Orthorhombic (Fe₂TiO₅)-monoclinic (Cr₂TiO₅) solid solution series: Synthesis by gel routes, coloring and NIR reflectivity evaluation

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ABSTRACT
CrₓFe₂₋ₓTiO₅ compositions of the solid solutions series from pseudobrookite Fe₂TiO₅ to monoclinic Cr₂TiO₅ have been prepared by the ceramic route and gel methods. At 1400°C, pseudobrookite crystallizes in the x = 0–0.4 range, both pseudobrookite and monoclinic Fe₂₋ₓTiO₅ coexist at x = 0.5, while in the range x = 0.7–1.5 monoclinic FeₓCr₁₋ₓTiO₅ crystallizes. Powders were 5 wt% glazed within a double-firing frit and the composition with x = 0.1 fired at 1000°C exhibits the best red color (L*a*b* = 43.2/18.8/12.5), showing an intense band at 520 nm in the UV–Vis–NIR absorption spectrum associated with Cr³⁺ in octahedral coordination. The unit cell volume of the pseudobrookite decreases smoothly with the chromium amount, associated with the entrance of Cr³⁺ replacing Ti⁴⁺, while the volume of the Fe₂₋ₓTiO₅ unit cell increases with the entrance of Fe³⁺ replacing Cr³⁺. The use of flux agents, the compaction pressure and the gel methods increase the crystallization of pseudobrookite but do not improve the reddish color, which is associated with the concentration of Cr⁴⁺ in the pigment. The optimized pigment composition Cr₀.₁Fe₁.₉TiO₅ also shows a high NIR reflectance (55% in powder, 54% in glazed sample).

1. Introduction
Pseudobrookite Fe₂TiO₅ is a reddish brown to ochre-yellow colored mineral that was first described by Pauling [1] in 1930. The structure of pseudobrookite (general formula AB₂O₅) shows orthorhombic symmetry (Cmcm space group) and gives its name to a large group of isostructural phases. The group of Ti pseudobrookites, including FeTi₂O₅, MgTi₂O₅, Fe₂TiO₅, Al₂TiO₅, Ga₂TiO₅, and Ti₃O₅, have an extraordinary structural flexibility to accommodate many distinct metals (with +2, +3 or +4 oxidation states) in their two different and distorted octahedral cationic sites, A (4c) and B (8f), giving rise to a number of solid solutions with general formula [M³⁺₂⁺,M²⁺⁺₄⁺,Ti]A [Ti,M²⁺]='M³⁺]B [O₅]. This property, along with their high melting point and high refractive index (2.4 for Fe₂TiO₅) [2], allow Ti pseudobrookites to be excellent candidates for the development of new pigments. Indeed, some patents about yellow pigments based on Ti pseudobrookites have been already developed (Rademachers [3], Maloney [4], Katamoto [5] and Suzuki [6]), basically for low-temperature applications (paints, plastics, resins, etc.). Moreover, some recent studies show that Ti pseudobrookites may also be used as ceramic pigments for the coloration of glazes under more severe firing treatments [7–10].

Pseudobrookites are entropy-stabilized phases [11,12], that is to say, the cationic disorder contributes the entropic component to stabilize pseudobrookite phase at high temperatures. By decreasing the temperature, pseudobrookites decompose in the thermodynamically most stable phases, either a mixture of binary oxides M₂O₃ and TiO₂ (pseudobrookites M³⁺₂⁺Ti⁴⁺O₅), a mixture of ilmenite MTiO₃ and rutile TiO₂ (pseudobrookites M²⁺₂⁺Ti⁴⁺O₅) [12], or giving rise to a smaller symmetry phase (Ti₂O₅ case) [13]. In this regard, the higher or lower thermal stability of pseudobrookites is strongly dependent on its composition; this decomposition can be inhibited obtaining stabilized pseudobrookite at low temperatures or even at room temperature by adding different dopants or forming solid solutions.

The solid solution from Fe₂TiO₅ to FeTi₂O₅ was studied by Gray and Ward [14] and also by Navrotsky [15]. It has commonly been observed that naturally occurring minerals with pseudobrookite structure have intermediate compositions; thus, in addition to varying proportions of Fe²⁺ and Fe³⁺ [16], other ions such as Mn²⁺, Mn³⁺/Mn⁴⁺, Al³⁺, and Cr³⁺/Cr⁴⁺ frequently occur. It is well known that for the synthesis of iron pseudobrookite Fe₂TiO₅ from anatase an iron (III) oxide, a significant excess of titania with respect to the Fe₂TiO₅ stoichiometry is needed, in order to “achieve a complete reaction of the iron oxide” and to obtain a hematite-free pseudobrookite [17]. In effect, Seitz et al. [18] conclude from Rietveld analyses that the stoichiometry of hematite-free pseudobrookite is Fe₁.₉₅Ti₀.₀₅O₂ at 900°C and Fe₁.₉₅Ti₀.₉₅O₂ at 1400°C. Furthermore, the pseudobrookite phase obtained by sintering under air conditions.

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atmosphere does not have the Fe₂TiO₅ stoichiometric composition (it shows iron/titanium ratio lower than 2) and, moreover, this variation occurs with the temperature of thermal treatment. Seitz et al. propose two hypotheses to explain this variation of stoichiometric composition: (i) the thermal treatment under air leads to an average oxidation number intermediate between 2 and 3 for the iron ions, and (ii) the occurrence of cation vacancies, concomitantly to a dense anionic subnetwork. However, the Mösßbauer study performed on samples constituted by a single pseudobrookite phase strongly suggests that crystallization of a pure pseudobrookite phase from iron-deficient chemical compositions (iron/titanium < 2) is not due to stabilization of Fe²⁺ into the bulk but to the occurrence of cation vacancies [18]: a proposed formulation can be written as (Fe₃₊ₓ⁺Ti₂₋ₓ⁻)₈VₓO₅₋ₓ with the electroneutrality of the composition leading to the vacancy concentration z = x/(x + 10); for instance, z ∼ 0.006 (x ∼ 0.06) and z ∼ 0.009 (x ∼ 0.09) for the hematite-free pseudobrookite at 900 and 1400 °C respectively.

