

Comparison of blue pigments prepared by two different methods

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Abstract

The color efficiency of ceramic glaze blue pigments obtained by synthesis methods was compared. The fired pigments and enameled samples were characterized by XRD, UV-vis-NIR spectroscopy, CIE- $L^*a^*b^*$ color-measurements, and SEM. The pigments obtained by the Pechini method presented a better solubility in the molten glazes than the pigments obtained by the mechanical mixture of the oxide precursors. The pigments obtained by the Pechini method also developed a bluer color hue than the pigments obtained by the mechanical mixture of the oxide method. © 2002 Published by Elsevier Science Ltd.

Keywords: Colour; Glazes; Mixing; Pechini method; Pigments; SnO₂

1. Introduction

Blue pigments have been widely used from early antiquity for surface decoration of stylistically different classes of pottery,¹ and also in the bulk coloration of polished, unglazed² ceramics. The traditional source of blue in currently known ceramic pigments contains Co, but this work deals with an exception and it will present an alternative to this system, the incorporation of antimony in to the host lattice of SnO₂. The aim of this work is the decrease of the environmental impact in the manufacturing process (Co is widely considered as toxic or hazardous), while also maintaining an optical coloring performance in the desired glaze. The coloring performance of pigments depends very much on their thermal stability, their chemical reactivity towards the glaze components, the coordination of host ions, and it also depends on the preparation methodology.

The coloring efficiency of different glaze blue pigments was compared, with the intention to reduce costs and to minimize the environmental impact, in the expectation of substituting cobalt for another less toxic element.

2. Experimental procedure

The polymeric precursor solution was prepared by the Pechini method, which has been used to synthesize polycationic powders.^{3,4} The process is based on the metallic citrate polymerization using ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used to chelate cations in an aqueous solution. The addition of a glycol such as ethylene glycol leads to the formation of an organic ester. Polymerization, promoted by heating the mixture, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix.

Fig. 1a schematically presents the preparation of the SnO₂ starting from a polymeric precursor solution. The tin citrate was separately prepared from SnCl₂·2H₂O and the dopant source used was Sb₂O₃. Nitric acid was used to improve solubility.

The powders were also prepared by the traditional ceramic procedure (mechanical mixture of the oxide precursors—OM). Fig. 1b schematically presents the preparation of this method. The [Sb]/[Sn] molar ratio used was 7%, in both methods.

The heat treatment range used was between 800 and 1200 °C, consisting in heating the powders up to the appropriate temperature in order to obtain a mono-phase structure for the pigments.

A mixture of glaze (commercial glaze—GERBI, Brazil) and the sieved pigments (weight volume ratio of

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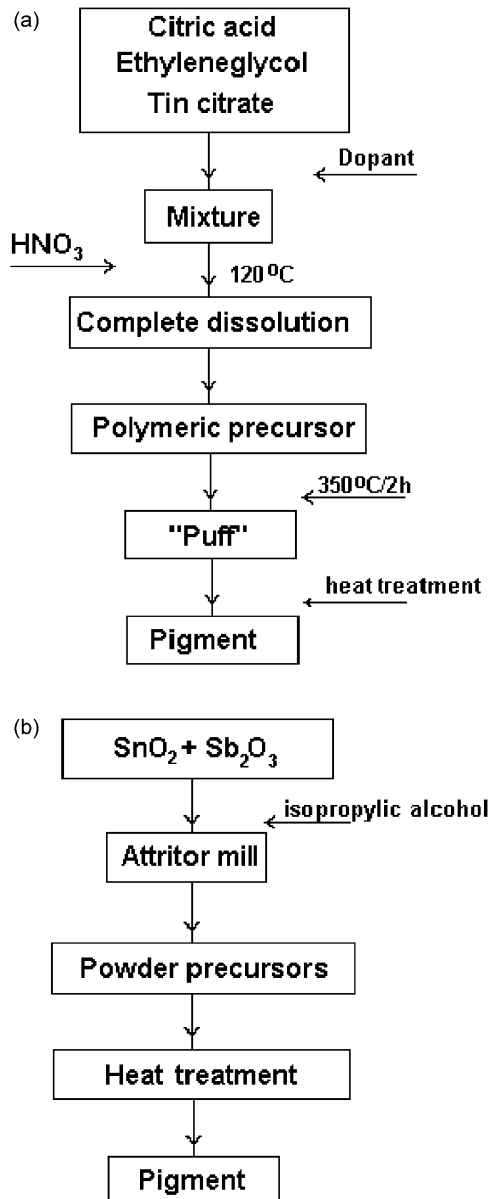


