

M-Doped Al_2TiO_5 ($M = \text{Cr}, \text{Mn}, \text{Co}$) Solid Solutions and their Use as Ceramic Pigments

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New ceramic pigments based on the tialite (Al_2TiO_5) structure, doped with Co (pink), Cr (green), or Mn (brown), were prepared through the pyrolysis of aerosols followed by calcination of the obtained powders at 1400°C . The expected decomposition of Al_2TiO_5 into a mixture of Al_2O_3 and TiO_2 on refiring was inhibited by Cr-doping and also by co-doping with Mg the Mn- or Co-doped samples. Microstructure and phase evolution during pigment preparation were monitored by scanning electron microscopy and XRPD. Unit cell parameters of tialite were determined by Rietveld refinement of the X-ray diffraction patterns, revealing in all cases the formation of solid solutions where the solubility of dopants in the Al_2TiO_5 lattice followed the trend $\text{Co} < \text{Mn} < \text{Cr}$. The valence state and possible location of dopants in the tialite lattice were investigated by X-ray photoelectron spectra and diffuse reflectance spectroscopies, which suggested the presence of Cr^{3+} ions in a large interstitial site of the tialite lattice with a distorted octahedral geometry, and of Mn^{3+} and Co^{2+} ions in the Al^{3+} octahedral sites of the tialite lattice in the former case, and in both Al^{3+} and Ti^{4+} octahedral sites in the latter. Testing the ceramic glazes assessed the technological behavior of pigments, which found that the color stability was reasonably good for the Mn-doped tialite and the Cr-doped pigment, although the latter suffered a small loss of green hue. The Co-doped pigment was found to be not stable in glazes, undergoing a cobalt-leaching effect.

I. Introduction

CERAMIC pigments are colored inorganic compounds with a high thermal and chemical stability used to color ceramic bodies. Many of these materials consist of an oxide matrix doped with transition metal cations that act as chromophore cations. One of the main research activities in this field is the search for new inorganic structures that, once doped with proper chromophore ions, result in new pigments that are cheaper, non toxic, or have more attractive shades than those currently used in the ceramic industry.^{1–6} Among the suggested candidates is pseudobrookite (Fe_2TiO_5), whose pigment performance has been recently reported.⁷

Tialite (Al_2TiO_5) is isomorphous with pseudobrookite. Its orthorhombic structure (space group *Bbmm*, $Z = 4$) contains two different highly distorted octahedral sites, where the Al(III) and Ti(IV) cations are located.⁸ It has been shown that these

cationic sites can accommodate certain amounts of other metal cations such as Si, Zr and Mg,^{9,10} Fe and Cr,¹¹ and lanthanides,¹² although no attention has been paid to the chromatic properties of the resulting solid solutions because most are not colored. This compound also presents a high melting point (1860°C)¹³ and an appropriate thermal stability. It must be mentioned that, although pure tialite is well known to decompose on firing at $900^\circ\text{--}1100^\circ\text{C}$, this process can be inhibited by the incorporation of certain metal cations into its crystalline lattice.^{11,12} Tialite has also a high mean refractive index (2.07, according to the Gladstone–Dale relationship), making this structure a good candidate for the development of new ceramic pigments.^{7,14}

The aim of this paper is to synthesize tialite powders doped with Cr, Co, or Mn cations and analyze their thermal, crystallochemical, and color properties in order to explore their potential as ceramic pigments. The synthesis route adopted for this purpose was that based on the pyrolysis of liquid aerosols generated from aqueous solutions of cation precursors, which presents several advantages when compared with the traditional ceramic procedure, such as simplicity, control of particle size distribution, and higher reactivity.^{15–17} In all cases, the chromophore ion content was varied in order to determine the maximum doping level and to optimize the optical properties of the resulting colored materials. Finally, different glazes were prepared with the optimum pigments in order to evaluate their behavior during processing and their performance as ceramic pigments.

II. Experimental Procedure

(1) Powder Preparation

Aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich, St. Louis, MO, >99%), titanium oxychloride ($\text{TiOCl}_2 \cdot \text{HCl}$, Fluka, Buchs, Switzerland, Ti content = 15%), magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Panreac, Castellar del Vallés, Spain, 99%), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Fluka, 97%), and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich, 98%) were used as the metal precursors as-received. The powder synthesis was carried out by the pyrolysis of liquid aerosols generated from aqueous solutions of these precursors following a procedure previously reported for other pigment systems,¹⁶ which can be summarized as follows. The starting solutions having the tialite stoichiometry (0.1 mol/dm³ $\text{Al}(\text{NO}_3)_3$ and 0.05 mol/dm³ TiOCl_2 for the samples only doped with Cr, Mn, or Co, and 0.09 mol/dm³ $\text{Al}(\text{NO}_3)_3$ and 0.005 mol/dm³ MgCl_2 0.055 mol/dm³ TiOCl_2 for the samples containing Mg) and variable concentrations of the chromophore (Table I) were sprayed into an expansion chamber using a glass nozzle and air at a constant pressure (0.5 kg/cm²) as the carrier gas. The generated aerosols flew through two consecutive furnaces kept at 250° and 800°C , respectively, in which the liquid

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droplets were dried and thermally decomposed, respectively. The resulting solid particles were finally collected on a glass filter with a very high efficiency.

The as-prepared powders were calcined at different temperatures up to 1400°C for 3 h by placing them in a platinum crucible and heating the furnace at 10°C min⁻¹ up to the maximum temperature.

For testing the glazes, aqueous suspensions—containing a 3 wt% of pigment and a 97 wt% of a transparent industrial frit (Colores Cerámicos SA, Onda, Castellón, Spain; composition (wt%): Al₂O₃ < 10%, B₂O₃ < 5%, CaO < 10%, SiO₂ > 60%, Na₂O < 10%, ZnO < 10%)—were prepared by ball milling. These slurries were deposited on double-firing wall tile bodies and further fired at 1050°C using the following thermal schedule: from room temperature to 800°C with a heating rate of 42°C min⁻¹, from 800° to 1050°C at 14°C min⁻¹; after 5 min at 1050°C, the furnace was switched off and the glazed tiles were left to cool down inside the furnace.

(2) Characterization Techniques

The size and morphology of the particles were examined by scanning electron microscopy (SEM) (Model JSM5400, JEOL, Tokyo, Japan). Energy dispersive X-ray analysis (EDX) (Oxford, Model Link, Model Pentafet, Link Analytical, Oxford, U.K.) installed in the SEM was used to gain information on the particles' composition.

The crystalline phases present in the solids were identified by X-ray diffraction (XRD) (Model D501, Siemens, Karlsruhe, Germany). Unit cell parameters were determined by a least squares refinement from the XRD data collected at intervals of 0.02° (2θ) for an accumulation time for an interval of 10 s, using silicon (20% by weight) as the internal standard. The crystallographic data for the Al₂TiO₅ structure were taken from the JCPDF file reported for this compound (JCPDS 41-258).

Information on the oxidation state of the chromophore species in the pigments was obtained from the X-ray photoelectron spectra (XPS) of the samples measured with a VG Escalab apparatus (Model 220, West Sussex, U.K.) using the AlKα excitation source. Calibration of the spectra was performed at the Ti2p peak taken at 458.5 eV.

