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Brown ceramic pigments based on chromium(III)-doped titanite obtained by spray pyrolysis

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Cr-doped titanite ($CaTiSiO_5$) pigments were synthesized through spray pyrolysis of aerosols generated from aqueous solutions containing colloidal silica, calcium chloride, titanium(IV) oxychloride and chromium(III) nitrate. This process yielded amorphous powders with spherical morphology and broad size distribution ($<10\ \mu m$) after thermal decomposition at 600 °C. The titanite phase was obtained by further calcination at 800 °C without any addition of flux agents. The brown color of the pigments can be attributed mainly to the existence of Cr(IV) ions occupying both, octahedral positions of Ti(IV) and tetrahedral position of Si(IV), together with a small amount of Cr(III) present as Cr_2O_3. The optimum pigment obtained by this method corresponded to a Cr/titanite mole ratio of 0.04.

1. Introduction

In recent years, Cr-doped metal oxide materials have been widely investigated as ceramic pigments [1–4] due to their interesting properties including high temperature resistance, chemical stability (low corrosion by the liquid phases formed during firing of bodies or glazes) jointly with suitable optical properties [5,6]. Among theses materials, Cr-doped malayaite ($CaSnSiO_5$) is recognized as one of the most important chromium pigment used in the ceramic industry for coloring glazes [7–10] due to it peculiar pink hue.

Titanite ($CaTiSiO_5$) is an isostructural titanium analogue of malayaite [11]. In spite of this similarity, this system has not been explored for coloring applications, although it has been reported that it could incorporate transition metal cations [12].

Currently, synthetic inorganic pigments are mainly prepared through solid-state reactions [6] which require several processing steps such as, initial ball milling of the raw materials (usually oxides and/or salts) for homogenization; calcination of these mixtures at high temperatures to obtain the desired crystalline phases and color and finally, wet milling to reduce particle size [13]. In order to decrease the calcination temperature of these mixtures and to develop purer color a variety of flux agents that usually cause negative environment effect [14,15] are frequently used. In addition, irregular and agglomerated grains with rough surface typically result from the solid-state method.

Several other preparation routes have been developed to improve the conventional synthesis method as well as the physical and chemical characteristic of the produced pigments, such as those based on coprecipitation [8], sol–gel [16–18], combustion [19] and hydrothermal [20] reactions, spray drying [21,22] and spray pyrolysis [23–25]. In particular, the latter technique (SP) has been shown to be an attractive alternative to the solid-state method for the synthesis of inorganic pigments [23–25] providing a variety of advantages, such as reducing the processing steps, precise control of stoichiometry in multicomponent formulations, phase purity and control of particle size and shape of the final product. In addition, as a consequence of the mixing of the starting compounds at molecular level attained with the SP procedures, the desired crystalline phase and color can be obtained at lower temperature than those involved in other procedures [8,16–22]. Finally, the SP technique is continuous, which is desirable for industrial applications.

The aim of this work is to explore the applicability of Cr-doped titanite ($CaTiSiO_5$) as ceramic pigment. For this purpose, several samples with titanite composition ($CaO:TiO_2:SiO_2$) and different Cr amount were synthesized by pyrolysis at 600 °C of aerosols generated from solutions of colloidal silica, calcium chloride, titanium oxychloride and chromium(III) nitrate. The obtained powders were then thermally treated at different temperatures until the complete

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transformation into pure titanite was achieved. The resulting pigments were characterized, in terms of their morphological, crystallochemical and optical properties.

2. Experimental

2.1. Synthesis procedure

A schematic diagram of the SP flow reactor used for the preparation of the pigments has been already described [24]. The Cr(III)-doped titanite samples [Cr/titanite molar ratio = 0.02; 0.04; 0.08] were prepared from aqueous solutions (250 cm^3) of equimolecular amount (0.05 mol dm^{-3}) of colloidal silica sol (Ludox TMA, Sigma Aldrich, 34 wt%), $CaCl_2 \cdot 2H_2O$ (Riedel-de Haën, 99%), Cl_2OTi $(HCl)_x$ [Fluka, Ti content ~15 wt%] and $Cr(NO_3)_3 \cdot 9H_2O$ (Panreac, 98%). These starting solutions were nebulized through a glass nozzle, using air as a carrier gas at a constant pressure (0.5 kg cm^{-2}), which was enough to ensure a steady flow of the solutions to the nozzle. After the atomization stage, the aerosol was introduced into an expansion chamber and then transported through two consecutive furnaces where the temperature was kept at 300 and 600 °C, respectively. Inside the first furnace the droplets undergo evaporation of the solvent and precipitation of the precursors, whereas the thermolysis of the latter occurred at higher temperature in the second heater. The resulting solid particles were collected using a glass filter. These powders were further heated in an electric furnace at higher temperatures with a heating rate of 600 °C/h for 4 h, for crystallization and color development.

