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Environmental-friendly yellow pigment based on Tb and M (M = Ca or Ba) co-doped Y₂O₃

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Abstract

A yellow inorganic ceramic pigment with general formula Y_{1.86-x}M_xTb_{0.14}O_{3-x/2} (M = Ca and/or Zn) with x = 0.06, 0.32 and 0.64 were synthesized by a modified Pechini method. XRD, SEM and HRTEM/EDX analysis showed the formation of solid solution at 1300 °C when x = 0.06 and 0.32. The best b* yellow coordinates were obtained for Ca and Zn co-doped Y_{1.86}Tb_{0.14}O₃ samples. The intensity of the yellow colour in the samples is related to the presence of Tb⁴⁺ ions. Samples with higher concentration of Tb⁴⁺ ions lead to a better yellow colour. The chemical stability of these pigments was determinate in an industrial glaze. The glazing tests indicated that the powder samples with x = 0.06 and 0.32 fired at 1300 °C were stable in the glaze. These results make it a potential candidate for environmental friendly yellow ceramic pigment to be used in applications such as pigment for glazes or inkjet printers.

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Keywords: Ceramic yellow pigment; Environmental friendly; Lanthanide; Yttrium oxide; Pechini method

1. Introduction

Inorganic pigments are an integral part of many decorative and protective coatings. They are used for mass colouration of materials such as plastics, glaze, ceramics and porcelain enamels. Ceramic pigments are basically white or coloured substances with high thermal stability and chemical resistance enabling their further processing at high temperatures.

There is interest to develop new yellow-coloured inorganic materials to substitute industrial pigments that are based on toxic metals hazardous to human health and the environment. Most of the ceramic pigments used in the ceramic industry are based on transition and heavy metals as chromophore ions.¹ The strong environment regulations adopted by the European Union has increased the develop of new compositions of inorganic pigments more environmental friendly, without toxic elements such as Pb, Hg, Cd, Sb, As, Co, Cr, Ni, etc.

The development of new solids with interesting colour applications is being attractive topic for researchers and industries;

especially materials where the substitution of transition ions by lanthanide ions is produced. The used of lanthanides is growing due to their known low toxicity and the unique optical properties make them a promising material in a wide range of applications, that includes inorganic pigments for ceramic glazes, tunable lasers, or X-ray imaging.^{2–7}

Praseodymium yellow (Pr-doped ZrSiO₄) has been widely used in ceramic industries due to its stability at high temperatures and low toxicity^{8–10} but this pigment requires high temperature calcinations and long times during preparation, which trends to induce particle grown of the pigment. This effect does not allow applications in which fine dispersion of the pigment is essential, for example, paints or inks. For applications such as inkjet printers, the particle size must be less than 1 μm and the re-milling process, commonly used to reduce the particle size in the ceramic industry, is not useful for this praseodymium-zircon pigment. When the milling process is used, the intensity of the yellow colour decreases. This problem is common in other pigments based on zircon solid solution such as vanadium zircon blue, and it leads to the obtain low intensity colours. Moreover, the high temperature needed also produce inhomogeneity in the final product.¹¹

Based on environmental considerations, different lanthanides-based yellow inorganic pigments have been

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study for researchers as alternative to the existing toxic pigments.^{12–15} Among several non-toxic yellow pigments, CeO₂ and related materials have attracted much attention due to their opacity, low toxicity and thermal stability.^{16–18} However, the chromatic properties of these materials are not very attractive as compared with the pigments currently used in the ceramic industry.

Recently, Vishnu et al.¹⁹ have developed a new class of yellow pigment based on solid solutions of mixed oxides with the general formula Sm_{6-x}W_{1-y}Zr_xMo_yO_{12-δ}. This pigment, synthesised by solid state route, seems a good colorant for plastics and possess good chromatic properties.

Therefore, substitution of toxic elements by lanthanide ions represents an alternative and successful way to prepare more environmentally benign coloured materials. The main limitation in the use of lanthanide elements is that their *f-f* electronic transitions are forbidden by the selection rules.²⁰ Thus, it will give rise to compounds with low-intensity colours when these elements are present in their most usual oxidation states.

Yttria (Y₂O₃) has recently received special interest due to its high chemical durability, and refractory properties.^{21,22} Usually, high pressure (>40 MPa) and/or high temperatures (>1600 °C) are needed to obtain polycrystalline Y₂O₃ dense ceramics.^{23–30} It has been reported that the sintering temperature of Y₂O₃ can be reduced by doping with a divalent cations such as Ca²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Sr²⁺ or Zn²⁺.^{31–33} The most effective dopant was Ca²⁺ (1 mol%) which reduced the sintering temperature for a relative density of 90% from 1700 °C to 1500 °C under conventional sintering in air.

Lanthanide ions doped yttrium oxide materials has attracted considerable interest, due to their important optical properties such as their excellent luminescent efficiency, colour purity, and chemical and thermal stability.^{34,35} Among the lanthanides ions, Tb doped Y₂O₃ materials have been widely studied due to their important luminescence properties when they are prepared as nanoparticles.³⁶ In order to evaluate the effect of the particle size, different authors have prepared nanocrystalline Tb doped Y₂O₃ host materials and the optical properties have been measured.^{37–39} Goldburt et al.³⁷ showed the influence of particle size in the phosphor efficiency and the luminescence behaviour. Psuja et al.³⁹ studied the cathodoluminescent properties of Tb doped yttria nanocrystallites, and showed that the most intensive luminescence was observed for samples sintered at 900 °C where the grain size was in the order of 40 nm. Soo et al.⁴⁰ synthesized nanocrystals of Y₂O₃ doped with different concentrations of Tb³⁺, and showed the effect of the nanoparticles agglomeration on the optical properties.

