Study of nanoparticles based on Cr and Sb doped TiO_2 as pigments for inkjet technology applications

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Abstract

Nanoparticles of the ceramic pigment with composition $Ti_{0.97}Cr_{0.015}Sb_{0.015}O_2$ were prepared by microemulsion-mediated solvothermal method at 180 ºC. Anatase or rutile single phase was obtained depending on the synthesis conditions. Scanning electron microscope analysis showed the formation of nanospheres with particle size around 600 nm. The anatase to rutile transformation temperature was determined by Raman spectroscopy. The evolution of the colour was studied, and it was related with the polymorphic transition. Yellow nanopigments were obtained at low temperature and huge orange colour was observed at high temperature. Nanopigments prepared at 180 ºC 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 nanoparticles were ~ -57 mV. The size, shape, colour and electrostatic stability of these nanoparticles make them potential candidates to be applied in glazes or inkjet printers as orange ceramic pigments.

Keywords: nanoparticles, pigment, titanium dioxide, orange ceramic pigment, inkjet

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 nanopigments, TiO_2 have a massive potential market.

Ceramic nanopigments have been developed for inkjet decoration of ceramic tiles using quadrichromic technology, being a new field of application. The nanopigments are able to overcome some actual problems of the inkjet industrial processes [11]. The use of pigmenting particles at the nanoscale is necessary for inkjet applications [12,13]. At present in the industry, these nanoparticles are basically obtaining by different milling steps [14,15]. The use of nanopigments in inkjet technology can solved problems like nozzle clogging, dispersion or instability caused by micronized pigments, and moreover, remove the milling stages [16].

Wet chemistry methods are one of the best options to prepare TiO_2 nanoparticles. The literature reports approaches for the synthesis of nanoparticles of titania, including thermal hydrolysis [17,18], sol-gel [19,20], hydro/solvothermal method [21,22] and microemulsion processes [23,24]. Among them, solvothermal and microemulsion methods are extensively used for the preparation of nanomaterials.

Solvothermal method has many advantages such as:

1) The final product can be obtained directly at relatively lower reaction temperature.
2) Crystalline products with different composition, structure, and morphology could be prepared modifying the synthesis conditions like temperature, pH, times or reactant concentration.
3) It produces high purity particles compare with traditional solid-solid routes.
4) The equipment and processing required are simpler, and the control of the reaction conditions is easier than other methods.

Therefore, the solvothermal synthesis is a good method for the preparation of oxide ceramic fine powders [21]. However, large sizes of TiO_2 nanocrystals and poor dispersion stability are usually appear in the materials prepared by solvothermal methods.

Microemulsions with nanosized aqueous cores have been extensively used as the reaction media for preparation of nanomaterials [25,26]. 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 [27] or $Ca_{10}(PO_4)_6(OH)_2$ [28]. Shenm *et al.* [29] have successfully synthesized rutile and anatase with microemulsion-mediated hydrothermal 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 extensively studied [30,31]. 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. In order to prevent grain growth of the nanoparticles, Somiya *et al.* [32] prepared nanomaterials by hydrothermal microemulsion process. 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 ºC, where the development of the colour occurs during the anatase-rutile transformation [33]. 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% [34].

In this work, nanoparticles of Cr,Sb-doped TiO_2 ceramic pigment were prepared by microemulsion-mediated solvothermal method, being able to control the phase (anatase or rutile) mediated the control of pH of the aqueous phase and the time of the solvothermal treatment. Calcinations were unnecessary because the solvothermal treatment promoting the crystallization under mild temperatures, obtaining the desired phase at low temperature. Studies of the rutile-anatase transformation were also conducted in this work. These Cr,Sb-doped TiO_2 nanoparticles obtained at low temperatures 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 4.5g and 1.5g per gram of pigment to obtain anatase (A) or rutile (R) single phase, respectively [29].

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 ºC 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 ºC was annealed at different temperatures between 750 and 1080 ºC for 2 hours and cooled slowly inside the furnace.