Fig. 1. Synthesis routes for the powders obtained by the: (a) Pechini method and (b) oxide mixture method.

the pigment: glaze equals to 12 g of pigments: 100 ml of liquid glaze) was homogenized in a ball mill during 10 min. The slip was poured on the ceramic biscuits obtaining an uniform glaze layer, which was then fired following a fast heat treatment (up to 500 °C with heating ratio of 10 °C/min, from 500 to 1180 °C heated at 15 °C/min, a plateau of 1180 °C for 1 h and a cooling back to room temperature at 10 °C/min).

The determination the crystalline phases and the cell volume was carried out, using SiO₂ as an external standard, by X-ray diffraction (XRD) patterns, which were obtained with a Siemens D-5000 Diffractometer with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$ and $\theta = 19\text{--}110^\circ$), at room temperature.

For the refinement and microstructural analyses, the DBWS⁵ program was used based on the Rietveld method, and the function profile chosen was the pseudo-Voigt, which allows a good adjustment in order to accentuate asymmetries of the profile at low angles.

The surface area measurements of the pigments were accomplished in a Micromeritics, ASAP 2000 equipment, using N₂ as the adsorption/desorption gas. The mean diameter obtained by applying the BET method,⁶ d_{BET} , is represented by:

$$d_{\text{BET}} = \frac{6}{A_s \cdot \rho}$$

where A_s is the specific surface area (m²/g) and ρ is the theoretical density of the phase ($\rho_{\text{SnO}_2} = 6.99 \text{ g/cm}^3$).⁷

UV-vis-NIR spectroscopy (diffuse reflectance) of the fired pigments was performed with a Varian 5G spectrophotometer. In addition, the L^* , a^* and b^* color parameters and diffuse reflectance of enameled samples were measured through the Gretac Macbeth Color-eye spectrophotometer 2180/2180 UV, in the 300–800 nm range, using the D65 illumination. The CIE- $L^*a^*b^*$ colorimetric method, recommended by the CIE (Commission Internationale de l'Eclairage)⁸ was followed. In this method, L^* is the lightness axis [black (0) → white (100)], b^* is the blue (–) → yellow (+) axis, and a^* is the green (–) → red (+) axis, and ΔE is the hue variation.

Scanning electronic microscopy (SEM) was used to characterize the fired pigments by employing a Zeiss DSM, 940 A.

Transmission electronic microscopy (TEM) was used to characterize the powder pigments by employing a Philips CM200.

3. Results and discussion

Figs. 2–13 illustrate the XRD, UV-vis-NIR, SEM and TEM of the different studied systems. It is observed that the system obtained by OM is less reactive and consequently needs a higher temperature (1000 °C) to obtain a single homogeneous phase, whereas, for the system obtained by the Pechini method at 800 °C, the cassiterite phase has already been formed. In the OM diffractograms at 800 and 900 °C (Figs. 3 and 5), the presence of three phases is observed: SnO₂ (major phase 87 and 89.5%, respectively), monoclinic Sb₂O₄ (3 and 4%) and orthorhombic Sb₂O₄ (10 and 5.5%), respectively. Tables 1 and 2 present the SnO₂ values of lattice parameters as well as unit cell volume at both systems at the different thermal treatment temperatures. The unit cell volume for OM and Pechini systems increases up to the temperature of 1100 °C and decreases at higher

temperatures indicating that from 1100 °C on, the system may be expelling the dopant but no second phase was detected by the XRD. The antimony oxide may be evaporated, since it is known that from this temperature on such a fact occurs.⁹

The microdeformation observed in this study was larger for the powders obtained by the Pechini method than for the powders obtained by the OM method, what indicates that the dopant is in the form of a solid solution indeed, causing a deformation in the lattice of SnO₂