Diffuse reflectance spectroscopy was performed by a Perkin Elmer spectrophotometer (Model λ35, Norwalk, CT) under the following conditions: 350–1100 nm range, 0.03 nm step size, BaSO₄ integrating sphere, BaSO₄ pellet as the white reference material. The powders were allocated in a sample holder with a quartz glass window. Reflectance (R_{∞}) was converted to absorbance (K/S) by the Kubelka–Munk equation, $K/S = (1 - R_{\infty})^2 \cdot (2R_{\infty})^{-1}$.¹⁸ Absorbance bands in the 9000–26000 cm⁻¹ range were deconvoluted in gaussian peaks (PFM, OriginLab, Northampton, MA) in order to obtain energy (centroid) and splitting (full-width at half-maximum, FWHM). The experimental errors, including background correction and reproduc-

ibility, are ~2% (energy), ~5% (splitting). Every band was attributed by fitting its energy in the relevant Tanabe–Sugano diagrams¹⁹ (d³ for Cr³⁺, d⁴ for Mn³⁺, and d⁷ for Co²⁺). Crystal field strength $10Dq$ was determined by the energy of spin-allowed transitions for Cr³⁺ and Co²⁺,^{20–22} or by the method of orbital baricentre for Mn³⁺.²⁰ Interelectronic repulsion Racah parameters were calculated by the energies of spin-allowed bands (B and C for Co²⁺, and B_{35} for Cr³⁺) or spin-forbidden ones (B_{55} and C for Cr³⁺).^{18,21,22} The attribution of the main bands was verified by calculating expected energies on the basis of $10Dq$ and B values.^{18,21–23} The nephelauxetic ratio β was calculated as $\beta = B/B_0$, where B is experimental and B_0 is the value of the free ion.^{18,21–23}

The color of the pigments was evaluated according to the Commission Internationale de l'Eclairage (CIE) through $L^*a^*b^*$ parameters.²⁴ In this system, L^* is the color lightness ($L^* = 0$ for black and $L^* = 100$ for white), a^* is the green (–)/red (+) axis, and b^* is the blue (–)/yellow (+) axis. These parameters were measured (illuminant D65, standard observer 10°) using a Dr. Lange colorimeter (Model LUCI 100, Berlin, Germany) and a white ceramic tile (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as the standard reference. Before measurements, the samples were gently ground in an agate mortar.

III. Results and Discussion

(1) Microstructure and Phase Evolution During Pigment Preparation

Table I shows the nominal composition in terms of the chromophore/tialite molar ratio of all samples prepared by the pyrolysis of aerosols procedure, which will be hereafter named as indicated in the table. All samples, irrespective of the chromophore ion, consisted of spherical particles with a broad size distribution (< 10 μm), as expected from the method used here for aerosol generation.^{15–17} An illustrative example of such particles (sample Cr5) is shown in Fig. 1(A), in which it can be also observed that they seem to be composed of much smaller, strongly aggregated subunits and that some of them were hollow (see the inset of Fig. 1(A)), indicating the preferential precipitation of the salt precursors near the surface of the aerosol droplets during the drying process in the first furnace.²⁵

After spray pyrolysis, all samples were amorphous to XRD; for this reason they were further calcined at increasing temperatures up to the tialite crystallization. As observed in Fig. 2(A), which corresponds to sample Cr5, TiO₂ with an anatase structure (JCPDS 21-1272) was the first crystalline phase appearing after heating at 800°C. This phase transformed into rutile (JCPDS 21-1276) at 1000°C, which was accompanied by the crystallization of Al₂O₃ corundum (JCPDS 46-1212). The tialite (JCPDS 41-258) crystallization started at 1200°C, ending this process on calcination at 1400°C, although a very small amount of unreacted corundum still remained in the sample.

Table I. Composition of the Doped-Tialite Samples

Sample name	Tialite stoichiometry	Ti/Al	Cr/Tialite mol ratio	Mn/Tialite mol ratio	Co/Tialite mol ratio	Mg/Al
Cr5	Al ₂ TiO ₅	0.5	0.05			
Cr10	Al ₂ TiO ₅	0.5	0.10			
Cr14	Al ₂ TiO ₅	0.5	0.14			
Cr20	Al ₂ TiO ₅	0.5	0.20			
Mn5	Al ₂ TiO ₅	0.5		0.05		
Mn8	Al ₂ TiO ₅	0.5		0.08		
Mn11	Al ₂ TiO ₅	0.5		0.11		
Mn14	Al ₂ TiO ₅	0.5		0.14		
Co5	Al ₂ TiO ₅	0.5			0.05	
Co8	Al ₂ TiO ₅	0.5			0.08	
Co11	Al ₂ TiO ₅	0.5			0.11	
MgMn5	Al _{1.8} Ti _{1.1} Mg _{0.1} O ₅	0.61		0.05		0.055
MgCo5	Al _{1.8} Ti _{1.1} Mg _{0.1} O ₅	0.61			0.05	

