Synthesis, through pyrolysis of aerosols, of $YIn_{1-x}Mn_xO_3$ blue pigments and their efficiency for colouring glazes

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ABSTRACT

Mn-doped $YInO_3$ blue pigments have been synthesised at a much lower temperature (1100 °C) than that required by the traditional solid state method (1400 °C). The developed procedure, which is based on the pyrolysis at 600 °C of aerosols generated from aqueous solutions of Y, In and Mn nitrates followed by an annealing treatment at 1100 °C, yields spherical pigments particles with heterogeneous size in the optimum range required for ceramic applications (<10 μm). The amount of Mn introduced in the $YInO_3$ matrix has been systematically varied in order to evaluate the effects of the Mn content on the colour properties of the pigments. It has been found that the optimum pigment composition (bluer colour with the lowest Mn content) is given by the formula $YIn_{0.90}Mn_{0.10}O_3$. The technological performance of these $YIn_{1-x}Mn_xO_3$ blue pigments has also been evaluated by testing their efficiency for colouring ceramic glazes of different composition (boracic and plumbic) and properties, aiming to find a less toxic alternative for the Co-based pigments commonly used by the ceramic industry.

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1. Introduction

With the exception of the turquoise blue pigment of vanadium zircon, $(Zr,V)SiO_4$, the traditional chromophore used for ceramic pigments with blue tint is the cobalt ion incorporated into different crystalline structures: cobalt orthosilicate (Co_2SiO_4), cobalt aluminate $(CoAl_2O_4)$, cobalt stannate (Co_2SnO_4), cobalt zinc aluminate $[(Co,Zn)Al_2O_4]$, cobalt chromite $(CoCr_2O_4)$, and zinc silicate doped with Co(II) cations, $[(Co,Zn)_2SiO_4]$ [1]. Among them, cobalt aluminates are preferred, since an intense navy blue hue can be obtained with the lowest cobalt content and therefore, a lower cost. Nevertheless, cobalt and its related salts are considered to be toxic and/or hazardous substances under current legislation. In fact, excessive exposure to cobalt-containing dusts in the workplace, or to excessive concentration in drinking waters, can cause damage to lungs, heart and skin. In addition, cobalt is considered an occupational carcinogen.

During the last few years, several attempts have been carried out to minimise the negative environmental effects of Co and/or to reduce cost in the blue ceramic pigments manufacture. These research efforts involve either optimizing the Co content in some of the above mentioned structures (willemite) [2] or searching for new formulations [3–7]. In particular, corundum $(\alpha\text{-}Al_2O_3)$ has been codoped with Fe and Ti [3] resulting in a blue colour probably due to the formation of a $Fe_{1-x}Ti_xAl_2O_3$ spinel [4]. Hibonite $(CaAl_{12}O_{19})$ based compounds codoped with Co and Ti (bluish hue) [5] or with Ni and Sn (turquoise shade) [6] have been also proposed. Finally, it has been shown that the addition of molybdenum oxide to corundum results in a greyish-blue mordant pigment [7].

Therefore, the search for intense blue inorganic pigments that are environmentally benign, earth-abundant and durable is an important issue that still remains as a challenge today [8]. Very recently, Smith et al. have discovered that when calcining at 1300 °C a mixture of Y_2O_3, In_2O_3 and Mn_2O_3 with appropriate stoichiometry and annealing protocol, a surprisingly intense bright-blue colour is obtained, which has been attributed to the introduction of Mn^{3+} into the trigonal bipyramidal sites of In^{3+} of the hexagonal $YInO_3$ structure [8]. They also demonstrated that this blue colour appeared over much of the $YIn_{1-x}Mn_xO_3$ solid-solution range, although $YInO_3$ and $YMnO_3$ are white and black, respectively. Therefore, these pigments might be an interesting alternative to the Co containing ceramic pigments, providing that they are thermally and chemically stable under the drastic conditions (high temperature, attack by the glaze components, etc.) involved in processing [9], which up to our knowledge, has not been yet proved.

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A first aim of this paper is to evaluate, for the first time, the technological performance of these recently discovered Co-free $YIn_{1-x}Mn_xO_3$ blue pigments for the ceramic industry. For this purpose, we test here their efficiency for colouring ceramic glazes of different composition (boracic and plumbic) and properties. It should be also mentioned that Smith et al. [8], have prepared these pigments by the traditional ceramic procedure from oxide precursors, which involves several calcination cycles at high temperatures ($\geq$1300 °C) accompanied by intermediate grinding process to help the diffusion of the metal cations required for the $YInO_3$ formation and to control particle size. In this paper, we also report a new procedure for the synthesis of these pigments based on the pyrolysis of liquid aerosols generated from aqueous solutions of common cations salts, which results in several important advantages from the economic point of view, when compared with traditional ceramic procedure [10–13]. In particular, the pyrolysis method usually involves a significant decrease of the temperature of pigment formation and a certain control of particle size distribution within the optimum range established for ceramic applications ($<$10 μm) [9], without requiring grinding processes. Moreover, the method reported herein yields spherical particles, which along with its continuous character, might make it very interesting for novel ink-jet technologies recently developed for ceramic tile decoration, which demand the availability of pigment particles with a spherical shape [14].

