems, such as TiO_2 [27-28], it would bring about a position of the ν_3 band that is shifted to rather high energies. At all events, Dq values, fluctuating between 970 and 1270 cm^{-1} , are just indicative, since the position of the very weak bands ν_1 and ν_2 is uncertain.

3.2.5. Nickel doping

The DRS patterns of Ni-doped zirconium titanate are similar in all samples: a complicated structure with several weak peaks characterises the IR-to-green region, while a rapidly growing absorbance occurs from blue to the near UV (Fig. 10). These effects can be explained by crystal field transitions of Ni^{2+} in an octahedral site, being the main band at $\sim 24000\text{ cm}^{-1}$ attributable to the ν_3 transition ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3P)$ and the three peaks in the 11000-14000 cm^{-1} range to a threefold splitting of the ν_2 transition ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3F)$. The further couple of peaks in the 15000-17000 cm^{-1} interval could be due to a split spin-forbidden transition ${}^3A_{2g}({}^3F) \rightarrow {}^1E_g({}^1D)$ though its position would be expected in the green-blue region, according to the Tanabe-Sugano diagram [12]. In this framework, the weak increase of absorbance below 10000 cm^{-1} is expected to be the tail of the ν_1 transition ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{2g}({}^3F)$. This interpretation is supported by Dq values (in d^8 configuration $10Dq = \nu_1$) just below 900 cm^{-1} . The splitting of the ν_2 transition is about 1500 cm^{-1} .

3.2.6. Praseodymium doping

The substitution of praseodymium for zirconium does not produce any colouring, as it gives rise just to a very low absorbance in the entire visible range, apart some weak peaks attributable to f-f transitions of the lanthanide. In contrast, the same replacement in zircon develops an intense yellow colour due to the total absorption of the violet light [29]. This different behaviour can be justified both in terms of diverse point symmetry (C_2 in zirconium titanate versus D_{2d} in zircon) and mean metal-oxygen distance of the Pr ion (2.047 Å in zirconium titanate instead of 2.196 Å in zircon).

3.2.7. Vanadium doping

The optical spectra exhibit a gradual increase of absorbance toward the UV region, with two weak bands around 16000 and 23000 cm^{-1} (Fig. 11) that are referable to V^{3+} in octahedral environment and particularly to the parity forbidden transitions $\nu_1 = {}^3T_1({}^3F) \rightarrow {}^3T_2({}^3F)$ and $\nu_2 = {}^3T_1({}^3F) \rightarrow {}^3T_1({}^3P)$. Values of Dq and B_{35} are found to vary in a limited range: 1680-1710 cm^{-1} and 770-840 cm^{-1} respectively. However, these spectra cannot be successfully deconvolved unless a third band – with an intermediate wavenumber between ν_1 and ν_2 of V^{3+} – is involved. This band, centred approximately at 20000 cm^{-1} , may be referred to the ${}^2T_{2g}({}^2D) \rightarrow {}^2E_g({}^2D)$ transition of V^{4+} in an octahedral site, that is likely to occur because the precursor is a pentavalent vanadium oxide. The occurrence of the V^{4+} ion in ceramic pigments, already found in zircon and baddeleyite, gave rise to a clearly split transition, for instance 12500 and 15700 cm^{-1} in zircon [30-32]. In any case, the very low resolution of our spectra does not allow any inference about this kind of peak splitting.

3.3. Technological properties

The chromatic performances of currently used ceramics pigments is contrasted with those of zirconium titanate pigments (Fig. 12). These latter exhibit the following colours: light green (Co), greenish yellow (Ni), light brown-tan (Fe and Mn), orange-buff (Cr and V). All these colours are less saturated than the correspondent industrial pigments. As a matter of fact, Co and CoSb samples are quite close to the field of Co-chromite, while CrW, MnW and VSb samples develop colours in between of V-zirconia and Cr-rutile. Ni samples exhibit an original green-yellow hue, however much less intense than the mixture of yellow and turquoise zircon [6,17,32]. Zirconium titanate pigments behave in a different way into low temperature versus high temperature ceramic glazes and frits as well as in through-body applications. This ceramic behaviour was assessed by considering the chromatic changes in different matrices (frit, glazes, body) and temperatures (Tab. 6 and Fig. 13).

3.3.1. Low temperature applications

Once the pigments are applied in a typical boric-alkaline frit, utilised for ceramic products fired at low temperatures (e.g. double-fired porous tiles, earthenware and majolica tableware) the colour achieved at 950°C is the same of the Co-, Mn- and Ni-doped zirconium titanate, while the orange-buff hue of Cr- and V-bearing pigments is even enhanced in saturation once dispersed into the glass.

The behaviour of zirconium titanate in the chemically aggressive environment of the molten frit – rich in lead, zinc, and magnesium among others – is rather good for Cr-, Mn- and V samples, that do not change appreciably their colour increasing the firing temperature to 1000°C. In the same condition, a colour virage (from green to light brown) occurs in the case of frit containing Co- and Ni-doped pigments.

3.3.2. High temperature glazes

The thermal stability of zirconium titanate appears to be dramatically reduced in ceramic applications such as glazed tiles, that couple high temperature (from 1100 to over 1200°C) with very aggressive chemical environments, due in particular to high concentrations of calcium, zinc and magnesium into the molten glaze. Zirconium titanate is partially decomposed in *monoporosa* or stoneware firing conditions, so that its colour fades in every case to a light brown hue. Exception is made of glazes containing the Co pigment, which become gradually bluer at increasing firing temperatures; in this case, the breakdown of zirconium titanate makes it available an increasing amount of Co²⁺ dissolved in silicate melts, where it imparts a well-known blue coloration to silicate melts, a phenomenon known as “cobalt bleeding” [33,34].

3.3.3. Through-body applications

The pigment dispersion in an opaque medium, such as a porcelain stoneware body, brings about both a colour dilution and contamination by the light yellow hue of the ceramic matrix. These phenomena account for the consistent reduction of colour saturation occurring in coloured bodies, when compared to the correspondent zirconium titanate pigments, and the shift toward the colour of the undoped body (Fig. 14). Within this general trend, the Co and V pigments appear to be more resistant to the attack of the liquid phase developed at the high temperature of porcelain stoneware firing (1200-1250°C) because the colours of bodies are still relatively close to those of pigments. In contrast, zirconium titanates containing Ni, Mn or Cr are heavily attacked by the liquid phase, since their coloration approaches that of the undoped body.

4. Discussion

As previously described, the results of crystal structure analysis suggest that all the studied srilankite-type pigments are characterized by an essentially disordered structure, although the shortening of the *b*-axis in doped and co-doped samples could be taken as an indication for a progressively increased degree of Zr-Ti ordering. Assuming that the variation of the *b*-axis is mainly (or only) controlled by the order/disorder kinetics, the combination of diffraction and spectroscopic data can be used to explain the quite regular variation of the *c*-axis as being proportional to the ionic radii differences (Figure 2c). In fact, spectroscopy data revealed the following valences for the different chromophore ions (Shannon [35] ionic radii in parentheses): Co²⁺ (0.75 Å), Cr³⁺ (0.62 Å), Fe³⁺ (0.65 Å), Mn²⁺ (0.83 Å) and Mn³⁺ (0.65 Å), Ni²⁺ (0.69 Å), V³⁺ (0.64 Å) and V⁴⁺ (0.58 Å). By considering these valences for each ion, it is expected that the Cr³⁺, Fe³⁺ substitution for Ti⁴⁺ (0.61 Å) and the Co²⁺, Mn²⁺ substitution for Zr⁴⁺ (0.72 Å) would increase the *c*-axis length, while the V⁴⁺ substitution for Ti⁴⁺ and the Ni²⁺ substitution for Zr⁴⁺ would shorten the *c* axis. The expected variations are actually confirmed by the unit cell modifications from XRD, with the only exception of Ni-doped samples. Regarding the C+C series, it can be observed in Figure 2 that W generally induces a decreasing of both the *a*- and *c*-axis, while the Sb co-doping determines a decrease of the *a* cell parameter and a lengthening of the *c* axis. Simply based on these considerations, the presence of W⁵⁺ (0.62 Å) or W⁶⁺ (0.60 Å) and Sb³⁺ (0.76 Å) can be inferred from the refined unit cell parameters. The inferred trivalent state of Sb ions, however, disagrees with the assumption that Sb⁵⁺, similarly to W⁵⁺, would balance Cr³⁺, Mn³⁺, Fe³⁺ and V³⁺ in replacement of Ti⁴⁺. In the case of Sb³⁺ incorporation, the charge balance could be accomplished through a mechanism of oxygen vacancies. Therefore, we suggest that charge mismatch is compensated by counterion substitution only in the case of W addition, while samples co-doped with Sb should present anion

vacancies. This latter hypothesis would require additional investigation, for instance, by neutron diffraction, to be supported. The valence of doping and co-doping ions is likely to remarkably affect the presence and amount of impurity phases. In fact, DRS spectroscopy suggests unexpected valences for Ni, Mn and Co ions (Ni^{2+} , $\text{Mn}^{2+,3+}$ and Co^{2+}) replacing Zr^{4+} , compared to the predicted ones (Ni^{3+} , Mn^{2+} and Co^{3+}) in substitution of Ti^{4+} . This would lead to a batch enrichment in ZrO_2 that would crystallize as baddeleyite. The different amount of accessory phases from the series C with respect to the series C+C is due to the fact that W^{5+} or W^{6+} substitutes Ti^{4+} while Sb^{3+} substitute Zr^{4+} , therefore co-doping with Sb should lead to higher amounts of ZrO_2 .

