

Synthesis of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($0 \leq x \leq 0.5$) rutile solid solutions from alkoxides

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In this study, $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($0 \leq x \leq 0.5$) rutile solid solutions have been synthesized from gels built from hydrolysis-condensation of Cr (III) acetylacetonate, NbCl_5 and Ti (IV) isopropoxide mixture (polymeric gel). Characterization of these solid solutions was carried out by X-ray diffraction, ultraviolet-visible and infrared spectroscopy, differential thermal and thermogravimetric analysis and CIELAB (Commission Internationale de l'Eclairage $L^*a^*b^*$) parameter measurements. The results obtained by the polymeric gel method were compared with those obtained by traditional ceramic synthesis. This comparison reveals some differences with regard to synthesis temperatures and reaction mechanisms. The formation of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($0 \leq x \leq 0.5$) rutile solid solutions by the ceramic method requires temperatures of about 1200°C and soaking times of several days. These solid solutions are synthesized at 1000°C in 24 h by the polymeric gel method. In ceramic synthesis, the CrNbO_4 compound with rutile structure appears as an intermediate compound in the formation of rutile solid solutions. In polymeric gel synthesis, however, the CrNbO_4 rutile compound was not detected in the samples.

1. Introduction

The preparation of solid solutions by the conventional ceramic method presents some drawbacks. The necessary high temperatures give rise to loss of volatile reagents and consequently to deviation of the stoichiometric conditions of the initial systems. Sol-gel techniques are used in preparing V-ZrSiO₄ solid solutions [1] and some garnets [2]. This synthesis method forms a gel in which particle size and the high degree of homogeneity allow a significant increase in the efficiency of the process at lower temperatures.

Rutile TiO₂ is an important material with diverse applications in pigments, the electronic industry and electrochemistry. There are many papers dealing with the synthesis of solid solutions based on rutile structures [3, 4]. In previous papers on synthesis by the ceramic method and on the characterization of $\text{M}^{\text{III}}\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($\text{M}^{\text{III}} = \text{Ga}$ [5], $\text{M}^{\text{III}} = \text{Al, Cr, Fe}$ [6]) the presence of a $\text{M}^{\text{III}}\text{NbO}_4$ compound was detected; this seems to appear as an intermediate compound. When $\text{M}^{\text{III}} = \text{Cr}$ (where CrNbO_4 is isostructural with rutile), solid solutions with rutile structure are formed in the complete range of compositions.

The aim of this study is the synthesis and characterization of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($0 \leq x \leq 0.5$) rutile solid solutions by the polymeric gel method. The results obtained are reported and are compared with those obtained by the ceramic method.

2. Experimental procedure

Samples of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ ($0 \leq x \leq 0.5$) based on the rutile structure were prepared by the ceramic and polymeric gel methods. The starting materials used in the ceramic method were TiO₂ anatase (Probus), Cr₂O₃ (Merck) of reagent grade chemical quality, and Nb₂O₅ (BDH), 99.5%. In the ceramic method, appropriate amounts of the starting materials were mixed and homogenized in acetone in a planetary ball mill for 20 min. Residual acetone was removed by evaporation. The dried mixtures were put into refractory crucibles and fired at temperatures between 600 and 1300°C for various soaking times. In the polymeric gel method, the starting materials used were Cr(III) acetylacetonate (Janssen), NbCl_5 (Merck) of reagent-grade chemical quality and Ti (IV) isopropoxide (Janssen), 98%.

To obtain the polymeric gel samples, a solution of NbCl_5 in ethanol was refluxed with continuous stirring at 70°C for 12 h. Cr (III) acetylacetonate was added to the resulting solution, acidifying with 3M HNO₃ and refluxing at 70°C for 12 h. Subsequently, Ti(IV) isopropoxide was added and the mixture was refluxed for 24 h with continuous stirring. The molar ratios of H₂O:Ti(IV) isopropoxide and H⁺:Ti(IV) isopropoxide used were 5:1 and 0.3:1, respectively. The gels were dried (a) by i.r. lamp, (b) by air-drying at room temperature (20°C), and

(c) by slow drying, covering the gel with a plastic film to slow down solvent loss by evaporation. The film was drilled with a needle to control the speed of evaporation [7]. Homogeneous green-coloured gels were obtained. The dried gels were put into refractory crucibles and fired at temperatures between 300 and 1000 °C for various soaking times. Colourations of fired samples were yellow–brown ($x = 0.10$), brown ($x = 0.25$) and brown–green ($x = 0.40$ and $x = 0.50$).