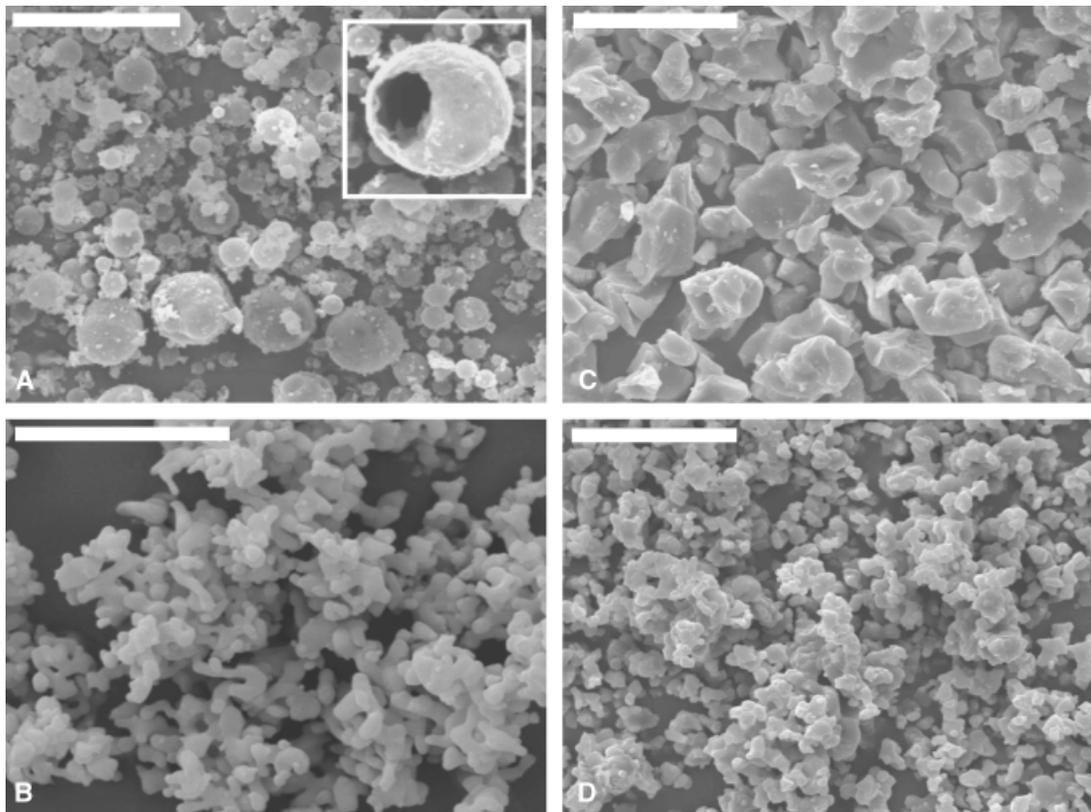


Fig. 1. Scanning electron micrographs (SEM) obtained for (A) sample Cr5, as-prepared (a magnified view of a single particle is shown in the inset for a better observation of its hollow nature); (B) sample Cr5 calcined at 1400°C; (C) sample Mn5 calcined at 1400°C; (D) sample Co5 calcined at 1400°C. Magnification bar = 20 μm.

The thermal behavior of the other Cr-doped samples was similar (data not shown).

In the case of the Mn-doped samples, the only noticeable difference in the crystallization behavior with respect to the Cr-doped system was the occurrence of a very weak and unidenti-

fied peak at $\sim 46^\circ 2\theta$ in the XRD diffraction patterns of the samples with a Mn content $\geq 8\%$ after firing at 1400°C, whose intensity increased with Mn content (Fig. 2(B)).

The thermal evolution of the Co-doped samples was also similar to the Cr-doped case, except that for a Co content

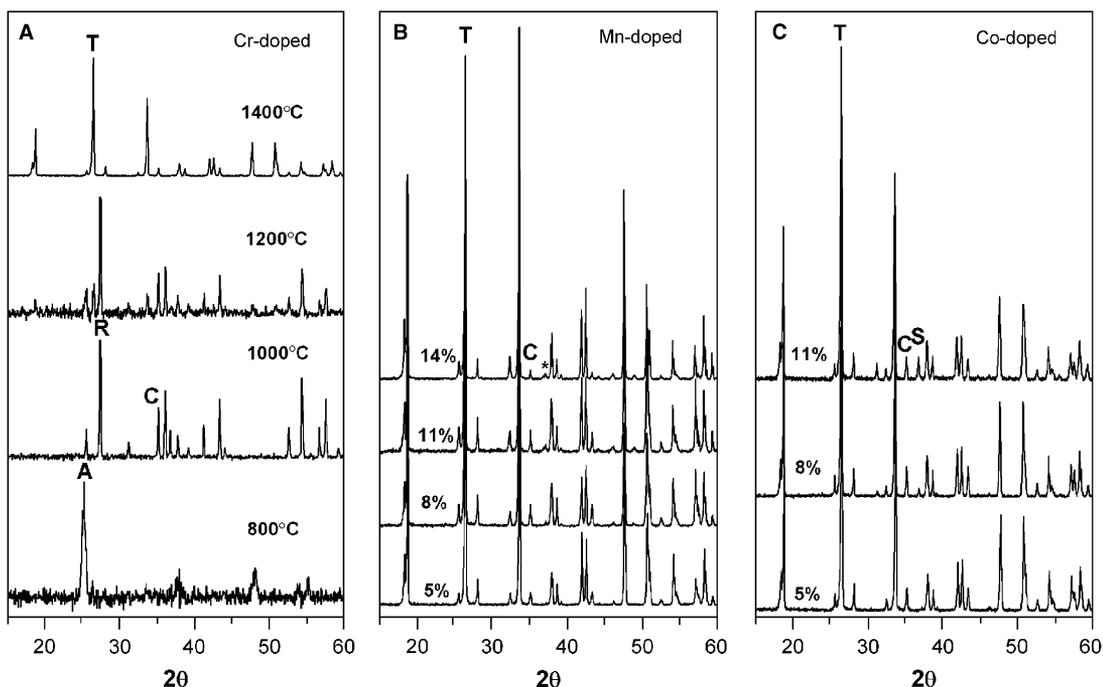


Fig. 2. X-ray diffraction (XRD) patterns of (A) sample Cr5 heated at different temperatures; (B) Mn-doped samples with different Mn contents heated at 1400°C; (C) Co-doped samples with different Co contents heated at 1400°C. Symbols designating the most intense reflections of phases: T = tialite; R = TiO₂ rutile; A = TiO₂ anatase; C = Al₂O₃ corundum; S = CoAl₂O₄ spinel. Peak marked with an asterisk could not be identified.

$\geq 8\%$, a small amount of CoAl_2O_4 spinel (JCPDS 38-814) was detected by XRD after calcination at 1400°C , in addition to tialite (Fig. 2(C)).

In all cases, the thermal treatment gave rise to particle sintering, resulting in irregular grains of similar size in the Cr- and Co-doped samples (Figs. 1(B) and (D), respectively) and of coarser size ($<15\ \mu\text{m}$) in the Mn-doped samples (Fig. 1(C)).

(2) Tialite Crystal Structure

Table II shows the unit cell parameters determined for all doped tialite systems calcined at 1400°C and for an undoped sample obtained by a similar procedure for comparison. As observed, a volume cell expansion was detected in all cases, evidencing the formation of M/tialite ($M = \text{Cr}, \text{Mn}, \text{or Co}$) solid solutions. It was also observed that for Cr and Mn doping, the unit cell parameters increased progressively in the whole range of studied compositions (up to a 20% of Cr and 14% of Mn), suggesting that the maximum cation solubility was not attained in these two cases. On the contrary, for the Co-doped samples, these parameters reached a maximum for sample Co8 (Co content = 8%). Because a certain amount of unreacted CoAl_2O_4 was detected for this sample (Fig. 2(C)), it can be concluded that the Co solubility in the tialite lattice is $<8\%$ (Co/tialite mol ratio).

The extent of unit cell expansion depends on the type of dopant (Fig. 3). Tialite exhibits a regular growth of unit cell parameters with increasing amount of Co or Mn doping; an exception is made for tialite Co11, which is always out of the general trend of Co-doped pigments, confirming that the actual cobalt content in the solid solution is lower than the nominal amount. The lattice expansion occurs mainly along the a and b axes, and it is larger for Co than for Mn doping. In contrast, the Cr-doped tialite lattice undergoes an anisotropic distortion, as it exhibits a smaller expansion mainly along the c axis, with little changes of the a and b parameters (Fig. 4).

(3) Valence State of Chromophores

To elucidate the chromophore oxidation state in these solid solutions, XPS spectroscopy was used. For this purpose, we selected the samples with the highest doping level below the solubility limit (Cr20, Mn14, and Co5). As observed in Fig. 5, the spectrum of the Cr-doped sample displayed two Cr2p peaks at 576.6 ($\text{Cr}2p_{3/2}$) and 586.3 ($\text{Cr}2p_{1/2}$) eV, which can be attributed to either Cr(III) or Cr(IV) cations, because the binding energy for both cations is very similar.^{26,27} However, crystallographic considerations seem to discard the presence of Cr(IV). Thus, if these cations were present, they would most likely occupy the Ti(IV) sites for electroneutrality. This situation would result in a cell contraction because the ionic radius of Cr(IV) (0.55 Å) is smaller than that of Ti(IV) (0.605 Å),²⁸ which is in contrast to the unit cell expansion detected for this system (Table II).

