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Pigments based on Cr and Sb doped TiO_2 prepared by microemulsion-mediated solvothermal synthesis for inkjet printing on ceramics

Marc Jovaní [a], María Domingo [a], Thales R. Machado [a, b], Elson Longo [c], Héctor Beltrán-Mir [a, *], Eloisa Cordoncillo [a]

[a] Departamento de Química Inorgánica y Orgánica, Universitat Jaume I de Castellón, Avda. Sos Baynat s/n, 12071 Castellón de la Plana, Spain
[b] LIEC-Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Departamento de Química, UFSCar-Universidade Federal de São Carlos, Rod. Washington Luis km 235, P.O. Box 676, 13565-905 São Carlos, São Paulo, Brazil
[c] LIEC-Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Instituto de Química, UNESP-Universidade Estadual Paulista Júlio de Mesquita Filho, P.O. Box 355, 14801-907 Araraquara, São Paulo, Brazil

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ABSTRACT

A ceramic pigment with nominal composition $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$ was prepared by microemulsion-mediated solvothermal method at 180 °C. Anatase or rutile single phase was obtained depending on the synthesis conditions. Scanning electron microscope analysis showed the formation of spheres with particle size around 600 nm. The anatase to rutile transformation temperature was determined by XRD and Raman spectroscopy. The evolution of the colour was studied, and it was related with the polymorphic transition. Yellow pigments were obtained at low temperature and huge orange colour was observed at high temperature. Powders prepared at 180 °C were tested with an industrial frit. Similar chromatic coordinates of an industrial orange ceramic pigment obtained at high temperatures were observed. ζ-potential values of the particles were ~−57 mV. The size, shape, colour and electrostatic stability of these particles make them potential candidates to be applied in glazes or inkjet printers as orange ceramic pigments.

1. Introduction

Titanium dioxide, TiO_2, has a wide range of applications. Since its commercial production in the early twentieth century, it has been widely used as a pigment [1], sunscreens [2,3], paints [4], toothpaste [5], etc. Titanium dioxide occurs mainly in three crystalline forms: rutile, anatase and brookite. Rutile is the stable phase, and anatase and brookite are metastable. Both anatase, space group I4/amd, and rutile, space group $P4_2/mnm$, are tetragonal. Structures consist of TiO_6 octahedra, sharing four edges in anatase and two edges in rutile [6,7].

Nowadays, the field of nanotechnology has generated a great deal of interest because materials have numerous new properties in nanosize-scaled. These size-dependent properties include new phase transition behaviour, different thermal and mechanical properties, interesting surface activity and reactivity, and unusual optical, electrical and magnetic characteristics [8–10]. In this way, and more closely in the field of pigments, TiO_2 have a massive potential market. Study of the particle size of TiO_2 is essential because it affects phase and thermal stability as well as surface and bulk properties [11–13]. The knowledge of the particle size is crucial to predict the behaviour of the nanoparticles in industrial processes, like in the case of ceramic decoration which the use of high temperatures are required [14].

Ceramic submicronic pigments have been developed for inkjet decoration of ceramic tiles using quadrichromic technology, being a new field of application. These pigments with particle size less than 1 μm are able to overcome some actual problems of the inkjet industrial processes [15]. The use of pigmenting particles at the nanoscale is necessary for inkjet applications [16,17]. At present in the industry, these particles are basically obtaining by different milling steps, producing submicronic particles with no round shape [18,19]. The use of submicronic pigments in inkjet technology can solved problems like nozzle clogging, dispersion or instability caused by micronized pigments, and moreover, remove the milling stages [14].

Wet chemistry methods are one of the best options to prepare TiO_2 nanoparticles. The literature reports approaches for the

* Corresponding author. Tel.: +34 964 728245; fax: +34 964 728214.
E-mail address: mir@uji.es (H. Beltrán-Mir).

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synthesis of nanoparticles of titania, including thermal hydrolysis [20,21], sol–gel [22,23], hydro/solvothermal method [24,25] and microemulsion processes [26,27]. Among them, solvothermal and microemulsion methods are extensively used for the preparation of nanomaterials.

Solvothermal method has many advantages such as: (a) the final product can be obtained directly at relatively lower reaction temperature, (b) crystalline products with different composition, structure, and morphology could be prepared modifying the synthesis conditions like temperature, pH, times or reactant concentration, and (c) it produces high purity particles compare with traditional solid–solid routes.

Therefore, the solvothermal synthesis is a good method for the preparation of oxide ceramic fine powders [24]. However, large sizes of TiO_2 nanocrystals and poor dispersion stability usually appear in the materials prepared by solvothermal methods.

Microemulsions is a powerful method for obtaining ultrafine and nanometric particles with controlled size and shape [28]. TiO_2 nanomaterials prepared by micelle method have often amorphous structure, and calcination is usually necessary in order to induce high crystallinity [10].