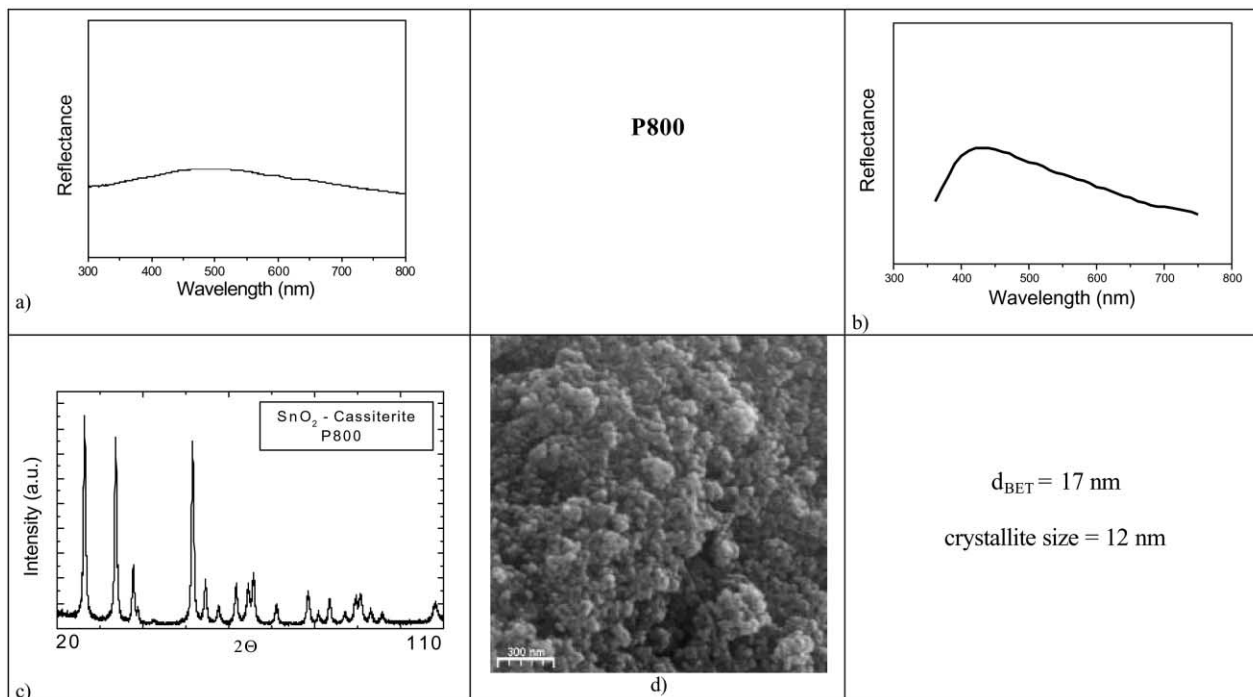


Fig. 2. Spectra of the SnO₂:7%Sb₂O₃ system obtained, after a heat treatment at 800 °C, by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