The resulting materials were examined with a Philips powder diffractometer, using CuK_α radiation and Ni filter, to study the development of the crystalline phases. Rutile unit cell parameters were measured using the LSQC and POWCAL computer programs [8]. In order to refine d values, $\alpha\text{-Al}_2\text{O}_3$ was employed as an internal standard in an X-ray diffractogram run between 50 and 100 (degrees 2 θ) at low goniometer speed. The POWCAL and LSQC programs calculate the crystallographic unit cell parameters of the sample by comparing its refined d values with the standard values.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in a Perkin–Elmer instrument in air atmosphere, using a platinum crucible and a heating rate of 20 °C min^{-1} . Finely powdered alumina was used as a reference material. Infrared spectroscopy (KBr pellets) was employed to study the structural evolution of the solid solutions. The i.r. spectra were recorded with a Perkin–Elmer spectrophotometer in the 4000–2000 cm^{-1} range. U.v.–vis spectroscopy (diffuse reflectance), in the 190–800 nm range, allowed the Cr (III) site in these rutile solid solutions to be studied.

CIELAB colour parameter measurements [9], conducted with a colorimeter using a standard illuminant D , were used to differentiate the samples in terms of colour. L^* is the lightness axis (black (0) to white (100)), a^* is the green (–) to red (+) axis, and b^* is the blue (–) to yellow (+). On an x – y CIE chromatic diagram, the dominant reflected wave-number (λ) was measured.

3. Results and discussion

3.1. X-ray diffraction

The evolution of the crystalline phases detected at different temperatures in the air-dried polymeric gel samples is reported in Table I. The non-doped polymeric sample ($x = 0$) develops rutile around 500 °C. When the substitution degree (x) increases, the

rutile phase appears at higher temperatures in the gel samples. Rutile solid solutions are obtained in the complete range of compositions at 1000 °C in these samples.

In the ceramic samples, TiO_2 (anatase) \rightarrow TiO_2 (rutile) phase transformation and CrNbO_4 formation were observed to take place at 1000 °C. The synthesis of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ rutile solid solutions by the ceramic method requires temperatures of about 1200 °C and soaking times of several days.

Fig. 1a shows the evolution with temperature of the crystalline phases in a ceramic sample with $x = 0.25$. It may be observed from this figure that the CrNbO_4 compound appears as an intermediate compound in the formation of solid solutions. After the synthesis of TiO_2 (rutile) and CrNbO_4 (rutile), Ti(IV) ions are replaced by Cr(III) and Nb(V) ions in the TiO_2 , with the concurrent substitution of Cr(III) and Nb(V) ions by Ti(IV) ions in the CrNbO_4 structure, forming the solid solutions. Fig. 1b shows the evolution with temperature of crystalline phases in the air-dried gel sample with $x = 0.25$. It can be observed that no crystalline phase is detected in this sample with heat treatment at 400 °C. In the 500–700 °C temperature range, anatase and rutile phases are observed, with a single rutile phase forming at 1000 °C. It can be seen from Table I and Fig. 1b that the CrNbO_4 rutile compound is not detected in the gel samples. Both the lower temperatures involved in the formation of solid solutions and the absence of CrNbO_4 compound formation seem to be due to a greater homogeneity in the samples prepared by the polymeric gel method than in the samples prepared by the ceramic method.