2.2. Characterization

Differential thermal (DTA) and thermogravimetric (TGA) analyses were carried out in air using Mettler Toledo equipment, model TG/DTA 851e. The sample was heated at a heating rate of 5 °C min^{-1} in a platinum crucible.

The crystalline phases present in the powders were characterized by X-ray diffraction (XRD) using a Siemens D501 diffractometer. The measurements were performed in the 10–70° 2θ range with $\Delta 2\theta$ steps of 0.05°.

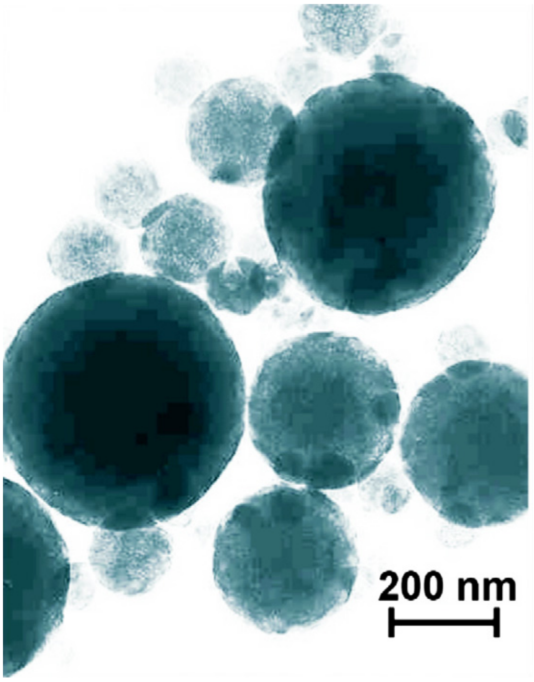

Fig. 1. TEM micrograph of sample Cr4, as prepared.

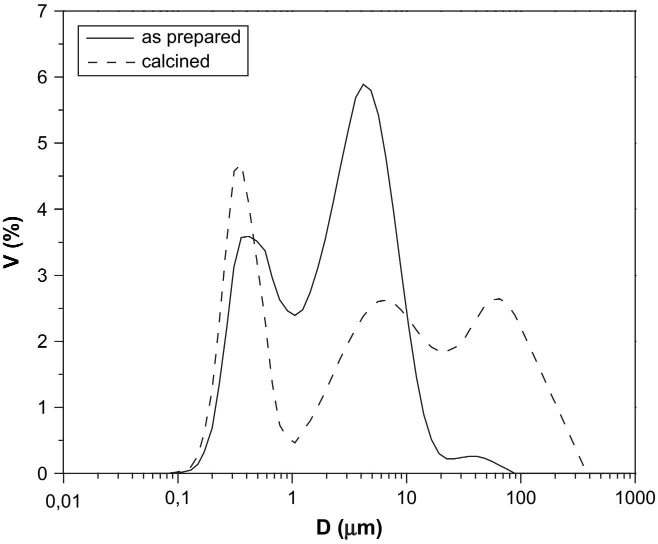

Fig. 2. Particle size distribution curve for sample Cr4, as prepared and calcined at 1000 °C.

The particle morphology and size were studied using scanning electron microscopy (SEM, Jeol JSM5400) and transmission electron microscopy (TEM, Philips 200 CM). Energy dispersive X-ray analysis (EDX, Philips DX4), installed in TEM microscope, was also used to gain information on the particle composition. Particle sizing was performed by laser diffraction using Malvern Mastersizer S equipment.

UV–visible spectroscopy of the fired samples was measured using a Cary 500 Scan Varian spectrophotometer in the 300–1400 nm range (step 0.1 nm). The diffuse reflectance spectra (DRS) were obtained using an integrating sphere, $BaSO_4$ as a white reference and a D_{65} illuminant (observer at 10°).