Powders of samples at 180 ºC, 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 colorant. A commercial transparent frit was chosen. The frit composition used is given in Table 2. 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 minutes. This cycle involve five steps: ramping to 800 ºC in 18 min, heating from 800 ºC to glaze firing temperature in 17 min, 5 min hold at 1080 ºC, cooling to 600 ºC 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 Endeavor diffractometer with CuK_α radiation. Data were collected by step-scanning from $2\theta = 20$ to 70^o with a step size of 0.05^o 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 colorimetric 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: $K/S = 2(1- R_\infty) \times 2 R_\infty^{-1}$ [35]. 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.

3-Results and discussion

3.1- Optimization of the crystalline phase and microstructural characterization

Microemulsions were heated at 180 ºC for variable times to optimize the preparation of a rutile or anatase single phase. Several factors such as temperature, time and pH needs to be considered to obtain single phases [26,30,31]. 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.

Phase analysis of the samples after the treatment at 180 ºC was performance by powder XRD. XRD patterns of TiO_2 synthesized 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 hours 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 when the reaction time was increasing. R3 and R2 samples shown single phase of rutile, and A1 sample shown single phase of 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 the 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 [36]. Peaks located at 235, 432 and 602cm^{-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} [37], 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 the micra are required for inkjet applications [11]. Therefore, the average grain size of the R2 and A1 samples were analyzed 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 nanoparticles were observed and the grain size distribution was around 600 nm in both samples. The production of inkjet inks involves a problem of the pigment sedimentation in the dispersant [11]. In this way, measurements of ζ-potential were performed in water with 0.1% of sodium hexametaphosphate (65-70%, Aldrich) [38], 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 [16]. Note that high ζ-potential values (positive or negative) are better to avoid sedimentation and therefore, to be applied in inkjet technology.

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

The anatase-rutile phase transition involves a volume contraction, and it depends on variables such as size, morphology, etc. [7]. In this work, Sb,Cr-doped TiO_2 nanospheres with anatase phase (A1), obtained at 180 ºC, were fired at different temperatures between 750 and 1080 ºC to study the anatase-rutile phase transition. The evolution of the colour with the phase transition was also studied. Raman spectra were analyzed at each temperature and the chromatic coordinates were obtained. Fig. 5 shows the evolution with temperature of the TiO_2 polymorphs by Raman spectroscopy. The anatase-rutile transformation occurred at temperatures higher than 850 ºC, and it was essentially completed at 1000 ºC. The chromatic coordinates of the samples at different temperatures are shown in Table 3 and Fig 6. A1 sample presents a slight yellow coloration at 180 ºC. It is possible to relate the increase of a^* and b^* chromatic coordinates with the phase transitions between 750 ºC and 1080 ºC. The b^* coordinate increase from 23 to 36 suggesting that there is a relation between the polymorph transformation and the increase of b^* coordinate. However, the a^* coordinate show an approximately linear increase with temperature over the range 750 – 1000 ºC. It is important to highlight a constant b^* value in the interval between 900 and 1000 ºC. 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 1080ºC, the value of b^* increase significantly.

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 rectangular. This fact suggests the elongation of the particles in the polymorphic transition.

3.3. Stability of the nanoparticles as a pigment

In order to determine the stability of the nanopowders prepared at 180 ºC after glazing, a nanopowder/frit mixture was prepared and fired according the cycle set out in the experimental part at the maximum temperature of 1080 ºC. The pieces with the glaze were also characterized by UV-Vis and values of the CIELab parameters were obtained. Diffuse reflectance spectra of A1, R2 and a commercial ceramic pigment fired at higher temperatures (>1200 ºC) and glazed in the same conditions are presented in Fig 8 for the 230-800 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 ~260 nm attributed at the metal-ligand charge transfer ($Ti^{4+}\leftrightarrow O^{2-}$); a second band centred at ~340 nm corresponding to the substitution of the Ti(IV) by Cr(III) in an octahedral coordination ($Ti^{4+}\leftrightarrow Cr^{3+}$); and finally, a band centred at ~410 nm attributed to the *d-d* transition of the Cr(III) [$^4A_2(^4F)\rightarrow{}^4T_1(^4F)$] in an octahedral coordination [39]. The intensity of this low energy band was different depending of the sample. Higher absorption of the *d-d* transition $^4A_2(^4F)\rightarrow{}^4T_1(^4F)$ was observed for the anatase (A1) glazed sample and this intensity was similar to the glazed commercial pigment. The precursor of titanium in solid-solid reactions is usually anatase, which transforms to rutile during the synthesis at high temperatures [40]. 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, the colour of both samples in a standard frit was similar to the coloration of the commercial ceramic pigment obtained at high temperatures.