In this work, the synthesis of M²⁺ (Ca and/or Zn) and Tb³⁺ codoped Y₂O₃ ceramics by a modification of the Pechini's method is reported to obtain new yellow pigments. Thus, in order to generate an alternative environmental friendly coloured materials without toxic chromophore elements, the optical properties of Y₂O₃: M²⁺, Tb³⁺ ceramics are reported. Structural and microstructural characterization of the materials is also studied by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX) and ultraviolet–visible spectroscopy (UV–Vis). In order

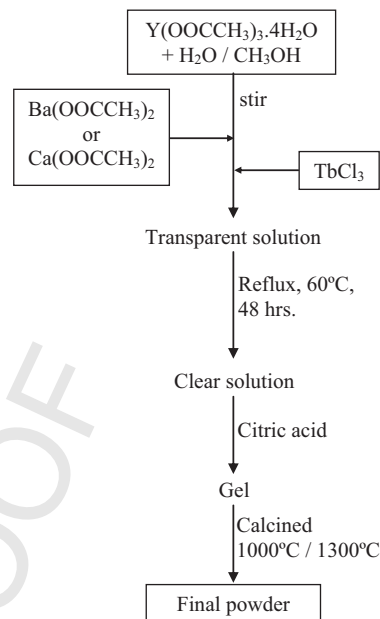


Fig. 1. Scheme of the synthesis procedure.

to obtain the best colouration of the pigment and small particle size, the synthesis temperature and the concentration of dopants is also evaluated. As far as we aware, the colour properties of Tb doped Y₂O₃ materials for ceramic pigment applications has not been previously reported.

2. Experimental

Samples were prepared by a modified Pechini procedure⁴¹ using Y(OOCCH₃)₃·4H₂O (99.9%, Strem Chemicals), Ba(OOCCH₃)₂·H₂O (98%, Sigma–Aldrich), Ca(OOCCH₃)₂·H₂O (98%, Sigma–Aldrich), Zn(OOCCH₃)₂ (98%, Sigma–Aldrich) TbCl₃ (99.9%, Strem Chemicals), as precursors. All reagents were of analytical grade and used without further purification. Distilled water and absolute methanol (Scharlab, 99.9%) were used as solvents. A scheme of the general preparation of the samples is shown in Fig. 1.

Yttrium precursor was dissolved in water and methanol with a Y(OOCCH₃)₃:H₂O:CH₃OH molar ratio 1:1.4:25. Then, Ba(OOCCH₃)₂·H₂O, Ca(OOCCH₃)₂·H₂O or Zn(OOCCH₃)₂, and finally TbCl₃, were added and the mixture was stirred for 20 min. This mixture was transferred into a balloon flask and, heated at 60 °C (reflux) for 48 h. The resulting solution was cooled until room temperature and then, citric acid (metal: citric acid, 1:1 molar ratio) was added. A gel was formed and it was dried in air at room temperature. Finally, the powder was annealed at temperatures of 1000 °C and 1300 °C.

2.1. Preliminary study

A preliminary study was conducted to determine the optimum working conditions (temperature, time and composition) in which compositions listed in Table 1 exhibited a good yellow colour after annealing. The chemical stability and the final

Table 1
Compositions prepared for the preliminary study.

Ref.	Composition
YT	$Y_{1.86}Tb_{0.14}O_3$
YTB	$Y_{1.8}Tb_{0.14}Ba_{0.06}O_{2.97}$
YTC	$Y_{1.8}Tb_{0.14}Ca_{0.06}O_{2.97}$

Table 2
Frit composition.

Composition (wt%) ^a						Temperature/°C
SiO ₂	B ₂ O ₃	Al ₂ O ₃	RO ^b	BaO	R ₂ O ^b	
63	5	12	6	1	10	1080

^a The percentages do not represent quantitative analyses.

^b R = alkaline or alkaline earth metals.

colour of the prepared powders in a glaze were also evaluated. Compositions for this preliminary study were selected based on previous study by Kumini et al.,⁴² in which Tb doped Y_2BaZnO_5 produced yellow colour materials. Three compositions were proposed: one composition based on Tb doped Y_2O_3 solid solution with formula $Y_{2-x}Tb_xO_3$ ($x = 0.14$) as a reference; and two more compositions (YTB and YTC) in which Tb ($x = 0.14$) and small amounts of Ba or Ca were used as codopants. Samples were annealed in air at 1000 °C and 1300 °C for 2 and 6 h, respectively. The heating rate was 10 °C/min. After heat treatment the powder was milled and sieved at 0.06 mm. To achieve reducing conditions, samples sintered at 1300 °C in air and pressed into pellets were returned to a tubular furnace at 1300 °C for 1 h in 5% H_2 /95% N_2 atmosphere and then quenched in liquid N_2 .

The annealed compositions (4% in weight of the pigment) were mixed with one industrial frit using water as a dispersing medium, and 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, corresponding 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.

2.2. Compositional study

Based on the results obtain in the preliminary study, where Ca and Tb doped Y_2O_3 samples exhibited more intense

yellow colouration (see Section 3), different compositions with Ca were prepared. Charge composition mechanism according to the formula $Y_{1.86-x}Ca_xTb_{0.14}O_{3-x/2}$ was proposed to introduce calcium as dopant. Moreover, different compositions with Zn and Ca codoped $Y_{1.86}Tb_{0.14}O_3$ were also prepared. Zn was also introduced based on the previous study by Kumini et al.⁴² The effect of calcium and zinc concentration on pigment colour was studied by means of six compositions based on $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ ($M = Ca$ and/or Zn) with $x = 0.06, 0.32$ and 0.64 , which are indicated in Table 3. In this compositional study, the concentration of dopant ions was increased in order to explore the colouration when the expensive yttrium reagent was decreased. Three trends are observed in Table 3: (I) three compositions (including the composition of the preliminary study, YTC) with different amounts of Ca; (II) one composition with a fix amount of Zn; and (III) three compositions with different amounts of Ca and Zn as codopants.

Samples were fired at 1000 °C and 1300 °C, with soaking times of 2 and 6 h, respectively. After the heat treatment the compositions were milled and sieved at 0.06 mm. Then, powder samples were also applied with an industrial frit (same conditions used in the preliminary study).

2.3. Characterization

Phase analysis of the annealed samples was performed by powder XRD with a Siemens D5000 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 10 s of counting time at each step, and accumulating over two XRD cycles. The goniometer was controlled by the “Siemens DIFFRACT Plus” software, which also determined diffraction peak positions and intensities. The instrument was calibrated with an external Si standard.