Fig. 2 shows diffractogram of the sample with $x = 0.1$ in the three different drying processes (a–c), after heat treatment at 600 °C, showing the influence of the drying process in the formation of solid solutions. The anatase/rutile ratio is smaller in slower-drying processing. Thus rutile phase formation seems to arise earlier in the samples which undergo slower drying.

Table II shows the unit cell parameters obtained by the POWCAL and LSQC programs in the rutile solid solutions synthesized by the gel method. The a and c parameters are seen to increase linearly in all the composition range ($0 \leq x \leq 0.5$), in agreement with the replacement of titanium by the larger chromium and niobium ions. On the other hand, the data shows the expansion of a to be smaller than that of c , and the

TABLE I Evolution of crystalline phases of air-dried samples prepared by the polymeric gel method with firing temperature

T (°C)/ t	$x = 0.0$	$x = 0.10$	$x = 0.25$	$x = 0.40$	$x = 0.50$
300 °C/12 h	R (w), T (vw)	T (vw)	A	A	A
400 °C/12 h	R (w), T (vw)	T (w)	A	A	N (vw)
500 °C/12 h	R (m)	T (w)	T (vw), S (vw)	N (w)	N (w)
600 °C/12 h	R (m)	T (w), S (vw)	T (w), S (vw)	N (m)	N (m)
700 °C/12 h	R (m)	T (vw), S (s)	T (vw), S (w)	N (m), S (vw)	N (m), C (w)
800 °C/12 h	R (f)	S (s)	S (m), N (w)	N (w), C (vw), S (w)	N (m), C (w)
900 °C/12 h	R (f)	S (s)	S (s)	N (vw), S (s)	N (vw), S (s)
1000 °C/12 h	R (f)	S (s)	S (s)	S (s)	S (s)

A, amorphous phase; crystalline phases: R, TiO_2 rutile; T, TiO_2 anatase; N, Nb_2O_5 ; C, Cr_2O_3 ; S, rutile solid solution; peak intensity: vw, very weak; w, weak; m, medium; s, strong.