2. Experimental

2.1. Synthesis of pigments and glazes preparation

Four compositions were prepared by pyrolysis of aerosols (Table 1) having a different manganese content (Mn/Y mole ratio = 0, 5, 10 and 20%), in order to evaluate the effect of this parameter on the optical properties of the final pigments. The liquid aerosols were generated from aqueous solutions of appropriate metal salts (yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$, Aldrich, 99.9%; indium nitrate, $In(NO_3)_3 \cdot 3H_2O$, Aldrich, 99.9%; manganese nitrate, $Mn(NO_3)_2 \cdot 4H_2O$, Fluka, 97%)) following a procedure previously reported [10], which can be summarised as follows. The starting solutions having a fixed $Y(NO_3)_3$ concentration (0.05 mol dm^{-3}) and variable amounts of $In(NO_3)_3$ and $Mn(NO_3)_2$ as stated in Table 1, were sprayed into an expansion chamber using a glass nozzle and air at constant pressure (0.5 kg cm^{-2}) as a carrier gas. The aerosols so generated were introduced into two consecutive furnaces kept at 250 and 600 °C, respectively, in which the liquid droplets were first dried and then, thermally decomposed. The resulting solid particles were finally collected on a glass filter with a very high efficiency.

The obtained powdered samples were placed in platinum crucibles and calcined at different temperatures (up to 1100 °C) for 3 h, using a heating rate of 10 °C min^{-1}.

A commercial Co-based ($CoAl_2O_4$) pigment, supplied by Colores Cerámicos S. A. (5003-L), was also used for comparison.

In order to explore the applicability of the Mn-doped $YInO_3$ pigments for colouring glazes, two transparent industrial frits (supplied by Colores Cerámicos S.A.) with different processing temperatures were assayed; a plumbic one (quantitative composition (wt. %): Al_2O_3 = 5%; B_2O_3 = 5%; CaO = 5%; K_2O = 5%; Na_2O = 5%; PbO = 25%; SiO_2 = 50%) suitable for processing temperatures $\geq$780 °C, and a boracic one (qualitative composition: $K_2O < 10\%$; $MgO < 10\%$; $CaO < 20\%$; $ZnO < 20\%$; $B_2O_3 < 10\%$; $Al_2O_3 < 10\%$; $SiO_2 < 50\%$; $TiO_2 < 10\%$) with higher processing temperatures ($\geq$1000 °C). For the preparation of glazes, aqueous suspensions containing a 0.75 wt. % of pigment and a 99.25 wt. % of the frit were prepared by ball milling. These slurries were deposited on double-firing wall tile bodies and further fired for 6 h at different temperatures in a gradient furnace (Pirometrol S.L.) using a heating rate of 200 °C/h. After this treatment, the furnace was switched off and the glazed tiles were left to cool down inside the furnace.

2.2. Characterization techniques

The morphology of the particles, as prepared and after calcination at 1100 °C, was examined for all samples by scanning electron microscopy (SEM-FEG) (Model S4800, Hitachi) and their volumetric particle size distribution was obtained from laser diffraction measurements (Malvern Mastersizer S).

The quantitative composition of the as prepared samples (In/Y and Mn/Y mol ratio) was determined by the ICP technique (Model
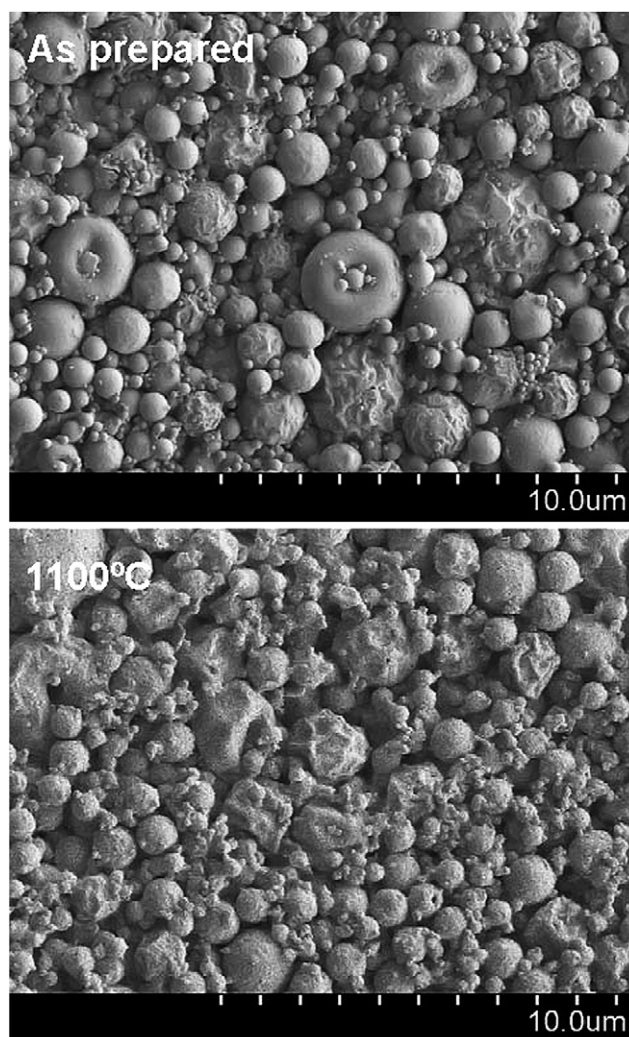
Table 1
Nominal and experimental composition of the Mn-doped $YInO_3$ pigments.