Scanning electron micrographs of the samples were taken on a 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 coated by a graphite film.

The characterization by high-resolution transmission electron microscopy (HRTEM) was carried out on JEOL 2100 microscope, with an accelerating voltage of 200 kV, coupled with an EDX (Inca Energy TEM 200, Oxford). EDX spectra were recorded with a 2 mm probe size. The spectra were further processed with the help of INCA software, version, 4.05, from Oxford Instruments.

Table 3
Compositions prepared. Reference is shown in brackets.

Composition		
Trend I	Trend II	Trend III
$Y_{1.8}Tb_{0.14}Ca_{0.06}O_{2.97}$ (YTC)		$Y_{1.8}Tb_{0.14}Ca_{0.03}Zn_{0.03}O_{2.97}$ (CZ006)
$Y_{1.54}Tb_{0.14}Ca_{0.32}O_{2.84}$ (C032)	$Y_{1.54}Tb_{0.14}Zn_{0.32}O_{2.84}$ (Z032)	$Y_{1.54}Tb_{0.14}Ca_{0.16}Zn_{0.16}O_{2.84}$ (CZ032)
$Y_{1.22}Tb_{0.14}Ca_{0.64}O_{2.68}$ (C064)		$Y_{1.22}Tb_{0.14}Ca_{0.32}Zn_{0.32}O_{2.68}$ (C064)

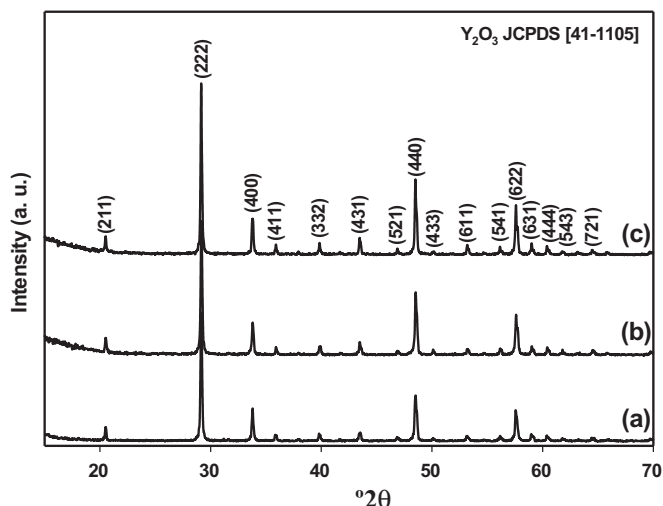


Fig. 2. XRD patterns for (a) Y_{1.86}Tb_{0.14}O₃ and (b) Y_{1.8}Tb_{0.14}Ca_{0.06}O_{2.97}, and (c) Y_{1.8}Tb_{0.14}Ba_{0.06}O_{2.97} sintered at 1300 °C for 6 h.

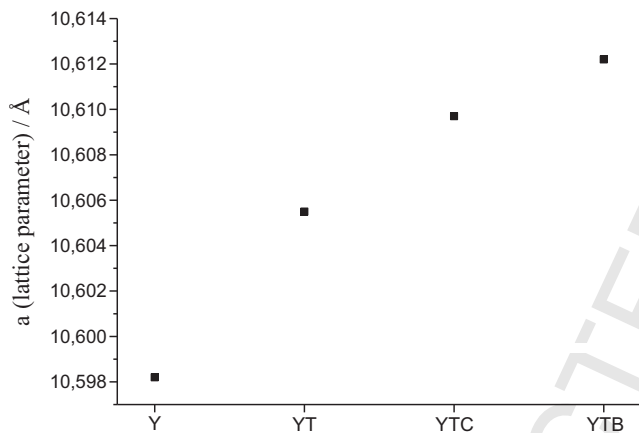


Fig. 3. Variation in the lattice parameters of Y₂O₃:Tb and (Ca or Ba) solid solution.

UV-Visible diffuse reflectance spectroscopy and colorimetric study of the samples were performed on a CARY 500 SCAN VARIAN spectrophotometer in the 300–700 nm range. BaSO₄ was used as a reference. The CIE Lab colour parameters *L*^{*}, *a*^{*}, and *b*^{*} on the unglazed and glazed fired compositions were determined by coupling an analytical software for colour measurements to the Varian spectrophotometer, using a standard illuminant D, 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 4
Crystal size by Scherrer's equation of YT, YTB, and YTC samples annealed at 1000 °C and 1300 °C.

Ref.	Crystal size (nm)	Crystal size (nm)
	1000 °C	1300 °C
YT	149.25	288.02
YTB	205.20	456.02
YTC	149.24	328.34

Photoluminescence (PL) measurements were performed at room temperature by CARY ECLIPSE VARIAN fluorescence spectrophotometer in the 450–650 nm range. Emission spectra were excited at 290 nm.

3. Result and discussion

3.1. Preliminary study

XRD analysis was performed for samples fired at 1000 and 1300 °C. Single phase was obtained at both temperatures for