Based on the advantages of each method, a combination of microemulsion with solvothermal method has been explored to prepare nanomaterials such as $SrCO_3$ nanostructures [29] or $Ca_{10}(PO_4)_6(OH)_2$ [30]. Microemulsions with nanosized aqueous cores have been used as the reaction media for preparation of TiO_2 nanomaterials [31,32]. Shen et al. [33] have successfully synthesized rutile and anatase with microemulsion-mediated solvothermal method. They studied the preparation of rutile or anatase modifying the synthesis conditions such as the amount of urea in aqueous phase of the microemulsion. The effect of pH on TiO_2 phase structure have been also studied [12,34]. Regarding these studies, the low pH favours the formation of rutile phase while more alkaline media favours anatase phase formation. Other studies were done in order to control the growth of the particles. Somiya et al. [35] prepared nanomaterials by hydrothermal microemulsion process in order to prevent grain growth of the nanoparticles. They conclude that the aqueous micelles in microemulsions act as microreactors to confine the growth of TiO_2 powders.

As it mention before, TiO_2 has been widely used as a pigment. In the industry, where the solid solution used is $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$, the pigment is manufactured starting from anatase with chromium (III) oxide as chromophore element and antimony (III) oxide as counterions in presence of several mineralizers. In this case, the colour is acquired by calcinations at high temperatures around 1200 °C, where the development of the colour occurs during the anatase-rutile transformation [36]. Anatase to rutile transformation is reconstructive, therefore, transformation involves breaking and reforming bonds [7]. This reconstructive transformation involves a contraction of the c-axis and involving a volume contraction around 8% [37].

In the literature, synthesis of Cr–Sb–TiO_2 pigment was carried out by different preparation routes. C. Gargoni et al.[38] prepared samples of composition $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$ with rutile phase by several routes: ceramic method, heterogeneous ammonia coprecipitation method, homogeneous urea coprecipitation method, Pechini polyester method, and aqueous-organic coprecipitation method in a water-ditehylenglycol. Authors concluded that final colour in a conventional glaze from powders obtained by non-conventional methods was worse than colour obtained from powders prepared by the ceramic method. Other authors [14,39] used the polyol non-conventional method to synthesize nanoparticles of this pigment. Stable ceramic inks were prepared with a nanometric size by this method.

In this work, Cr,Sb-doped TiO_2 ceramic pigments were prepared by microemulsion-mediated solvothermal method. As far as we know, synthesis of this pigment has not been yet reported using this method. This route allows an accurate control of the phase and the particle size of the pigment, and therefore, it is possible to determine the influence of these properties to the final colour at high temperature in ceramic decoration. In spite of this method have been used to prepare TiO_2, the incorporation of the Cr and Sb to this structure have not been reported using this method. In the literature [33] and, as well as in this study, the phase (anatase or rutile) was controlled by the pH of the aqueous phase. However, time of the solvothermal treatment has been studied in this work due to the presence of the chromophores ions. These ions must be incorporated in the structure to form a solid solution, and therefore, they can also affect to the final phase present and the kinetic conditions of the reaction. Due to it, the time of the reaction is an important parameter to consider here. Studies of the rutile-anatase transformation were also conducted in this work.

Microemulsion-mediated solvothermal method has been able to synthesise pigments with optimal colouration, controlling the phase, shape and size of the particles to be applied in inkjet printing of ceramics. For this application, the inorganic pigment was obtained at high temperature by the traditional solid–solid reaction. However, in this method, calcinations were unnecessary because the solvothermal treatment promoting the crystallization of the phase at low temperatures. Therefore, these Cr,Sb-doped TiO_2 submicroparticles obtained at low temperatures (180 °C) would have potential applications in the field of ceramic inks.

2. Experimental

Samples of $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$ solid solution were prepared by a microemulsion-mediated solvothermal route. The synthesis procedure was as follows: first, 10 mL of Triton X-100 (surfactant), 3 mL of n-hexanol (cosurfactant 98%) and 16 mL of cyclohexane (Sigma–Aldrich, ≥99.5%) were mixed under magnetic stirring, making up the oil phase. Second, 2 mL of $TiCl_4$ (Fluka, ≥99%) solution, previously prepared in an acid medium of HCl 4M, 2 mL of H_2O and the specifics amounts of $CrCl_3 \cdot 6H_2O$ (Probus, 93%) and $SbCl_3$ (Sigma–Aldrich, ≥99%), together with the necessary amount of urea (Fluka, ≥99.5%) to obtain the desired phase, were mixed under magnetic stirring (aqueous phase). The amount of urea was fixed to 4.5 g and 1.5 g per gram of pigment to obtain anatase (A) or rutile (R) single phase, respectively [33].