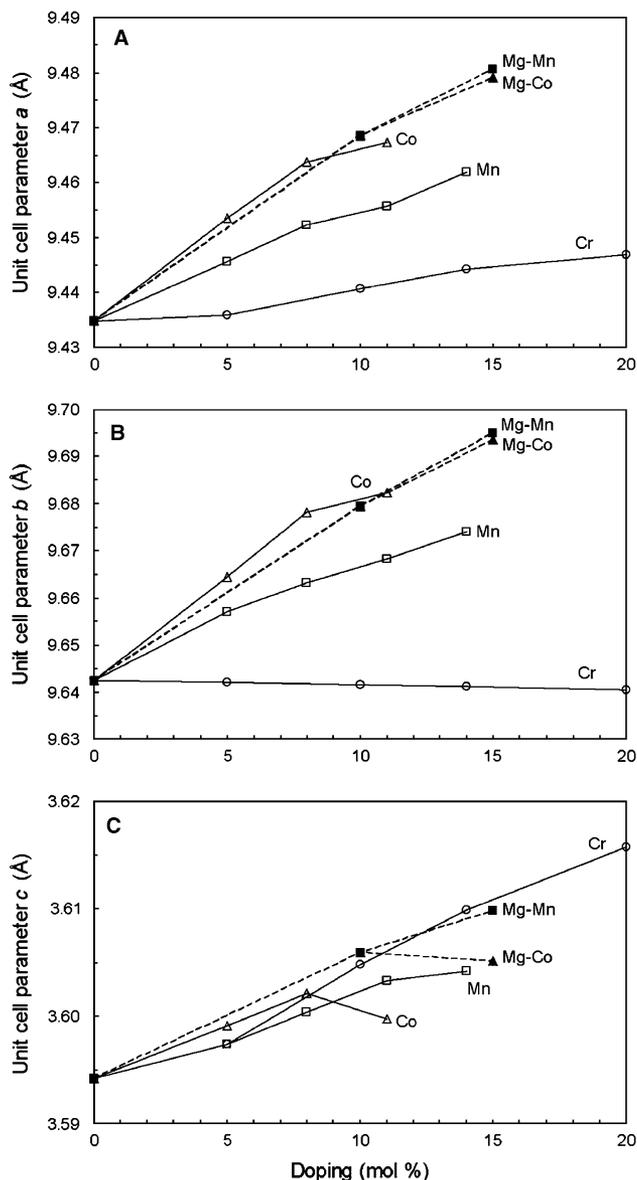


Fig. 3. Changes of unit cell parameters a (A), b (B) and c (C) of tialite samples heated at 1400°C with increasing Co, Cr, or Mn doping and with Mg-Co or Mg-Mn co-doping.

The position of the Mn2p XPS peaks of the Mn-doped sample (641.5 and 653.1 eV, respectively) and the absence in the XPS spectrum of a satellite at about 648 eV, characteristic of

Table II. Unit Cell Parameters and Unit Cell Volume of the Doped-Tialite Samples Fired at 1400°C

Sample	a (Å)	b (Å)	c (Å)	$V(\text{Å}^3)$
Undoped tialite	9.4348 ± 0.0004	9.6424 ± 0.0004	3.5942 ± 0.0002	326.98 ± 0.04
Cr5	9.4359 ± 0.0003	9.6421 ± 0.0004	3.5974 ± 0.0002	327.30 ± 0.04
Cr10	9.4407 ± 0.0012	9.6416 ± 0.0010	3.6048 ± 0.0004	328.12 ± 0.11
Cr14	9.4443 ± 0.0003	9.6411 ± 0.0003	3.6099 ± 0.0001	328.69 ± 0.03
Cr20	9.4468 ± 0.0005	9.6404 ± 0.0004	3.6157 ± 0.0002	329.28 ± 0.05
Mn5	9.4456 ± 0.0009	9.6571 ± 0.0009	3.5974 ± 0.0004	328.14 ± 0.10
Mn8	9.4522 ± 0.0008	9.6632 ± 0.0008	3.6004 ± 0.0003	328.85 ± 0.08
Mn11	9.4557 ± 0.0011	9.6682 ± 0.0012	3.6033 ± 0.0005	329.41 ± 0.12
Mn14	9.4618 ± 0.0005	9.6740 ± 0.0006	3.6042 ± 0.0002	329.90 ± 0.07
Co5	9.4535 ± 0.0007	9.6645 ± 0.0007	3.5991 ± 0.0003	328.83 ± 0.07
Co8	9.4637 ± 0.0010	9.6782 ± 0.0011	3.6021 ± 0.0005	329.92 ± 0.12
Co11	9.4673 ± 0.0012	9.6823 ± 0.0014	3.5997 ± 0.0005	329.97 ± 0.13
Mg-doped tialite	9.4685 ± 0.0004	9.6794 ± 0.0004	3.6059 ± 0.0002	330.48 ± 0.03
Mg/Mn5	9.4805 ± 0.0006	9.6950 ± 0.0006	3.6098 ± 0.0003	331.79 ± 0.07
Mg/Co5	9.4790 ± 0.0007	9.6935 ± 0.0007	3.6051 ± 0.0003	331.25 ± 0.08

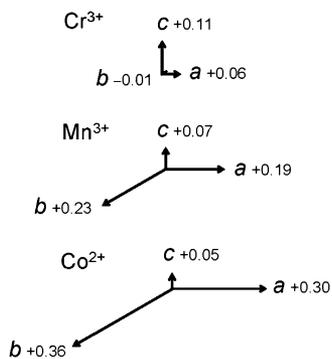


Fig. 4. Trends of unit cell parameters of tialite pigments with doping (pm per mole of dopant).

Mn(II), seem to indicate only the presence of Mn(III) and/or Mn(IV) cations in this sample. These species cannot be distinguished by this technique because their binding energy is very close.²⁹ Again, the unit cell expansion on Mn doping (Table II) and the size of Mn(III) (0.645 Å) and Mn(IV) (0.53 Å) cations²⁸ drive to discard the existence of the latter because of crystallographic considerations similar to the those above-mentioned for the Cr system.

The Co2p XPS spectrum of the Co-doped sample showed two peaks at 780.6 and 796 eV, respectively, along with two satellites at a lower binding energy, whose relative intensity clearly manifests that only the Co(II) species are present in the sample.³⁰ Therefore, it can be assumed that the solid solution is formed in this system by the simultaneous substitution of two

Al(III) for one Co(II) and one Ti(IV) cations in order to maintain electroneutrality, as it has been previously suggested for other divalent cations/tialite solid solutions such as Mg(II).⁹ As a consequence, some free alumina would be available for the formation of a cobalt aluminate spinel, which should also be taken into account to explain the small amount of this phase detected in the sample with the higher Co content (8%).