Yellow-ochre to reddish maroon or brown hues can be obtained by substituting iron or titanium ions with other metallic cations in pseudobrookite (e.g., Mg⁺²). Pseudobrookite-based pigments were first developed in the 1970s in order to get heat-resistant colorants for thermoplastics, industrial paints, and other applications involving low-temperature treatments [18]. Dondi et al. [8] have studied the potentialities of these types of compounds for ceramic pigment applications, i.e., applications involving high-temperature treatment. The colors achievable with pseudobrookite pigments are significantly dependent on the composition of ceramic matrices, varying from saturated brown shades achieved in low temperature glasses to a lighter brown in stoneware glazes, while the colors fade to a light gray in highly opacified glasses for wall tiles, where the high CaO and ZnO content contributes to rapid dissolution of the pigment [8]. According to Dondi et al., the color is originated by several light absorptions in the visible spectrum due to both d⁶ electrons transitions and a magnetically-coupled paired transition between iron ions in adjacent lattice sites. A doubling of the "A₁→T₁ and "T₁ bands is related to the occurrence of Fe³⁺ in both octahedral sites of pseudobrookite [5]. Recently, Gargori et al. [19] described a red-brown ceramic pigment based on chromium-doped ferrian armalcolite (MgFe)₂(FeTi₃)O₁₀, which belongs to the pseudobrookite group X₂YO₅, with X and Y being usually Fe (2 + and 3 +), Mg, Al, and Ti. End members of this group are armalcolite ((Mg,Fe)₂Fe₃O₁₀), pseudobrookite (Fe₂TiO₅), ferropsudobrookite (Fe₃TiO₅), and karrooite (MgTi₂O₅).

The compound Cr₂TiO₅ could be synthesized as a stoichiometric single phase above 1660 °C in air [20]. Application of selected area electron diffraction, high resolution electron microscopy and powder X-ray diffraction studies showed that Cr₂TiO₅ is isomorphic with CrFe₂TiO₅, which shows V₃O₅ oxvanite monoclinic type structure (space group C2/c), showing cell parameters a = 7.020(1) Å, b = 5.025(1) Å, c = 9.945(2) Å and β = 111.43(2)° (ICPDS 73-0409). It was found that Cr₂TiO₅ is unstable relative to a mixture of Cr₂O₃ (ss) and a so-called "E" phase below 1660 °C [20].

In the literature there is a controversy about the existence of a monoclinic polymorph for Fe₂TiO₅ orthorhombic pseudobrookite. Shiojiri et al. [21] reported a doubtful new monoclinic structure for Fe₂TiO₅. The crystal structure of metal pseudobrookite (Fe₂TiO₅) is determined by Shiojiri et al. from high-resolution electron microscopy images and their computer simulated images, with the aid of electron diffraction and X-ray powder diffraction. The new structure would have a monoclinic unit, containing eight molecules, with a = 2.223, b = 0.373, c = 0.980 nm, and β = 116.2°. [22]. Other authors detect a monoclinic Fe₂TiO₅ (ICPDS 73-1898, having lattice parameters a = 10.101, b = 5.037, c = 7.024 Å) with XRD peaks associated with nanostructured materials, which show a wide profile and relatively low intensity of peaks due to the low particle size of the involved nanoparticles [22,23]. A monoclinic form of Fe₂TiO₅, metastable in nature, has been artificially grown as single crystals from a flux containing various amounts of the basic oxides and characterized by Mößbauer spectroscopy [24], but the occurrence of this controverted polymorph from a solid state reaction is unusual. The most comprehensive work on orthorhombic Fe₂TiO₅ and its solid solution with Fe₃TiO₅ is the paper of Guo et al. [25], which shows that the whole solid-solution series has the pseudobrookite (Ccmm) structure type. Guo et al. emphasize that no diffraction peaks associated to monoclinic specimen were detected in any of the samples prepared for their study. Therefore Guo et al. found no evidence for the monoclinic phase reported by Shiojiri et al. [21].

The monoclinic CrₓFe₂₋ₓTiO₅ unstable at room temperature, is isostructural with VₓO₇-type gamma-TiO₅, CrFeTiO₅ and VₓTiO₅ [26]. In this communication chromium-doped pseudobrookite compositions of the CrₓFe₂₋ₓTiO₅ solid solutions series from pseudobrookite Fe₂TiO₅ (x = 0) to Cr₂TiO₅ (x = 2) have been studied in order to stabilize a red-brown pigment in CaO-ZnO-SiO₂ ceramic matrices. The effect of several flux agents as mineralizers and the use of non-conventional synthesis methods such as ammonia coprecipitation (CO), citrate route or metal-organic decomposition method (MOD) and a polymeric gel (GP) method have also been studied.

On the other hand, the synthesis of pigments showing high NIR reflectance (the so-called “cool pigments”) is highly demanded nowadays, since they can help reduce the temperature of the external walls and therefore the temperature inside of buildings, thus reducing the power consumption during hot weather. Therefore, the NIR reflectance of an optimized CrₓFe₂₋ₓTiO₅ composition is compared with a commercially available (Zn-Fe-Cr) brown spinel (CPMA 13-37-7) [27] in order to evaluate the pigment suitability as an energy-saving material.