Then, the aqueous phase was added dropwise to the oil phase under stirring mediated a peristaltic pump at room temperature, forming a clear microemulsion. The microemulsion was mixed under magnetic stirring for 48 h and, then, placed in a Teflon-lined stainless steel autoclave and heated at 180 °C in an oven for variable times. The precipitate was collected by centrifugation and washed repeatedly with ethanol. After this process, samples were dried in air at room temperature. A scheme of the general preparation of the samples is shown in Fig. 1, and the different treatment conditions used in each case (time and the amount of urea) are shown in Table 1.

It is well known that the anatase-rutile phase transition involves a volume contraction, and it depends on variables such as size, morphology, etc. [7]. Therefore, in order to study the anatase-rutile phase transition in these samples, the powder with anatase phase obtained at 180 °C was annealed at different temperatures between 750 and 1080 °C for 2 h and cooled slowly inside the furnace.

Powders of samples at 180 °C, where single phase and optimal colour were obtained, were mixed with one industrial frit (4% in weight of the pigment) using water as a dispersing medium. Then, the dispersion was applied to white twice-fire bodies, to verify composition stability as a ceramic colourant. A commercial transparent frit was chosen. The frit composition used is given in Table 2.

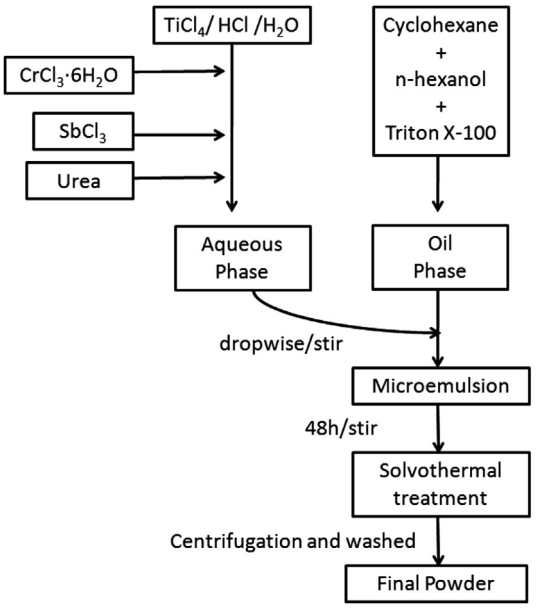

Fig. 1. Scheme of the TiO_2 sample preparation.

After drying, the pieces were fired in an electric kiln. The heat treatment applied, corresponds to a standard firing cycle used in a ceramic tile industry where the highest temperature of the cycle was 1080 °C for 5 min. This cycle involve five steps: ramping to 800 °C in 18 min, heating from 800 °C to glaze firing temperature in 17 min, 5 min hold at 1080 °C, cooling to 600 °C in 20 min, and finally cooling to room temperature in 15 min.

2.1. Characterization

Phase analysis of the samples was performed by powder XRD using a Bruker D4 Endeavour diffractometer with CuK_α radiation. Data were collected by step-scanning from $2\theta = 20$ to 70° with a step size of 0.05° and 1.5 s of counting time at each step.

Scanning electron micrographs of the samples were taken on a field emission scanning electron microscope (SEM) JEOL 7001F, equipped with a spectrometer of energy dispersion of X-ray (EDX) from Oxford instruments, using acceleration voltage = 15 kV. Samples for microstructures and microanalysis determinations were deposited in an aluminium holder and sputtered by platinum. Dynamic Light Scattering (DLS, ZetaSizer-NanoSeries Malvern Instruments, Malvern, UK) was also used to measure the ζ-potential of the as-prepared powder samples.

Raman spectra were recorder on a RFS/100/S Bruker Fourier transform (FT-Raman) spectrometer, with a Nd:YAG laser excitation light at 1064 nm in a spectral resolution of 4 cm^{-1}, in order to confirm the polymorphic phase (anatase or rutile).

UV–Visible diffuse reflectance spectroscopy and colourimetric study of the glazed fired samples were performed on a CARY 500 SCAN VARIAN spectrophotometer in the 200–800 nm range. $BaSO_4$ was used as a reference. Reflectance (R_∞) was converted to absorbance (K/S) by the Kubelka-Munk equation: $K/S = 2(1 - R_\infty) \times 2\, R_\infty^{-1}$ [40]. The positions of the main absorbance peaks in the optical spectra were determined through a deconvolution procedure that allowed obtaining more accurately values for the electronic transitions. The CIELab colour parameters L^*, a^*, and b^* of the glazed fired compositions and the anatase powders at different temperatures were determined by coupling an analytical software for colour measurements to the Varian spectrophotometer, using a standard illuminant D65, to differentiate the pigment in terms of colour. L^* is the lightness axis [black (0) to white (100)], a^* is the green (<0) to red (>0) axis, and b^* is the blue (<0) to yellow (>0) axis.

Table 1
Different treatment conditions to obtain rutile (R) or anatase (A) phase.

Ref.	Urea(g)/Pigment(g)	Time (h)
R1	1.5	17
R2	1.5	24
R3	1.5	48
A1	4.5	17
A2	4.5	24
A3	4.5	48

Table 2
Frit composition.