	In/Y nominal	Mn/Y nominal	In/Y ICP	Mn/Y ICP
$YInMnO_3$	1.00	–	0.98	–
$YIn_{0.95}Mn_{0.05}O_3$	0.95	0.05	0.94	0.048
$YIn_{0.90}Mn_{0.10}O_3$	0.90	0.10	0.89	0.087
$YIn_{0.80}Mn_{0.20}O_3$	0.80	0.20	0.84	0.184

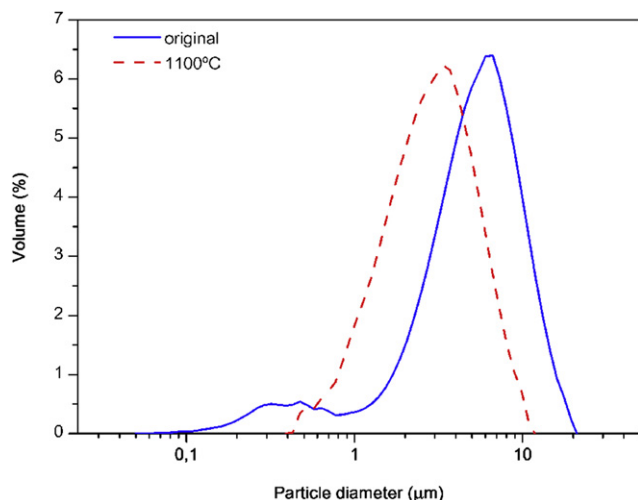**Fig. 1.** FEG-SEM micrographs of sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared and after heating at 1100 °C.

Fig. 2. Volumetric particle size distribution obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared and after heating at 1100 °C.

Ultima 2, Horiba Jobin Yvon). Energy dispersive X-ray analysis (EDX) (Bruker X Flash Detector 4010) installed in the scanning electron microscope was also used to gain information on the composition of single particles.

The Fourier transformed infrared spectra (FTIR) were recorded in a Nicolet 510 Fourier transform spectrometer. For this purpose, the samples, as prepared and after heating at 400 and 1100 °C, were diluted in KBr pellets. The X-ray photoelectron spectra (XPS) were measured with a VG Escalab apparatus (Model 220) using the MgKα excitation source. Calibration of the spectra was done at the $In3d_{5/2}$ peak taken at 446.6 eV [15].

Thermogravimetric analyses (TGA) were performed (Q600 TA Instrument) for all compositions in the range 25−1100 °C, under an air atmosphere and using a heating rate of 10 °C min^{-1}.

The crystalline phases present in the as prepared and calcined samples were identified by X-ray diffraction (XRD) (Model X'Pert Pro, Panalytical). Unit cell parameters of the pigments calcined at 1100 °C were determined by Rietveld refinement, using the X'Pert HighScore Plus software, from the XRD data collected at intervals of 0.02° (2θ) for an accumulation time for interval of 10 s. Silicon (20%
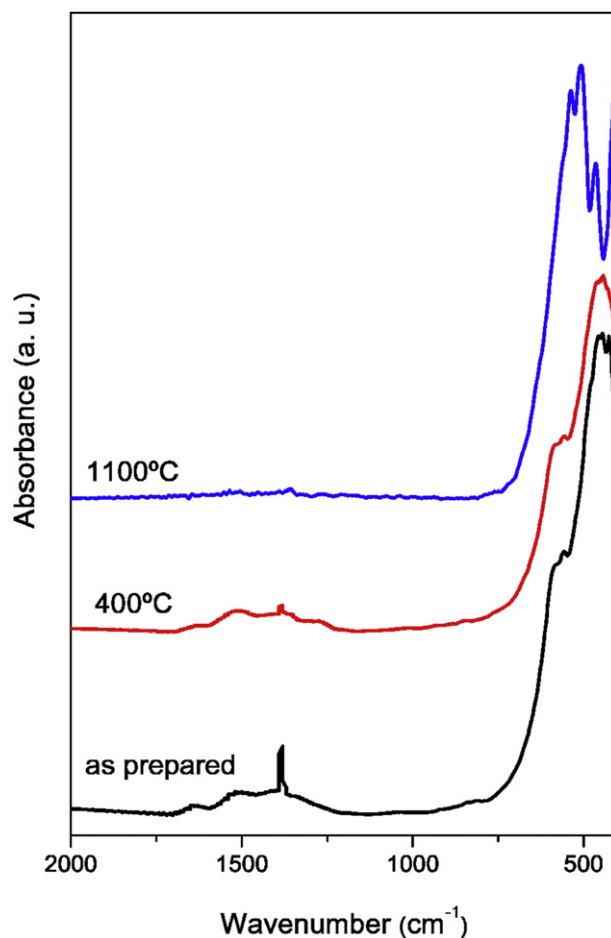