2. Materials and methods

2.1. Samples preparation

CrₓFe₂₋ₓTiO₅ compositions have been prepared by the ceramic route (or solid state reaction method), using as precursors Fe₂O₃ and TiO₂ (anatase) supplied by Panreac S.A., and Cr₂O₃ supplied by Riedel. In this ceramic method the precursors were homogenized in a planetary frit of the CaO-ZnO-SiO₂ system (1050 °C) in order to characterize its pigmenting properties.

The effect of the presence of flux agents on the reactivity of the system was studied by addition of several mineralizers (10 wt%) to the ceramic mixture x = 0.1 and fired successively at 1000 and 1100 °C with soaking times of 3 h. The tested mineralizers were: a) two low temperature mineralizers such as H₂BO₃ (melting point m.p. 170.9 °C) and NH₄Cl (decomposes at 338 °C), b) a middle temperature mineralizer Li₂CO₃ (m.p. 723 °C), and c) a relatively high temperature flux agent NaF (m.p. 993 °C). On the other hand, x = 0.1 samples (both non-mineralized and mineralized with NH₄Cl) were pelletized at 100 bar in a conventional press and fired at 1000 °C for 2 h, in order to study the effect of powder compaction on the reactivity and color of the pigment.

Moreover, the effect of three non-conventional methods of preparation based on gel techniques was also studied for the optimized x = 0.1 composition. In the coprecipitation or colloidal-gel method (CO), Cr(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O and titanium(IV) n-butoxide (for 10 g of CrₓFe₁₋ₓTiO₅ final product and all supplied by ALDRICH S.A.) were successively dissolved at room temperature and continuously stirred in 200 mL of water, then ammonia solution (15 wt%) were dropped to the stirred solution until pH = 8 is reached; finally, the obtained gel was dried at 110 °C. In the MOD (metal-organic decomposition) or citrate-gel method, the same precursors of CO method (for 10 g of CrₓFe₁₋ₓTiO₅ final product) were successively dissolved at room temperature and continuously stirred in 200 mL of water. Then cotic
acid, in a molar ratio citric acid: pseudobrookite = 1:2, was added to the stirred solution and the obtained solution was also dried at 110 °C. Finally in the GP (polymeric gel) method, the same precursors of CO route (for 10 g of Cr1.9Fe0.1TiO5 final product) were successively dissolved at room temperature and continuously stirred in 200 mL of ethanol. The solution was closed to the air by a polyethylene film and maintained for 24 h at room temperature with continuous stirring in order to promote the hydrolysis-polymerization of the mixture; then, the obtained gel was dried at 110 °C. All dried gels were fired at 500 °C for 1 h (charring procedure) for its stabilization, and then they were calcined at 1000 °C for 3 h along with the CE sample.

2.2. Samples characterization

X-Ray Diffraction (XRD) was carried out on a Siemens D5000 diffractometer using Cu Kα radiation, 10–70° 20 range, scan rate 0.02°/20 s, 4s per step and 40 kV and 20 mA conditions. In order to measure the parameters of the crystalline unit cell through POWCAL and LSQC programs [28], α-Al2O3 was added (40 wt%) as internal standard, and XRD patterns were recorded at 20–70° 20 range under slower conditions (scan rate 0.01°/20 s, 10 s per step and 40 kV and 20 mA).

UV–Vis–NIR spectra of fired powder samples and also of 5 wt% glazed samples (in a conventional double-firing frit on the SiO2-CaO-ZnO system (1050 °C)) were collected using a Jasco V670 spectrometer through diffuse reflectance technique which gives data in absorbance using arbitrary units (A), or in reflectance units (R(%) using the Kubelka-Munk transformation model. The Kubelka-Munk (K-M) function model has a particularly simple solution in the case of reflection of radiant energy at boundary surfaces of mat (dull, scattering) surfaces [29,30]. L*a*b* color parameters of glazed samples were measured following the CIE-L*a*b* colorimetric method [31] using a X-Rite SP60 spectrometer, with standard lighting D65 and 10° observer. On this method, L* is a measure of lightness (100 = white, 0 = black) and a* and b* of chroma (−a* = green, +a* = red, −b* = blue, +b* = yellow). The optical reflectance spectrum was scanned in the range of 300–2500 nm for the optimized pigment, and the total solar reflectance (R) and the NIR solar reflectance (R_NIR) were obtained as the integral of the measured spectral reflectance and the solar irradiance divided by the integral of the measurement window between 300–2500 nm for R or 750–2500 nm for R_NIR, as in the Eq. (1):

\[ R = \frac{\int_{300}^{2500} R(\lambda) \, d\lambda}{\int_{300}^{2500} I(\lambda) \, d\lambda} \]

where, \( R(\lambda) \) is the spectral reflectance (W m\(^{-2}\)) measured from UV–Vis–NIR spectroscopy and \( I(\lambda) \) is the standard solar irradiation (W m\(^{-2}\) nm\(^{-1}\)) according to the American Society for Testing and Materials (ASTM) Standard G173-03 [32].

Microstructure characterization of powders was carried out by Scanning Electron Microscope (SEM) using a JEOL 7001 F electron microscope (following conventional preparation and imaging techniques). The chemical composition and homogeneity of the samples was determined by semi-quantitative elemental analysis with an EDX analyzer (supplied by Oxford University) attached to the microscope.