Concerning the coordination environment around the chromophore ions, the results from structure refinements provide an average picture which might be significantly different from the local situation around the absorbing ion, as inferred from spectroscopy. However it is of some interest to compare this long and short range information. The refined mean metal-oxygen distances are practically the same in all samples, but apical (M-O2) and equatorial (M-O1, M-O3) lengths of the (Ti,Zr) O_6 octahedron are very different, bringing about an increased distortion. In reality, it is more likely that each cation would occupy the octahedron with its own bond lengths, according to a model of partial relaxation of the zirconium titanate lattice [22,36]. More in detail, the doping with elements acting as chromophores or counterions causes elongation of (Ti,Zr) O_6 octahedra and increases the degree of distortion, compared to ZT, with the exception of samples VW and FeW (Fig. 15). The C series exhibits an elongation of the apical distance (M-O2) and a shortening of the mean equatorial metal-oxygen distances. The co-doping with W determines a flattening of the octahedra, except sample MnW, while concerning equatorial distances the variations were not relevant in most cases, except the considerable shortening in samples VW and FeW. Antimony addition brings about a wider range of situations; in fact, it determines an elongation of the octahedra in samples NiSb and CrSb, while in the other samples it is not easy to outline a unique trend concerning both the apical and equatorial distances.

The spectroscopic data are generally consistent with the above structural characteristics of zirconium titanate pigments; in fact, the crystal field theory predicts that the optical absorptions occur at energies that are dependent on the crystal field strength Dq and the mean metal-ligand distance R , according to the relationship:

$$10Dq = 5q \langle r^4 \rangle \langle R \rangle^{-n}$$

where q is the effective charge on the ligands, $\langle r^4 \rangle$ is the mean of the fourth power of d-electron-core distance, $\langle R \rangle$ is the mean metal-oxygen distance in the octahedron, and n is an exponent, widely varying between 2 and 9, that is theoretically equal to 5 in the point charge model approximation [12,37].

Literature data of Dq and $\langle R \rangle^{-5}$, measured on several oxides and silicates, are contrasted in Figure 6 for the various chromophores [11]. It results that Dq values of zirconium titanate pigments are at wavenumbers reasonably predicted by the CF theory on the basis of their $\langle R \rangle^{-5}$. In contrast, comparing the C and C+C series, no significant dependence of Dq and $\langle R \rangle^{-5}$ seems to arise, being the maximum variation in most cases $< 50 \text{ cm}^{-1}$ and $< 0.5 \text{ pm}$ respectively. Account must be taken that our spectroscopic measurements have an insufficient sensibility to small differences of Dq . Moreover, X-ray diffraction determines an averaged value of $\langle R \rangle$ that is known to be significantly different from the real value for the chromophore ion [22-37].

A threefold splitting of CF peaks is expected due to the low point symmetry (C_2) of the chromophore in the distorted octahedral site of zirconium titanate. It is possible to observe this splitting in ν_1 peaks of Cr^{3+} (and perhaps Mn^{3+}) as well as in ν_2 bands of Ni^{2+} and Co^{2+} . The full width at half maximum of these bands (δ , Table 4) is actually proportional to the degree of distortion of the octahedron (Δ_6 , Table 3) in the case of Co-, Cr- and Ni-

doped pigments, but for CrW. In particular the Mn^{3+} band exhibits a very wide splitting ($>4600\text{ cm}^{-1}$) that may be tentatively related to the well known Jahn-Teller effect of this ion in distorted sites, though the very scarcely resolved optical spectrum.

The nephelauxenic ratio β_{35} increases with the addition of W and further with Sb, suggesting an increasing ionicity degree of the chromophore-oxygen bonding in presence of counterions.

5. Conclusions

Zirconium titanate can be coloured with first row transition elements, giving rise to different colours depending on the metal used. In industrial-like synthesis conditions, zirconium titanate has a srilankite-type disordered structure, where Ti and Zr are randomly distributed in a unique octahedral site and the phase composition is enriched in Ti.

The addition of chromophores (Co, Cr, Fe, Mn, Ni, Pr or V) induces a cell volume contraction mainly due to the strong shortening of the b axis, which is possibly caused by an increasing degree of ordering (at the short range) while the average structure maintains a disordered state. The shortening of the b -axis is accompanied by a slightly lengthening of the c and a unit-cell parameters. These variations are not fully consistent with an averaged ionic radius, calculated by assuming the ion oxidation state and occupancy within the octahedral site. Associated to the unit-cell variations, the refined metal-oxygen distances and distortion degree of the $(\text{Zr,Ti})\text{O}_6$ octahedron vary across the series in such a way that any change in the apical M-O bond length seems to be counterbalanced by an opposite change of the equatorial ones. It follows that the averaged M-O distances are almost the same in all pigments but with a different distortion degree.

Doping of zirconium titanate promotes an exsolution of ZrO_2 , mainly due to the stoichiometry shift of the Zr:Ti ratio from 1:1 to nearly 1:2 of the srilankite-type phase but also related to the presence of Al_2O_3 impurity. Accordingly, coloured srilankite is almost systematically associated with baddeleyite. When Sb or W counter ions are added, in order to ensure the charge neutrality of the structure, it appears that different charge balancing mechanisms are operating: formation of anion vacancies seems to be present in the former case while a coupled heterovalent substitution is acting in the latter. This implies that only tungsten addition actually increases the Zr solubility in the zirconium titanate phase.

Optical spectroscopy indicates the occurrence of the following valences: Co^{2+} , Cr^{3+} , Fe^{3+} , Mn^{2+} , Mn^{3+} , Ni^{2+} , V^{3+} , V^{4+} . There is a reasonable agreement between Dq and metal-oxygen distance, as predicted by the crystal field theory. The effect of counterions on Dq is scarce, but a clear influence on B_{35} arose, implying a reduced covalent character of M-O bonding when Sb or W are added. However, the colour of pigments changes significantly upon the addition of a counterion with a complex dependence on Dq and B , not generalisable.

Zirconium titanate pigments exhibit different technological properties depending on the chromophore and on the different ceramic applications, where interesting green (Co), greenish-yellow (Ni) and orange-buff hues (V, Cr, Mn) are obtained. The colour development and stability is excellent in low temperature applications, such as glazes for double-fired wall tiles, majolica and earthenware. The technological performance of zirconium titanate is clearly reduced in high-temperature applications (such as body and glazes for porcelain stoneware) or especially in strongly aggressive molten glazes (such as those rich in CaO, ZnO and MgO used in *monoporosa* and stoneware tile decoration). At all events, the behaviour of srilankite-based pigments is not suitable for through-body applications.

The colouring performance of zirconium titanate pigments appears to be worse than expected on the basis of general CF considerations, taking into account the presence of a

unique octahedral site with a low point symmetry. The scarce colouring properties obtained seem to be connected with: simultaneous occurrence of multiple valences, absence of CT effects, large CF splitting due to site distortion and occurrence of local situations where the chromophore ion is hosted.

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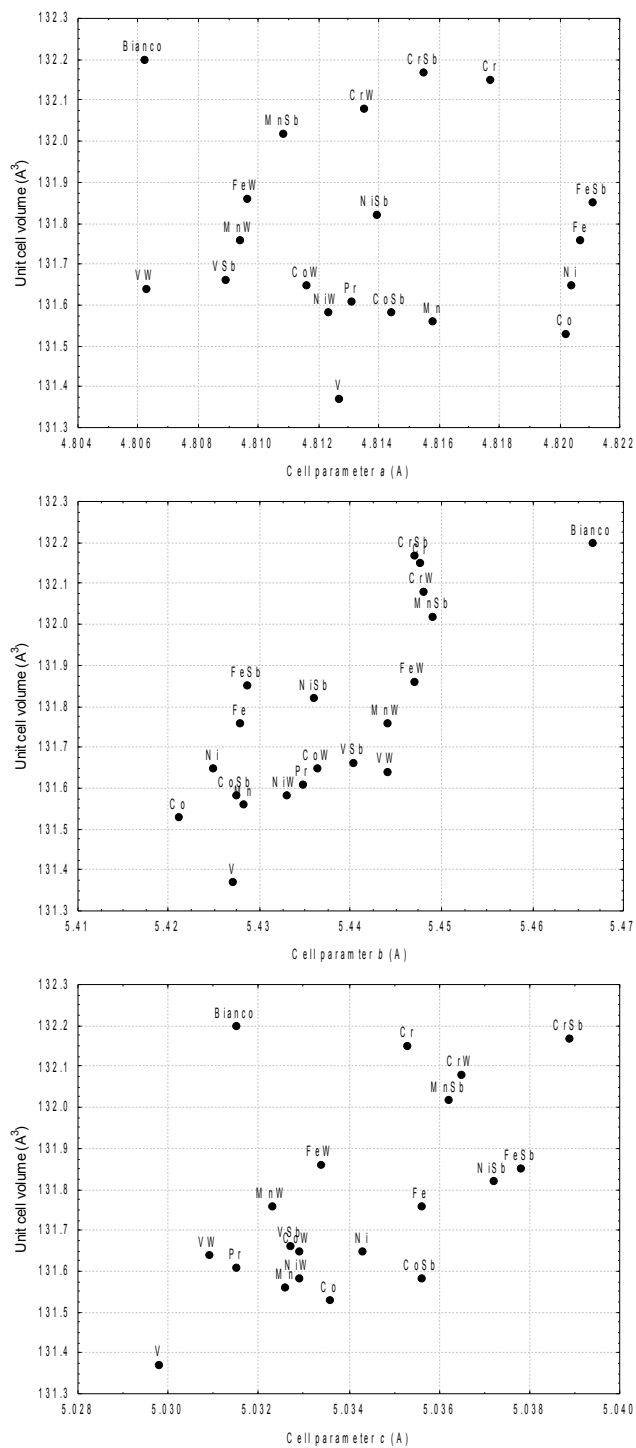


Figure 2 – Plot of the cell parameters $a(a)$, $b(b)$, $c(c)$ vs. unit cell volume.