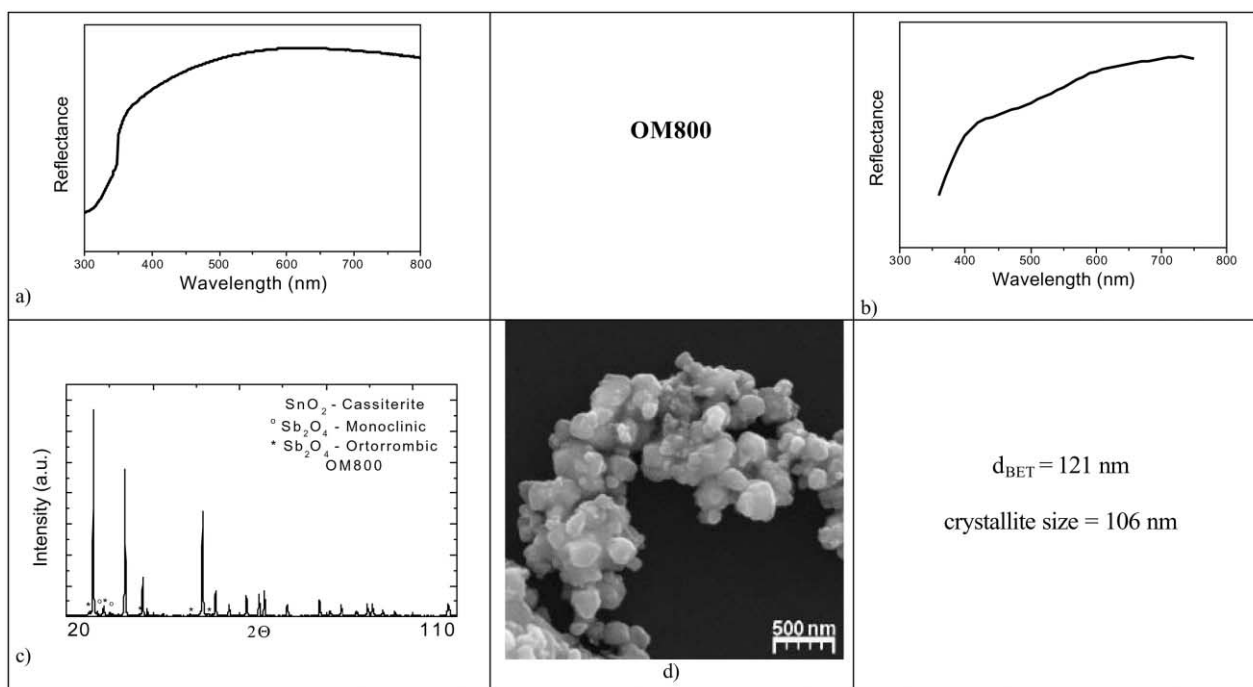


Fig. 3. Spectra of the SnO₂:7%Sb₂O₃ system obtained, after a heat treatment at 800 °C, by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

due to the fact that dopant addition causes nuclear-electronic repulse in the lattice, what occurs for in the OM system at higher temperatures.

As for the powders obtained by the Pechini method, the crystallite size and the particle size increased with

temperature. On the other hand, as for the powders obtained by OM, the crystallite size was kept approximately constant and the particle size increased with temperature, although at a smaller rate than in the case of the Pechini method. This is an indication that there