3. Results and discussion

3.1. X-Ray diffraction characterization (XRD)

XRD results obtained with fired powders are summarized in Table 1 and the corresponding XRD patterns of samples fired at 1400 °C are shown in Fig. 1. All fired samples are red-brown colored and its XRD patterns indicate the following evolution of crystalline phases:

a) At 1000 °C, hematite peaks predominate in the XRD pattern of sample with x = 0 (undoped pseudobrookite), samples with x = 0.1, 0.3, 0.5 and x = 0.7 show orthorhombic pseudobrookite as the main phase, that turns into monoclinic Fe-Cr2TiO5 in x = 0.5 and x = 0.7 samples. Samples with higher x values show predominant diffraction peaks associated with the reactants eskolaite (Cr2O3) and rutile (TiO2).

b) At 1200 °C, samples with x = 0 to x = 0.3 show strong diffraction peaks associated with orthorhombic pseudobrookite and weak peaks of residual hematite; at higher x values the monoclinic Fe-Cr2TiO5 predominates, but sample x = 2 still remains unreacted, since only the peaks associated with the reactants are detected.

c) At 1400 °C, samples up to x = 0.5 show pseudobrookite as predominant crystalline phase, but some residual hematite is also detected; at x = 0.5 both pseudobrookite and monoclinic Fe-Cr2TiO3 coexist, while at higher x values monoclinic Fe-Cr2TiO3 is detected. However, in sample x = 2 the peaks of monoclinic Cr2Ti2O7 are not detected and, instead, the XRD pattern shows the presence of a mixture of Cr2O3 (ss), Cr2Ti2O7 (the so-called “E” phase) [20], along with other unidentified peaks (Fig. 1). These peaks could probably be associated with the discrete homologous series of Cr2Ti2n−1O2n−1 (with n = 6, 7, 8) that were found to be stable as single phases in certain temperatures range, in agreement with S. Sōmiya et al. [33].

The described evolution of the crystalline phases agrees with previous reports: for instance, Seitz et al. [18] postulate the presence of cation vacancies that lead to a proposed formulation written as (Fe2+x−2Ti2n−2)+x−n−2Cr2n+2O2n, in order to explain that the pseudobrookite phase obtained under air conditions does not show the Fe2TiO4 stoichiometric composition and the fact that this composition varies with firing temperature. In effect, in the case of samples between x = 0 and x = 0.5, hematite always appears as residual phase along with pseudobrookite, which cannot be obtained as the single crystalline phase. In contrast, monoclinic Fe-Cr2TiO3 is obtained as single phase in samples between x = 0.7 to x = 1.5 (Fig. 1).

3.2. Color evolution of samples

CIE-L*a*b* color measurements of fired powders and of 5 wt% glazed samples into a CaO-ZnO-SiO2 conventional glaze are shown in Table 2. The results indicate that the progressive introduction of chromium decreases L* parameter (samples become darker) and also decreases both a* and b* parameters of the powders, in agreement with the visual perception. Likewise, when the firing temperature increases, the color evolution is similar and samples become darker and more bluish (all L*, a* and b* parameters decrease).

When the powders are 5 wt% glazed in a double-firing frit (1050 °C) the non-doped chromium sample becomes practically colorless: at 1000 °C this sample shows a very light yellowish color (L*:a*b* = 71.8/2.6/22.8, see Table 2), and also at 1400 °C (L*:a*b* = 71.3/1.1/9.5, see Table 2).
Table 2 and Fig. 2), associated with a L* value higher than 71. This result indicates that chromium is the responsible for the brown shade of the glaze. In these glazed samples, the best red-brown color is obtained at 1000 °C: the x = 0.1 sample with L*a*b* = 43.2/18.8/12.5 shows the highest red chroma (positive a* value) of the prepared samples, showing a relatively high intensity of color (low L*). As a reference or comparison, a commercial pink coral based on hematite inclusion into zircon crystals shows L*a*b* = 53/26/24, namely, higher a* red shade and lower intensity than the optimized sample x = 0.1, while the commercially available brown pigment based on Zn-Fe-Cr spinel (CPMA 13-37-7) [27] shows L*a*b* = 32.6/13.0/9.2, with higher intensity of color but lower a* red parameter [19].

On the other hand, as the firing temperature of powders increases (Table 2), a strong decrease of both L* and red a* parameters is detected. Likewise, the b* parameter turns into a blue shade (negative values) and the powders are black colored.

Similar evolution is observed in glazed samples (see Table 2):

a) At 1000 °C, associated to the lowest reactivity of the system (lowest crystallization of pseudobrookite or monoclinic Fe-Cr2TiO5); the reddish shade (evaluated by a*) is the best, varying from 12.0 (x = 1.5) to 18.8 (x = 0.1).

b) At 1200 °C, associated with large crystallization of pseudobrookite or monoclinic Fe-Cr2TiO5 phases: the intensity of the color decreases (higher L*) and the red shade also decreases to 8.8 (x = 1.5) and 12.2 (x = 0.1) respectively.

c) When the reactivity is completed at 1400 °C, the intensity continues to fall and the reddish value a* also decreases to 6.4–7.6.

From the above discussed XRD and CIEL*a*b* results, it can be pointed out that the red-brown color of glazed samples is associated with the presence of chromium (since the glaze becomes colorless without Cr (x = 0)), and it becomes green in sample x = 2 (showing eskolaite Cr2O3 and the E phase, Cr2Ti2O7, as detected phases) (Fig. 2). However, the best red-brown colors are not associated with a complete crystallization of pseudobrookite or monoclinic Cr2Ti2O5 phase; indeed, when its crystallization progresses with temperature, powders become practically black colored and glazed samples show low reddish shades (high values of L* and low values of both a* and b*).