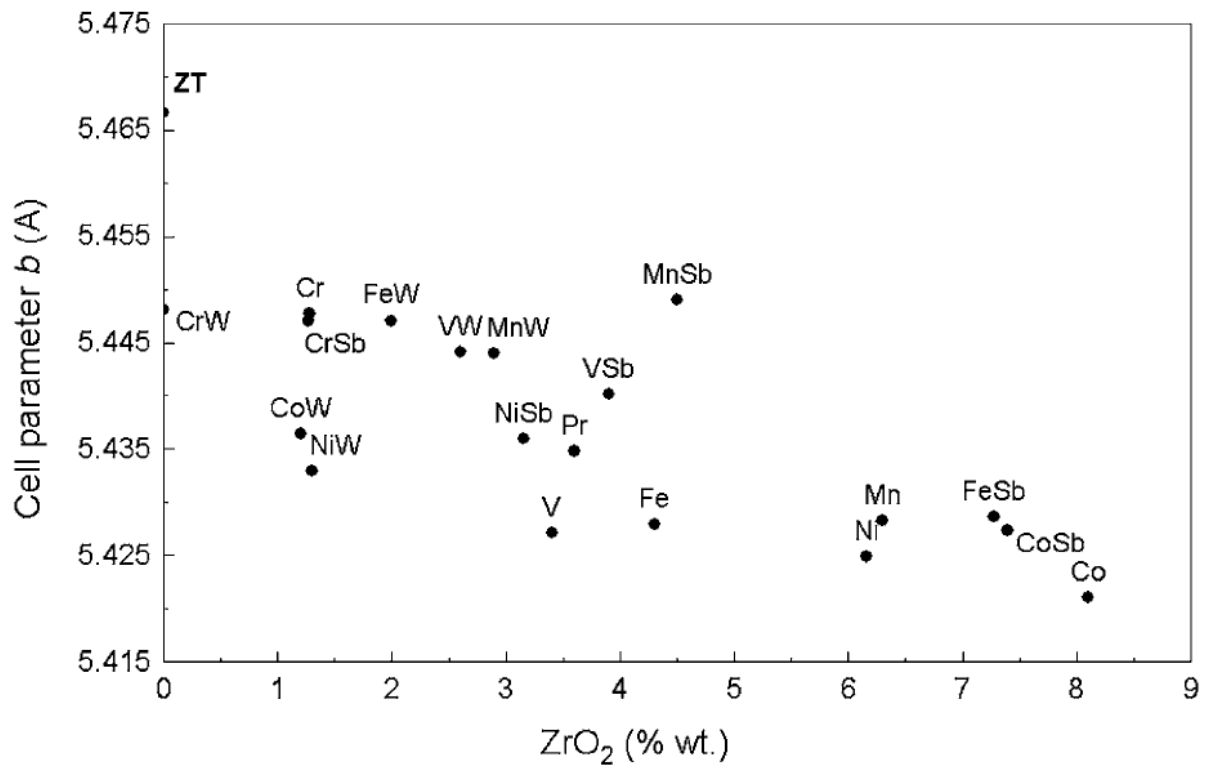


Figure 3 – Plot of the amount of the accessory phase ZrO₂ (expressed in % weight) vs. cell parameter *b*.

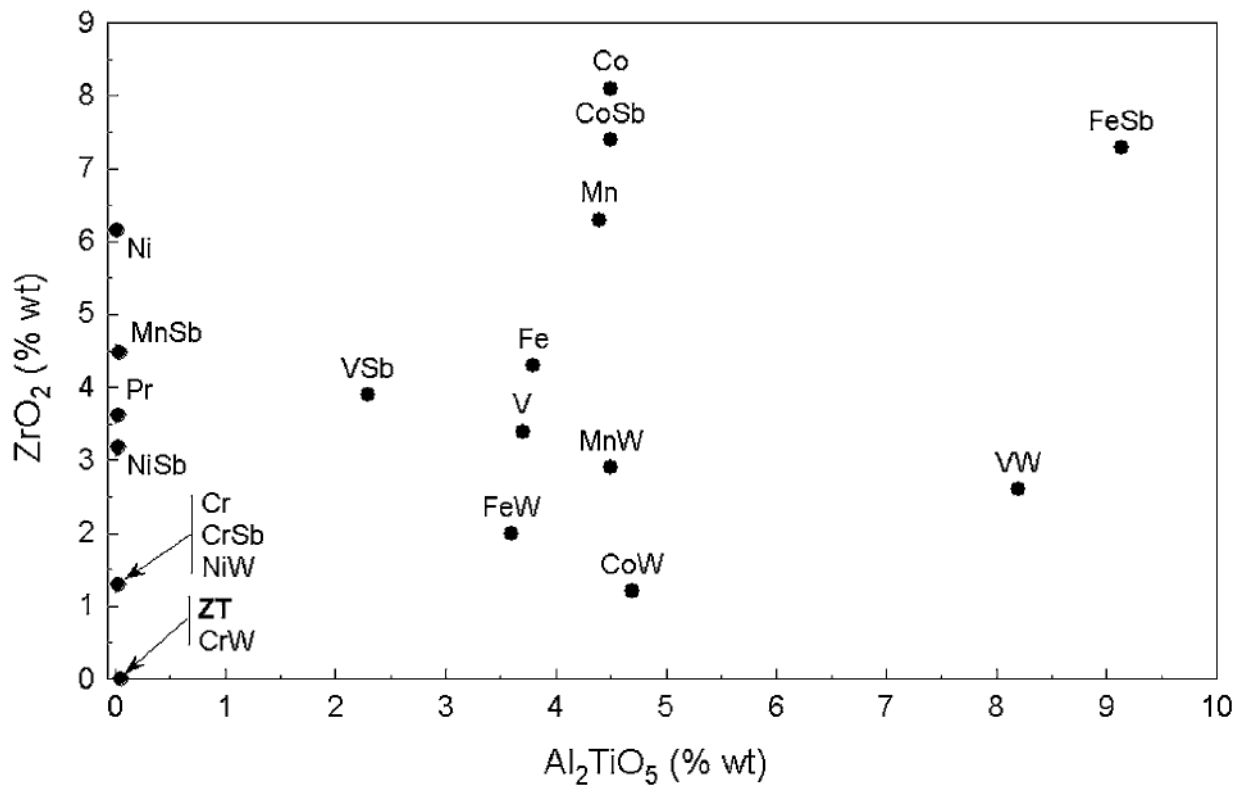


Figure 4 – Plot of the amount of the accessory phase Tialite (Al₂TiO₅) vs. amount of the accessory phase baddeleyite (ZrO₂).

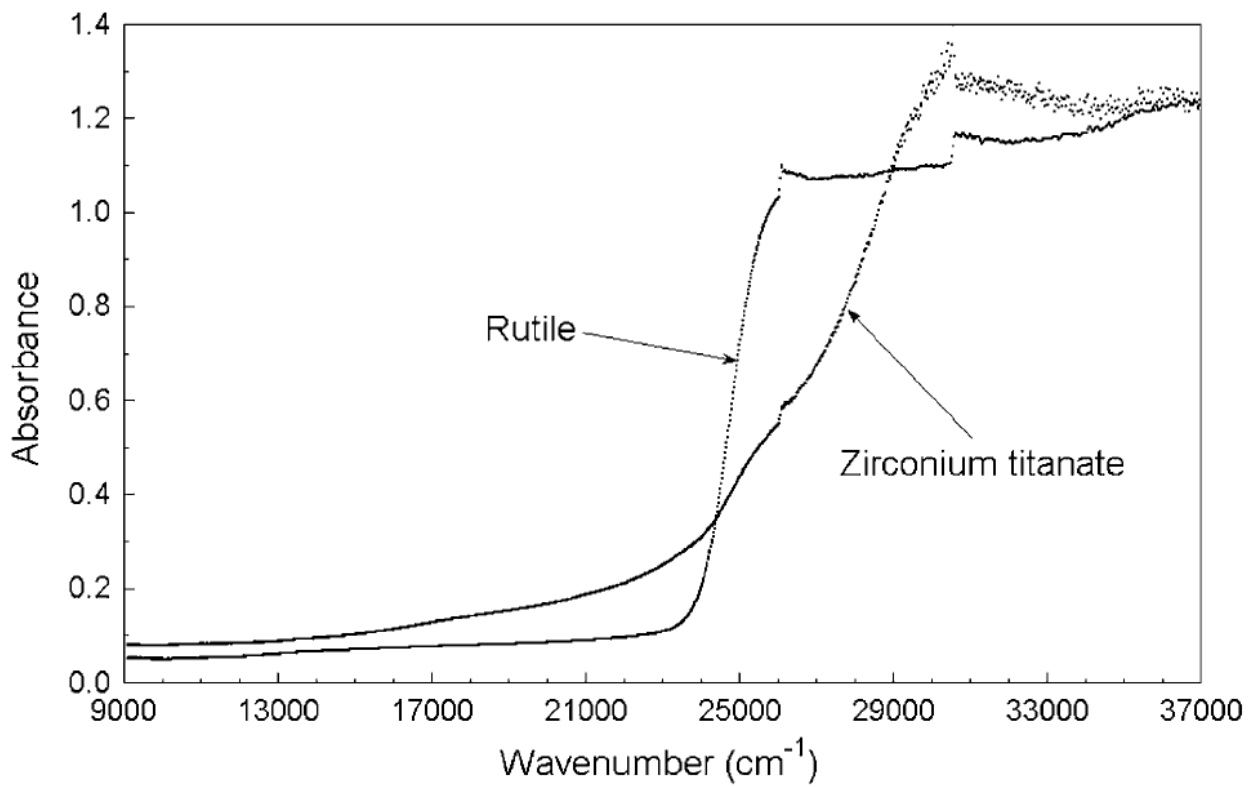


Figure 5 - UV-visible-NIR spectra of zirconium titanate and rutile.