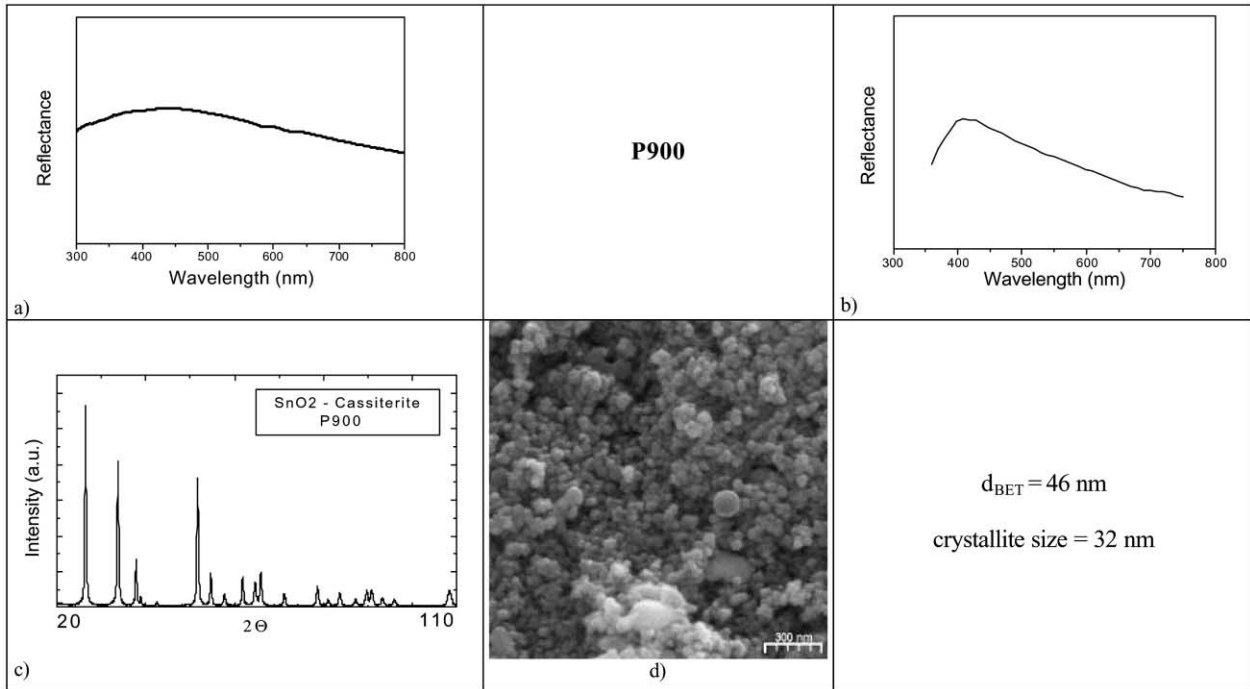


Fig. 4. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 900°C , by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

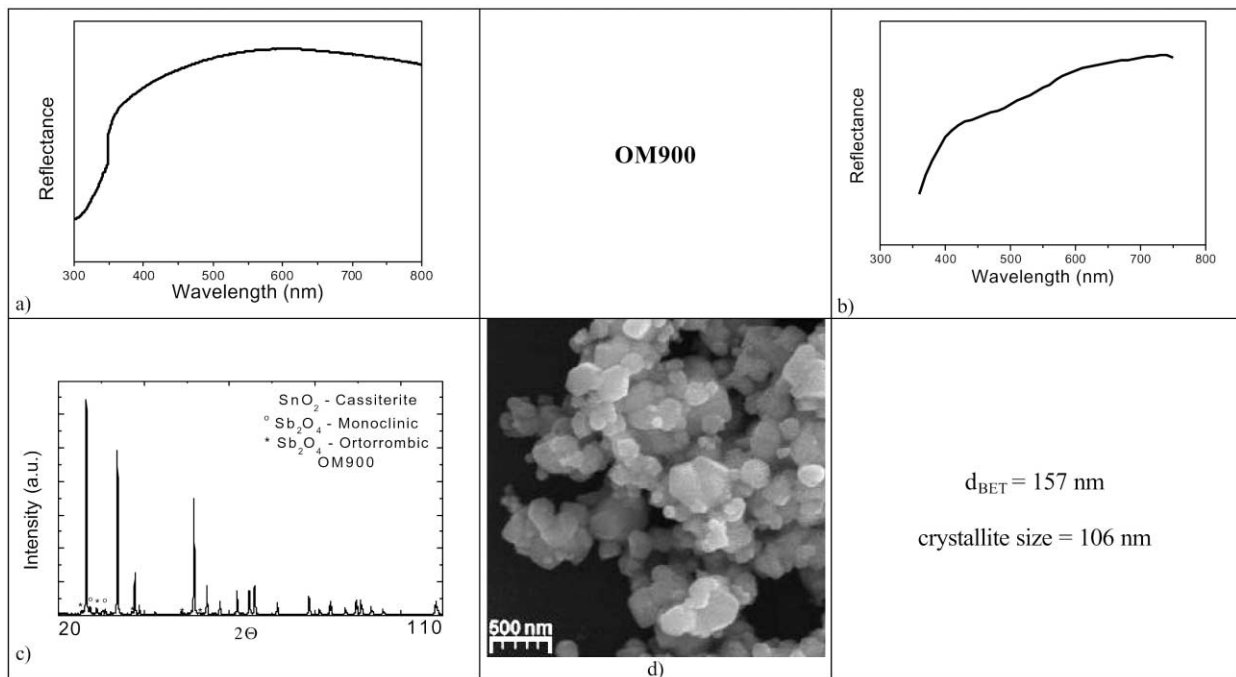


Fig. 5. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 900°C , by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

are no changes in the crystal growing mechanism. That is due to the fact that the Pechini system is formed by nanoparticles (30–60 nm) presenting a high reactivity, causing the coalescence at lower temperatures. The largest particles were observed at 1200 °C for the OM.