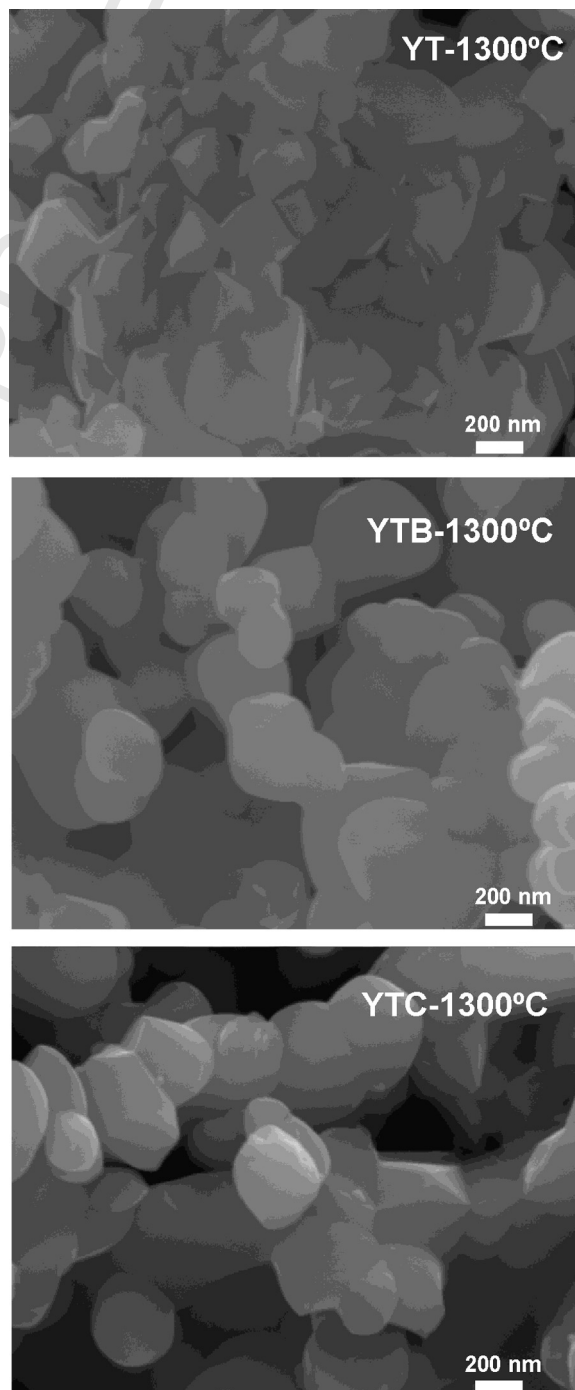


Fig. 4. SEM of powders annealed at 1300 °C.

all compositions as shown in Fig. 2 for 1300 °C. The patterns exhibit peaks which were assigned to Y₂O₃ (JCPDS 41-1105), which could suggest the formation of solid solutions for the three compositions studied. The diffraction peaks of yttria phase become sharper with the increase of annealed temperature. There was no evidence of any secondary phases, but if there are free Tb₂O₃ and CaO or BaO outside the Y₂O₃ lattice, would be too small to be detected by routine powder XRD due to the sensitivity threshold of the instrument.

The lattice parameters (*a*, for cubic phase) of the solid solutions have been determined and they are showing in Fig. 3. Main phase Y₂O₃ exhibits the cubic bixbyite structure (space group *Ia*3, No. 206) with a lattice parameter of 10.604 Å. The results indicated that there are changes in the lattice parameter, the value of *a* parameter change with the size of every cation. The variation in the unit cell parameters of Y₂O₃ indicated that dopants

with ionic radius larger than Y³⁺ (104 pm), e.g. Tb³⁺ (106.3 pm), Ca²⁺ (114 pm) or Ba²⁺ (149 pm),⁴³ increase the lattice parameter. This variation in the parameters of network suggests that terbium, barium, and calcium were incorporated into the Y₂O₃ structure. From the variation of the parameter, it is clear that a solid solution forms.

Crystal sizes of the samples sintered at 1000 °C and 1300 °C were obtained by Scherrer and they are shown in Table 4. Crystal size values of the sample followed the sequence YT < YTC < YTB. This result is in agreement with the ionic radii sizes of the Ca and Ba in each case. Values of crystal size increased from 1000 °C to 1300 °C.

Typical microstructures of the three samples fired at 1300 °C, obtained by SEM are shown in Fig. 4. There was no evidence of any secondary phase by EDX, and therefore, it was concluded that the three samples were single-phase solid solutions. Grain