3.3. UV–Vis–NIR absorption spectra

The UV–Vis–NIR absorption spectra of fired powders are shown in Fig. 3. The following bands are detected: (a) intense bands at 200–300 nm, (b) intense band centered at 400 nm overlapping with (a), (c) strong shoulder at 510 nm, (d) weak shoulder at 600 nm, (e) weak band at 700 nm, and (f) a very weak band at 900 nm. It is difficult to distinguish the presence of Cr3+, Cr4+ or Fe3+ ions in octahedral sites in UV–Vis–NIR absorption spectra of samples containing the ions in these positions simultaneously [34–36], because the bands of Cr3+ and Cr4+ are overlapped to a high extent with the absorption bands of iron (III). But the main characteristic of the Fe3+ ions in octahedral sites is
the strong absorption associated to the transitions $^6A_{1g}(S) \rightarrow ^4A_{1g}$, $^4E(G)$ at 450 nm and $^6A_{1g}(S) \rightarrow ^4T_{2g}(D)$ at 400 nm that dominates the absorption spectrum of the powders either at 1000 °C or 1200 °C (Fig. 3) [19].

UV–Vis–NIR absorption spectra of non-doped (without chromium) glazed samples are shown in Fig. 4; according to the colorless shade of the samples, only an intense absorption band due to the charge transfer associated to the glaze centered at 280 nm has been detected, along with a very weak band centered at 450 nm associated with Fe$^{3+}$ ions in octahedral sites. The UV–Vis–NIR absorption spectra of Cr-doped glazed samples are shown in Fig. 5 and the detected bands are the following: (a) intense band at 270 nm due to the charge transfer of the glassy matrix of the glazed samples, (b) intense band centered at 520 nm, (c) weak shoulder at 600 nm, (d) double weak bands at 700 nm, (e) weak shoulder at 850 nm, and (f) a very weak band at 900 nm. The strong absorption in the range 400–450 nm has disappeared, and along with the intense ion charge transfer of the bulk glaze, an intense band at 520 nm dominates the spectrum, indicating the presence of Cr$^{4+}$ in octahedral coordination with its characteristic absorption band centered at 520 nm [19,37,38]. On the other hand, the intensity (optical density) of absorption bands in the spectra of glazed samples increases when the amount of chromium increases from $x = 0$ to $x = 0.5$ (pseudobrookite crystallization field, Fig. 5.a) and decreases from $x = 0.5$ to $x = 1.5$ (monoclinic Fe-Cr$_2$TiO$_5$ crystallization field, Fig. 5.b). Finally, the weak shoulder at 600 nm and the double weak band at 700 nm, both of them detected more evidently when chromium amount increases in the pseudobrookite crystallization field (from $x = 0$ to $x = 0.5$), indicate a progressive presence of Cr$^{3+}$ in octahedral sites in agreement with literature [19,39,40]. On the other hand, the optical density of these Cr$^{3+}$ bands decreases with $x$ in the monoclinic Fe-Cr$_2$TiO$_5$ crystallization field (from $x = 0.5$ to $x = 1.5$), but the 520 nm band intensity associated to Cr$^{4+}$ in octahedral sites remains stable, indicating a saturation of Cr$^{4+}$ concentration at around $x = 0.5$. These results are in agreement with the evolution of the reddish $a^*$ parameter of glazed samples in Table 2: a$^*$ increases slightly from $x = 0.1$ to $x = 0.7$ samples, associated with the increase of optical density at 520 nm due to Cr$^{4+}$, and remains practically stable in the monoclinic Fe-Cr$_2$TiO$_5$ crystallization field (from $x = 0.7$ to $x = 1.5$, with values around $a^* = 6.7$), associated with a stable optical density of the 520 nm band of Cr$^{4+}$ in these samples.
Thereby, although the assignment of bands is difficult because of the overlapping of the absorptions of Cr$^{3+}$, Cr$^{4+}$ and Fe$^{3+}$ ions in octahedral coordination, the analysis of the UV–Vis–NIR absorption spectra shows that chromium is the chromophore in the glazes, predominating the oxidation state $+4$, although Cr$^{3+}$ concentration increases when chromium amount increases. This behavior is in agreement with the color and the evolution of the CIEL*a*b* values of glazed samples: the intensity of the color increases always with both chromium amount and temperature (L* diminishes) and the red-brown chroma tends to blue, due to the enhancement of the 600 nm (orange) absorption band when chromium amount or temperature increase.

3.4. Evolution of crystalline unit cell parameters with the amount of chromium

Unit cell parameters were measured in powders fired at 1400 °C (Table 3). The evolution of the volume of the crystalline unit cell with chromium amount (x) is shown in Fig. 6 and the following characteristics can be pointed out:

a) From x = 0 up to x = 0.5, in which the presence of Fe$_2$TiO$_5$ pseudobrookite dominates or coexists (x = 0.5) with Fe-Cr$_2$TiO$_5$ monoclinic phase, the volume of the pseudobrookite unit cell decreases smoothly with the chromium amount according to the entrance of Cr$^{4+}$ (Shannon-Prewitt ionic radius 0.69 Å in coordination VI) in the structure of the pseudobrookite, replacing Ti$^{4+}$ (0.745 Å in coordination VI) [41].

b) From x = 0.5 to x = 1.5, in which the Fe-Cr$_2$TiO$_5$ monoclinic phase coexists with Fe$_2$TiO$_5$ pseudobrookite (at x = 0.5) or dominates the system, the unit cell decreases smoothly with the chromium amount. Indeed it can be considered that the network of the Fe-Cr$_2$TiO$_5$ monoclinic phase grows progressively with the entrance of iron Fe$^{3+}$ (0.785 Å in coordination VI high spin) replacing Cr$^{3+}$ (Shannon-Prewitt ionic radius 0.755 Å in coordination VI). However, the increase in unit cell volume of the Fe-Cr$_2$TiO$_5$ monoclinic phase due to iron entrance (as the x value diminishes) is reduced by the presence of Cr$^{4+}$ in the structure (replacing Ti$^{4+}$ and acting as reddish chromophore) as it was shown by the UV–Vis–NIR absorption spectra of these samples.

c) For x = 2, the pure Cr$_2$TiO$_5$ monoclinic phase is metastable at room temperature and is not synthesized in this study at 1400 °C. Instead, a mixture of Cr$_2$O$_3$, Cr$_2$Ti$_2$O$_7$, the so-called “E” phase [20] and other unidentified peaks is detected (Fig. 1). In Table 4 and Fig. 6 the values of 33-0409 JCPDS XRD card have been used.