This effect is observed by the SEM micrographs, and these results are in agreement with the XRD data, where only at 1000 °C the formation of a homogeneous phase for the powders obtained by OM was noticed. According to TEM micrographs it was possible to confirm that

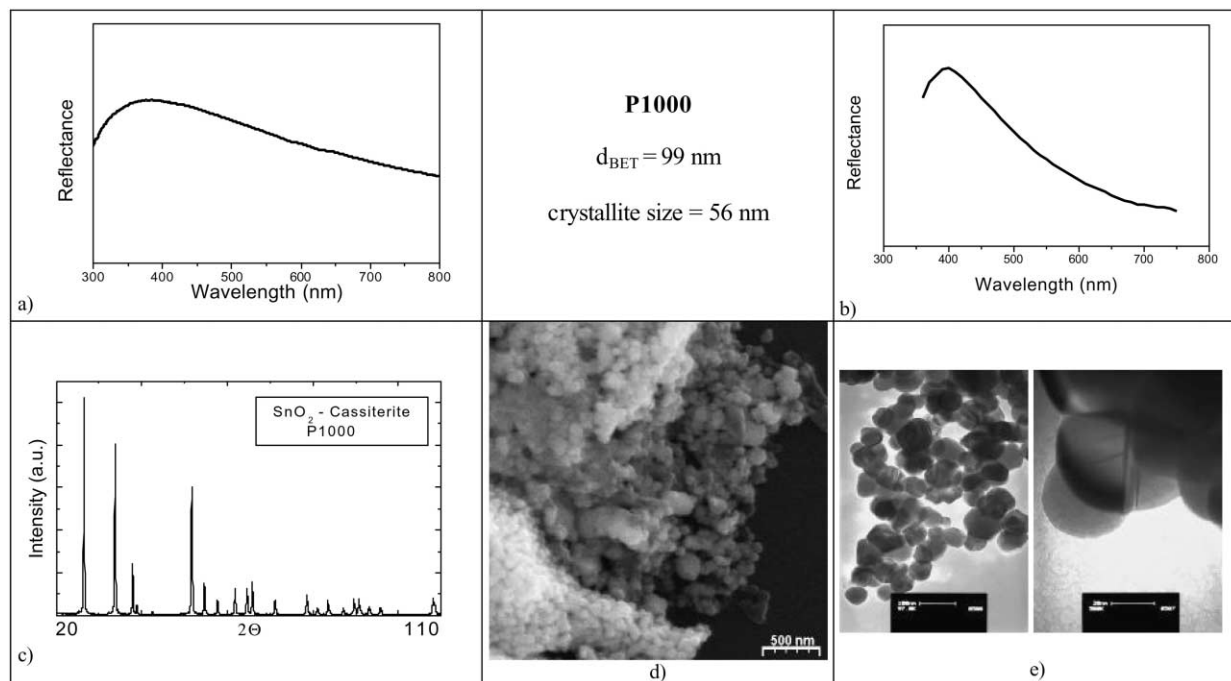


Fig. 6. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1000 °C, by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder, (d) SEM micrograph of the powder and (e) TEM micrograph for the powder.