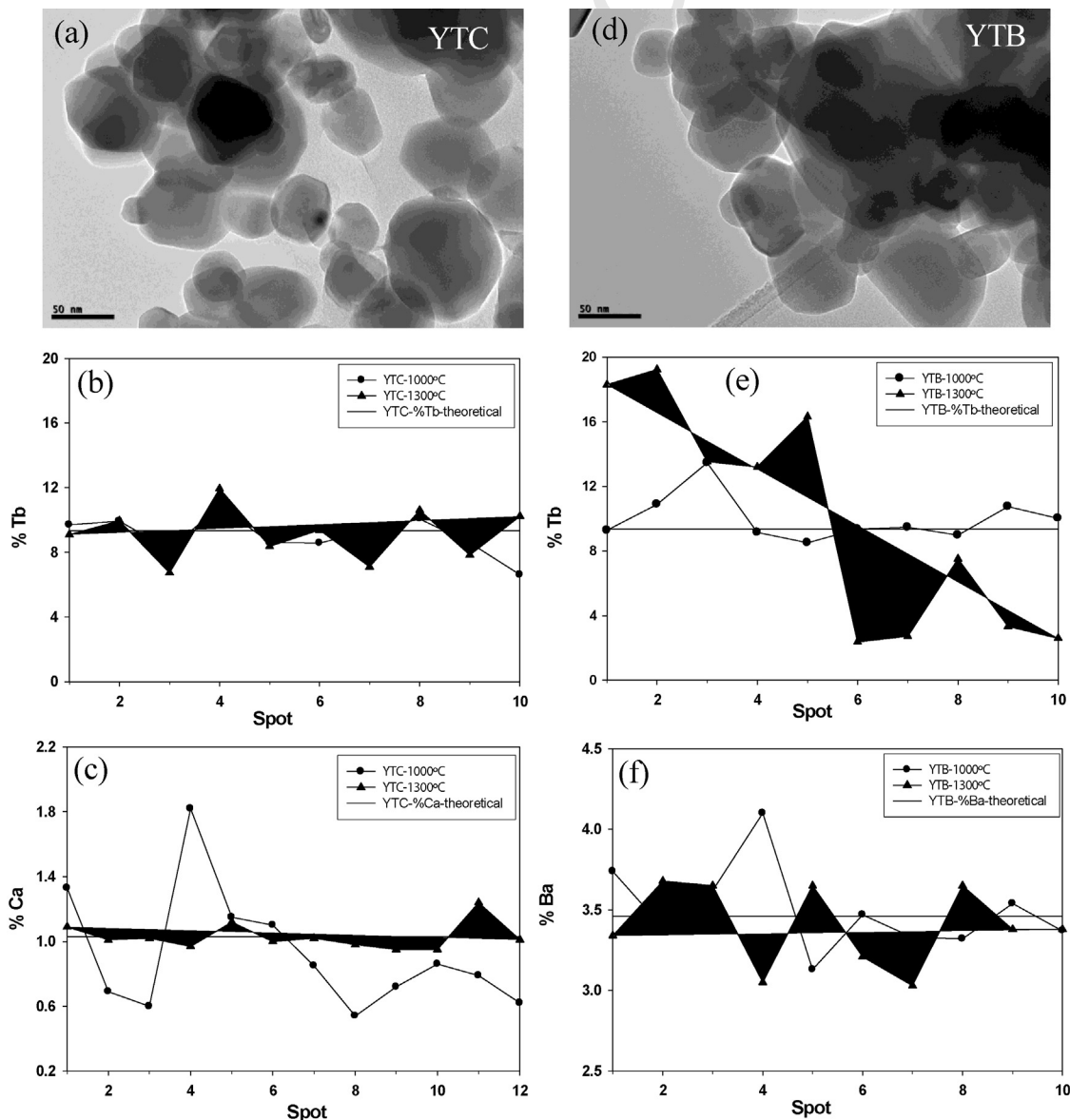


Fig. 5. Representative micrographs of HRTEM at 1300 °C and percentage (in % weight) of the experimental elements obtained by EDX elemental analysis, for YTC (a–c) and YTB (d–f) samples.

size was ~ 200 – 500 nm for all samples. These values of grain size are within the limit necessary for its possible application in inkjet printers (<1 μm , or 500 nm at the maximum of a Gaussian of size distribution).

HRTEM was conducted in order to analyse the homogeneity and distribution of the dopants through the sample, because the small amounts of Ca and Ba present were not easily detected by SEM. HRTEM micrographs and EDX analysis of different crystals (in weight percentage of each element) for YTC and YTB samples are shown in Fig. 5. Different results were observed depends on firing temperature and the sample. Two micrographs of YTC and YTB at 1300 °C are shown in Fig. 5a and d, respectively, as example of regions where the microanalysis was done.

For the YTC fired at 1000 °C and 1300 °C (Fig. 5a–c), the percentage of Tb was around 9.3% with a good distribution which is indicating that all the terbium was homogenous distributed through the solid solution at both temperatures, Fig. 5b. The Ca distribution was irregular in this sample and it depends of the temperature. Best distribution of the Ca in the crystal was observed at 1300 °C because all the spots analysed had a similar Ca percentage and close to the theoretical value, Fig. 5c.

For the YTB fired at 1000 °C and 1300 °C (Fig. 5d–f), non-homogeneous distribution of Tb and Ba was observed at 1000 °C and 1300 °C, which might be due to both elements agglomeration in some zones of this sample. Probably, the lattice structure of YTB have not been stabilised at both temperatures.

Once the structural evolution and homogeneity with temperature of the samples was established, the optical properties were investigated by UV/Vis absorption measurements. UV/Vis spectra of the terbium, calcium or barium doped Y_2O_3 samples, in the 300 – 700 nm wavelength range, are shown in Fig. 6a. All powders had yellow colouration after fired at 1000 and 1300 °C but the intensity of the colour was different. A broad absorption band in the blue region of the spectra, around 400 nm, was observed for all samples. This absorption band is the result of the presence of Tb^{4+} ions, since this band is ascribed to a $\text{Tb}^{4+}-\text{O}^{2-}$ charge-transfer band^{44–46} YTC samples showed the highest intensity between 350 and 480 nm in the blue region, and therefore, the most intense complementary yellow colour was observed for this sample at both 1000 and 1300 °C.

These results were consistent with the measurements of the chromatic coordinates of the compositions listed in Table 5. The b^* coordinate, which is the yellow component in the CIELab system, indicated that the highest values were obtained for the YTC samples where Ca was used as dopant. At the same time, the a^*

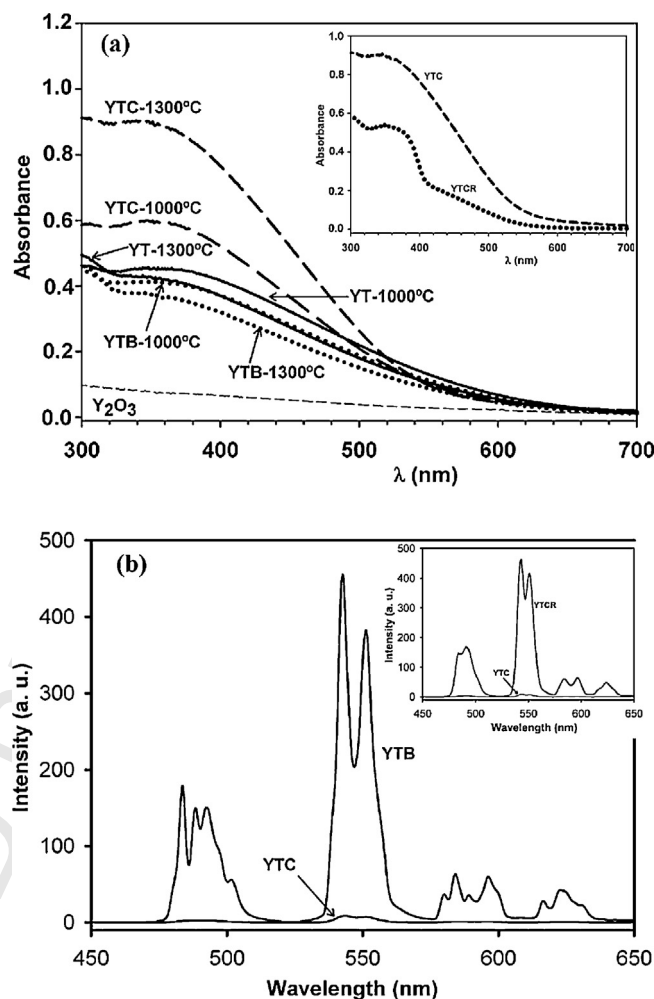


Fig. 6. (a) UV/Vis spectra of the YT, YTB and YTC samples, annealed at 1000 °C, and 1300 °C (Y_2O_3 is included for comparison); inset shows UV/Vis spectra of the YTC and YTCR samples annealed in air and in $5\% \text{H}_2/95\% \text{N}_2$, respectively; (b) photoluminescence spectra of YTB and YTC samples after annealed in air at 1300 °C; inset shows PL spectra of YTC and YTCR samples annealed at 1300 °C in air and in $5\% \text{H}_2/95\% \text{N}_2$, respectively.

parameter, which is the red component, showed the low value for this YTC sample. Regarding the L^* parameter, it remains almost constant for all samples. Moreover, the best yellow colouration that corresponds with the highest b^* value, was obtained at 1300 °C.