Fig. 4. FTIR spectra obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared and after heating at 400 and 1100 °C.

by weight) was used as internal standard. The crystallographic data for the $YInO_3$ structure were taken from reference [16].

The colour of the pigments in powdered form and of the glazes was evaluated according to the Commission Internationale de l'Eclairage (CIE) through L*a*b* coordinates [17]. In this system, L*
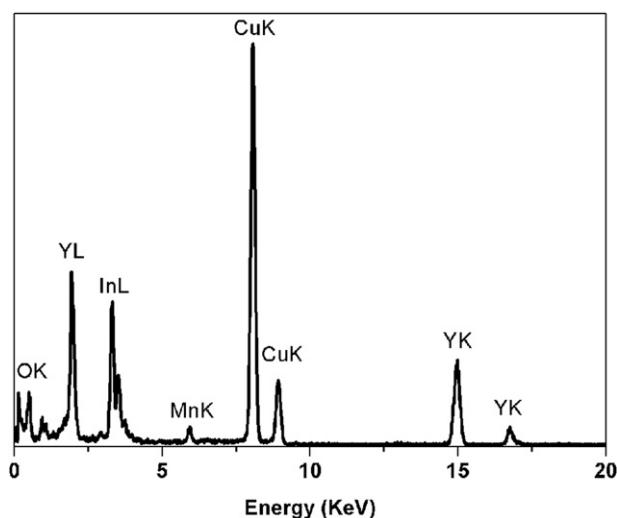

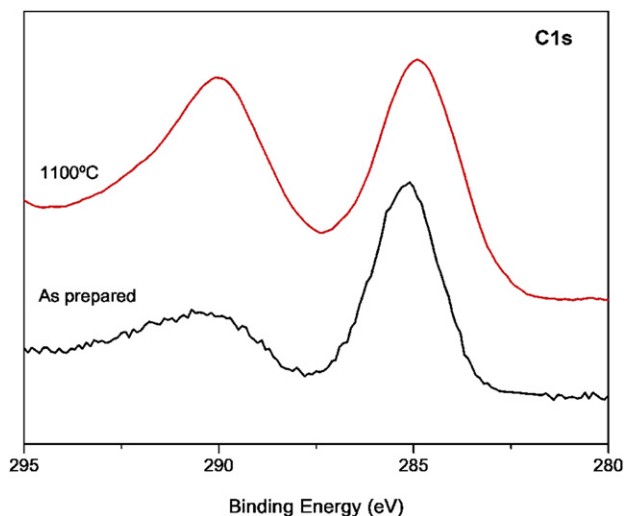**Fig. 3.** EDX spectrum obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared.

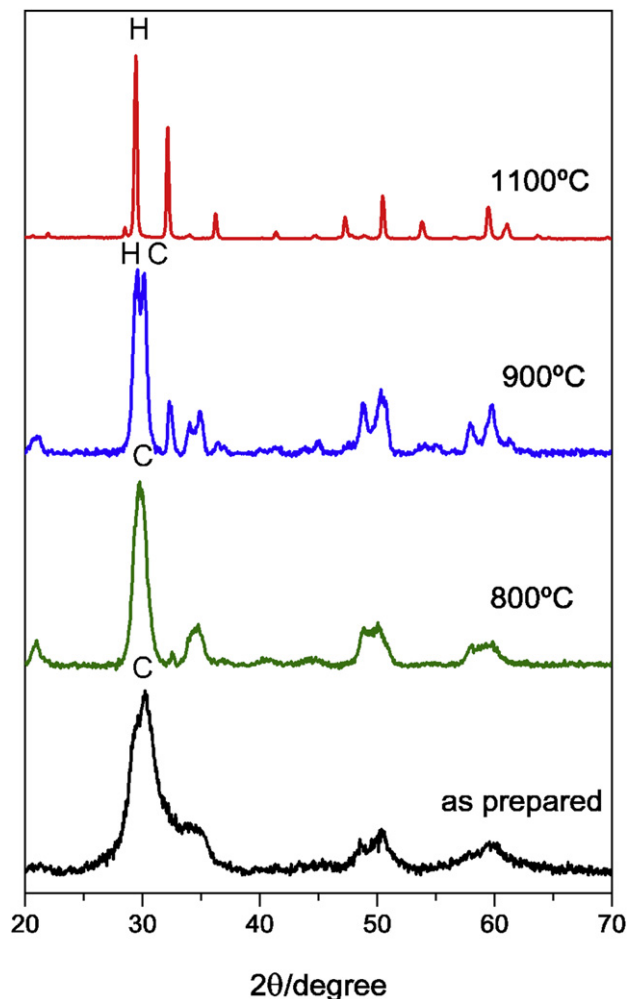**Fig. 5.** C1s XPS spectrum obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared and after heating at 1100 °C.