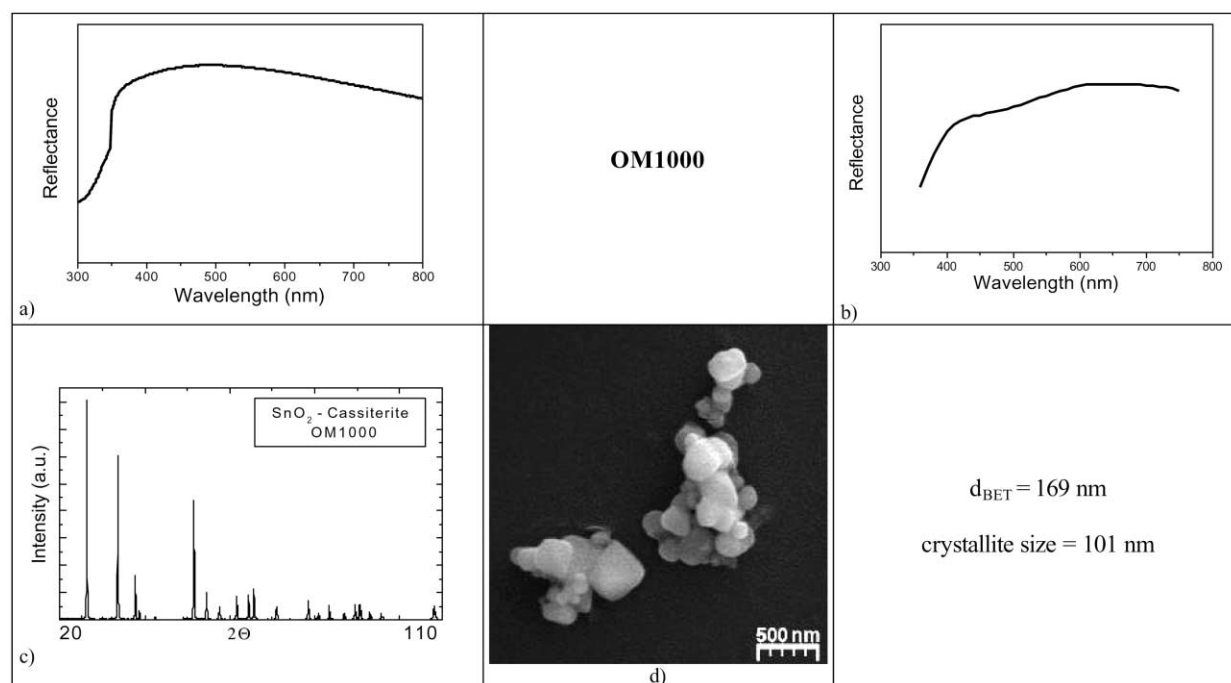


Fig. 7. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1000 °C, by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

this system is constituted of nanometric particles, which are very crystalline and homogeneous.

In these pigments, the SnO_2 -based matrix presents a white color, and this oxide is an opacifier within a vitreous system. Gray colors are formed by the doping (7%

in mol of Sb_2O_3) at calcination temperatures of 800 and 900 °C. For the Pechini method from 1000 °C, a bluish hue is acquired, confirmed by characteristic bands in the region from 380 to 420 nm. On the other hand, for the OM process, only at 1000 °C it is possible to obtain a