PL measurements and different thermal treatments (reducing conditions) were conducted in order to determine whether Tb^{4+}

Table 5

L^* , a^* and b^* coordinates of the YT, YTB and YTC samples after firing at 1000 °C for 2 h, 1300 °C for 6 h and after glazing. L^* , a^* and b^* coordinates of YTC after firing at 1300 °C in reducing atmosphere (YTCR) have been included.

Ref.	1000 °C Powder			1300 °C Powder/glaze		
	L^*	a^*	b^*	L^*	a^*	b^*
YT	88.72	5.18	23.40	90.70/95.75	3.63/−2.22	20.99/19.07
YTB	90.41	3.94	21.03	92.22/96.20	2.76/−1.70	18.40/15.33
YTC	90.36	2.66	30.62	89.71/90.42	2.20/0.01	44.79/55.28
YTCR	—	—	—	73.65/—	−0.71/—	10.65/—

ions were presented in the samples studied. The oxidation state of terbium ions, Tb^{3+} and Tb^{4+} , plays an important role for their fluorescence intensity. It is known that Tb^{4+} does not participate in the expected emission process and it acts as a fluorescence quenching center, reducing the fluorescence efficiency.^{47,48} This behaviour is also observed in Tb doped Y_2O_3 samples annealed under air, O_2 and/or H_2/Ar atmospheres.^{49,50}

The emission spectra at room temperature for YTC and YTB samples sintered in air at $1300^\circ C$ are shown in Fig. 6b. All these spectra were registered using the same wavelength excitation (290 nm) in the range 450–650 nm, where the characteristics $^5D_4 \rightarrow ^7F_J$ transitions of Tb^{3+} appear. The emission spectra for all samples, Fig. 6b, consists of four main lines at 488 nm ($^5D_4 \rightarrow ^7F_6$), 543 nm ($^5D_4 \rightarrow ^7F_5$), 586 nm ($^5D_4 \rightarrow ^7F_4$) and 622 nm ($^5D_4 \rightarrow ^7F_3$) which correspond to the emission bands of Tb^{3+} . However, the intensity of these bands was different depending of the sample composition. In particular, the intensity of the bands in YTC sample was lower than YTB.

In summary, the emission spectra together with UV-Vis analysis showed that the presence of Tb^{4+} was higher in the YTC sample.

In order to confirm these results, YTC sample was fired at $1300^\circ C$ in reducing atmosphere (5% H_2 /95% N_2), and the UV-Vis and emission spectra were obtained at room temperature in the same conditions than before. This sample was labelled as YTCR. Results obtained after this thermal treatment can be summarized as follow: first, the intensity of the yellow colour decreased after this process (see chromatic coordinates in Table 5); second, the intensity of the absorption band centered at ~ 400 nm in the UV-Vis spectra decreased after the reducing atmosphere (inset Fig. 6a); and third, the intensity of the Tb^{3+} transition bands increased when a reducing atmosphere was used (inset Fig. 6b). In conclusion, these results confirmed that the amount of Tb^{4+} in the YTC was higher than the YTB sample, and therefore, the intensity of the yellow colour was the best.

In order to determine the stability of the calcined powders (pigments) after glazing, a pigment/frit mixture was prepared and fired according to the cycle set out in the experimental part at the maximum temperature of $1080^\circ C$. The pieces with the glaze were also characterized by UV/Vis and values of the CIELab parameters are presented in Table 5. It can be observed that the yellow b^* coordinate for the sample YTC was improved and the L^* values were similar after glazing, and therefore, this composition was stable into the frit. These values were close to those for Pr doped $ZrSiO_4$.

In summary, after analysed all compositions prepared, it was concluded that Tb and Ca codoped Y_2O_3 samples sintered at $1300^\circ C$ was the best solid solution to obtain a good yellow colouration.

3.2. Compositional study

Regarding the results obtained after the preliminary study, different compositions based on $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ solid solution (M=Ca and/or Zn) with $x=0.06, 0.32$ and 0.64 were studied to accomplish the best composition of the yellow pigment (Table 3).

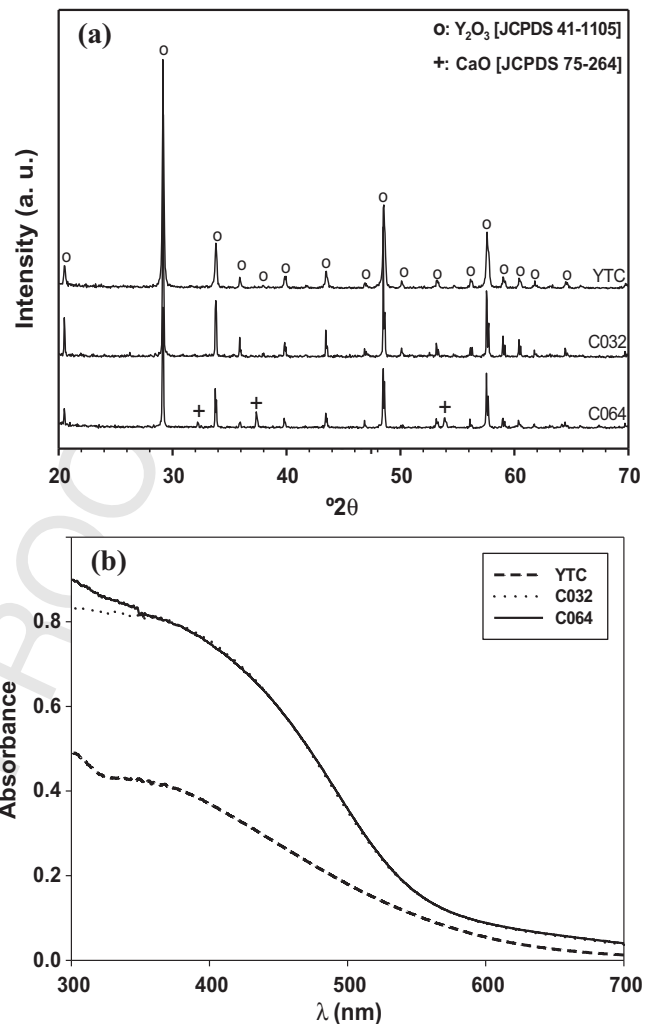
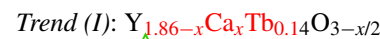


Fig. 7. (a) XRD and (b) UV-Vis spectra of YTC, C032, and C064 samples.