3.5. Effect of mineralizers

As indicated above, in order to study the effect of the presence of flux agents on the reactivity of the system, 10 wt% of several mineralizers were added to the ceramic mixture x = 0.1, which was then fired successively at 1000 and 1100 °C with soaking time of 3 h. The CIEL*a*b* color parameters of both non-mineralized and mineralized

| Sample | Crystalline Phase | a (Å) | b (Å) | c (Å) | β (°) | V(Å³) |
|--------|------------------|------|------|------|------|-------|
| x = 0  | Pseudobrookite   | 9.795(5) | 9.9699(2) | 3.72601(3) | - | 363.90(1) |
| x = 0.1| *                | 9.767(1) | 9.952(3) | 3.7354(6) | - | 363.32(1) |
| x = 0.3| *                | 9.735(1) | 9.9133(3) | 3.7354(6) | - | 360.47(1) |
| x = 0.5| *                | 9.712(1) | 9.873(2) | 3.733(2) | - | 357.96(1) |
| x = 0.5| Cr$_2$TiO$_5$    | 7.015(2) | 5.01(2)  | 10.145(4) | 110.67(4) | 332.96(2) |
| x = 0.7| *                | 7.008(3) | 5.006(3) | 10.102(5) | 110.80(2) | 331.30(3) |
| x = 1  | *                | 7.002(2) | 4.990(2) | 10.064(4) | 110.92(4) | 328.54(3) |
| x = 1.5| *                | 6.974(6) | 5.005(2) | 10.052(4) | 111.25(4) | 327.51(4) |
| x = 2  | *                | 7.01500 | 5.01400 | 9.9370 | 111.42 | 325.375 |

* The values for x = 2 (Cr$_2$TiO$_5$), metastable at room temperature and not synthesized in this study, are the values of 33-0409 JCPDS XRD card.
(10 wt% added mineralizer) samples with \( x = 0.1 \) (fired at 1000 °C) and 5 wt%-glazed into the conventional double-firing frit are shown in Table 4. Likewise, several XRD patterns of the sample with \( x = 0.1 \) fired at 1000 °C for 3 h are shown in Fig. 7.

According to the data of Table 4, all the mineralized glazed samples, with low temperature (\( \text{H}_3\text{BO}_3 \) and \( \text{NH}_4\text{Cl} \)), middle temperature (\( \text{Li}_2\text{CO}_3 \)) and relatively high temperature (\( \text{NaF} \)) flux agents, show similar \( \text{L*}^a\text{a*}^b\text{b*} \) values; although the best reddish value (higher \( \text{a*} \) parameter) is associated with the non-mineralized sample, very similar results are obtained with \( \text{NH}_4\text{Cl} \) addition. On the other hand, both non-mineralized and mineralized samples (\( x = 0.1 \)) with \( \text{NH}_4\text{Cl} \) were pelleted at 100 bar in a conventional press and fired at 1000 °C for 2 h, in order to analyze the effect of powder compaction (prior to firing treatment) on the reactivity and color of the pigment powders and corresponding glazed samples. The results shown in Table 4 indicate that the compaction pressure does not increase the intensity and reddish shade of glazes.

With regards to powders reactivity, the XRD patterns shown in Fig. 7 indicate that \( \text{NH}_4\text{Cl} \) addition as mineralizer (Fig. 7.c) gives rise to more intense peaks of pseudobrookite than non-mineralized sample (Fig. 7.a). Likewise, compaction pressure also increases the reactivity, both in non-mineralized and in \( \text{NH}_4\text{Cl} \)-mineralized samples, showing the pseudobrookite XRD peaks higher intensity in pelleted samples than its homologous non-pelleted samples. However, as it was previously discussed, the fact of having an increased reactivity, associated with a more advanced crystallization of pseudobrookite, does not involve obtaining better reddish nor more intense colors. The red color is associated with the \( \text{Cr}^{4+} \) amount into the pseudobrookite lattice rather than with the amount of pseudobrookite crystallization. This behavior is confirmed analyzing the effect of firing temperature on reactivity and the color: despite of the increase of reactivity of the system with temperature, the powders darken and glazed samples show lower reddish shades (high values of \( \text{L*} \) and low values of both \( \text{a*} \) and \( \text{b*} \)) when temperature (reactivity) increases.

### 3.6. Microstructure analysis

In order to analyze the microstructure of the pigment, some SEM studies were carried out. SEM micrographs of powders with \( x = 0.1 \) without mineralizer fired at 1000 and 1200 °C (for 3 h) are shown in Fig. 8. Spheroidal particles of 0.5–2 \( \mu \)m of average particle size are observed at 1000 °C, which increase slightly in size when temperature increases at 1200 °C. On the other hand, the performed SEM-EDX mapping analyses (Fig. 9) show that the Cr distribution in the particles is homogenous, although some segregation of Ti and Fe is observed in agreement with XRD results which show the presence of rutile and hematite as residual crystalline phases.