The color coordinates of the pigments were measured using a Dr. Lange, LUCI 100 colorimeter for the same illuminant (D_{65}) and a white ceramic tile (coordinates: $x = 76.7$, $y = 81.4$, $z = 86.4$) as a standard reference. The color was evaluated, according to the Commission Internationale de l'Eclairage (CIE) through $L^*a^*b^*$ parameters [26]. In this system L^* is the color lightness ($L^* = 0$ for black, $L^* = 100$ for white); a^* is red (+) and green (−) axis and b^* is the yellow (+) and blue (−) axis.

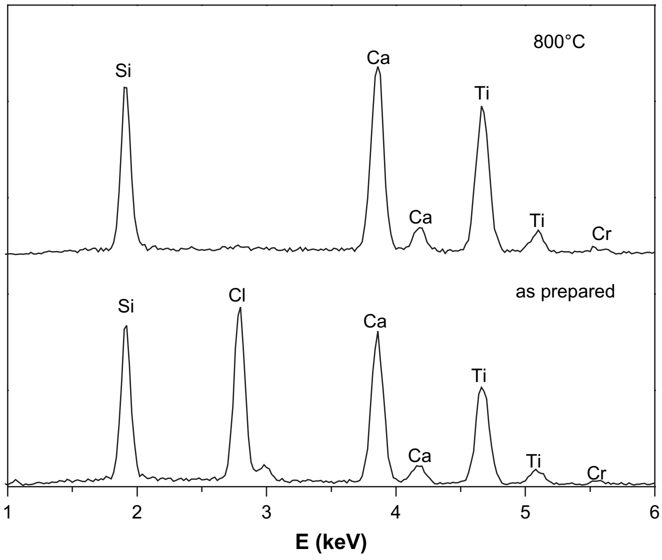

Fig. 3. EDX spectra obtained for sample Cr4, as prepared and calcined at 800 °C.

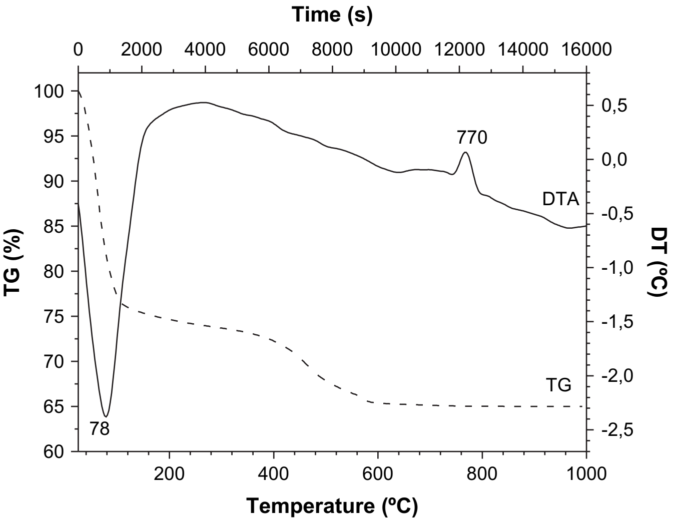

Fig. 4. Differential thermal and thermogravimetric analysis obtained for sample Cr4.

3. Results and discussion

In order to study the effect of chromophore concentration on the pigment properties different compositions with nominal composition of titanite (Ti/Si atomic ratio = 1) and variable Cr content were prepared. The samples with a Cr/Ti atomic ratio = 0.02, 0.04 and 0.08 were named as Cr2, Cr4 and Cr8, respectively. It should be clarified that all samples developed similar structural and morphological characteristics on thermal treatment. Thus, most of the characterization data hereafter presented corresponds to sample Cr4, which has been chosen as a representative example.

This sample consisted of dense spherical particles (Fig. 1) due to the volumetric precipitation of the precursors during the solvent evaporation process [27] with heterogeneous size. Thus, in the volumetric size distribution (Fig. 2) two broad maxima centered at 0.4 μm (40%) and 4 μm (60%) were detected. These particles were amorphous by X-ray diffraction.