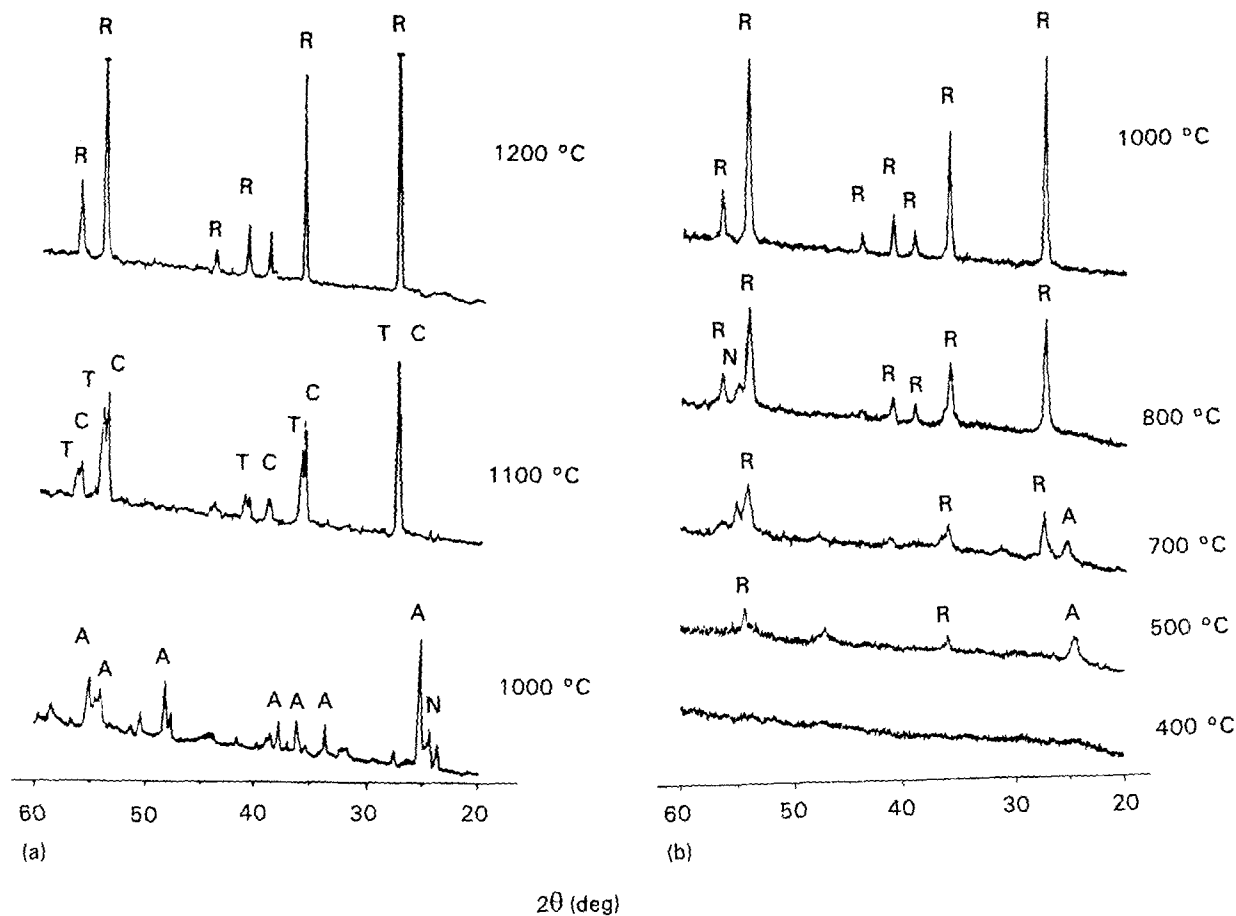


Figure 1 X-ray diffractogram of samples with $x = 0.25$ fired at several temperatures: (a) ceramic sample, (b) air-dried gel sample. Crystalline phases: A = anatase; T = TiO_2 (rutile); R = rutile (solid solution); N = Nb_2O_5 ; C = CrNbO_4 (rutile).

value of the ratio c/a therefore increases with x . Fig. 3 shows that the unit cell parameters in both gel and ceramic samples are similar.

3.2. Differential thermal and thermogravimetric analysis

The DTA and TGA curves of the air-dried sample with $x = 0$, are shown in Fig. 4a. The DTA curve exhibits an endothermic peak at 120–300 °C. In the same temperature range, a weight loss is detected in the TGA curves, which could be due to the evaporation of residual solvent entrapped in the micropores of the gel. There is also a broad exothermic peak in the 300–500 °C temperature range, associated with the oxidation of organic matter; this is in agreement with the weight loss in the same temperature range in the TGA curve. In the 525–625 °C temperature range, a weak exothermic peak is observed, but as no weight loss is detected in the TGA curve, this peak may be associated with crystallization of rutile (Table I).

Fig. 4b shows DTA curves of slowly dried samples with $x = 0$ and $x = 0.25$ in the 300–700 °C temperature range. It may be observed from Fig. 4b that the weak exothermic peak assigned to crystallization is exhibited at higher temperatures when x increases. This is in accordance with the X-ray results.

In the ceramic samples, the TiO_2 (anatase) \rightarrow TiO_2 (rutile) phase transformation and solid solution formation are not detected in the DTA curves. This may be related to smaller structural changes or to the slower reactions involved.