This novel method of synthesize nanospheres at low temperature presents a lot of benefits in front the method used in the ceramic industry. In the ceramic industry is necessary the use of high temperatures calcinations to prepare rutile-based orange pigments by the solid state method, requiring consumption of large amounts of energy. Secondary phases are normally obtained from this method, not allowing a control of the phases, the 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 this reasons, the novel synthesis method presented in this work to prepare nanopigments at low temperature allows several advantages compared to the traditional solid-solid method, used in the ceramic industry. A possible application of this method in the industry can produce great economic benefits, removing the milling stage and saving a high amount of energy in 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 ºC. The experimental conditions were optimised in order to obtain anatase or rutile phase. These samples prepared at 180 ºC 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. Nanospheres 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 ºC, and it was essentially completed at 1000 ºC. 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 ºC was the starting nanopowder. Orange colour was kept after the application on glazes. Therefore, the size, shape, colour and the electrostatic stability of these nanoparticles make it a potential candidate for orange ceramic pigment to be incorporated in the inkjet technology.

5. Acknowledgements

We thank the "Universitat Jaume I"-project No. P1 1B2013-65 (MJ, MD, HB, EC) for financial support. M.J. also thanks this project for a fellowship. We also thank to Juan Carlos Gallard (Ferro Spain S.A.) for the initial ideas.

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Figure captions

Fig. 1. Scheme of the TiO_2 sample preparation.

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

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

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

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

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

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

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

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

Highlights

- Nanoparticles of Cr,Sb-doped TiO_2 ceramic pigment were prepared by a microemulsion-mediated solvothermal method at 180 ºC.
- Anatase and rutile single phase were synthesized modifying the pH of the aqueos phase and the time of the solvothermal treatment.
- Nanospheres with particle size around 600 nm were obtained.
- Nanopigments prepared ate low temperature were tested with an industrial frit presented huge orange colour.
- The size, shape, colour and the electrostatic stability of these nanoparticles make it a potential candidate to be used in inkjet applications like a pigment.

Graphical abstract

Nanospheres based on Cr,Sb-doped TiO_2 with a potential use in the inkjet technology were obtained at low temperature (180 ºC).

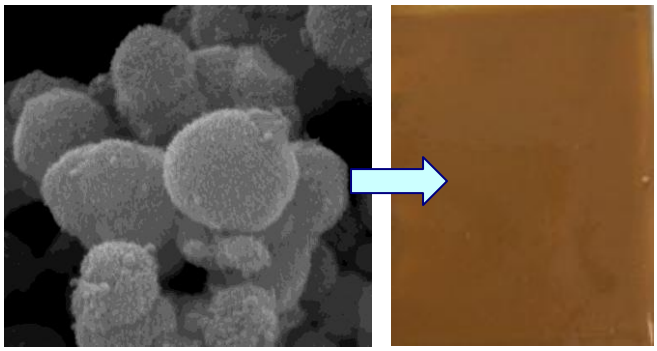

Figure 1

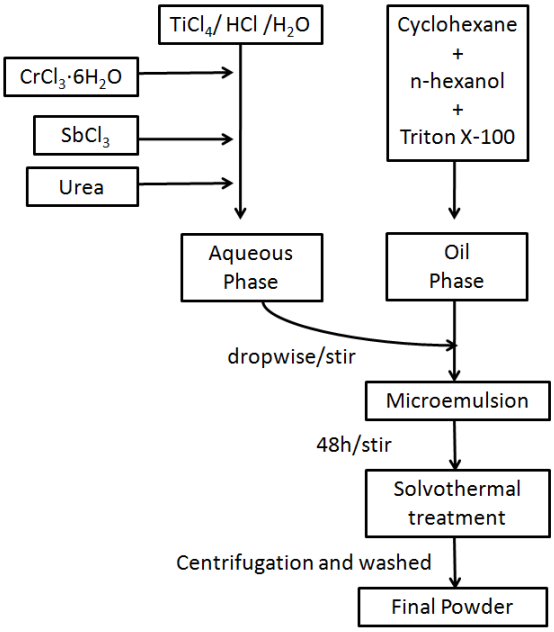

Fig 1.