The Ca/Ti (1.1), Si/Ti (1.0) and Cr/Ti (0.04) molar ratios measured by EDX for the sample Cr4 as prepared were in excellent agreement with the nominal composition prepared with the stoichiometry of titanite and a chromium content of 0.04, manifesting the effectiveness of the pyrolysis method to control the stoichiometry of multicomponent systems [27].

EDX spectroscopy gave additional information on sample composition. Thus, the spectrum showed as well an intense chlorine peak (Fig. 3), which probably indicates that the Ca or Ti precursors were not completely decomposed during the pyrolysis process.

In order to evaluate the thermal evolution of sample Cr4, differential thermal (DTA) and thermogravimetric (TGA) analyses were performed (Fig. 4). The obtained DTA curve revealed an intense endothermic peak at 78 °C with an associated weight loss of 24.8% in the range 25–200 °C that was attributed to absorbed moisture. A further mass loss of ~6.2% was detected on the TGA curve in the interval 450–750 °C. This effect could be associated with the elimination of chlorine, as suggested by the EDX analyses displayed in Fig. 3. It should be noted that the Cl content in the as prepared samples could be almost eliminated by a simple washing procedure with water as confirmed by EDX (data not shown), which therefore, would result in the suppression of the Cl emissions on calcination. An intense broad exothermic peak was also observed in the DTA curve at 770 °C which could be associated to the titanite crystallization. This was proved by the X-ray diffraction pattern of the sample heated at 800 °C (Fig. 5a), where titanite (JCPDS card no. 25-0177) was detected as the major crystalline phase, which was accompanied by a small amount of TiO_2 rutile (JCPDS card no. 21-1276) and $CaTiO_3$ perovskite (JCPDS card no. 3-065-3287). No significant changes were detected by XRD after calcination at 1000 °C, except the disappearance of the rutile phase (Fig. 5a).

Similar X-ray diffraction patterns were obtained for samples Cr2 and Cr8 heated at 1000 °C (Fig. 5b). It should be noted that the

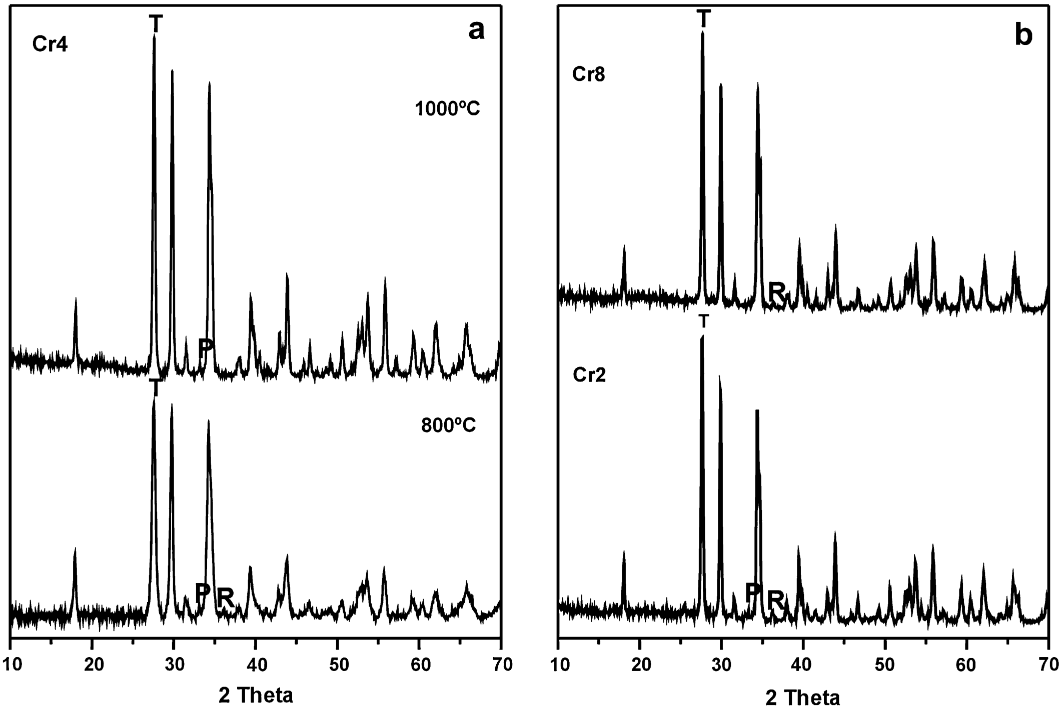

Fig. 5. X-ray diffraction patterns for sample Cr4 after heating at different temperatures (a) and for samples Cr2 and Cr8 calcined at 1000 °C (b). The most intense peaks of the titanite (T), rutile (R) and perovskite (P) crystalline phases labelled.