X-ray diffractograms of these compositions fired at $1300^\circ C$ are shown in Fig. 7a. All samples exhibit peaks that were assigned to yttrium (III) oxide (JCPDS File No. 41-1105). Small peaks of CaO were observed in the composition with high Ca concentration. Similar results were obtained at $1000^\circ C$ (not shown). Therefore, a solid solution was formed in the range $0 < x \leq 0.32$ for the Ca doped samples.

The evolution of the absorption spectra for the compositions fired at $1300^\circ C$, in the 380–780 nm wavelength range, is given in Fig. 7b. A band can be observed at $\lambda < 550$ nm attributed to the characteristic charge transfer process of the system. The position of the absorption edge depends on the terbium content. Therefore, this band did not move in these compositions because the terbium content was the same for all samples.

Measurements of the chromatic coordinates of these compositions after firing at $1300^\circ C$ (Table 6) indicate that sample C032 have the best yellow colour with the highest value of b^* . This result is consistent with the UV-Vis results where the most intensity absorption was observed for this sample.

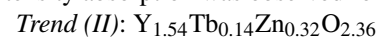


Table 6

 L^* , a^* and b^* coordinates of the samples after firing at 1300 °C for 6 h.

Ref.	L^*	a^*	b^*
YTC	89.71	2.20	44.79
C032	84.29	6.58	48.89
C064	84.87	6.58	45.05
Z032	82.71	8.24	37.15
CZ006	82.76	9.72	57.04
CZ032	82.11	8.77	55.41
CZ064	84.66	7.73	47.47
Pr-ZrSiO ₄	83.93	1.26	62.62

X-ray analysis of the composition Z032 where Zn substituted Y and fired at 1300 °C showed majority peaks that were assigned to yttrium (III) oxide and small peaks assigned to ZnO.

The absorption spectra of this sample (not shown) indicated the same absorption band at $\lambda < 550$ nm observed for the Ca doped samples (trend I), but the intensity of this one was the lowest. This result was confirmed with the chromatic coordinates because the yellow b^* coordinate was lower than the others (Table 6) and therefore, the yellow colouration was very weak. Since, the presence of Zn as the only alkaline dopant did not contributed to increase the intensity of the yellow colouration.

Trend (III): $Y_{1.86-x}Ca_{x/2}Zn_{x/2}Tb_{0.14}O_{3-x/2}$

X-ray diffractograms of these compositions fired at 1300 °C are shown in Fig. 8a. All samples were single phase and the diffraction peaks were assigned to yttrium (III) oxide (JCPDS File No. 41-1105). As the trend I, small peaks of CaO were observed in the composition with high Ca concentration. Similar results were obtained at 1000 °C (not shown). Therefore, a solid solution was formed in the range $0 < x \leq 0.32$ for the Ca and Zn doped samples.

The evolution of the absorption spectra for the compositions fired at 1300 °C, in the 380–780 nm wavelength range, is given in Fig. 8b. Similar absorption bands of charge transfer process were observed for all samples, and the intensity of these bands was the same for $x=0.06$ and 0.32 , and decreased for $x=0.64$.

Measurements of the chromatic coordinates of these compositions after firing at 1300 °C (Table 6) indicated that all samples showed the highest b^* values compared with those obtained for samples with only Ca or Zn as dopant. Good yellow colourations were obtained for CZ006 and CZ032 with chromatic b^* values close to those reported for Pr-ZrSiO₄ standard pigment. Therefore, there is an improved richness in the yellow colour with systematic replacement of Y³⁺ for Ca²⁺ and Zn²⁺ as can be observed from the increase in b^* values.

The low a^* value and high b^* value of the pigment with CZ032 make it a potential candidate for non-toxic yellow inorganic pigments. The chromatic properties, especially b^* of this pigment is comparable with the most used ceramic praseodymium yellow pigment ($b^* = 55$).

From these results and those obtained in the preliminary study, it could conclude that the sample of Y₂O₃ codoped with Tb, Ca and Zn (CZ032) was the best yellow pigment. Due to the colouration mechanism depends of the presence of Tb⁴⁺ ions, the different chemical characteristics of the codopant ions (ionic radii: Zn²⁺_(IC=6) = 88 pm, Ca²⁺_(IC=6) = 114 pm