Composition (wt%)[a]						
SiO_2	Al_2O_3	RO[b]	R_2O[b]	ZnO	ZrO_2	Temperature/°C
67	13	9.4	10	0.4	0.2	1080

[a] The percentages do not represent quantitative analyses.
[b] R = alkaline or alkaline earth metals.

3. Results and discussion

3.1. Optimization of the crystalline phase and microstructural characterization

Microemulsions were heated at 180 °C for variable times to optimize the preparation of a rutile or anatase single phase. Several

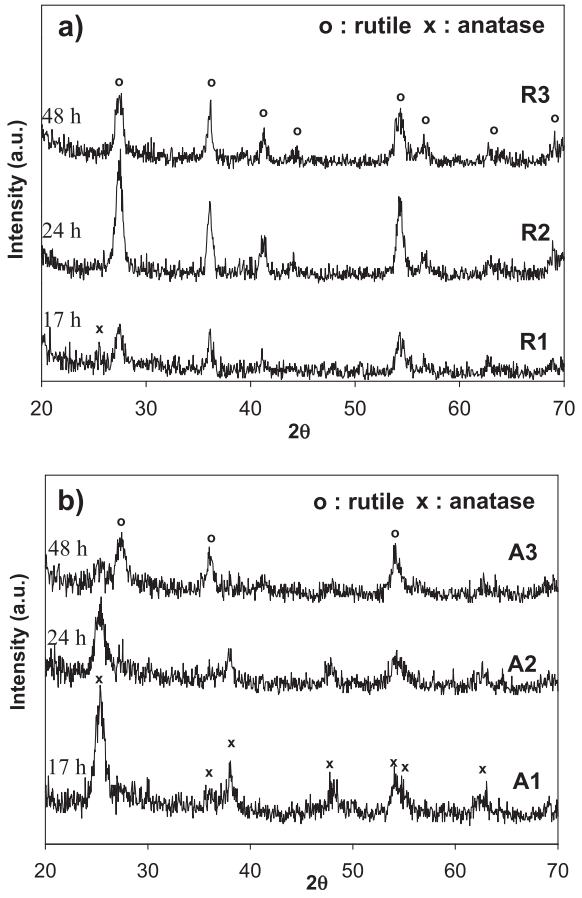

Fig. 2. XRD patterns of TiO_2 synthesised with different amounts of urea and different times of reaction at 180 °C in order to prepare rutile (a) or anatase (b) phases.

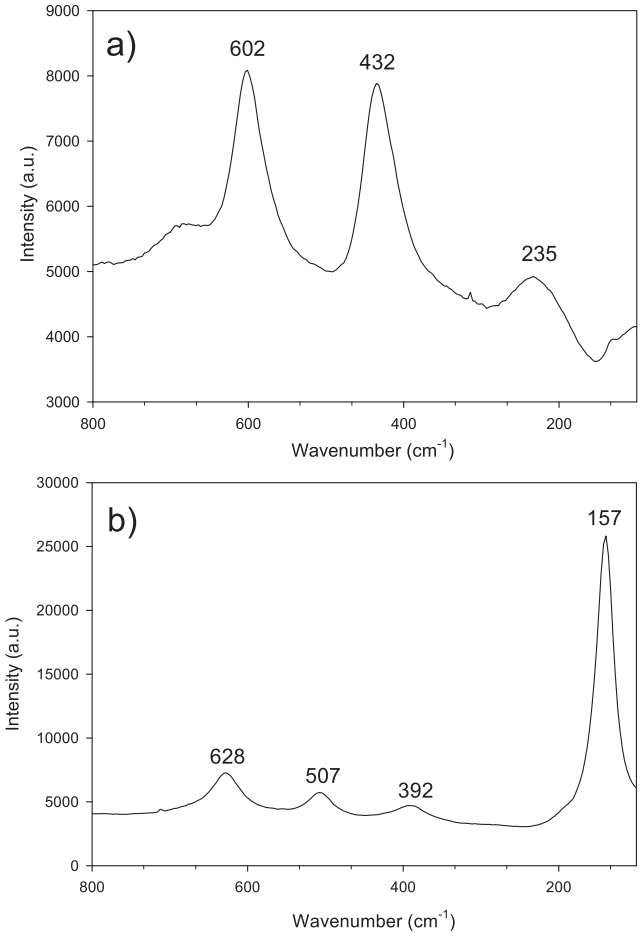

Fig. 3. Raman spectra for TiO_2 samples prepared with (a) 1.5 g of urea and after 24 h of reaction, R2, and (b) 4.5 g of urea and after 17 h of reaction, A1. Rutile or anatase phases were observed in (a) and (b), respectively.