Figure 2

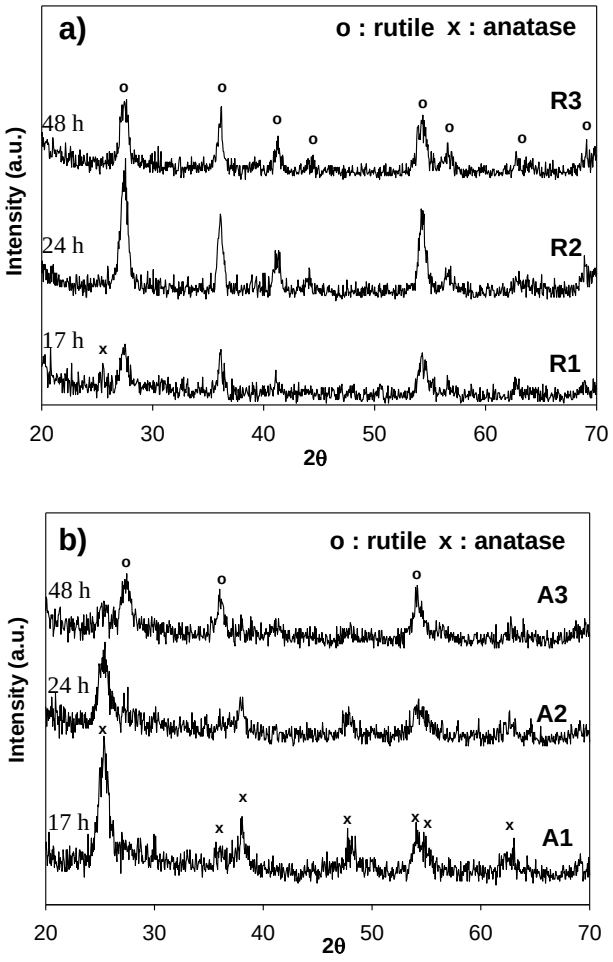

Fig 2.

Figure 3

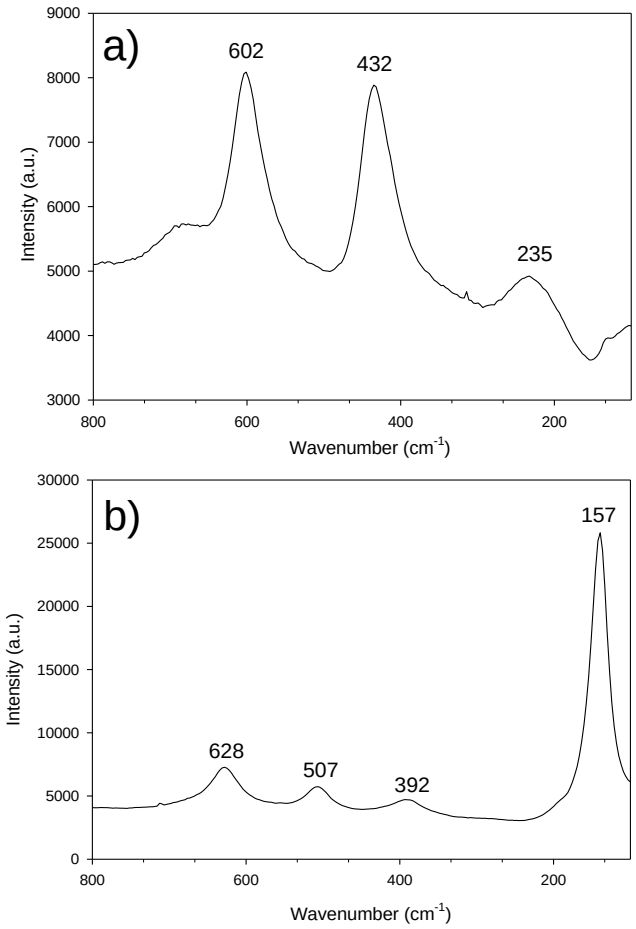

Fig 3.