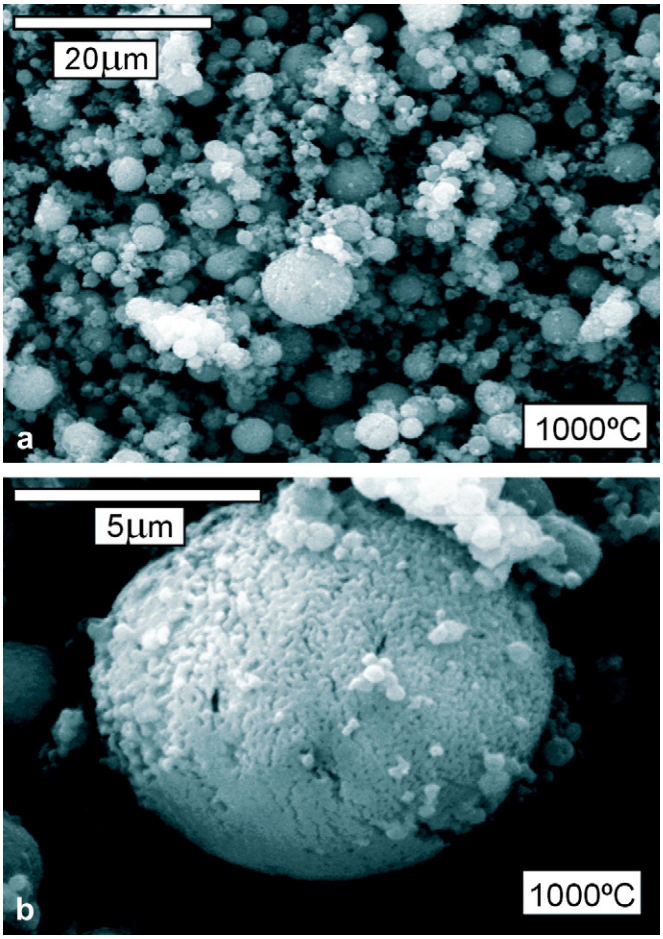

Fig. 6. SEM micrographs at different magnification of sample Cr4 heated at 1000 °C.

temperature required for titanite crystallization for our samples was significantly lower (800 °C) than that reported for samples synthesized by coprecipitaiton and sol–gel methods (1200 °C) [19] due to a more efficient mixing of components in the precursors.

It should be noted that after heating at 1000 °C the particles retained the spherical shape (Fig. 6a), although a certain particle sintering took place during this treatment as revealed by the particle size histogram shown in Fig. 2. A closer view of the heated sample (Fig. 6b) showed that the heated grains were polycrystalline.

The effects of the amount of chromophore on the color properties of the Cr-doped titanite pigments are summarized in Table 1. As it can be seen for as prepared sample Cr4, a negative a^*(−2.60), high b^* (24.90) and relatively high luminosity (L^* 69.20) values, corresponding to a yellow shade were detected. On further calcination at 800 °C, the pigment color turned to a light brown hue, which became darker (lower L^* and higher a^* and b^*) on further heating up to 1000 °C. As expected, a less intense coloration ($L^* = 64.40$) was observed for sample Cr2 calcined at 1000 °C in agreement with its lower chromium content (0.02). Finally, the increase of Cr/titanite molar ratio from 0.04 to 0.08 did not result in important changes in color intensity ($L^* = 55.40$) or hue ($a^* = 11.40$ and $b^* = 12.20$). Thus, it can be concluded that optimum pigment (best hue with lower Cr content) obtained through the described SP procedure was that with a Cr/Ti molar ratio = 0.04.