The occurrence of dopants such as Co(II), Cr(III), and Mn(III) is in agreement with the observed extent of lattice expansion, $\text{Co} > \text{Mn} > \text{Cr}$. This trend can be explained by the respective ionic radii in six-fold coordination,²⁸ Co(II) 0.745 Å, Mn(III) 0.645 Å, and Cr(III) 0.615 Å, which are larger than those of Ti(IV) 0.605 Å and Al(III) 0.535 Å. Interestingly, samples doped with Mg(II) (0.72 Å) follow rather faithfully the above trend, with an expansion close to that of the Co-doped tialite.

(4) Thermal Stability of Tialite Pigments

In order to investigate the thermal stability of the solid solutions formed after calcination at 1400°C, the same samples used for XPS characterization were further fired for 20 h at 900°C.¹¹ The XRD pattern obtained after this treatment for sample Mn14 revealed the complete decomposition of tialite, leaving TiO₂ (rutile) and corundum (Al₂O₃) as the main phases (Fig. 6(B)). Such decomposition was only partial in the case of Co doping (Fig. 6(C)), whereas it was completely inhibited in the Cr-doped sample, whose XRD patterns before (Fig. 2) and after firing (not shown) were very similar. This result is surprising and contrary to previous reports that indicated that Cr-doping has adverse effects on the tialite thermal stability.¹¹

In order to improve the thermal stability of these Mn- or Co-doped solid solutions, Mg(II) cations were also incorporated into the tialite lattice because they have been demonstrated to be highly efficient for such a purpose.⁹ For this study, we selected the Mn and Co contents resulting in the purest samples according to XRD (sample Mn5 and Co5) and 10% of Mg (Mg/tialite mol ratio), which involves a tialite stoichiometry given by the formula $\text{Al}_{1.8}\text{Ti}_{1.1}\text{Mg}_{0.1}\text{O}_5$ (Table I), in order to maintain electroneutrality. A sample only doped with Mg was also prepared for comparison. As observed in Fig. 6(A), tialite was completely developed in these samples after heating at 1400°C, as in the samples not containing Mg. It is important to note that, for the Co system, a small amount of CoAl_2O_4 was also detected by XRD, which was not present in the sample only doped with a similar amount of Co (Fig. 2(C)), indicating that the presence of Mg reduces the solubility of Co in the tialite lattice. This finding is not surprising, considering that Mg(II) and Co(II) are very similar in size and bonding geometry preferences and that the doping level in the Mg-Co co-doped sample is much higher (15%) than the solubility limit found for the Co/tialite system (<8%). It should also be mentioned that particle sintering was also detected after calcination in both cases, resulting in particles similar to those of the samples only doped with Mn or Co (Figs. 1(C) and (D)). The formation of solid solutions in the Mg-doped samples is corroborated by the increase of their unit cell parameters when compared with those of the undoped sample as the amount of dopants increased (Table II, Fig. 3). The presence of Mg(II) cations in these solid solutions seems to have little or no influence on the Mn or Co oxidation state, because the XPS spectra of the samples containing Mg are very similar to those of Mg-free samples (Fig. 5). Finally, the effectiveness of Mg doping for the stabilization of the Mn- or Co-doped tialite solid solutions was evidenced by the XRD patterns obtained in both cases after a further firing at 900°C for 20 h, which shows that tialite is the main crystalline phase (Figs. 6(B) and (C)).

(5) Color

The $L^*a^*b^*$ parameters and color of all synthesized tialite solid solutions are shown in Table III. As observed, Cr doping results in green pigments with a very similar hue (a^* and b^* values), irrespective of the doping level. The amount of dopant only affected in a significant manner the value of lightness (L^*),

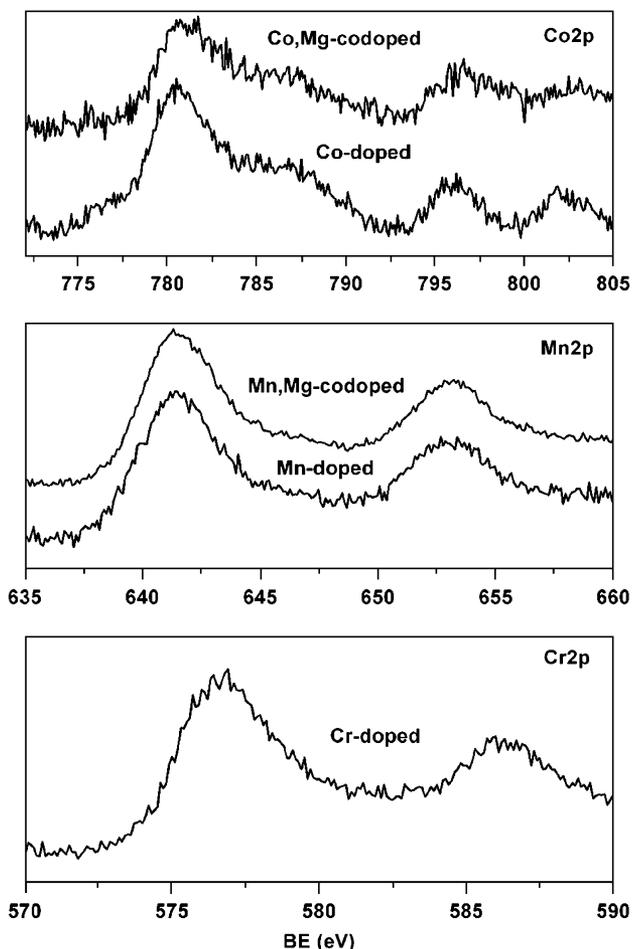


Fig. 5. XPS spectra recorded for the Cr-doped, Mn-doped, Mn-Mg co-doped, Co-doped and Co-Mg co-doped tialite samples heated at 1400°C.