Fig. 6. XRD patterns obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared and after heating at 800, 900 and 1100 °C. Symbols used to designate the most intense reflections of crystalline phases: C = cubic, H = hexagonal.

Table 2
L*a*b* coordinates of the Mn-doped $YInO_3$ pigments as prepared an after heating at 1100 °C and of a commercial $CoAl_2O_4$ pigment.

	Treatment	L*	a*	b*	Colour
$YIn_{0.95}Mn_{0.05}O_3$	As prepared	63.0	5.5	11.4	Brown
$YIn_{0.90}Mn_{0.10}O_3$	As prepared	53.6	5.7	10.4	Brown
$YIn_{0.80}Mn_{0.20}O_3$	As prepared	48.0	7.4	8.1	Brown
$YIn_{0.95}Mn_{0.05}O_3$	1100 °C	54.8	1.1	−31.2	Blue
$YIn_{0.90}Mn_{0.10}O_3$	1100 °C	49.5	0.5	−29.2	Blue
$YIn_{0.80}Mn_{0.20}O_3$	1100 °C	45.0	−0.6	−23.0	Blue
$CoAl_2O_4$	Commercial	44.8	2.1	−32.7	Blue

a white tile ceramic (chromaticity coordinates: $x = 0.315, y = 0.335$) as standard reference.

3. Results and discussion

3.1. Synthesis and characterisation of the samples

In all cases, the composition of the as prepared samples measured by ICP was in good agreement with the nominal values (Table 1), indicating the suitability of the pyrolysis of aerosols technique to control sample stoichiometry in multicomponent systems [18].

Most characterisation data hereafter presented correspond to sample $YIn_{0.95}Mn_{0.05}O_3$. All other studied compositions presented a similar behaviour, except when indicated. The as synthesized sample mostly consisted of spherical particles (Fig. 1, top), which is as expected, since the solution droplets behave as independent reactors [18]. However, some particles of rather irregular shape and a very rough surface were also detected, which can be due to a partial melting of the precursor salts particles formed on aerosol drying, before the final decomposition step [18]. It was also observed that the spheres presented a broad size distribution (typical for aerosols generated by using pneumatic methods [10–13]), with a maximum in their volumetric curve centred at 6.5 μm (Fig. 2).

EDX spectra obtained for several single particles of this sample were very similar, displaying the peaks corresponding to Y, In and Mn (Fig. 3), which manifested a high degree of chemical homogeneity, at least, at the particle level. Additional information on the composition of these particles was obtained by FTIR spectroscopy. Thus, their FTIR spectrum (Fig. 4) displayed the bands characteristics of the lattice vibration modes (<1000 cm^{-1}) along with some much less intense absorptions at 1640 cm^{-1}, due to adsorbed water [19], and at 1375 cm^{-1}, attributed to a small amount of residual nitrate anions [19]. The latter appeared overlapped with other much broader and weak feature in the 1580–1200 cm^{-1} region, which could be ascribed to the presence of carbonate anions [18]. This assignment was confirmed by the XPS spectrum of the sample, which showed, two peaks corresponding to the C1s level at 285 and 290 eV (Fig. 5). The first one is due to the adventitious C [15,20], whereas the latter is

is the colour lightness (L* = 0 for black and L* = 100 for white), a* is the green (−)/red (+) axis, and b* is the blue (−)/yellow (+) axis. These parameters were measured in a Dr. Lange colorimeter (Model LUCI 100) using an illuminant D65, a standard observer at 10° and
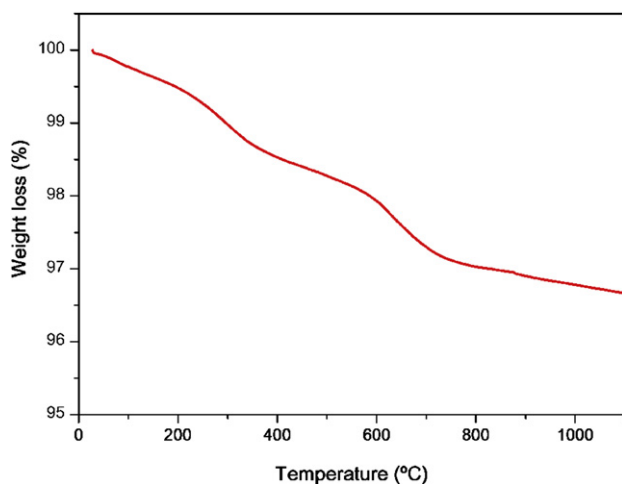