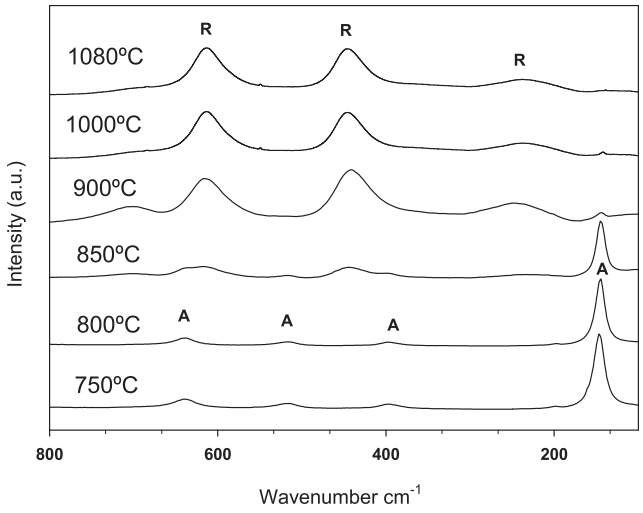

Fig. 5. Raman spectra of A1 sample fired at different temperatures.

factors such as temperature, time and pH needs to be considered to obtain single phases [12,32,34]. The aqueous phase with $TiCl_4$ solution in HCl has a very low pH, and therefore, the amount of urea plays an important role controlling the pH of this aqueous phase.

XRD patterns of TiO_2 synthesized at 180 °C with different times to obtain rutile or anatase are shown in Fig. 2(a) and (b), respectively. The crystalline phase evolution of TiO_2 was observed in both cases. Single phase of rutile [JCPDS 21-1276] was obtained when the treatment time was higher than 17 h and the amount of urea was fixed to 1.5 g, Fig. 2(a). Secondary phase of anatase [JCPDS 21-1272] was identified at short times of reaction. Therefore, the reaction needs more than 17 h for the formation of rutile single phase. When the amount of urea was adjusted to 4.5 g, anatase single phase was observed by XRD at short solvothermal treatment times, Fig. 2(b). Secondary phase of rutile appeared

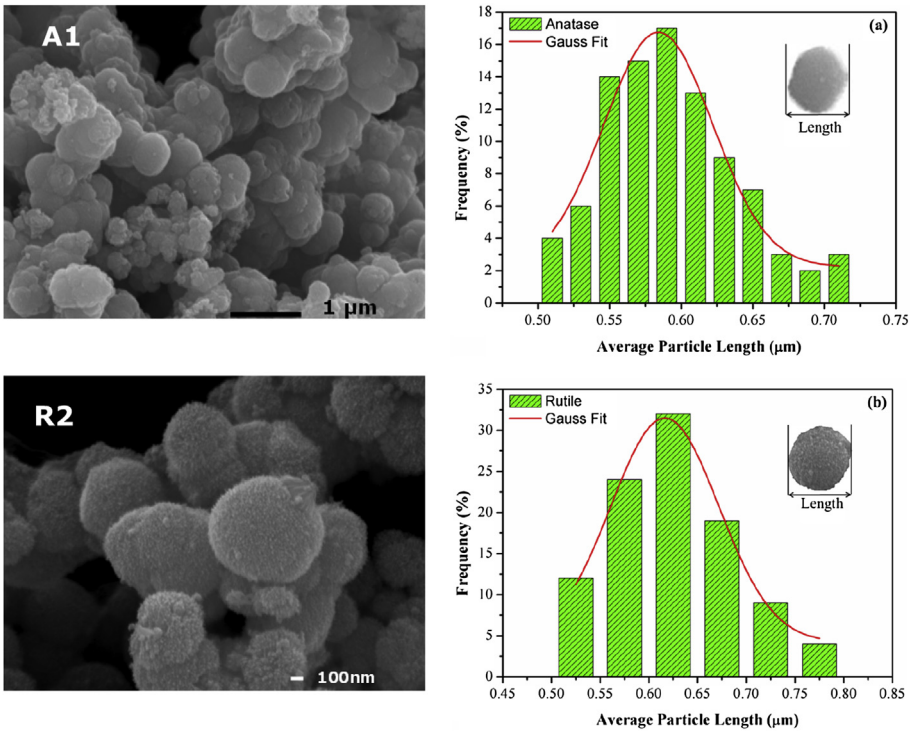

Fig. 4. SEM images of A1 (a) and R2 (b) powder samples with the average particle size in each case.

Table 3
Chromatic coordinates of A1 powder samples at different temperatures.