Figure 4

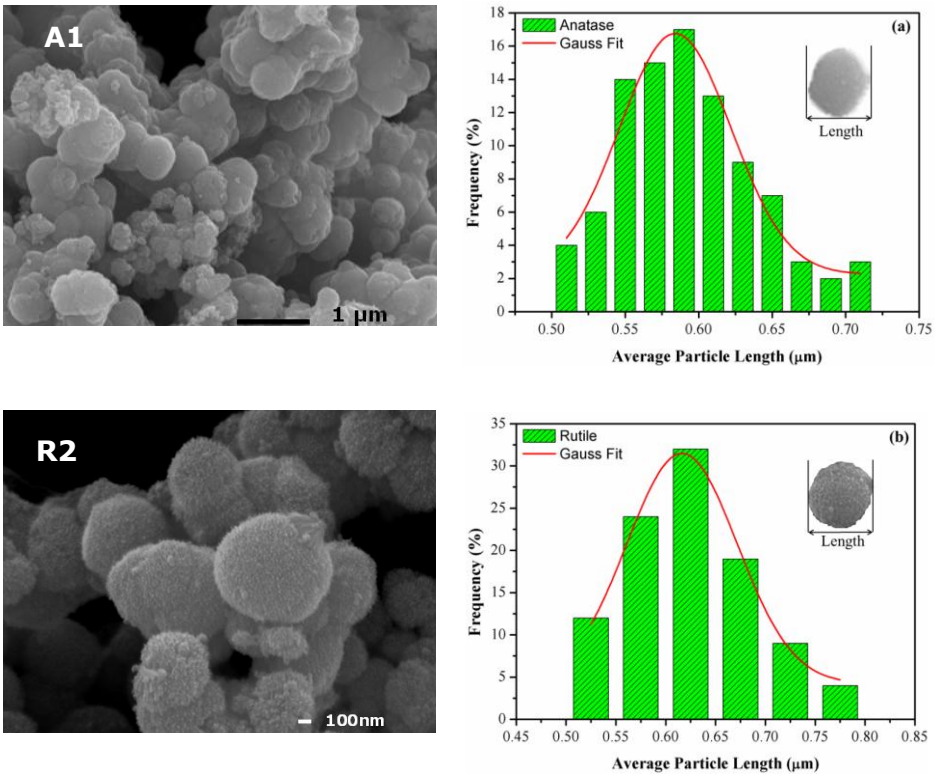

Fig 4.

Figure 5

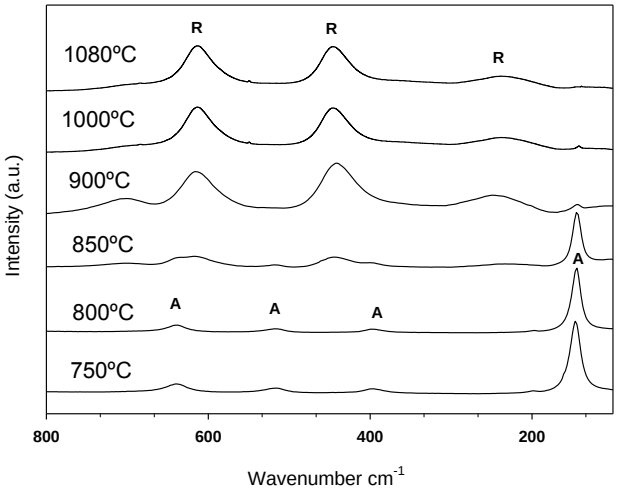

Fig 5.

Figure 6

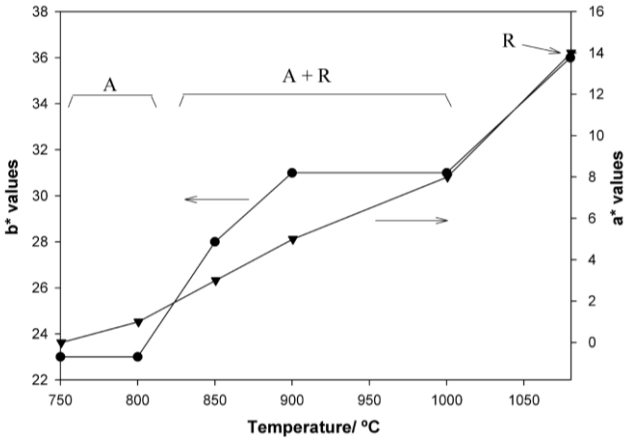

Fig 6.