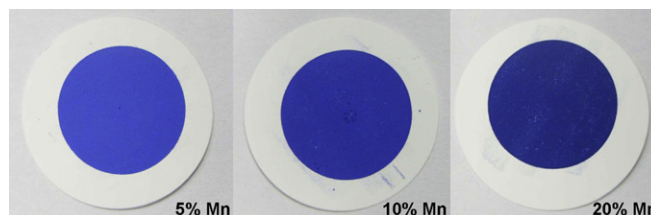**Fig. 7.** TGA curve obtained for sample $YIn_{0.95}Mn_{0.05}O_3$ as prepared.

Fig. 8. Photo of the Mn-doped $YInO_3$ pigments prepared by heating at 1100 °C with different Mn content, deposited on Millipore filters.

Fig. 11. L*a*b* coordinates of the glaze prepared with sample $YIn_{0.9}Mn_{0.1}O_3$ and the low temperature (plumbic) frit as a function of the processing temperature.
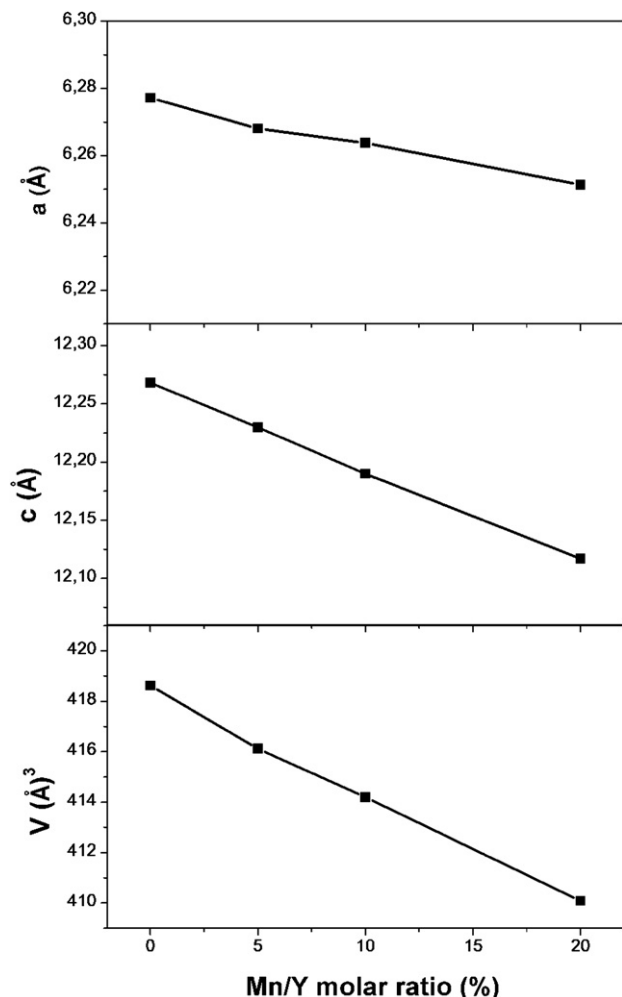
Fig. 9. Unit cell parameters and unit cell volume obtained for the Mn-doped $YInO_3$ pigments heated at 1100 °C as a function of the Mn content.

consistent with the presence of carbonate anions [20], which have been shown to be usually present on the particle surfaces of yttrium oxides under atmospheric conditions [20].

XRD (Fig. 6) revealed that in all cases, the prepared particles consisted of the cubic $YInO_3$ phase (JCPDS 25-1172) with low crystallite size, as suggested by the high reflection broadening. Therefore, they were annealed at increasing temperatures in order to
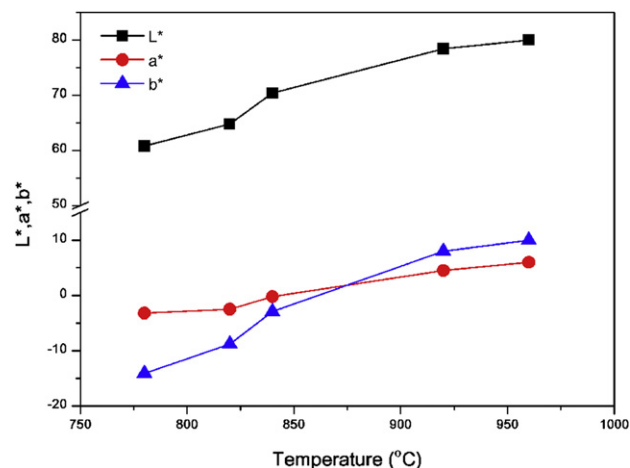
obtain the desired hexagonal phase (JCPDS 1-70-133), finding that the cubic-hexagonal transformation began at 900 °C and finished at 1100 °C (Fig. 6). It is important to note that this temperature is noticeably lower than that involved in the traditional ceramic procedure using oxide precursors ($\geq$1300 °C), which also requires several calcination cycles accompanied by intermediate grinding process to increase reactivity [8]. The milder conditions involved in our synthesis procedure can be attributed to the high degree of mixing of the component cations attained at the particle level, detected by the EDX analyses, which would favour the diffusion process required for phase transformation, as it has been previously observed for other pigment systems [10–12].