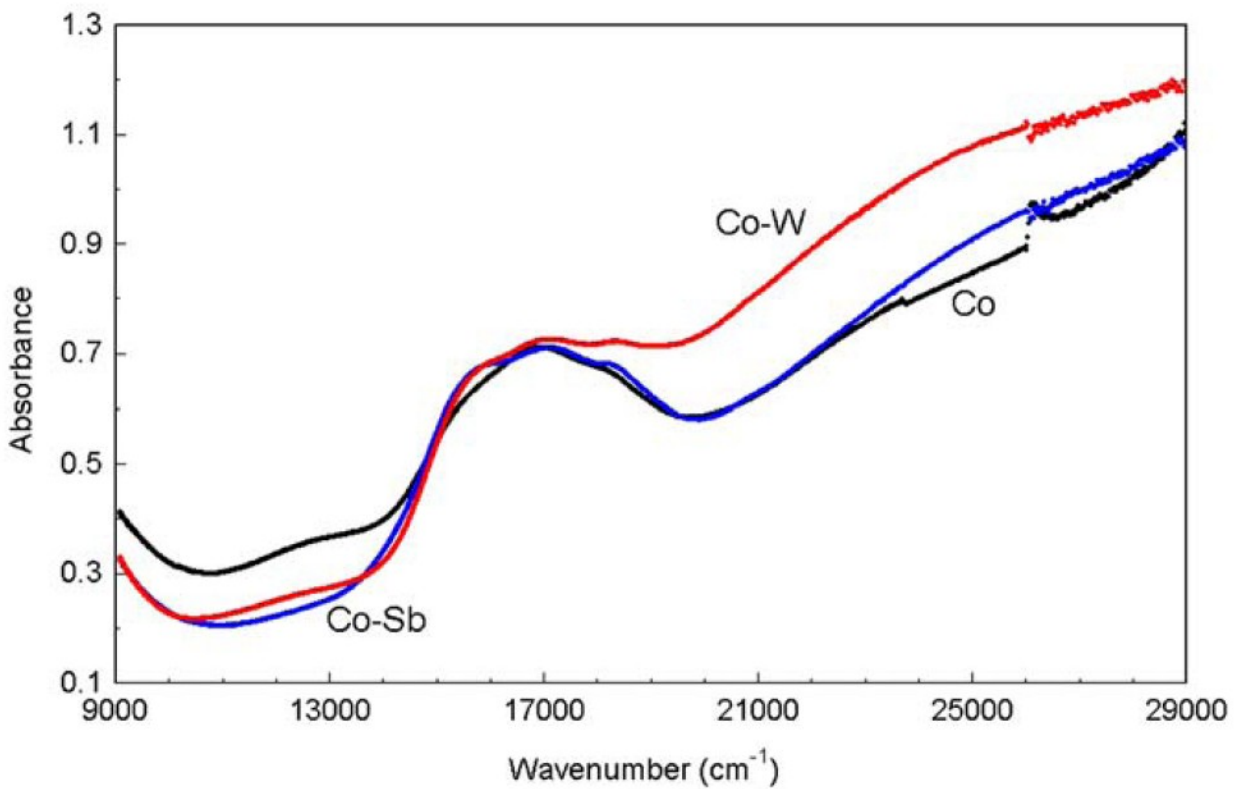


Figure 6. UV-visible-NIR spectra of zirconium titanate pigments doped with cobalt and co-doped with counterions.

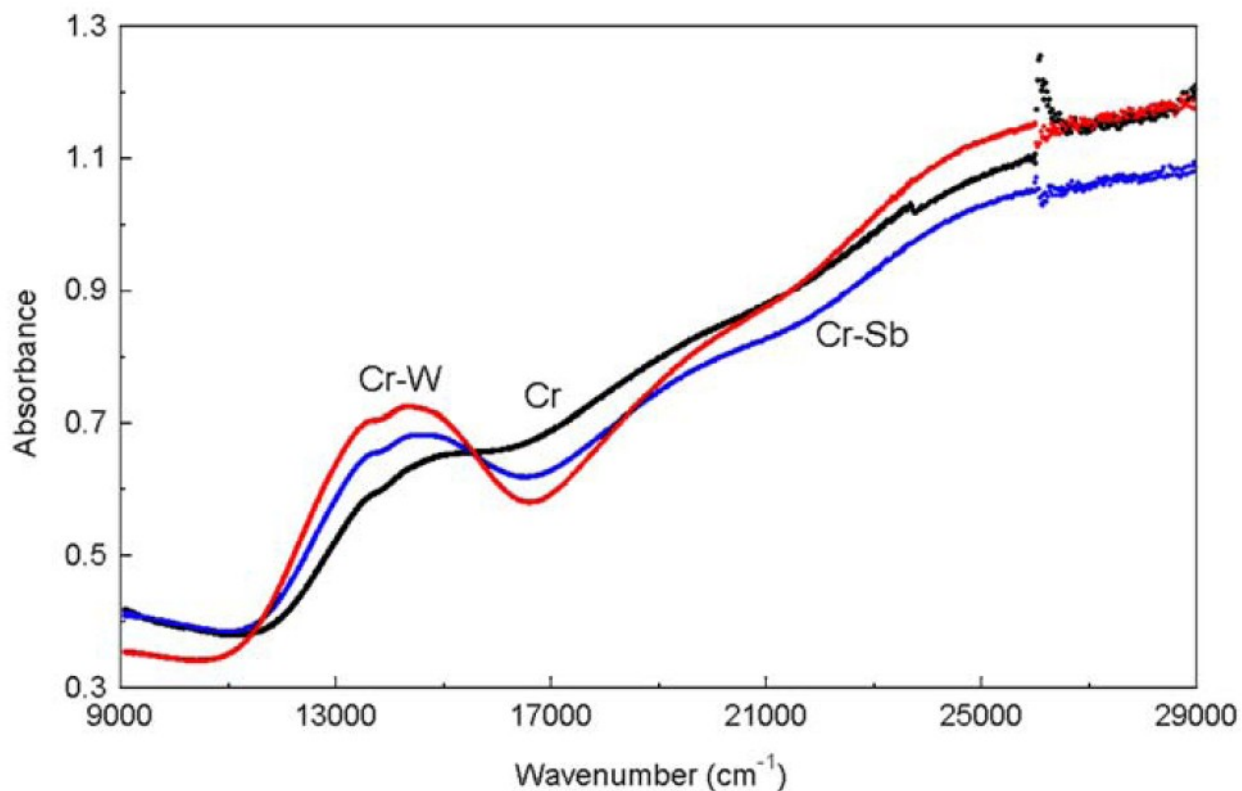


Figure 7. UV-visible-NIR spectra of zirconium titanate pigments doped with chromium and co-doped with counterions.

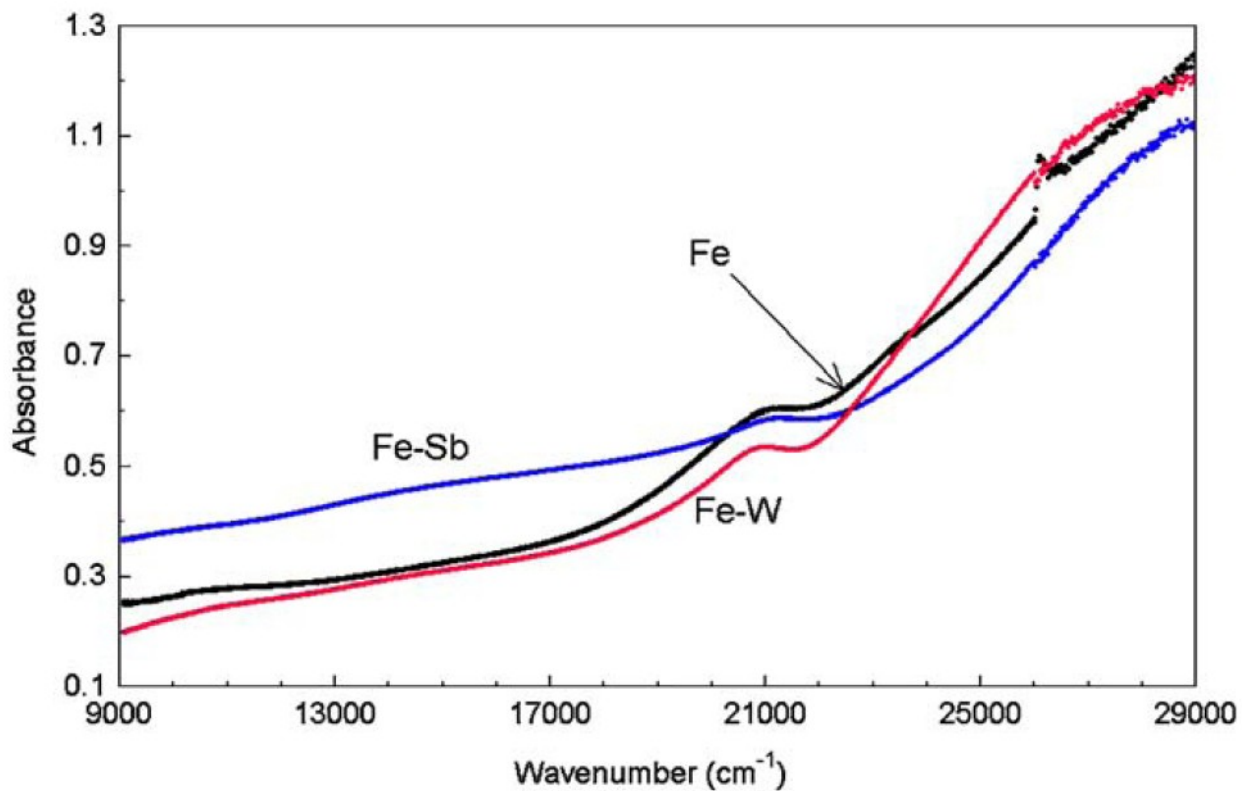


Figure 8. UV-visible-NIR spectra of zirconium titanate pigments doped with iron and co-doped with counterions.