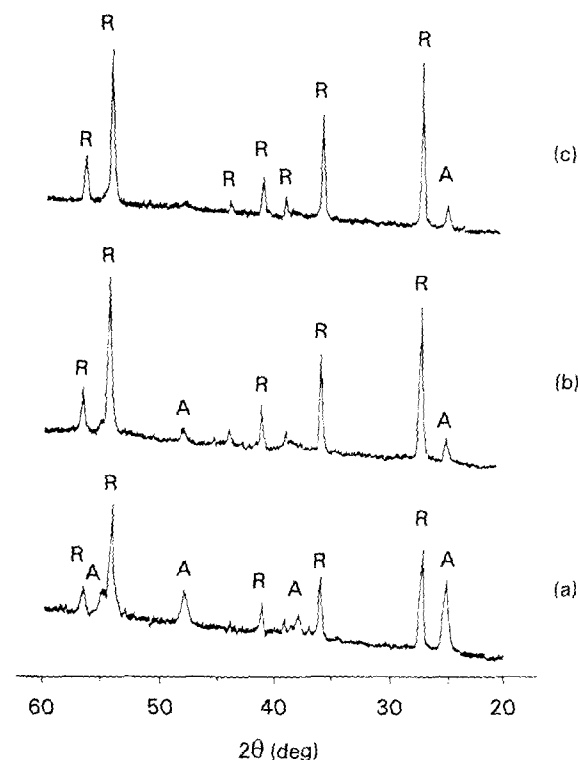


Figure 2 X-ray diffractograms of gel sample with $x = 0.10$ fired at 600 °C: (a) i.r. lamp dried, (b) air dried, (c) slowest dried. Crystalline phases: A = anatase; R = rutile.

3.3. Infrared spectroscopy

The infrared spectra of the raw and fired samples are shown in Fig. 5a and b. In the raw gels (Fig. 5a), the bands around 3400 and 1550 cm^{-1} are associated

TABLE II Rutile unit cell parameters from air-dried samples prepared by the polymeric gel method and fired at 1000 °C

x	a (nm)	c (nm)	V (nm ³)	c/a
0.10	0.46047 ± 0.00005	0.29689 ± 0.00008	6.295 ± 0.003	0.0645
0.25	0.46198 ± 0.00004	0.29879 ± 0.00005	6.377 ± 0.002	0.0647
0.40	0.46345 ± 0.00006	0.30020 ± 0.00008	6.448 ± 0.003	0.0648
0.50	0.4645 ± 0.0001	0.3012 ± 0.0003	6.498 ± 0.009	0.0648

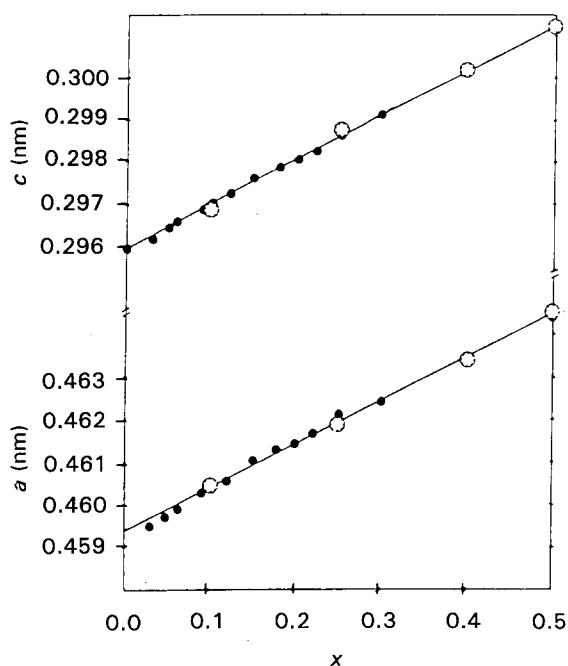


Figure 3 Unit cell parameters obtained by POWCAL and LSQC programmes in solid solutions based on rutile lattice, (●) ceramic samples, (○) gel samples.

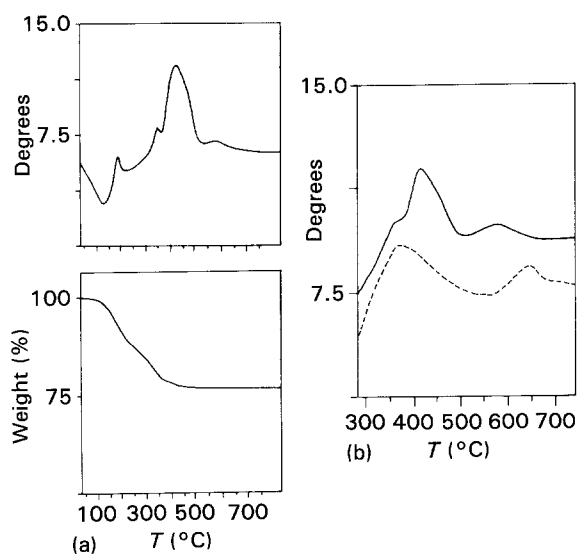


Figure 4 DTA and TGA curves, (a) DTA and TGA curves of air-dried sample with $x = 0$, (b) DTA curves of slowly dried samples with $x = 0$ (—) and $x = 0.25$ (---).