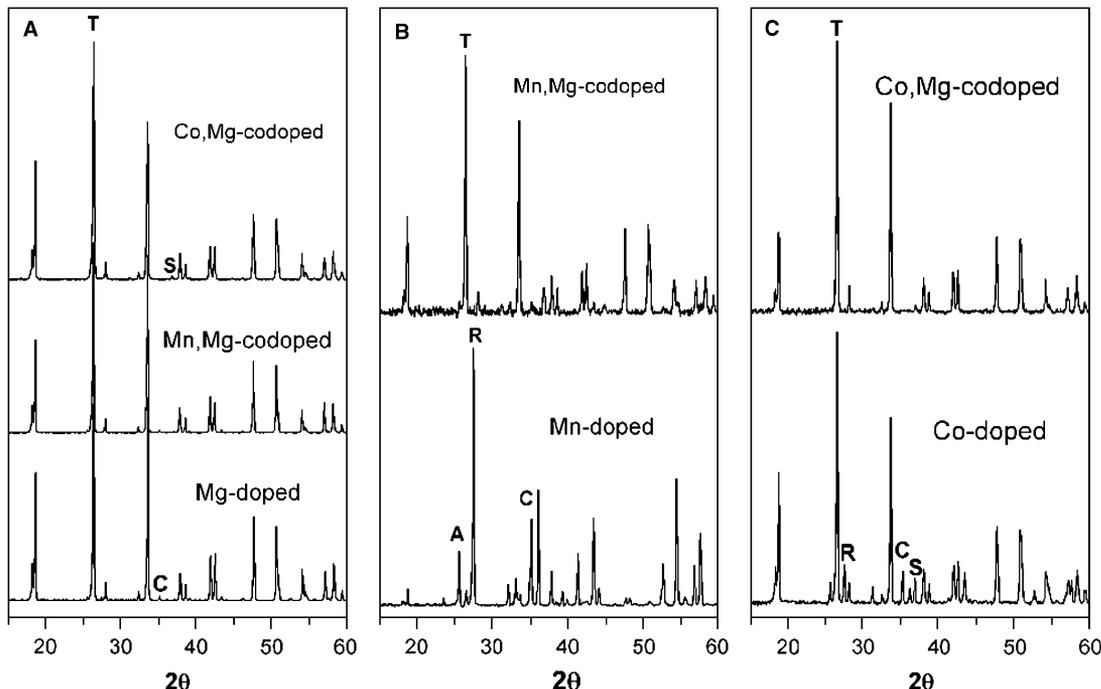


Fig. 6. X-ray diffraction (XRD) patterns of (A) Mg-doped, Mn-Mg co-doped, and Co-Mg co-doped tialite samples heated at 1400°C; (B) Mn-doped and Mn-Mg co-doped samples after a second firing treatment at 900°C for 20 h; (C) Co-doped and Co-Mg co-doped samples after a second firing treatment at 900°C for 20 h. Symbols designating the most intense reflections of phases: T = tialite; R = TiO₂ rutile; A = TiO₂ anatase; C = Al₂O₃ corundum; S = CoAl₂O₄ spinel.

which decreased (darker color) as the Cr content increased. From these parameters it can also be concluded that the optimum pigment (best color with the lower doping level) was that containing 14% of Cr, because the increase of this value up to 20% did not yield an important increase of L^* . All the Mn-doped pigments showed a brown color, whose intensity increased (L^* decreased) as the Mn content increased up to 11%, remaining almost constant for higher doping levels. The increase of the Mn amount also resulted in a progressive shift to more achromatic shades (a^* and b^* decrease). More appreciable color changes were detected for the Co-doped pigments when the amount of Co was varied. Thus, the more diluted sample (Co content = 5%) showed a pale salmon pink color that shifted to a beige hue when the Co content was increased up to 8% (sample Co). A further increase of the latter amount, up to 11% (sample Co11), resulted in a darker and more achromatic (lower a^* and b^*) shade. These color changes were probably due to the presence of a certain amount of CoAl₂O₄ in addition to the Co-tialite solid solution in samples Co8 and Co11, which was higher in the latter pigment, as detected by XRD (Fig. 2(C)). Therefore,

the most interesting Co-doped pigment is that with a Co content of 5% (Sample Co5).

The $L^*a^*b^*$ parameters of the Mg, Mn-codoped tialite pigment (sample MgMn5) were similar to those of the sample only doped with a similar amount of Mn (sample Mn5) and, therefore, showed a similar brown hue (Table III). However, the addition of Mg to the Co-tialite solid solution (sample MgCo5) resulted in a shift from pale salmon pink to a darker (lower L^*) and more achromatic dun color (Table III), likely due to the presence in this sample of the excess of CoAl₂O₄, as detected by XRD (Fig. 6(A)).

(6) Optical Spectroscopy

The UV-visible-NIR spectrum of the optimum Cr-doped tialite pigment (sample Cr14) exhibits the expected bands of Cr(III) in octahedral coordination (Fig. 7(A)): the intense spin-allowed transitions $^4T_{2g}$ and $^4T_{1g}$, as well as the weak spin-forbidden transitions 2E_g , $^2T_{1g}$, and $^2T_{2g}$.²⁰⁻²³ However, the spectrum also presents some unusual features, such as the strong absorbance at

Table III. $L^*a^*b^*$ Parameters and Colour Measured for the Doped-Tialite Pigments Fired at 1400°C and for the Glazes

Sample	L^* Pigment/Glaze	a^* ($g-r$) Pigment/Glaze	b^* ($b-y$) Pigment/Glaze	Color Pigment/Glaze
Cr5	70.9	-8.8	13.1	Green
Cr10	69.8	-8.3	13.2	Green
Cr14	65.7/51.0	-9.4/-1.6	15.2/25.8	Green/green
Cr20	63.5	-9.1	15.0	Green
Mn5	49.4/57.0	9.4/11.7	11.5/17.7	Brown/brown
Mn8	45.3	8.2	6.0	Brown
Mn11	42.4	6.2	6.0	Dark brown
Mn14	42.0/52.8	5.2/10.0	4.3/13.0	Dark Brown/brown
Co5	65.7/60.7	4.0/-1.5	13.8/3.3	Light salmon pink/gray
Co8	58.3	2.6	11.8	Beige
Co11	53.7	-1.2	6.3	Beige
MgMn5	50.6/60.9	10.1/10.6	12.0/17.8	Brown/brown
MgCo1	58.0/61.0	0.1/-0.9	9.2/8.3	Beige/gray

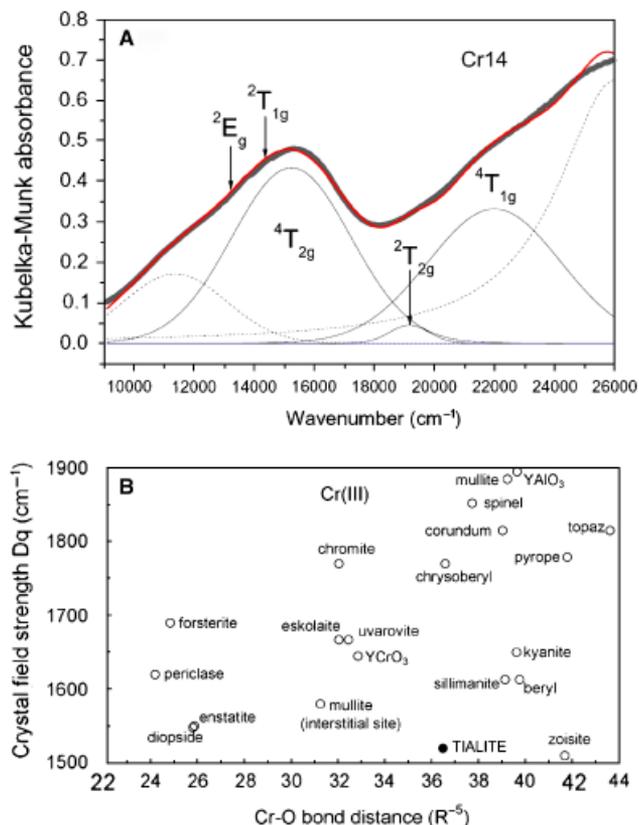


Fig. 7. Optical spectrum of the sample Cr14 heated at 1400°C and deconvoluted in the bands of octahedrally coordinated Cr(III) (A), and relationship between the Cr–O bond distance and crystal field strength for tialite compared with several oxides and silicates (B).