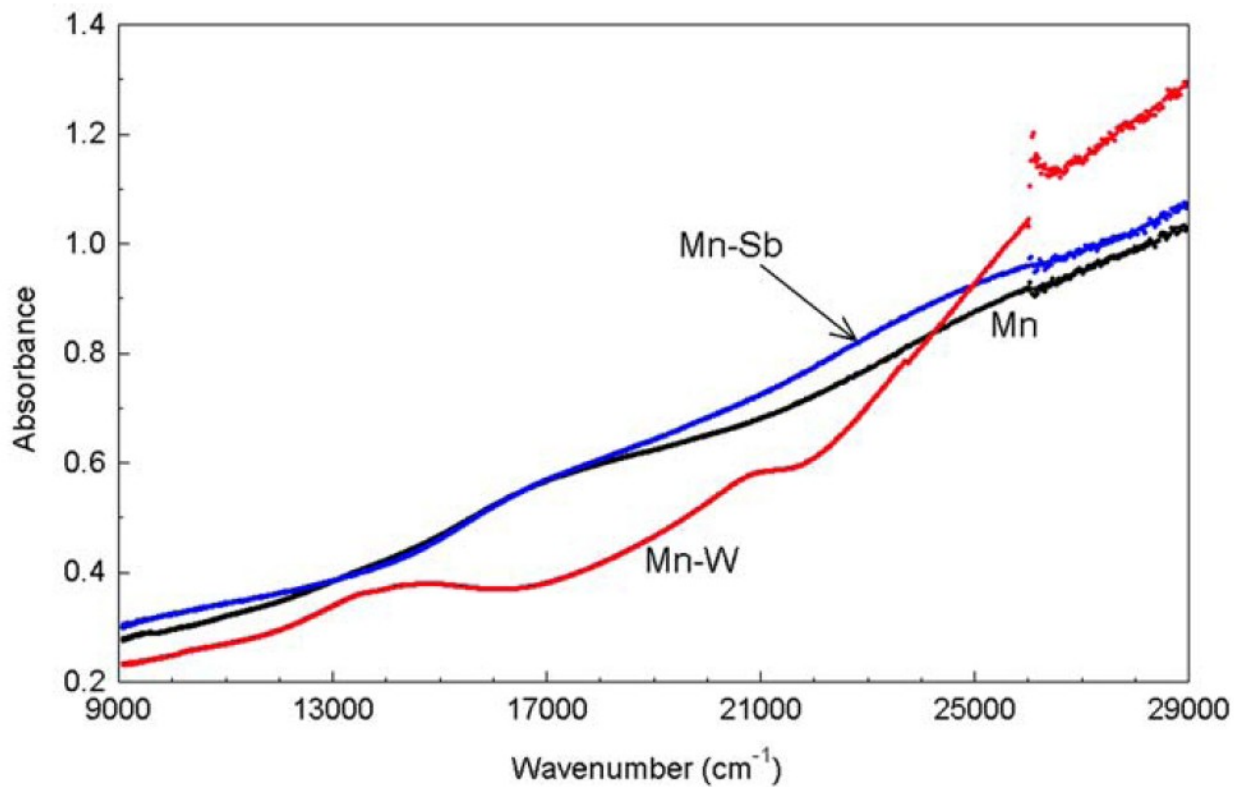


Figure 9. UV-visible-NIR spectra of zirconium titanate pigments doped with manganese and co-doped with counterions.

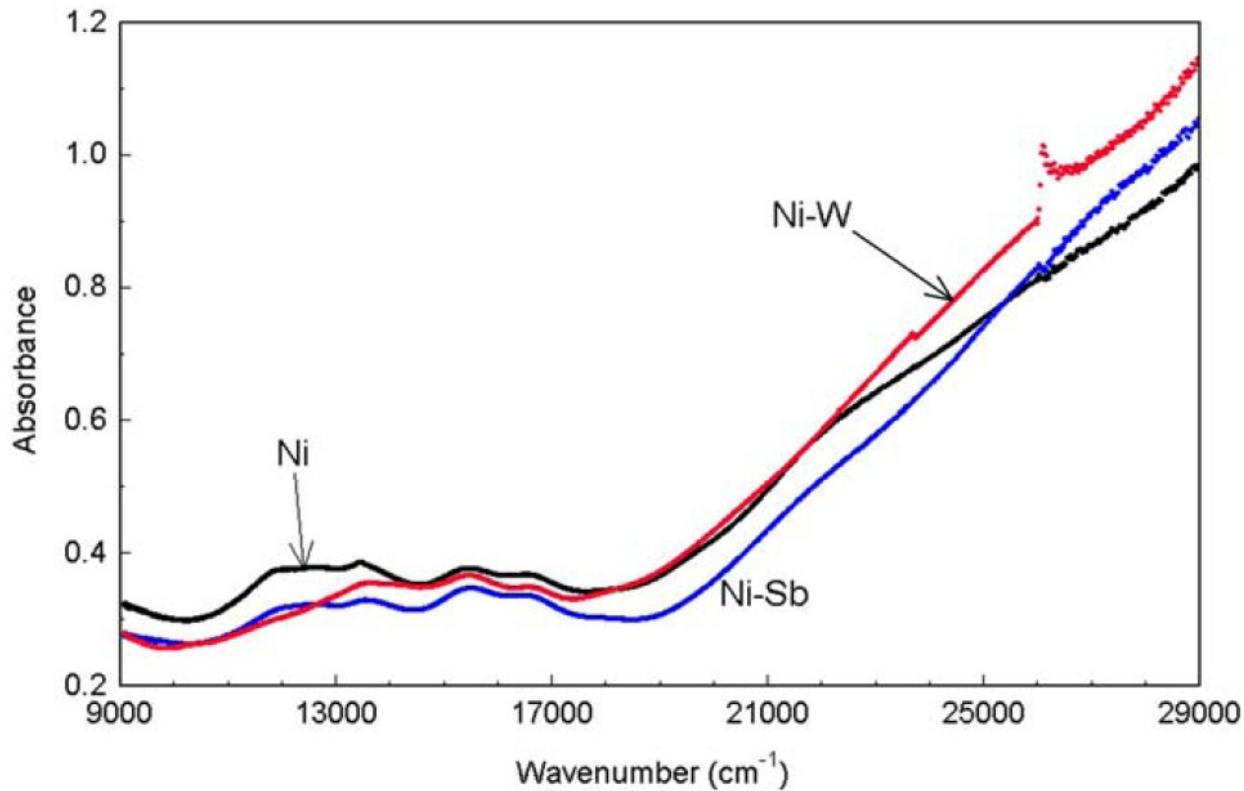


Figure 10. UV-visible-NIR spectra of zirconium titanate pigments doped with nickel and co-doped with counterions.

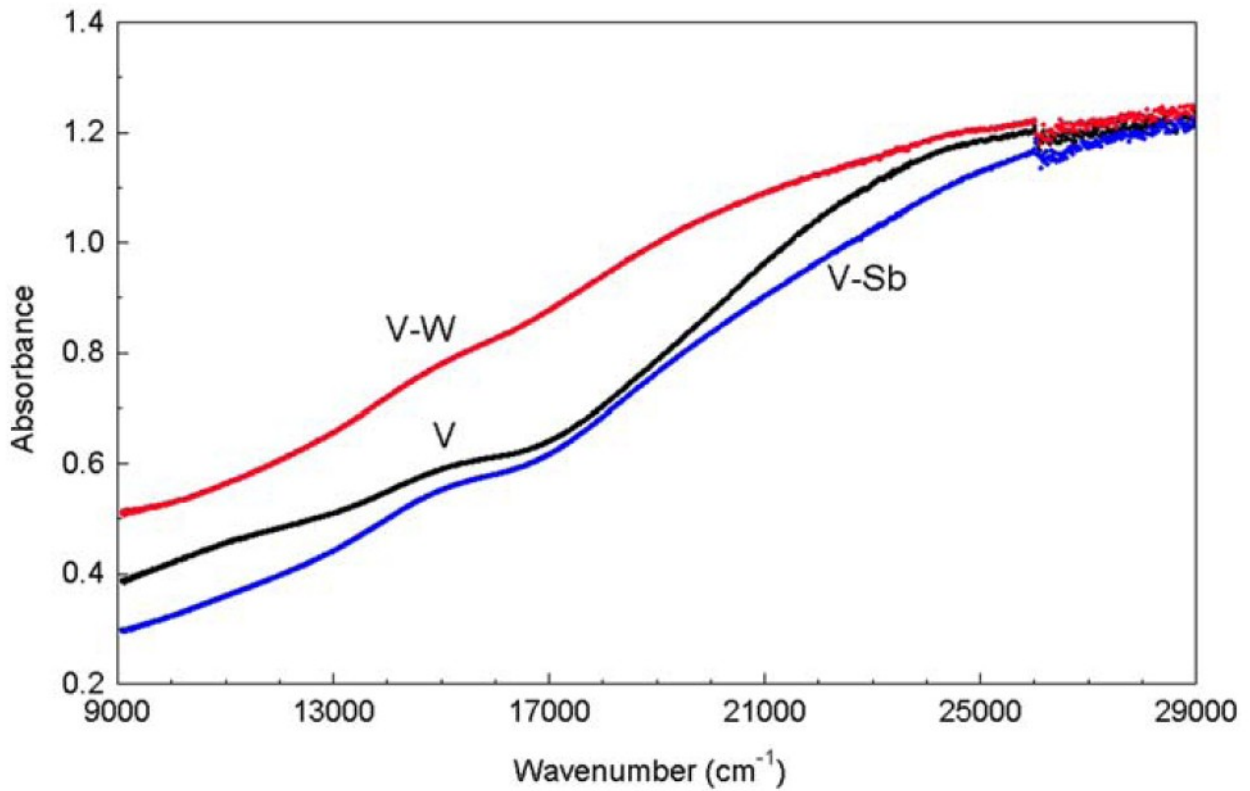


Figure 11. UV-visible-NIR spectra of zirconium titanate pigments doped with vanadium and co-doped with counterions.