	L*	a*	b*
180 °C (A1)	93	−5	21
750 °C	78	0	23
800 °C	76	1	23
850 °C	77	3	28
900 °C	77	5	31
1000 °C	72	8	31
1080 °C	70	14	36

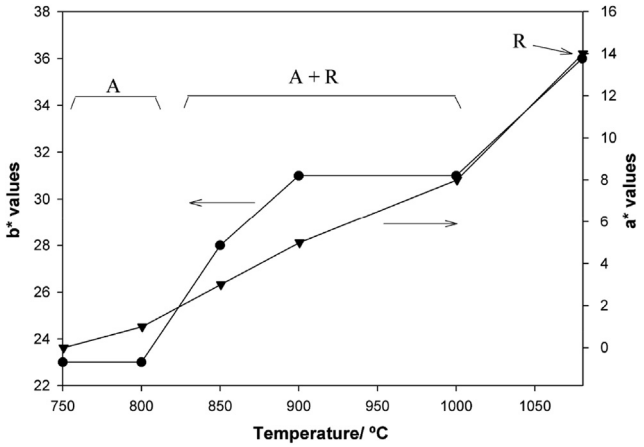

Fig. 6. CIELab chromatic coordinates of the A1 powder fired at different temperatures.

when the reaction time was increasing. R3 and R2 samples consist of single phase of rutile, while A1 sample is 100% anatase. R2 and A1 samples were chosen to continue the study due to both samples presents single phase by XRD and the shortest reaction times.

In order to confirm results obtained by XRD, TiO_2 powders were further characterized by Raman spectroscopy. Fig. 3 shows the Raman spectra of R2 and A1, showing the characteristic bands of the rutile and anatase single phase, respectively [41]. Peaks located at 235, 432 and 602 cm^{-1} can be assigned to the rutile phase, Fig. 3(a). No peaks that could be assigned to anatase TiO_2 or brookite were detected. In contrast, peaks located at 157, 392, 507 and 628 cm^{-1}, Fig. 3(b), can be assigned to the anatase phase, and no other peaks were observed. Peaks that could be assigned to the doping oxides, such as Cr_2O_3, located at 550 cm^{-1} [42], were not found. These results were consistent with the XRD results shown in Fig. 2.

Products prepared by ceramic method at high temperature must be milled to adjust the grain size of the pigments in function of their applications. It is important to know the microstructure and grain size of the samples to select one or other application. For example, grain sizes of below one micron are required for inkjet applications [15]. Therefore, the average grain size of the R2 and A1 samples were analysed by SEM. Micrographs and the grain size distribution of both powder samples are shown in Fig. 4. In both cases, there was no evidence of secondary phases by EDX, and therefore, single-phase of Cr,Sb–TiO_2 solid solutions were obtained. Spherical particles were observed and the grain size distribution was around 600 nm in both samples. Shape of the particles is also important for inkjet processes. Particles with rounded shape, as obtained in this work, are more suitable for inkjet fluid-dynamics instead of angular shapes, which are usually obtained from high energy ball milling. Production of inkjet inks involves a problem of the pigment sedimentation in the dispersant [15]. In this way, measurements of ζ-potential were performed in water with 0.1% of sodium hexametaphosphate (65–70%, Aldrich) [43], in order to determine the electrostatic stabilization of the R2 and A1 samples. Values of the ζ-potential were −57 mV and −56.5 mV, respectively. These negative values showed that the pigment can be dispersed, avoiding the sedimentation. ζ-potential values around 20 mV are obtained for the industrial pigment using glycol as dispersant [14]. Note that high ζ-potential values (positive or negative) are better to avoid sedimentation and therefore, to be applied in inkjet technology. But, other important properties such as surface tension, density or viscosity of the ink should be consider before the application [11].

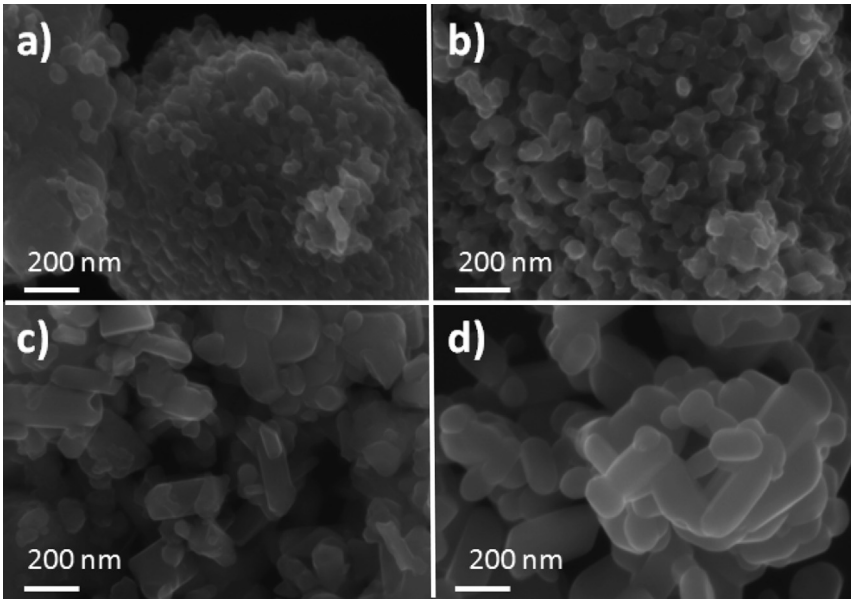

Fig. 7. Micrographs of the A1 sample at different temperatures: (a) 750, (b) 800, (c) 850 and (d) 900 °C.