the visible–UV border and the band at about 11 500 cm^{-1} . The former, which is not referable to any Cr–O or Al–O charge transfer,²¹ is perhaps due to a Ti–O metal–ligand charge transfer, as it occurs in titania.^{31,32} The latter is not ascribable to any Cr(III) transition. The resulting optical parameters of six-fold-coordinated Cr(III) are crystal field strength $Dq = 1520 \text{ cm}^{-1}$, Racah $B_{35} = 690 \text{ cm}^{-1}$, $B_{55} = 618 \text{ cm}^{-1}$, and $C = 2873 \text{ cm}^{-1}$; these values correspond well with the calculated energies of Cr(III) bands (Table IV). However, the crystal field Dq is not consistent with the metal–oxygen bond distance, because in Al_2TiO_5 , the mean Al–O distance is 1.94 Å and the expected Dq should be around 1750 cm^{-1} , according to the main trend of oxides and silicates.²⁰ A Dq as low as 1520 cm^{-1} matches a large crystallographic site, having a metal–oxygen distance of at least 2 Å (Fig. 7(B)). In any case, there are crystal structures that do not strictly follow the crystal field theory model, because the Cr(III) is in interstitial sites, e.g. mullite,³³ or in strongly distorted sites, e.g. zoisite.³⁴ Interestingly, the spin-allowed bands of Cr14 are very broad, almost at the limit for crystal field transitions (e.g. FWHM over 4000 cm^{-1}); this may imply a strong local distortion of the CrO_6 site. A possible interstitial site in the tialite lattice is present along “channels” parallel to the b axis, where a strongly distorted octahedral site is envisaged with a mean M–O distance of around 2 Å.³⁵

The spectra of all Mn-doped samples (even that co-doped with Mg) were similar each other and exhibited a strong absorbance of the green–blue–violet light and another absorbance peak in the near infrared; the main difference was absorbance, which clearly increased with manganese content from Mn5 to Mn14 and slightly diminished with Mg co-doping (Fig. 8(A)). There are clues of at least four main bands peaking at about 11 000, 16 000, 19 000, and 22 000 cm^{-1} , respectively; however, the deconvolution requires two further bands at about 10 000 and 25 000 cm^{-1} (Fig. 8(B)). These features may be attributed to Mn(III), in agreement with XPS results and the crystallographic

Table IV. Energy and Splitting of Bands of Six-fold-Coordinated Cr(III) (Sample Cr14) and Co(II) (Sample Co5)

Cr(III) transitions (${}^4A_{2g} \rightarrow$)	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	Band splitting FWHM (cm^{-1})
${}^4T_{2g}$	15 210	15 240	4660
${}^4T_{1g}$	21 870	21 990	5200
2E_g	12 010	12 940	–
${}^2T_{1g}$	14 080	14 570	–
${}^2T_{2g}$	19 200	19 160	–
Co(II) transitions	Calculated energy (cm^{-1})	Experimental energy (cm^{-1})	FWHM (cm^{-1})
${}^4T_{1g} ({}^4F) \rightarrow$			
${}^4T_{2g}$	8890	9220	1970
${}^2T_{2g}$	13 760	15 180	2950
${}^4A_{2g}$	17 780	17 440	1610
${}^4T_{1g} ({}^4P)$	18 810	18 780	1430
${}^2A_{1g}$	21 720	20 030	1440

considerations above discussed, which typically undergoes the Jahn–Teller effect with a strong splitting of the energy of orbitals e_g and t_{2g} .^{20,21} From this standpoint, the splitting of the lowest energy field state is thought to be responsible for the peak at $\sim 11\,000 \text{ cm}^{-1}$, while double splitting of the t_{2g} orbitals may be claimed for the bands at a higher energy. In all events, this simple interpretation is able to explain just the main optical features: one band in the infrared and the two intense bands at approximately 19 000 and 22 000 cm^{-1} ; the apparent doubling of bands, involving those at $\sim 16\,000$ and 25 000 cm^{-1} , might be due to distinct contributions from the two slightly different octahedral sites or to the unidentified phase (Fig. 2(B)). According to this interpretation, the crystal field strength is estimated to be

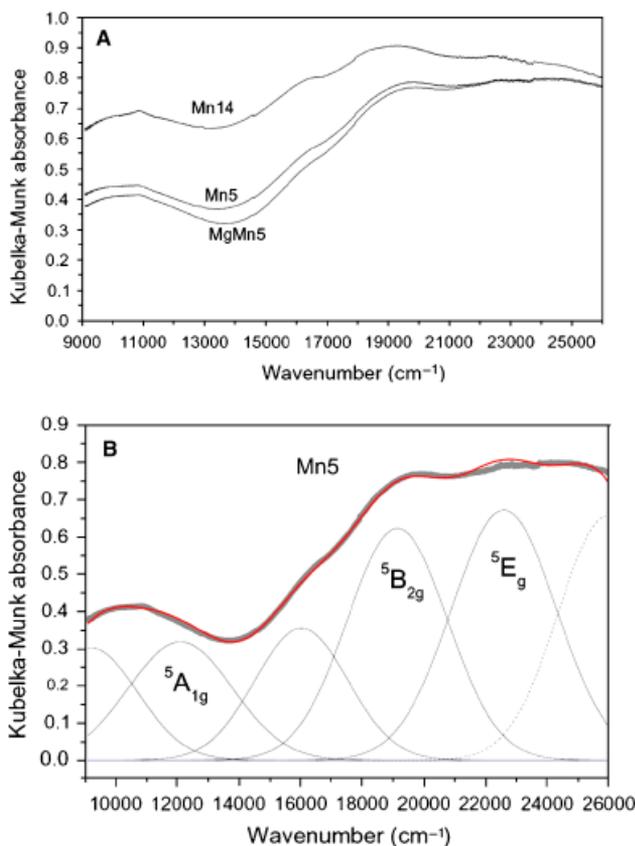


Fig. 8. Optical spectra of manganese-doped tialite samples heated at 1400°C (A), and the deconvoluted spectrum of the sample Mn5 with the bands of Mn(III) in six-fold coordination (B).