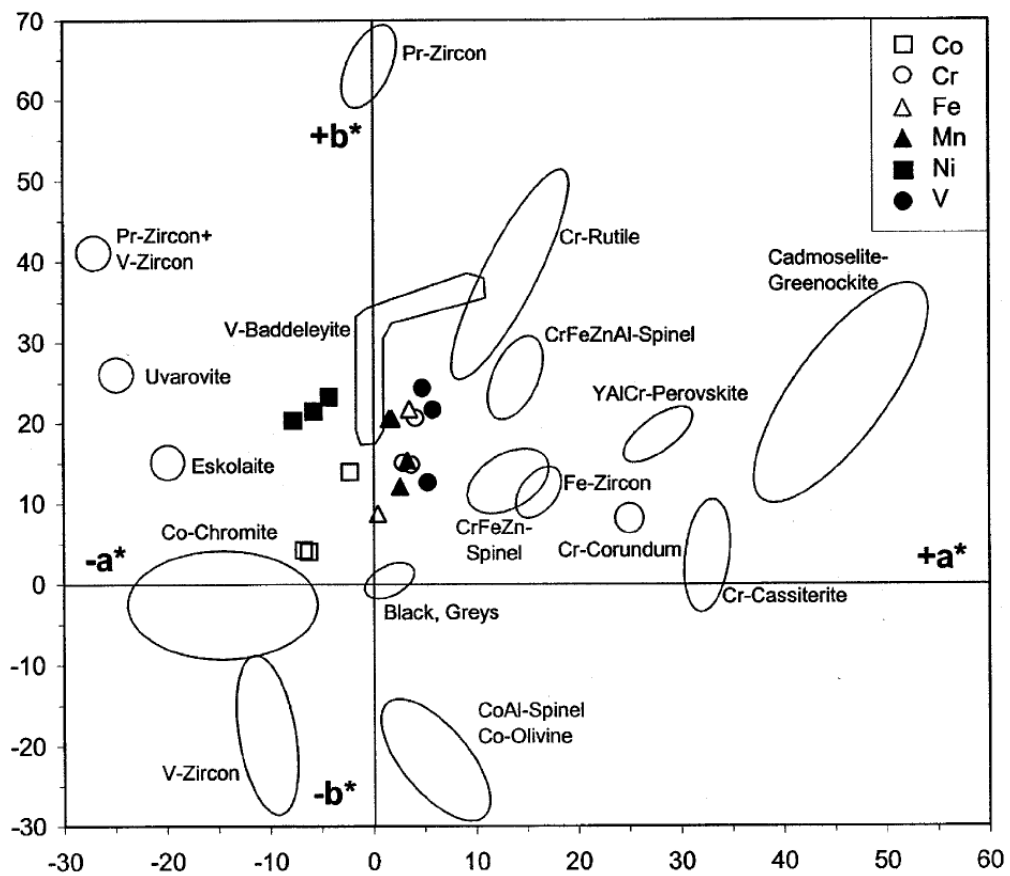


Figure 12. Chroma plot for industrial and zirconium titanate pigments.

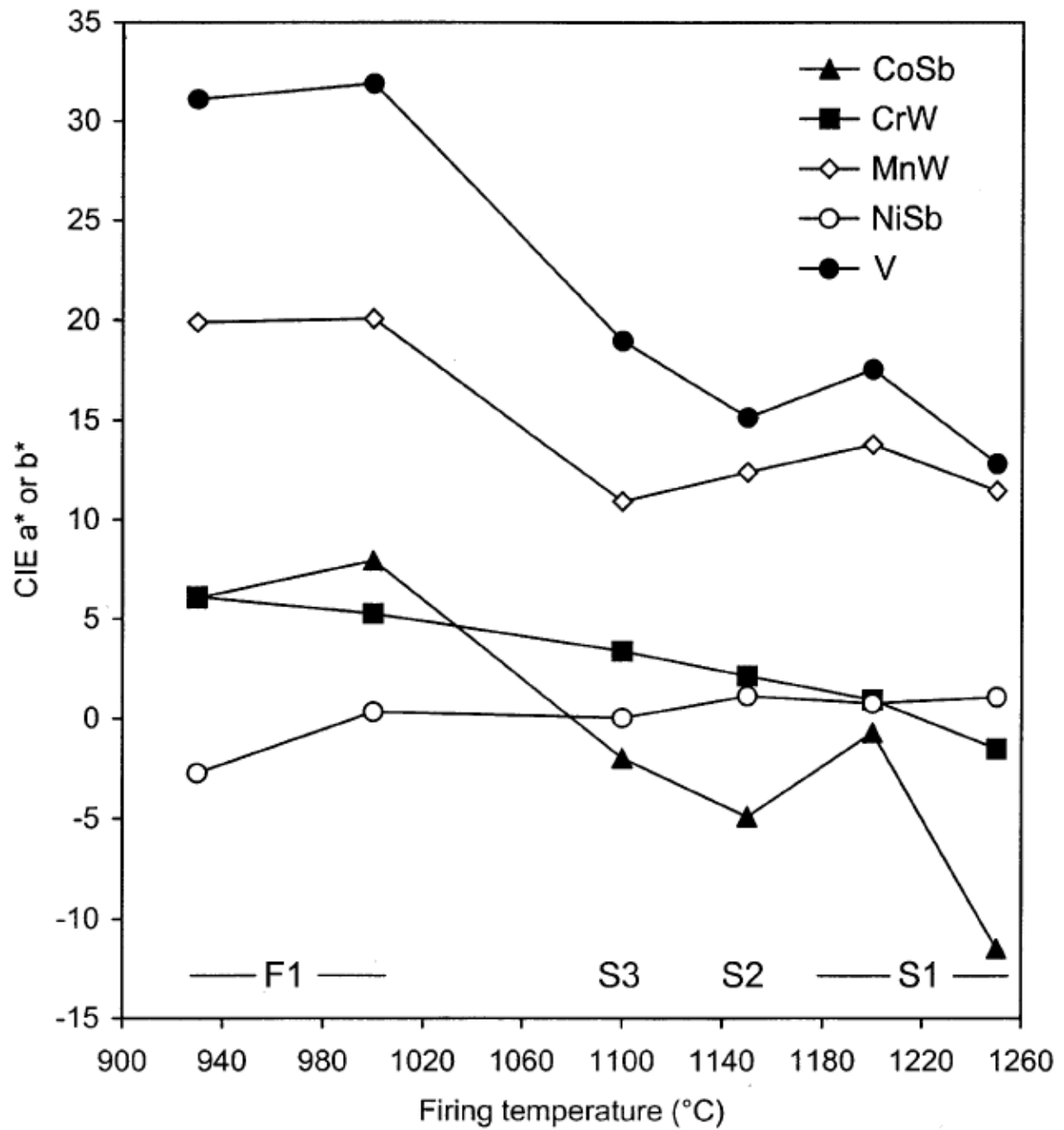


Fig. 13. Colour change (a^* for Cr- and Ni-doped, b^* for Co-, Mn- and V-doped) versus maximum firing temperature of zirconium titanate pigments applied in frit (F1) and glazes (S1, S2 and S3).

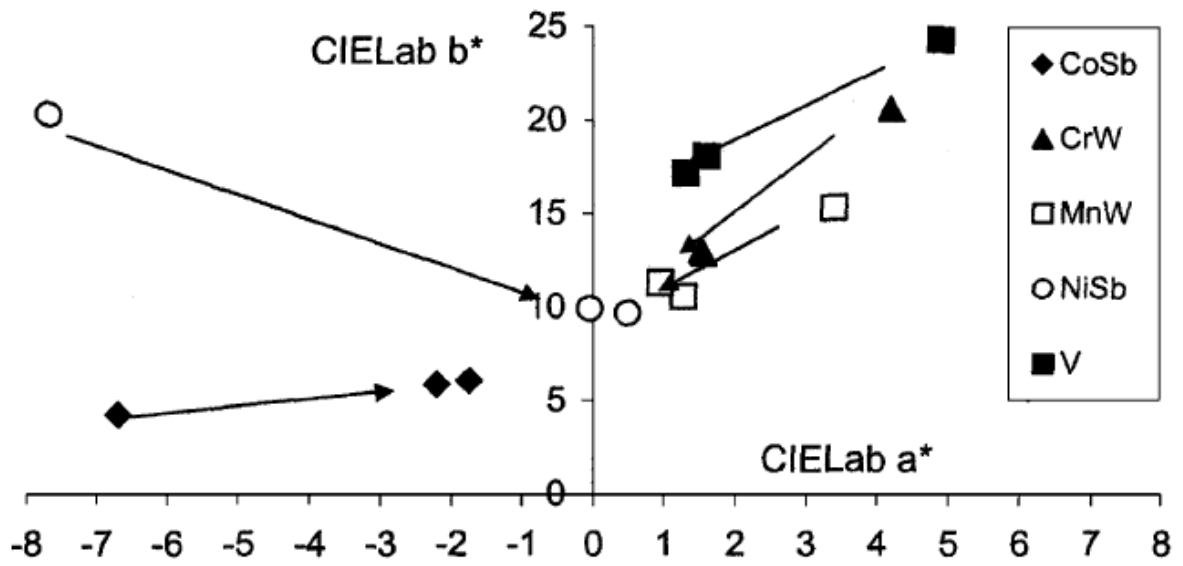


Fig. 14. Colour change of zirconium titanate pigments applied in porcelain stoneware body.