3.2. Study of the anatase-rutile transformation and evaluation of the colouring performance of the pigment

Fig. 5 shows the evolution with temperature (from 750 to 1080 °C) of the TiO_2 polymorphs by Raman spectroscopy. The anatase-rutile transformation occurred at temperatures higher than 850 °C, and it was essentially completed at 1000 °C. The chromatic coordinates of the samples at different temperatures are shown in Table 3 and Fig. 6. A1 sample presents a slight yellow colouration at 180 °C. It is possible to relate the increase of a^* and b^* chromatic coordinates with the phase transitions between 750 °C and 1080 °C. The b^* coordinate increase from 23 to 36 suggesting that there is a relation between the polymorph transformation and the increase of b^* coordinate. It could be explain either by the incorporation of the Cr and Sb in different environments or, as suggest Matteucci et al. [36,44], because there is a change of the Sb oxidation state. However, a^* coordinate show an approximately linear increase with temperature over the range 750–1000 °C. It is important to highlight a constant b^* value in the interval between 900 and 1000 °C. In this range, the main polymorph is rutile but anatase phase exist as minor phase. These results suggest that the phase transformation is still going on at this range of temperatures, probably due to the necessary time for the reconstruction of the structure, from anatase to rutile. After the reconstructive transformation was occurred, and single phase of rutile was obtained at 1080 °C, the value of b^* increase significantly.

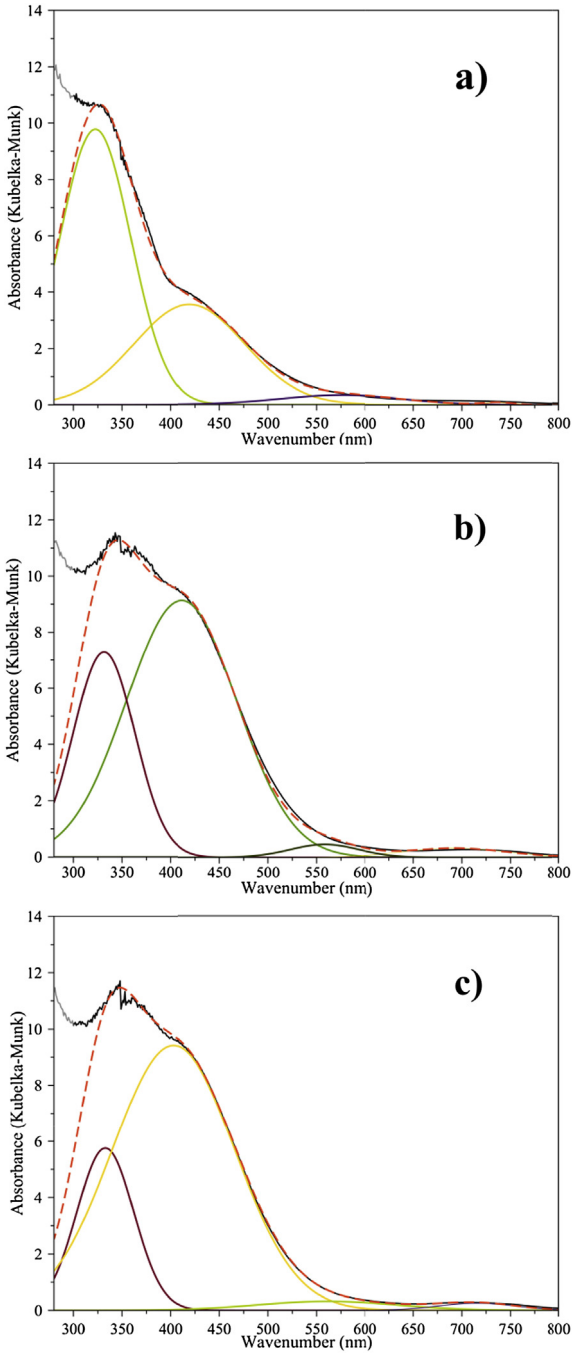

Fig. 8. Diffuse Reflectance spectra for R2 (a), A1 (b) and a commercial ceramic pigment (c) after glazing with deconvolution of optical bands.

In order to assess the morphology of the powders during the phase transformation, SEM analysis was made at each temperature. Fig. 7 shows the micrographs for the evolution of the morphology at different temperatures. Shape of the particles was different depending on the polymorph. When anatase is presented, the particles were almost spherical with certain agglomeration, Fig. 7(a) and (b). During the transition, when rutile phase was the majority phase, the particles were prismatic. This fact suggests the elongation of the particles in the polymorphic transition.