with stretching vibrations of OH groups and molecular H₂O, respectively [10]. The bands around 1350 and 850 cm⁻¹ are assigned to NO₃⁻ [11]. In the 800–400 cm⁻¹ range, the bands are attributed to M–O bonds (M = Ti, Nb, Cr). It can be seen from Fig. 5b that the bands associated with stretching vi-

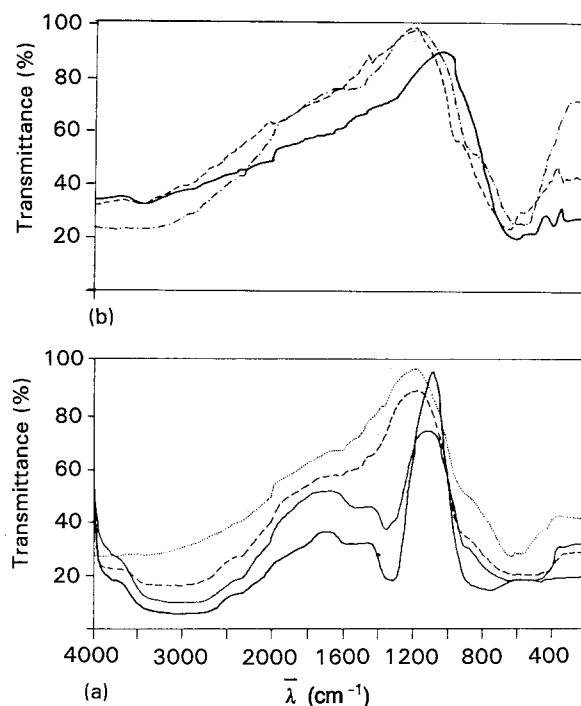


Figure 5 I.r. spectra of gels. (a) Raw gels: (—) $x = 0$; (---) $x = 0.10$; (-·-) $x = 0.25$; (····) $x = 0.50$; (b) gels fired at 500 °C: (—) $x = 0.10$; (---) $x = 0.25$; (-·-) $x = 0.50$.

brations of the OH groups and molecular H₂O decrease with the firing temperature of the samples, because physically absorbed water and bonded hydroxyl groups are lost. In the infrared spectra of the fired samples, the bands assigned to NO₃⁻ are not detected.

3.4. UV–V spectroscopy

Fig. 6 shows the u.v.–vis spectra of Cr₂O₃, the gel samples with $x = 0.10, 0.25$ and 0.50 fired at 1000 °C and the ceramic sample with $x = 0.25$ fired at 1200 °C. The polymeric gel samples show similar u.v.–vis spectra to the ceramic samples, differing in the smaller absorbance of the gels compared to that of the ceramic samples. The observed bands are associated to Cr(III) in octahedral coordination as follows.

A broad asymmetric band around 650–780 nm assigned to ⁴A₂(F) → ⁴T₂(F) (first octahedral Cr(III) transition).

A broad band is also observed with greater intensity than the former, extended around 340–560 nm. The maximum around 515 nm is attributed to ⁴A₂(F) → ⁴T₁(F) (second octahedral Cr(III) transition).