Figure 7

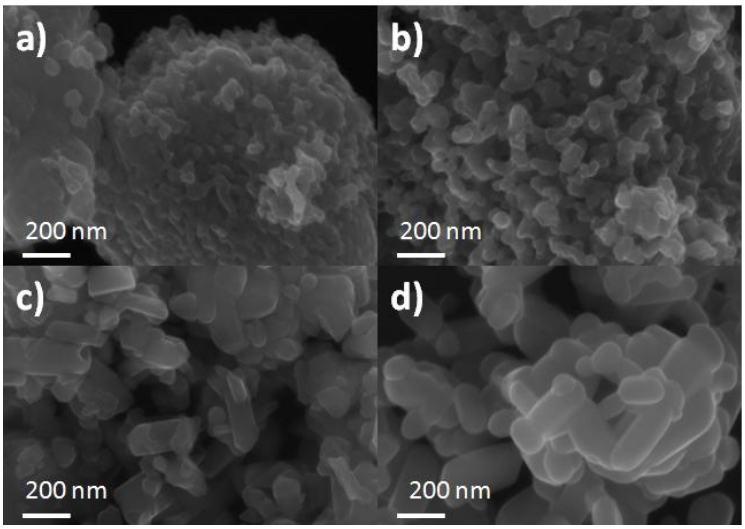

Fig 7.

Figure 8

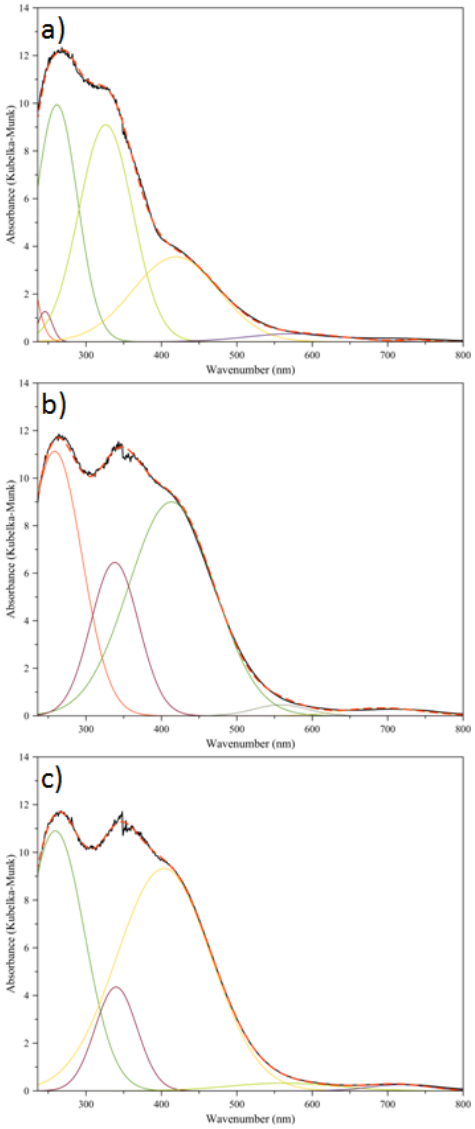

Fig 8.

Figure 9

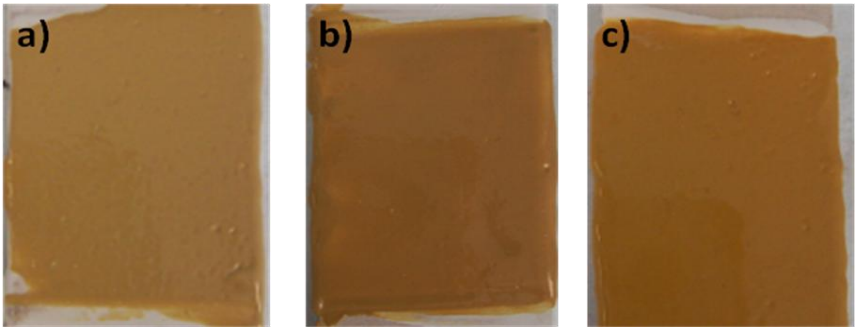

Fig. 9.

Table 1

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

Table 3

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

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

Table 4

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 1080ºC		
	L*	a*	b*
R2	65	12	39
A1	64	16	41
Commercial (>1200ºC)	60	16	47