### 3.7. Non-conventional methods

The XRD patterns of gel powders (\( x = 0.1 \)) dried at 110 °C are shown in Fig. 10; nitrates crystallization (such as ammonium nitrate, \( (\text{NH}_4)^\text{NO}_3 \)) is detected in all dried samples, due to the employment of nitrates as precursors, although GP dried gel appears practically amorphous. In the case of gels fired at 500 °C for 1 h, the XRD patterns (not shown) are typical of amorphous samples, due to nitrates decomposition at this temperature. The XRD patterns of gel powders fired at 1000 °C for 3 h are shown in Fig. 11: all fired powders appear more reactive than CE powder, showing low intensity XRD peaks associated with residual hematite and rutile, which are even not detected in CO sample. Similarly to the case of ceramic samples, the increase of

| Mineralizer          | \( \text{L*}^a\text{a*}^b\text{b*} \) |
|----------------------|-----------------------------------|
| Non-mineralized      | 43.2/18.8/12.5                    |
| \( \text{H}_3\text{BO}_3 \) | 46.6/13.9/6.6                    |
| \( \text{NH}_4\text{Cl} \) | 42.8/17.2/9.2                    |
| \( \text{Li}_2\text{CO}_3 \) | 39.8/14.8/6.6                    |
| \( \text{NaF} \) | 45.0/9.7/6.3                     |
| Non-mineralized and pelleted | 45.8/15.0/5.4                  |
| \( \text{NH}_4\text{Cl} \) mineralized and pelleted | 42.1/15.4/8.1                  |

Table 4: CIEL*a*b* of \( \text{Fe}_2(\text{Cr}_x\text{Ti}_{1-x})\text{O}_5 \) 5 wt% glazed samples: \( x = 0.1 \), fired at 1000 °C and 10 wt% added mineralizer.
reactivity is not associated with a better red-brown coloring; in effect, the UV-Vis-NIR absorption spectra of gel powders (x = 0.1) fired at 1000 °C, once glazed (5 wt%) within a double-firing frit (Fig. 12), show that the 520 nm band associated with Cr⁴⁺ in glazed sample exhibits higher intensity for CE sample followed by CO, GP and finally MOD sample. Accordingly, the measured L*a*b* values for these glazed samples (Table 5) indicate that gel samples show a lower red parameter (a*) than CE sample. Finally SEM micrographs of x = 0.1 gel powders fired at 1000 °C for 3 h (Fig. 13) show that the particles conforming the agglomerates are homogeneous and present an average size around 200 nm. The spheroidal particles may be better differentiated in CO sample; instead, the particles are more heterogeneous in CE sample (Figs. 8 and 9), with particle sizes compressed between 0.5 and 2 µm.

3.8. NIR reflectivity of the optimized pigment

The reflectance values R and R_NIR (calculated by Eq. (1) in the range 350–2500 nm or in the range 750–2500 nm, respectively) of the optimized Cr₁Fe₁.₉TiO₅ compared with a commercially available (Zn-Fe-Cr) brown spinel (CPMA 13-37-7) are shown in Table 6: both powder and glazed samples show higher reflectance than the reference brown pigment in all the analyzed wavelength ranges (total and NIR),
indicating the pigment suitability as an energy-saving material (cool pigment). The reflectance spectra in the 350–2500 nm range of the optimized Cr1Fe1.9TiO5 pigment (both as powder and 5 wt% glazed in double-firing frit) are shown in Fig. 14.

### 4. Conclusions

Reddish ceramic pigments based on the solid solution series between Fe2TiO5 (orthorhombic pseudobrookite) and Cr2TiO5 (monoclinic) have been synthesized and characterized. CrxFe2-xTiO5 compositions were prepared by the ceramic route. In order to analyze the pigmenting capacity, the powders were 5 wt% glazed into a conventional double-firing frit (1050 °C). At 1400 °C the reactivity is completed and pseudobrookite crystallizes in the range x = 0–0.4, both pseudobrookite and monoclinic Fe-Cr2TiO5 coexist at x = 0.5, while in the range x = 0.7–1.5 monoclinic Fe-Cr2TiO5 crystallizes as the only

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**Fig. 10.** XRD of non-conventional powders x = 0.1 dried at 110 °C. CRYSTALLINE PHASES: AN (ammonium nitrate (NH4)NO3). METHODS: CO (coprecipitation), MOD (metal-organic decomposition), GP (polymeric gel).

**Fig. 11.** XRD of non-conventional powders x = 0.1 fired at 1000 °C/3 h. CRYSTALLINE PHASES: P (Cr-Cr2TiO5 pseudobrookite) H (Hematite Fe2O3), R (Rutile): METHODS: CE (ceramic), CO (coprecipitation), MOD (metal-organic decomposition), GP (polymeric gel).

**Fig. 12.** UV–Vis–NIR absorbance spectra of gel powders x = 0.1 fired at 1000 °C 5 wt% glazed in double-firing frit: METHODS: CE (ceramic), CO (coprecipitation), MOD (metal-organic decomposition), GP (polymeric gel).

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**Table 5**

| TABLE 5 CIEL*a*b* of non-conventional samples Fe2(CrxTi1-x)O5 x = 0.1 sample, fired at 1000 °C. METHODS: CO (coprecipitation), MOD (metal-organic decomposition), GP (polymeric gel). |
| --- | --- | --- | --- |
| CE | CO | MOD | GP |
| Dried gels | - | 43.5/8.1/8.6 | 42.4/5.2/6.2 | 50.7/8.0/13.9 |
| Fired powder | 46.2/6.8/7.6 | 42.4/1.3/0.8 | 43.0/2.2/0.8 | 44.0/3.0/1.8 |
| 5 wt%. glazed | 43.2/18.8/12.5 | 41.2/16.1/15.6 | 43.0/5.2/0.8 | 44.0/6.0/1.8 |

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and becomes green in unreacted sample $x = 2$ (showing eskolaite Cr$_2$O$_3$ and the valence $+4$ dominates, although Cr$_3^+$ concentration increase.