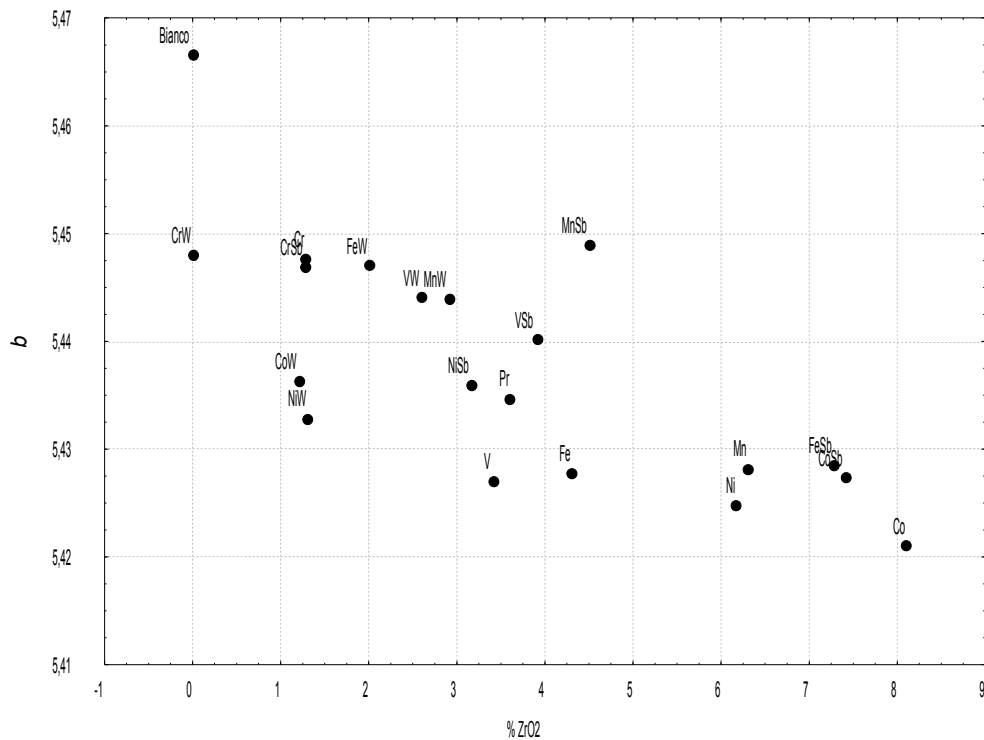


Figure 15. The mean equatorial metal oxygen distances vs. the apical distances (M-O₂).

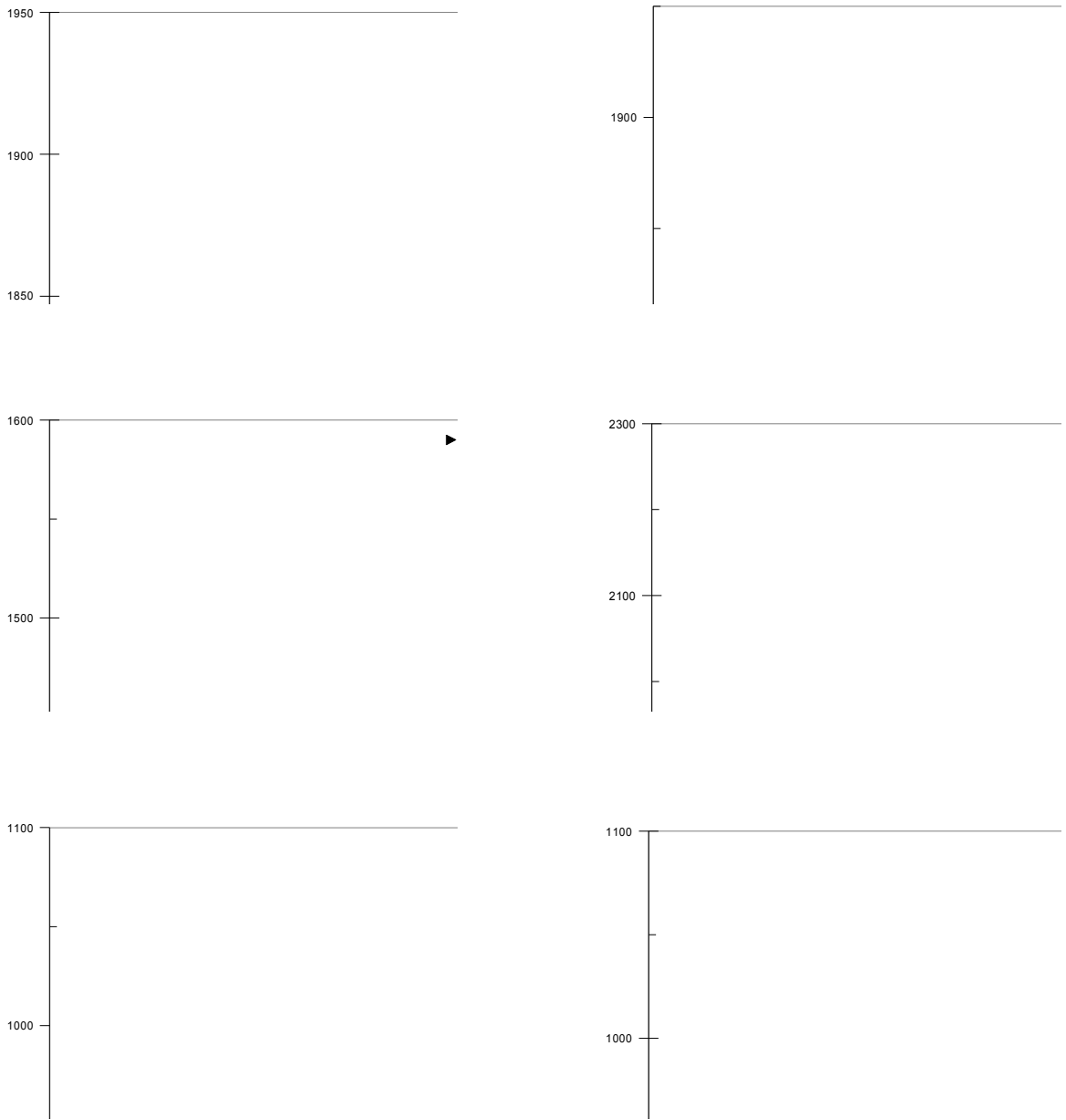


Figure 16. Relationship between crystal field strength Dq and the metal-oxygen distance $\langle R \rangle^{-5}$ for zirconium titanate and industrial ceramic pigments.

Table 1

Results of Rietveld refinements of X-ray diffraction patterns of zirconium titanate pigments: number of variables and Observations, figures-of-merit, Gaussian and Lorentzian profile coefficients, amount of accessory baddeleyite (ZrO_2), tialite (Al_2TiO_5) and rutile (TiO_2).

Sample	No. of variables	No. of observations	Figures-of-merit		ZrO ₂ (% wt.) (% wt.)
			RF ²	R _{wp}	
ZrTi	30	228	0.05	0.14	0.0(3)
Co	43	225	0.07	0.15	4.5(5)
CoSb	30	225	0.06	0.18	4.5(3)
CoW	30	226	0.11	0.24	4.7(4)
Cr	30	227	0.09	0.15	0.0(2)
CrSb	52	227	0.07	0.19	0.0(2)
CrW	32	227	0.11	0.19	0.0(2)
Fe	52	226	0.07	0.17	3.8(3)
FeSb	43	226	0.06	0.17	9.1(4)
FeW	35	226	0.07	0.16	3.6(2)
Mn	50	226	0.08	0.19	4.4(3)
MnSb	40	227	0.06	0.16	0.0(2)
MnW	50	226	0.07	0.18	4.5(3)
Ni	35	226	0.08	0.16	0.0(2)
NiSb	35	227	0.07	0.14	0.0(2)
NiW	35	225	0.08	0.18	0.0(2)
V	40	224	0.06	0.15	3.7(3)
VSb	41	226	0.06	0.17	2.3(4)
VW	40	226	0.12	0.30	8.2(4)
Pr	35	227	0.08	0.11	0.0(2)

Notes: Figures in parentheses are standard deviations in the last decimal figure. R_F² is only referred to zirconium titanate reflections. The number of reflections is referred to zirconium titanate ones.

Table 2

Main chemical and physical features of ceramic matrices used in technological testing:

Porcelain stoneware body (PSB), boric-alkaline frit (F1), glazes for porcelain stoneware (S1),

Stoneware (S2) and *monoporosa* tiles (S3).

% wt.	PSB	F1	S1	S2	S3
CaO	4	<1	9	14	13
MgO	4	<1	3	4	<1
PbO	0	6	0	4	0
ZnO	0	4	0	5	3
B ₂ O ₃	0	12	0	4	2
Temperature of softening T ₁ (°C)	1210*	930	1210	1150	1100
Temperature of half sphere T ₂ (°C)	n.d.	1265	1275	1200	1195
Temperature of melting T ₃ (°C)	n.d.	1290	1305	1235	1230
Refractive index (1)	1.490	1.505	1.525	1.545	1.560
Viscosity at T ₁ (MPa s)	4.4	4.9	4.7	5.0	5.3
Surface tension at T ₁ (mN m ⁻¹)	330	295	380	395	385

*Temperature of maximum densification

Table 32

Structural data of zirconium titanate pigments: unit-cell parameters (*a*, *b*, *c*, volume), occupancy of Zr in the octahedral site, expressed as atoms per unit formula (a.p.u.f.), isotropic displacement parameters ($U_{iso} \cdot 100$) and atomic positions.