3.3. Stability of the particles as a pigment

In order to determine the stability of the powders prepared at 180 °C after glazing, a micropowder/frit mixture was prepared and fired according the cycle set out in the experimental part at the maximum temperature of 1080 °C. The pieces with the glaze were also characterized by UV–Vis and values of the CIELab parameters were obtained. Diffuse reflectance spectra of R2, A1 and a commercial ceramic pigment fired at higher temperatures (>1200 °C) and glazed in the same conditions are presented in Fig. 8 for the 270–800 nm wavelength range. Three main absorption bands are identified in the three spectra after the deconvolution: a broad band located at high energy and centred at ~340 nm (ultraviolet region) attributed to the bandgap of the rutile [45]; and two bands centred at ~445 and 560 nm attributed to the d–d transitions of the Cr(III) [$^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ and $^4A_2(^4F) \rightarrow {}^4T_2(^4F)$, respectively] in an octahedral coordination [39]. Higher absorption of the d–d transition $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ was observed for the A1 glazed sample and this intensity was similar to the glazed commercial pigment. Precursor of titanium in solid–solid reactions is usually anatase, which transforms to rutile during the synthesis at high temperatures [38]. The intensity of the absorption bands could be related with the chromatic coordinates shown in Table 4. Good chemical and thermal stability into the frit was obtained and pigments acquired orange colour after glazing with the frit for both samples. Chromatic coordinates were slightly higher for the A1 and similar to those obtained for the commercial ceramic pigment in glaze (similar a* values). Photographs of the samples before and after mixed with the frit are shown in Fig. 9. In summary, colour of both samples in a standard frit was similar to the colouration of the commercial ceramic pigment obtained at high temperatures. Therefore,

Table 4
CIELab parameters of R2 and A1 samples after glazing (frit). CIELab parameters of a commercial ceramic pigment are included as comparison.

	Powder/Glaze 1080 °C		
	L*	a*	b*
R2	65	12	39
A1	64	16	41
Commercial (>1200 °C)	60	16	47

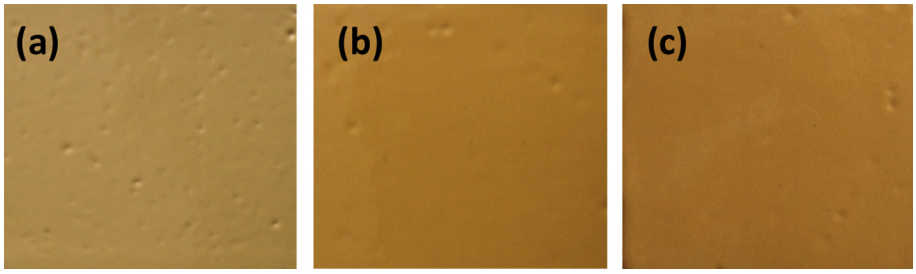

Fig. 9. Photographs of the ceramic tiles for R2 (a), A1 (b) and the commercial pigment (c) after mixed with the frit.

synthesis route has produced orange pigments after glazing, similar of those commercial pigments. It is important to note that these pigments with smaller particle size are stable in glazes, and they developed similar colour of the commercial pigment.

This novel method to synthesize spherical submicron particles at low temperature would presented benefits with respect to the method used in the ceramic industry, which makes use of high temperature calcination. Moreover, secondary phases are normally obtained from traditional ceramic route, not allowing a control of the phase, shape and size. A milling stage must be implemented to adjust the grain size of the pigment due to the high particle size caused by high-temperature calcinations. For these reasons, the novel synthesis method presented in this work to prepare pigments at low temperature would allowed several advantages compared to the traditional solid–solid method, used in the ceramic industry. A possible application of this method in the industry can avoid the milling stages and the calcinations at high temperature.

4. Conclusions

Anatase and rutile single phase of a yellow ceramic pigment based on Cr,Sb–TiO_2 were obtained by microemulsion mediated solvothermal method at 180 °C. The experimental conditions were optimised in order to obtain anatase or rutile phase. These samples prepared at 180 °C were single phase by XRD, Raman spectroscopy and SEM/EDX. The solvothermal treatment time needed to obtain single phase of anatase or rutile in the $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$ solid solution was 17 h and 24 h, respectively. Spherical particles were formed in both cases with an average particle size of 600 nm and a ζ-potential value around −57 mV. The polymorphic transition temperature and the changes of the morphology that this transformation involves were determined by Raman and SEM. The anatase-rutile transformation occurred at temperatures higher than 850 °C, and it was essentially completed at 1000 °C. Elongation of the particles in the polymorphic transition was observed. There is also a correlation between the polymorph transformation and the increase of the chromatic coordinates measured by UV–Vis, leading to a huge orange colour pigment. Samples have a good chemical and thermal stabilization into the frit, presenting similar chromatic coordinates to those of the commercial ceramic pigment obtained at high temperatures, especially when the anatase solid solution at 180 °C was the starting powder. Orange colour was kept after the application on glazes. Therefore, size, shape, colour and electrostatic stability of these particles, prepared by microemulsion-mediated solvothermal route, make it a potential candidate for orange ceramic pigment to be incorporated in the inkjet technology.

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