Glazed samples show that chromium is the chromophore in the glazes (high L* and low a* and b* values). UV practically black colored and glazed samples show poor reddish shades when chromium amount increases always with both chromium amount and temperature (L* diminishes) and the red-brown chroma tends to blue, due to the enhancement of the 600 nm (orange) absorption band occurring when the chromium amount or temperature increase. The best reddish shade for samples fired at 1400 °C (when the reactivity is completed) is obtained in $x = 0.5$ sample, since at higher $x$ values (in the monoclinic Fe-Cr$_2$TiO$_5$ crystallization field, from $x = 0.7$ to $x = 1.5$) the 520 nm band intensity associated to Cr$^{4+}$ in octahedral sites remains stable, indicating a saturation of the chromophore Cr$^{4+}$ concentration.

In the pseudobrookite crystallization field ($x = 0$ to $x = 0.5$) the volume of the pseudobrookite unit cell decreases smoothly with the chromium amount according to the entrance of Cr$^{4+}$ (Shannon-Prewitt ionic radius 0.69 Å in coordination VI) in the structure of the pseudobrookite, replacing Ti$^{3+}$ (0.745 Å in coordination VI). In the Fe-Cr$_2$TiO$_5$ monoclinic crystallization field ($x = 0.5$ to $x = 1.5$) the volume of the unit cell decreases smoothly with the chromium amount: namely, it grows progressively with the entrance of iron Fe$^{3+}$ (0.785 Å in coordination VI) replacing Cr$^{3+}$ (Shannon-Prewitt ionic radius 0.755 Å in coordination VI).

The effect of flux agents analyzed by 10 wt% addition of several mineralizers to the ceramic mixture ($x = 0.1$) shows that all mineralized glazed samples present similar L* a*b* values; although the best reddish value (higher a* parameter) corresponds to the non-mineralized sample, a very similar value is obtained with NH$_4$Cl addition. On the other hand, both non-mineralized and mineralized (with NH$_4$Cl) precursor mixtures with $x = 0.1$ composition were pelletized at 100 bar in a conventional press and fired at 1000 °C for 2 h, showing that the compaction pressure does not increase the intensity (lower L*) and reddish shade (higher a*) of the glazes color. Indeed, although the use of mineralizers and compaction pressure leads to a higher crystallization of pseudobrookite with respect to non-mineralized and non-pelletized samples, this is not associated with better reddish colors. Thus, this result confirms that the red color is rather associated with the Cr$^{4+}$ amount into the pseudobrookite lattice and not with the amount of pseudobrookite crystallization.

The preparation of the optimized $x = 0.1$ sample by non-conventional methods, such as co-precipitation (CO), metal-organic decomposition (MOD) and polymeric gel (PG) routes, show that all the fired gel samples appear more reactive than CE powder, showing low intensity peaks associated with residual hematite and rutile. However, this reactivity increase is not associated with a better red-brown coloring, similarly to the results obtained in the studies with mineralizers and pressure. SEM microscopy observations indicate that the gel particles are homogeneous and show an average size around 200 nm; in contrast, the particles are more heterogeneous in CE sample, having a particle size between 0.5 and 2 μm at 1000 °C which increases slightly when temperature increases at 1200 °C. The inset of Fig. 14 shows the best red color in the double firing at 1000 °C and temperature (L* diminishes) and the red-brown chroma tends to blue, due to the enhancement of the 600 nm (orange) absorption band occurring when the chromium amount or temperature increase.

The best reddish shade for samples fired at 1400 °C (when the reactivity is completed) is obtained in $x = 0.5$ sample, since at higher $x$ values (in the monoclinic Fe-Cr$_2$TiO$_5$ crystallization field, from $x = 0.7$ to $x = 1.5$) the 520 nm band intensity associated to Cr$^{4+}$ in octahedral sites remains stable, indicating a saturation of the chromophore Cr$^{4+}$ concentration.

### Table 6

|                  | M     | M glazed | P     | P glazed |
|------------------|-------|----------|-------|----------|
| R(%) (350–2500 nm) | 23    | 30       | 35    | 39       |
| R$_{max}$ (%) (750–2500 nm) | 33    | 46       | 55    | 54       |
| L*a*b*            | 42.5/5.2/13.0/ | 46.2/6.8/18.8/ | 43.3/18.8/ | 6.1       |
|                  | 9.2   | 7.6      | 12.5  |          |

![Fig. 13. SEM micrographs of x = 0.1 gel powders fired at 1000 °C/3 h: METHODS: CO (coprecipitation), MOD (metal-organic decomposition), GP (polymeric gel).](image1)

![Fig. 14. Vis-NIR reflectance spectra of optimized CE sample x = 0.1 fired at 1000 °C/3 h: P (powder), G (5 wt% glazed in double firing frit).](image2)
residual crystalline phases detected by XRD.

The optimized pigment composition Cr$_x$Fe$_{3-x}$TiO$_5$ fired at 1000 °C (3 h) show higher NIR reflectance (55% in powder, 54% in glazed sample) than the reference Zn-Fe-Cr brown pigment in all the analyzed wavelength ranges (total and NIR), indicating the pigment suitability as an energy-saving material (cool pigment).

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