Table V. Energy (cm^{-1}) of Mn(III) Bands, Orbital Baricentres, and Crystal Field Strength Calculated as Difference between the 5E_g and ${}^5T_{2g}$ Orbitals

Orbital		Mn5	MgMn5	Mn14	
5E_g	e_g	${}^5B_{1g}$	Ground state		
		${}^5A_{1g}$	10930	11150	11210
${}^5T_{2g}$	t_{2g}	5E_g	19090	19310	19210
			22770	22520	22650
Baricentre of 5E_g orbitals		5465	5575	5605	
Baricentre of ${}^5T_{2g}$ orbitals		20930	20915	20930	
Crystal field strength ($10Dq$)		15465	15340	15325	

on average $Dq = 1530 \text{ cm}^{-1}$ (Table V). This value is in fair agreement with the relationship between Dq and the Mn(III)–O distance in known structures. For instance, tialite presents values of Dq and Mn–O distance close to those of andalusite, where Mn(III) occupies a very distorted octahedral site of aluminum (average Al–O distance 1.94 \AA).^{20,36}

The spectra of samples Co5 and MgCo5 are significantly different, even by a fingerprinting approach (Fig. 9). It appears that the sample only doped with Co (Co5) has mostly Co(II) in six-fold coordination because its spectrum is similar to that of Co-olivine (Fig. 9(A)), which has only Co(II) in octahedral coordination,^{37,38} while the sample co-doped with Mg and Co (MgCo5) contains essentially Co(II) in tetrahedral coordination. In fact, the energies of the main bands of the latter sample correspond to those of Co-doped willemite (Fig. 9(A)), which has only four-fold-coordinated Co(II).^{39,40} The spectrum of sample Co5 has been interpreted as deconvoluting five bands, attributed to three spin-allowed transitions, ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{2g}$, ${}^4A_{2g}$, ${}^4T_{1g}({}^4P)$, and two spin-forbidden ones, ${}^4T_{1g}({}^4F) \rightarrow {}^2T_{2g}$ and ${}^2A_{1g}$ (Fig. 9(B)). The broad absorbance at the UV–visible border is likely to be due to Ti–O charge transfer. These bands fit

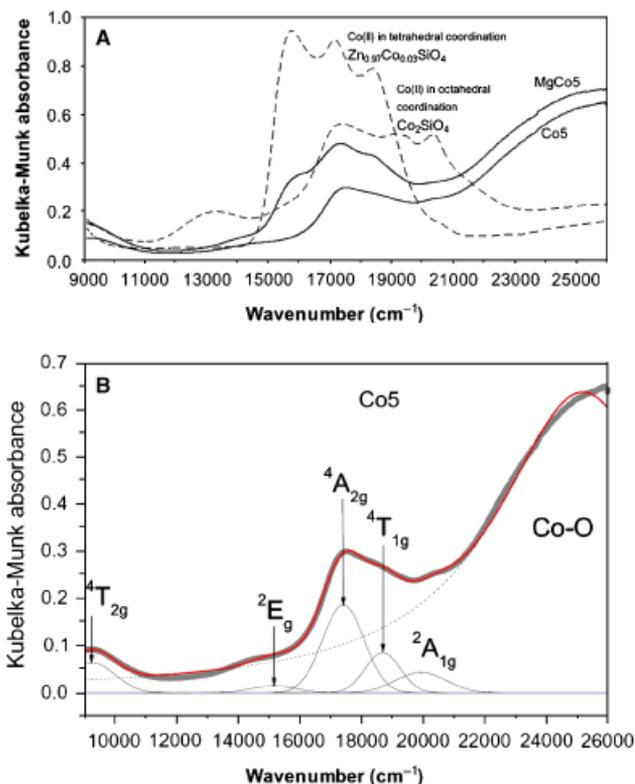


Fig. 9. Optical spectra of tialite samples doped with cobalt (Co5) and co-doped with Mg–Co (MgCo5) and heated at 1400°C , compared with spectra of octahedrally coordinated Co(II) in olivine and tetrahedrally coordinated Co(II) in willemite (A), and the deconvoluted spectrum of sample Co5 with the bands of Co(II) in six-fold coordination (B).



Fig. 10. Ceramic glazes prepared with Cr-doped (Cr14), Mn-doped (Mn5), and Co-doped (Co5) tialite pigments.

the Tanabe-Sugano diagram for a crystal field strength $Dq = 946 \text{ cm}^{-1}$ and a Racah $B = 760 \text{ cm}^{-1}$ ($C = 4B = 3040 \text{ cm}^{-1}$); these values reasonably match with the calculated energies of Co(II) bands (Table IV). In the literature, there are too few data of the crystal field strength of Co(II) to allow a reliable relationship with crystal structure and infer the Co–O distance. The bands corresponding to tetrahedral Co(II) in the spectrum of sample MgCo5 must be attributed to the presence of the above-mentioned small amount of CoAl_2O_4 spinel detected by XRD (Fig. 6(A)).

(7) Technological Behavior

The industrial applicability of the colored tialite-based systems was assessed by choosing the optimum Cr pigment (sample Cr14) and the Mn and Co pigments with the doping levels that gave rise to the purest tialite (samples Mn5, Co5, MgMn5, and MgCo5). In all cases, glazes free of defects were obtained, as illustrated in Fig. 10 for samples Cr14, Mn5, and Co5, although some appreciable differences in color with respect to that of the powdered samples were detected (Table III). Thus, a darker (lower L^*) green shade was observed for the Cr-doped pigment, which also showed a higher value of a^* (less green) and b^* (more yellow) components. In the case of Mn doping, a lighter (higher L^*) and more orange (higher a^* and b^*) brown color was observed after glaze firing. Similar parameters and tendencies were observed for the tiles decorated with the Mg–Mn co-doped pigment. This similarity suggests that the Mn-tialite solid solution was not affected during the thermal treatment used in the glaze test, even in the absence of Mg, probably because of the short holding time at high temperature. The most significant hue shift induced by the application in glaze was observed for the Co-doped pigment, which changed from pale salmon pink to gray, probably as a consequence of the exsolution of the Co cations from the tialite lattice during this process (the so-called *cobalt leaching*^{38,41}). This interpretation may be supported by the similar gray color obtained for the glaze prepared with the Mg–Co co-doped pigment (Table III), which already presented an excess of CoAl_2O_4 before enameling (Fig. 6(A)).

IV. Conclusions

New ceramic pigments with the tialite structure doped with Cr, Mn, or Co cations were for the first time obtained by the pyrolysis of aerosols followed by a further calcination of the obtained powders at 1400°C . In all cases, tialite solid solutions were achieved, but at high doping levels for Co and Mn, and spinel-like secondary phases were also present. The solubility of dopants in the Al_2TiO_5 lattice is growing in the series $\text{Co} < \text{Mn} < \text{Cr}$. The expected decomposition of Al_2TiO_5 into $\text{Al}_2\text{O}_3 + \text{TiO}_2$ on re-firing over 900°C was inhibited in the Cr-doped pigments, and it was also prevented by co-doping with Mg^{2+} cations the Co- or Mn-doped tialite solid solutions. Spectroscopic data indicate that Mn^{3+} and Co^{2+} ions are accommodated at the octahedral sites of the tialite lattice, mainly substituting for Al^{3+} in the former case and for both Al^{3+} and Ti^{4+} ions in the latter, implying an expansion of the unit cell, mostly along the a and b axes, proportional to the difference in

ionic radii. Cr^{3+} seems to rest in a large interstitial site, with a distorted octahedral geometry, implying an anisotropic lattice expansion mainly along the c axis. The colors achieved are green, brown, and pink, as expected in the case of Cr^{3+} , Mn^{3+} , and Co^{2+} in octahedral coordination, respectively. The color stability after application in ceramic glaze is satisfactory for the Mn-doped tialite and the Cr-doped pigment, although the latter suffers a small loss of green hue, perhaps related to the peculiar location of chromium ions in the Al_2TiO_5 structure. The Co-doped pigment is not stable in the glaze, as it underwent a typical cobalt-leaching effect, with the diffusion of Co ions into the glassy phase.

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