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)	Occupancy of Zr (a.p.u.f.)	$U_{iso} \cdot 100$	
						(Zr,Ti)	(O)
ZT	4.806(4)	5.467(0)	5.032(7)	132.20	0.50(2)	2.0(1)0.0264	2.8(1)0.3488
Co	4.820(3)	5.421(2)	5.034(3)	131.53	0.44(2)	3.0(1)0.0282	3.5(1)0.0357
CoSb	4.814(5)	5.427(4)	5.036(6)	131.58	0.44(6)	2.7(1)0.0265	3.5(1)0.0384
CoW	4.812(1)	5.436(9)	5.033(1)	131.65	0.44(6)	3.1(1)0.0398	3.5(1)0.0482
Cr	4.818(2)	5.448(8)	5.035(6)	132.15	0.39(9)	2.7(1)0.0314	3.5(1)0.0316
CrSb	4.816(1)	5.447(9)	5.039(1)	132.17	0.38(5)	2.4(2)0.0270	2.7(1)0.0325
CrW	4.814(3)	5.448(0)	5.037(7)	132.08	0.37(9)	2.8(3)0.0295	3.5(1)0.0392
Fe	4.821(8)	5.428(1)	5.036(7)	131.76	0.47(2)	3.0(2)0.0294	3.5(1)0.0375
FeSb	4.821(1)	5.429(0)	5.038(0)	131.85	0.40(4)	2.3(2)0.0274	3.0(2)0.0340
FeW	4.810(9)	5.447(2)	5.033(4)	131.86	0.40(4)	2.5(2)0.0250	2.9(3)0.0286
Mn	4.816(7)	5.428(3)	5.033(5)	131.56	0.43(7)	2.8(3)0.0280	3.5(3)0.0374
MnSb	4.811(0)	5.449(2)	5.036(1)	132.02	0.36(6)	2.7(3)0.0270	3.5(3)0.0356
MnW	4.809(6)	5.444(2)	5.032(3)	131.76	0.39(3)	3.0(2)0.0304	3.5(2)0.0516
Ni	4.820(9)	5.425(6)	5.034(3)	131.65	0.37(7)	2.8(2)0.0290	3.1(2)0.0326
NiSb	4.814(9)	5.436(1)	5.037(3)	131.82	0.48(6)	3.1(2)0.0313	3.5(2)0.0388
NiW	4.812(6)	5.433(3)	5.033(6)	131.58	0.38(8)	3.3(2)0.0336	3.5(2)0.0434
V	4.813(6)	5.427(3)	5.030(9)	131.37	0.44(5)	2.7(2)0.0259	3.5(2)0.0344
VSb	4.809(3)	5.440(2)	5.033(6)	131.66	0.39(3)	2.9(2)0.0294	3.5(2)0.0459
VW	4.806(4)	5.444(7)	5.031(5)	131.64	0.51(6)	2.1(3)0.0242	3.5(2)0.0424
Pr	4.813(0)	5.435(7)	5.032(4)	131.61	0.40(2)	2.9(1)0.0300	3.2(1)0.0280

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Table 3

Metal-oxygen distances and degree of distortion of the octahedral site in zirconium titanate pigments.

	(Ti,Zr)-O distances (Å)				Site di Δ ₆
	Apical distances M-O2 [x2]	Equatorial distances		Mean of the 6 distances <M-O>	
		M-O1 [x2]	M-O3 [x2]		
Zr	2.192(5)	1.930(5)	2.001(5)	2.041	2.0
Co	2.238(4)	1.947(4)	1.949(4)	2.045	4.0
CoSb	2.230(4)	1.935(4)	1.964(4)	2.043	4.0
CoW	2.201(4)	1.900(4)	2.025(4)	2.042	3.0
Cr	2.210(4)	1.923(4)	1.994(4)	2.042	3.0
CrSb	2.235(5)	1.908(5)	1.981(4)	2.041	4.0
CrW	2.204(5)	1.922(5)	2.002(4)	2.043	3.0
Fe	2.279(4)	1.909(4)	1.946(4)	2.045	6.0
FeSb	2.230(5)	1.927(5)	1.961(5)	2.039	4.0
FeW	2.169(4)	1.964(4)	1.986(4)	2.040	2.0
Mn	2.201(5)	1.914(5)	2.016(5)	2.044	3.0
MnSb	2.214(5)	1.944(5)	1.975(5)	2.044	3.0
MnW	2.236(5)	1.917(5)	1.973(5)	2.042	4.0
Ni	2.226(5)	1.926(4)	1.978(5)	2.043	4.0
NiSb	2.238(5)	1.919(4)	1.977(4)	2.045	4.0
NiW	2.221(4)	1.949(5)	1.953(5)	2.041	3.0
V	2.224(4)	1.904(4)	1.994(4)	2.041	4.0
VSb	2.205(5)	1.931(4)	1.985(4)	2.040	3.0
VW	2.122(4)	1.905(4)	2.081(5)	2.036	2.0
Pr	2.238(3)	1.911(3)	1.991(3)	2.041	4.0

Notes: Δ₆ is the distortion parameter of the octahedra and is calculated as $[1/3 \cdot 10^3 \cdot \sum_i (M-O_i - \langle M-O \rangle)^2 + (M-O_i - \langle M-O \rangle)^2] / [\langle M-O \rangle^2]$.

Table 4 - Optical spectroscopic data: crystal field transitions. crystal field strength (Dq). crystal field stabilization energy (CFSE). Racah parameters B₃₅ and β₃₅.

Ion	Sample	Crystal field transitions (cm ⁻¹)			Peak splitting	Dq	(k)
		ν ₁	ν ₂	ν ₃	δ (cm ⁻¹)	(cm ⁻¹)	
Co ²⁺	Co	n.d.	16890	23030	2740	898	
	CoSb	n.d.	16580	23380	2600	882	
	CoW	n.d.	16450	23120	2560	875	
Cr ³⁺	Cr	14310	18570	n.d.	1250	1425	
	CrSb	14170	20390	n.d.	1330	1487	
	CrW	14100	19430	n.d.	1320	1447	
Fe ³⁺	Fe	13010	17830	20430		(1207)	
	FeSb	n.d.	15600	21110		(1407)	
	FeW	13920	15580	20660		(1316)	
Mn ²⁺	Mn	14450	19050	23930		(1047)	
	MnSb	10950	18510	23860		(1269)	
	MnW	14430	20130	24350		(972)	
Mn ³⁺	Mn	16750			4600	1675	
	MnSb	14730			7560	1473	
	MnW	17280			5700	1728	
Ni ²⁺	Ni	n.d.	13640	23310	1540	879	
	NiSb	n.d.	13250	24080	1580	874	
	NiW	n.d.	13320	23800	1490	885	
V ³⁺	V	16100	23410	n.d.		1696	
	VSb	15780	23400	n.d.		1678	
	VW	16000	23740	n.d.		1710	
V ⁴⁺	V	19800				1980	
	VSb	19540				1954	
	VW	20040				2004	

Crystal field transitions. Co²⁺: ν₂=⁴T_{1g}(⁴F)→⁴A_{2g}(⁴F). ν₃=⁴T_{1g}(⁴P); Cr³⁺: ν₁=⁴A_{2g}(⁴F)→⁴T_{1g}(⁴F). ν₂=⁴T_{2g}(⁴F); Fe³⁺ and Mn²⁺: ν₁=⁶A₁(⁶S)→⁴T₁(⁴G). ν₂=⁴T₂(⁴G). ν₃=⁴E.⁴A(⁴G); Mn³⁺: ν₁=⁵E_g(⁵D)→⁵T_{2g}(⁵D); Ni²⁺: ν₂=³A_{2g}(³F)→³T_{1g}(³F). ν₃=³T_{1g}(³P); V³⁺: ν₁=³T₁(³F)→³T₂(³F). ν₂=³T₁(³P); V⁴⁺: ν₁=²T_{2g}(²D)→²E_g(²D). Splitting is of ν₁ (Cr. Mn) and ν₂ (Co. Ni). Racah β₃₅=B₃₅/B₀ where B₀ (cm⁻¹). Co²⁺: 989; Cr³⁺: 933; Fe³⁺: 1029; Mn²⁺: 960; Ni²⁺: 1042; V³⁺: 886 [20-21]. Values between brackets are indicative.

Table 5

Colourimetric characteristics of selected srilankite pigments dispersed in ceramic glazes (F1: double-firing frit; S3: *monoporosa* glaze; S2: stoneware glaze; S1; porcelain stoneware glaze) and in a porcelain stoneware body (G) and fired at different maximum temperatures (T) for annealing times of 5 to 10 min.

Pigment	F1 (T=930 °C)			F1 (T=1000 °C)			S3 (T=1100 °C)		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
CoSb	64.20	-6.83	6.05	84.69	1.11	7.94	79.34	-3.59	-1.11
CrW	63.18	6.11	29.59	70.47	5.26	33.59	78.81	3.38	12.11
MnW	66.51	5.88	19.91	71.90	5.43	20.09	83.60	2.31	10.11
NiSb	83.42	-2.73	23.20	87.50	0.33	17.94	89.41	0.03	10.11
V	59.22	8.04	31.10	64.78	8.55	31.89	82.12	3.01	10.11

Pigment	S1 (T=1200 °C)			S1 (T=1250 °C)			G (T=1200 °C)		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
CoSb	73.28	-2.31	-0.71	66.18	-1.39	-11.50	79.88	-1.75	-1.11
CrW	76.56	0.93	18.33	73.19	-1.53	15.11	80.13	1.56	12.11
MnW	79.69	1.87	13.78	81.39	1.21	11.46	82.79	1.28	10.11
NiSb	82.40	0.75	13.54	81.59	1.06	13.27	85.21	0.49	10.11
V	80.29	2.21	17.55	80.13	1.53	12.82	81.25	1.30	10.11