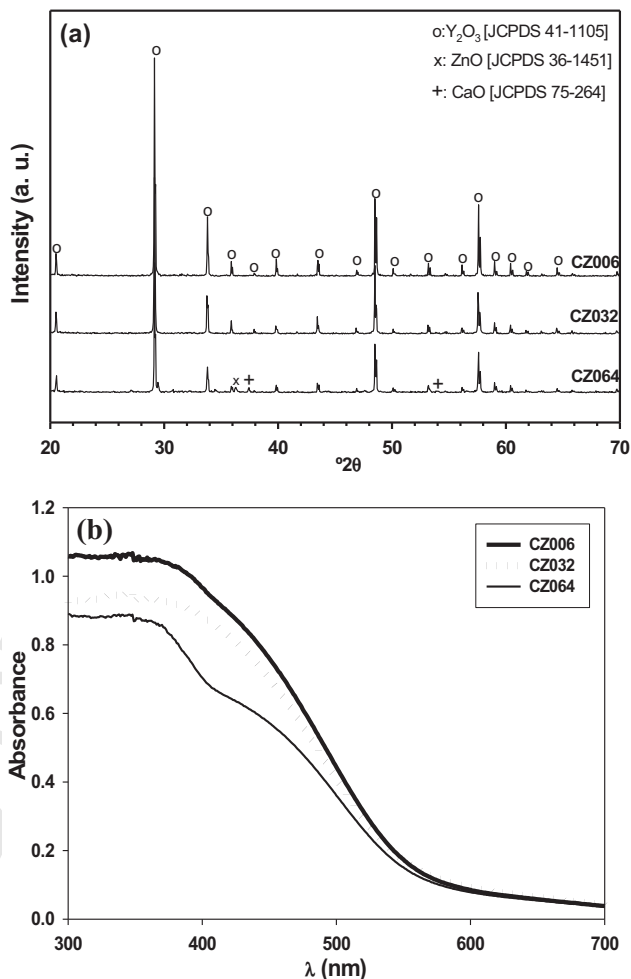


Fig. 8. (a) XRD and (b) UV-Vis spectra of CZ006, CZ032, and CZ064 samples.

and Ba²⁺_(IC=6) = 149 pm,⁴³ or electronegativity values in Pauling scale: Zn²⁺ 1.65, Ca²⁺ 1.0 or Ba²⁺ 0.85) leads to a higher Tb³⁺–Tb⁴⁺ conversion. In this work, sample doped with Ca and Zn allowed the formation of more Tb with the oxidation state +4, and consequently, obtaining of the best yellow colouration.

3.2.1. Evaluation of the colouring performance of the pigment

Fired compositions having the best chromatic properties were evaluated for its colouring performance by incorporating it into a transparent industrial frit and therefore, to verify composition stability as ceramic pigment. Typically 4 wt% of the pigment sample was used for the purpose (see Section 2). The colour coordinates of glazes are shown in Table 7.

Pigment colour was also yellow after glazing with the frit. Yellow b^* coordinates were comparable with the value obtained for the industrial Pr-ZrSiO₄ yellow pigment mixed with the same frit, and this value was higher for two compositions. These compositions are CZ006 and CZ032 where Ca and Zn doped Y_{1.86-x}Tb_{0.14}O_{3-x/2} solid solution was formed. Moreover, a^* values for these compositions are very close to that of praseodymium pigment. Good chemical and thermal stability into the frit was obtained and good yellow colouration was

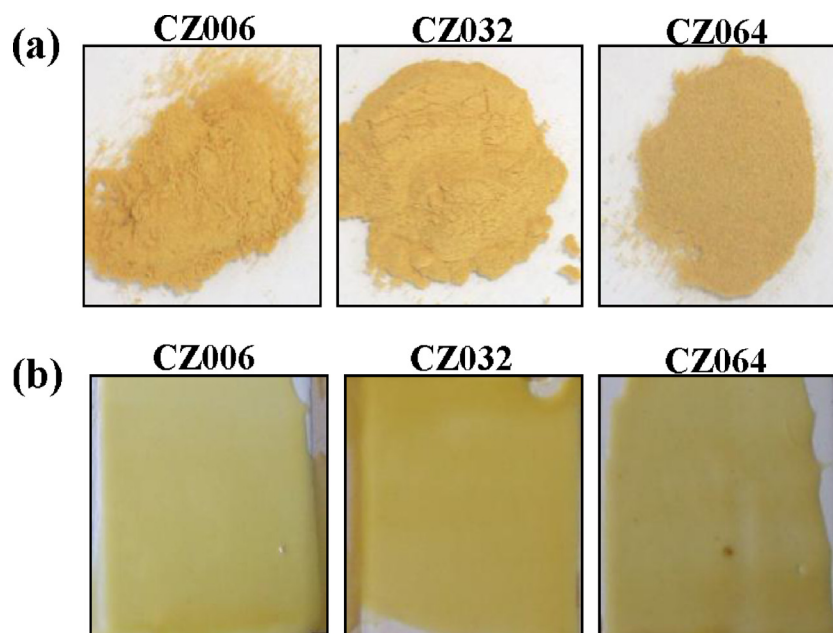


Fig. 9. Photographs of CZ006, CZ032 and CZ064 powders (a) fired at 1300 °C; and ceramic tiles (b) of the same samples after mixture with a frit.

observed for $Y_{1.54}Ca_{0.16}Zn_{0.16}Tb_{0.14}O_{2.84}$ composition, where the amount of Y^{3+} element was reduced using both Ca and Zn ions. Photographs of these compositions, before and after mixed with the frit, are shown in Fig. 9. Therefore, these results make it a potential candidate for environmental yellow ceramic pigment.

Further studies are in process to apply these pigments in inkjet printers, because small size particles and high quality yellow colour were obtained at high temperatures, without subsequent milling processes involving a decrease of its optical properties.

4. Conclusions

New environmentally inorganic yellow pigments having the general formula $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ ($M = Ca$ and/or Zn) with the composition range $0.06 < x < 0.64$ were prepared by a modification of Pechini method.

The limit of the $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ solid solution was found for the composition $x = 0.32$ when Ca, Zn or a mixture of them were used as a dopants. These samples, fired at 1000 and 1300 °C, were single phase by XRD, SEM and HRTEM/EDX analysis. Good yellow b^* coordinates were obtained with similar values of those observed for industrial yellow pigments. The intensity of the yellow colour in the samples was related to the presence of Tb^{4+} ions. Samples of Tb, Ca and Zn codoped Y_2O_3

leads to a better yellow colour. All these powders fired at 1300 °C were found to be stable in transparent frit, which is consistent with the formation of solid solution at these temperatures. Yellow colour was kept after the application on glazes. Therefore, these compositions could be good candidates to be applied in ceramic tiles or inkjet printers as yellow pigments.

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Table 7

CIE Lab parameters of the samples after glazing (frit).

Ref.	L^*	a^*	b^*
C032	83.39	-0.56	40.58
C064	84.14	-1.77	37.05
CZ006	82.33	0.69	47.86
CZ032	79.42	2.04	55.10
CZ064	80.35	1.17	44.55
Pr-ZrSiO ₄	81.50	-1.60	45.30

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