The thermal evolution of this sample was also followed by TGA, which indicated that the amount of the above mentioned (water, nitrates and carbonates) contaminants was rather low. Thus, a weight loss of $\sim$1.5% was detected in the 25–400 °C range (Fig. 7), caused by the release of water and the decomposition of the nitrate anions, as indicated by the almost disappearance of the 1375 cm^{-1} band in the FTIR spectrum registered after calcination at 400 °C (Fig. 4). The additional weight loss ($\sim$1.5%) observed in the 400–1100 °C range, was due to carbonate decomposition, as confirmed by the FTIR (Fig. 4) and XPS (Fig. 5) spectra obtained after annealing at 1100 °C, in which the signals corresponding to such anions were absent (Fig. 4) or minimised (Fig. 5).

It should be also noted that after the heat treatment, the particles roughly retained their original shape (Fig. 1, bottom),
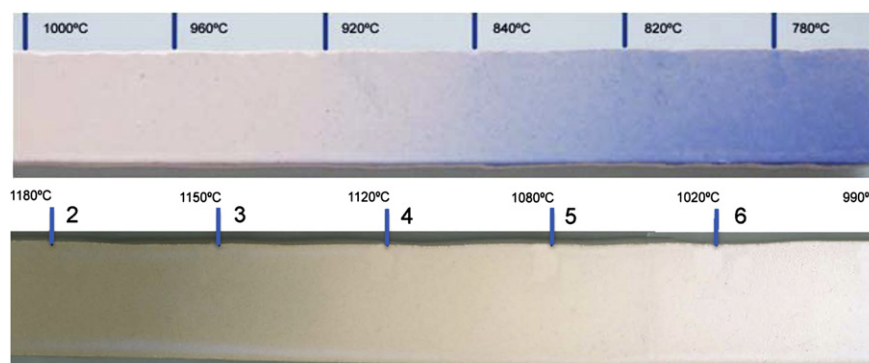

Fig. 10. Photo showing the colour development with temperature for the glazes prepared with sample $YIn_{0.9}Mn_{0.1}O_3$ and two different frits: plumbic (top) and boracic (bottom).
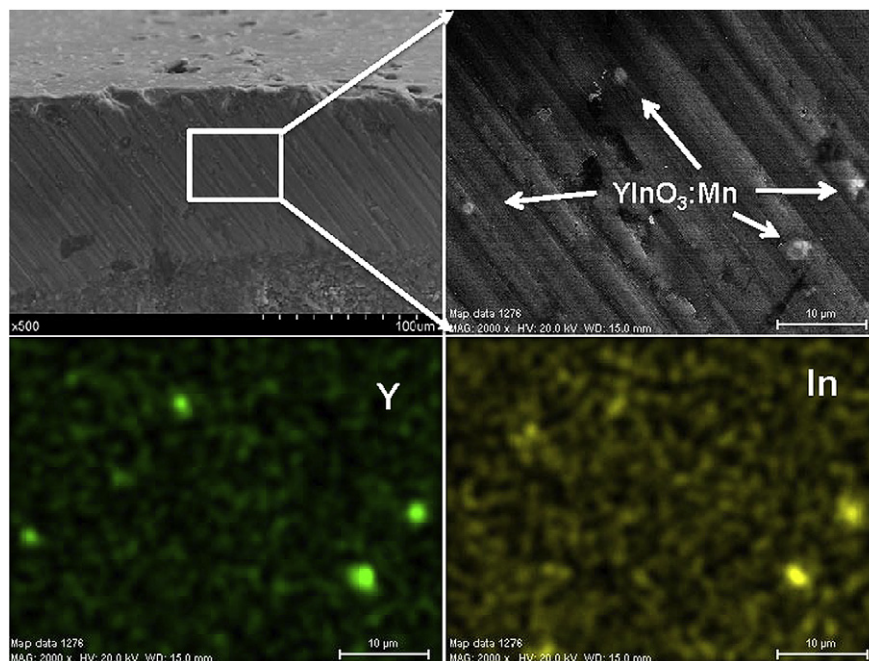
Fig. 12. FEG-SEM micrographs (a and b) and Y (c) and In (d) EDX mapping obtained for the glaze prepared at 780 °C with the plumbic frit and sample $YIn_{0.9}Mn_{0.1}O_3$.

although a slight reduction of the mean particle size was detected (Fig. 2) probably due to the release of contaminants on calcination. Nevertheless, the resulting particle size was kept within the range at which ceramic pigments develop their optimum colorimetric properties (1–10 μm) [9].