A band around 210–320 nm, in this range can appear the allowed third transition of Cr(III) in

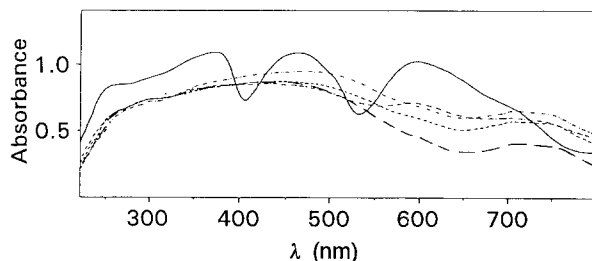


Figure 6 U.v.-visible spectra: (—) Cr_2O_3 ; (---) gel sample with $x = 0.10$ fired at 1000°C , (---) gel sample with $x = 0.25$ fired at 1000°C , (-·-·-) ceramic sample with $x = 0.25$ fired at 1200°C , (- - - -) gel sample with $x = 0.50$ fired at 1000°C .

TABLE III L^* , a^* , b^* parameters in air-dried polymeric gel samples fired at 1000°C and ceramic samples fired at 1300°C

x	Parameter	Gel sample	Ceramic sample
0.10	L	43.48	36.63
	a	20.08	22.14
	b	38.96	34.20
	λ (nm)	586	589
	x	0.487	0.499
	y	0.409	0.397
0.25	L	39.65	33.55
	a	13.75	15.96
	b	28.35	29.03
	λ (nm)	584	585
	x	0.449	0.474
	y	0.400	0.402
0.50	L	38.61	29.52
	a	1.91	7.74
	b	21.12	21.76
	λ (nm)	578	587
	x	0.393	0.431
	y	0.404	0.404

λ (nm) is the dominant wavenumber (at which the reflectance (%) is maximum in the visible range).

octahedral coordination, ${}^4A_2(\text{F}) \rightarrow {}^4T_1(\text{P})$, and the $\text{O}(\text{-II}) \rightarrow \text{Ti}(\text{IV})$ ligand metal charge transfer.

In these structures the $\text{Cr}(\text{III})$, $\text{Nb}(\text{V})$ and $\text{Ti}(\text{IV})$ occupy deformed octahedral sites. The unfolding and displaced bands may be explained by the lesser symmetry of $\text{Cr}(\text{III})$ in the rutile structure than in the Cr_2O_3 compound.

3.5. CIELAB parameter measurements

Table III shows the CIE L^* , a^* and b^* parameters of the ceramic samples fired at 1300°C , and of the polymeric gel samples fired at 1000°C . To achieve a better comparison, L^* , a^* and b^* measurements were carried out on glazes obtained from a $\text{PbO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3$ transparent glaze composition containing a 3% sample addition. The samples had previously been washed with hot 0.3 M HNO_3 . The L^* parameter is observed to be lower in the ceramic samples, whilst the a^* and λ parameters (observed from the x - y chromatic diagram) are lower in the polymeric gel samples. Table III indicates greater brightness (L^*), an increase in the amount of green (a^*), a trend to yellow (λ) and a lower colour saturation (x , y) in the polymeric gel samples.

4. Conclusions

1. The formation of $\text{Cr}_x\text{Ti}_{1-2x}\text{Nb}_x\text{O}_2$ rutile solid solutions by the ceramic method requires temperatures of about 1200°C with soaking times of several days, whilst the CrNbO_4 compound appears as an intermediate compound in this formation. In the polymeric gel samples, TiO_2 rutile (sample with $x = 0$) develops at temperatures of around 500°C . When the substitution degree (x) increases, rutile solid solutions are obtained at higher temperatures, although at 1000°C a rutile phase is formed in the complete range of compositions. Both lower temperatures and the absence of the CrNbO_4 compound formation seem to be due to a greater homogeneity in the samples prepared by the polymeric gel method than by the ceramic method.

2. The a and c parameters are observed to increase linearly over the whole composition range ($0 \leq x \leq 0.5$), in accordance with the substitution of titanium by the larger chromium and niobium ions. Unit cell parameters in both gel and ceramic samples are similar.

3. The CIELAB parameter measurements indicate greater brightness and lower colour saturation in the polymeric gel samples. The lower colour saturation may be due to a greater homogeneity in these samples.

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