Table 1
$L^*a^*b^*$ parameters and colors of the Cr-doped titanite pigments calcined at different temperatures

Sample	Temperature (°C)	L^*	a^*	b^*	Color
Cr4	As prepared	69.20	−2.60	24.90	Yellow
Cr4	800	61.80	9.60	6.30	Light brown
Cr4	1000	58.40	12.80	10.80	Brown
Cr2	1000	64.40	10.30	11.60	Brown
Cr8	1000	55.40	11.40	12.20	Brown

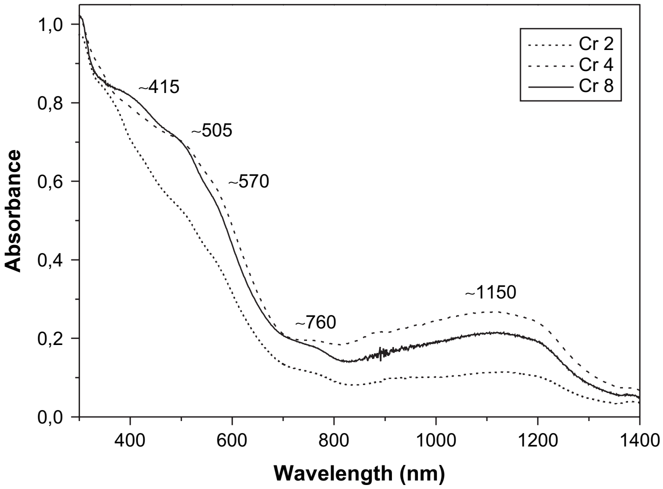

Fig. 7. Diffuse reflectance spectra obtained for Cr-doped titanites heated at 1000 °C for 4 h.

In order to study the crystallochemical features of the chromophore in the titanite lattice and therefore, the origin of the pigments color, UV–visible spectroscopy analyses were performed. The diffuse reflectance spectra corresponding to all studied samples are shown in Fig. 7. In all cases, a wide band at ~1150 nm and several absorption effects at ~760, ~570, ~505, and ~415 nm were detected.

The wide band in the near-IR part of the spectrum (at ~1150 nm), which is similar to that previously found for Cr-doped malayaite at ~1200 nm, can be attributed to the $^3A_2 \rightarrow {}^3T_1$ electric dipole allowed transitions of Cr(IV) in tetrahedral coordination following the assignment proposed by several authors [28,29]. The shoulder at ~760 nm could be associated to spin-forbidden transitions of Cr(III) ion in agreement with previous observation for Cr-doped cassiterite, Cr-doped malayaite [29] and Cr-doped zirconium titanates [30]. The absorption at ~505 nm should have the same origin than a similar band detected at ~515 nm for Cr-doped malayaite [28] and Cr-doped $Y_2Sn_2O_7$ pyrochlore [23] which was attributed to the d–d electron transitions of Cr(IV) ion hosted in distorted octahedral symmetry. Finally, the two shoulders at ~415 nm and ~570 nm could be assigned to the $^4A_{2g}\,(F) \rightarrow {}^4T_{1g}\,(F)$ and $^4A_{2g}\,(F) \rightarrow {}^4T_{2g}\,(F)$ electronic spin allowed transitions of Cr(III) in octahedral environment, respectively [31–33].

From the above considerations it can be concluded that two types of chromium species, are present in the titanite matrix. Cr(IV) cations which seem to occupy both, octahedral sites of Ti(IV) and tetrahedral sites of Si(IV), as in Cr-doped malayaite and Cr(III) cations which may be present as Cr_2O_3. These findings would explain the brown coloration of the Cr-doped titanite pigments which would result from the combination of a pink coloration coming form Cr(IV) cations dissolved in the titanite matrix (as in Cr-doped malayaite) [28] and the green color associated to Cr_2O_3 species.

4. Conclusions

It has been shown that the thermal decomposition at 600 °C of aerosols generated from aqueous solutions of colloidal silica, calcium chloride, titanium(IV) oxychloride and chromium(III) nitrate yields amorphous powders consisting of dense sphere particles with broad size distribution (in the 0.1–15 μm range). On calcination at 800 °C, crystallization of titanite ($CaTiSiO_5$) was detected without the addition of flux agents. This temperature is much lower than that required by other synthesis methods (1200 °C), due to a more efficient mixing of components in the precursors. The formation of titanite was accompanied by the development of a brown coloration which according to UV–visible spectroscopy might be due to the presence of both Cr(IV) and Cr(III) ions in the titanite matrix.

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