The colour of the samples, characterised by $L^*a^*b^*$ coordinates, is shown in Table 2. As observed, a change from brown (values of a^* and b^* close to the achromatic point) for the as prepared samples, to blue (Fig. 8) took place simultaneously to the cubic-hexagonal phase transformation, which in agreement with Smith et al. [8], was associated to the formation of a solid solution between Mn(III) cations and the hexagonal $YInO_3$ lattice. Such a process was confirmed by the measurement of the unit cell parameters of the prepared samples, which are shown in Fig. 9, along with those of an undoped sample for comparison. As observed, a progressive unit cell contraction was detected as increasing the doping level, due to the substitution of In(III) by Mn(III) cations whose ionic radius is lower (0.66 Å) than that of In(III) (0.81 Å) [21].

The effects of the amount of chromophore on the colour properties of the Mn-doped $YInO_3$ blue pigments are evidenced in Table 2. As observed, as the Mn content increased from 5 to 10% (nominal Mn/Y ratio), the lightness (L^*) decreased (from 54.8 to 49.5) and the blue coordinate (b^*) increased slightly (from −31.2 to −29.2), whereas the value of a^* remained almost unaltered (from 1.1 to 0.5). i.e., the colour became more intense, with a very small change in hue. A further increase of the Mn/Y ratio to 20%, also gave rise to a decrease of luminosity (from 49.5 to 45), but in this case, it was accompanied by a significant increase of the b^* component (from −29.2 to −23), which indicates a darkening of the blue hue. Consequently, we estimated that the sample with a Mn/Y mole ratio of 10% is the optimum pigment (bluer colour with the lowest Mn content), which was then selected for testing the technological performance of this system. The comparison of the colour properties of this optimum pigment with those of a commercial Co-based ($CoAl_2O_4$) sample revealed that the blue component (b^*) and luminosity (L^*) of the latter were lower ($b^* = −32.7$, $L^* = 44.8$) than

those of our pigment ($b^* = −29.2$, $L^* = 49.5$) (Table 2). This finding indicated that the Co-based pigment was slightly bluer and more intense than that based in Mn-doped $YInO_3$.

3.2. Technological behaviour

Although the glazes prepared with the $YIn_{0.90}Mn_{0.10}O_3$ pigment were free of defects, their colour was strongly influenced by the characteristics of the enamelling process, i.e. the composition of the frit and mainly, the processing temperature. Thus, as observed in Fig. 10, the glaze prepared with the boracic frit (firing temperature ≥ 1000 °C) did not show the blue colour characteristic of the studied pigment but a beige tint which turned to grey at the higher temperatures (>1120 °C). However, in the glaze prepared with the plumbic frit (firing temperature ≥ 780 °C), the blue colour was retained in the 780–820 °C range, although it progressively disappeared (the blue component, b^*, and luminosity, L^*, increased) at increasing temperature up to 1000 °C (Fig. 11). This behaviour suggests that Mn-doped $YInO_3$ reacts with the frits components above ∼800 °C. The analysis of a cross-sectional view of this glaze under the FEG-SEM microscope confirmed this interpretation. Thus, as observed in Fig. 12, the pigments grains could be clearly identified in the blue zone of the glaze (∼780 °C) by an EDX mapping registered for the majority elements of the pigment (Y and In). However, after a careful analysis of the beige zone (∼1000 °C), no pigment grains could be found indicating that they were dissolved by the frits during enamelling at >820 °C. Therefore, it can be concluded that the Mn-doped blue pigments are suitable for their use for colouring glazes only in low-temperature processes (third-fire).

4. Conclusions

Mn-doped $YInO_3$ blue pigments consisting of spherical particles of broad size distribution (<10 μm) have been synthesised by pyrolysis at 600 °C of aerosols generated from aqueous solutions of Y, In and Mn nitrates, followed by an annealing treatment at

1100 °C. This temperature of pigment formation is much lower than that required by the solid state traditional procedure (1400 °C) due to the high degree of mixing of the component cations attained at the particle level, which would favour the diffusion process required for crystallization. The optimum pigment composition (bluer colour with the lowest Mn content) is given by the formula $YIn_{0.90}Mn_{0.10}O_3$. This system can be considered as a less toxic alternative for the blue Co-based pigments and can be used for colouring glazes in low-temperature processes (third-fire). In addition, the developed Mn-doped $YInO_3$ pigments might have potential applications in ceramic decoration through ink-jet systems, due to its spherical morphology.

Acknowledgements

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