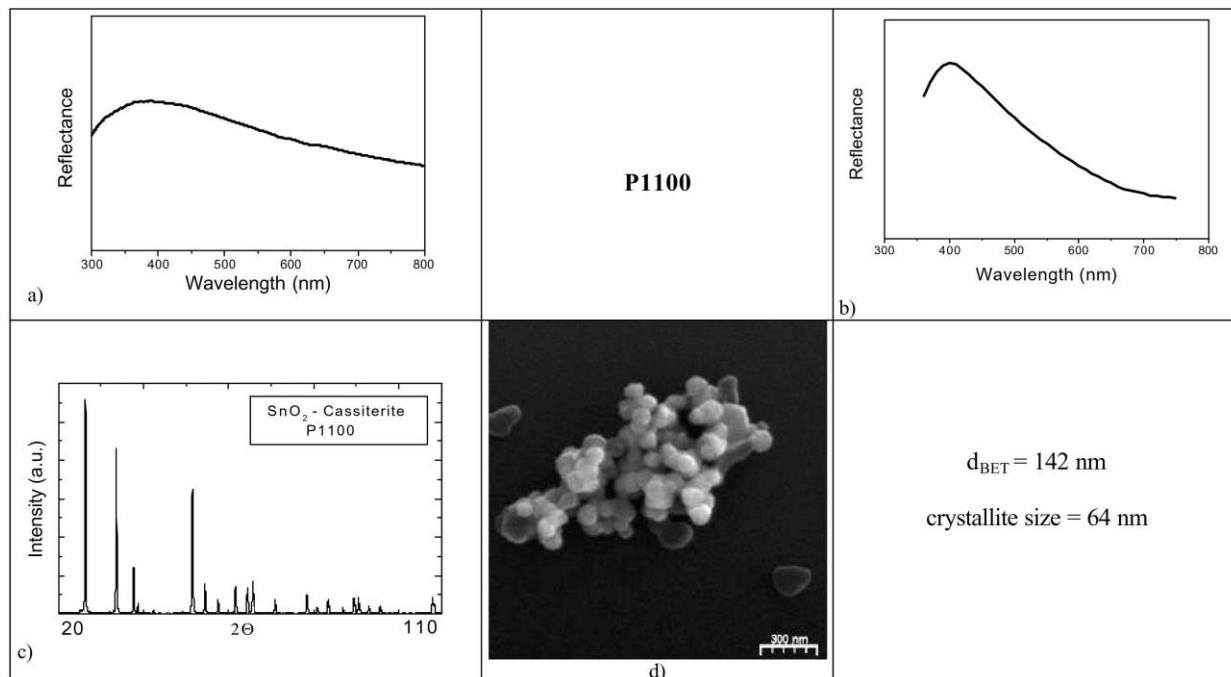


Fig. 8. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1100 °C, by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

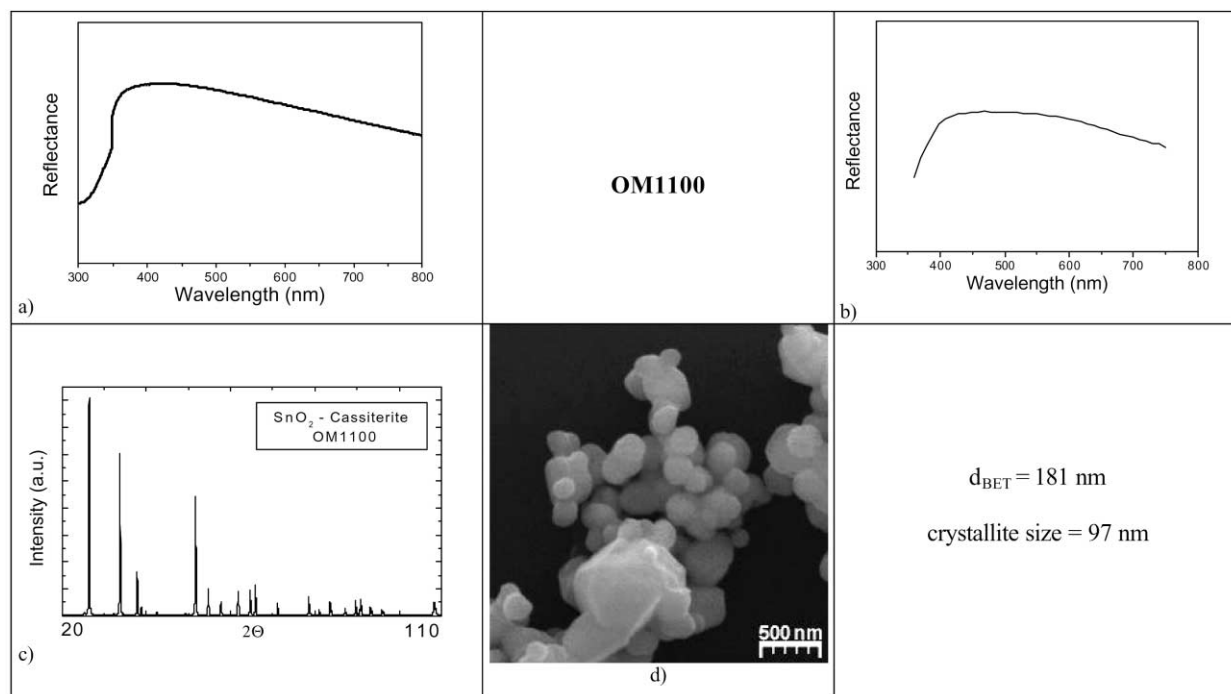


Fig. 9. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1100 °C, by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

slightly blue hue, whose intensity, increases with the increase in the temperature.

From 1000 °C the bands are overlapped, what indicates that the color of the pigment has already been defined. Concerning the samples prepared by the

Pechini method, the behavior found for the calcination temperatures of 800 and 900 °C was the opposite of the one observed by the OM process, obtaining a lower reflectance at this temperature range. As for the system prepared by OM, a higher reflectance of the powders

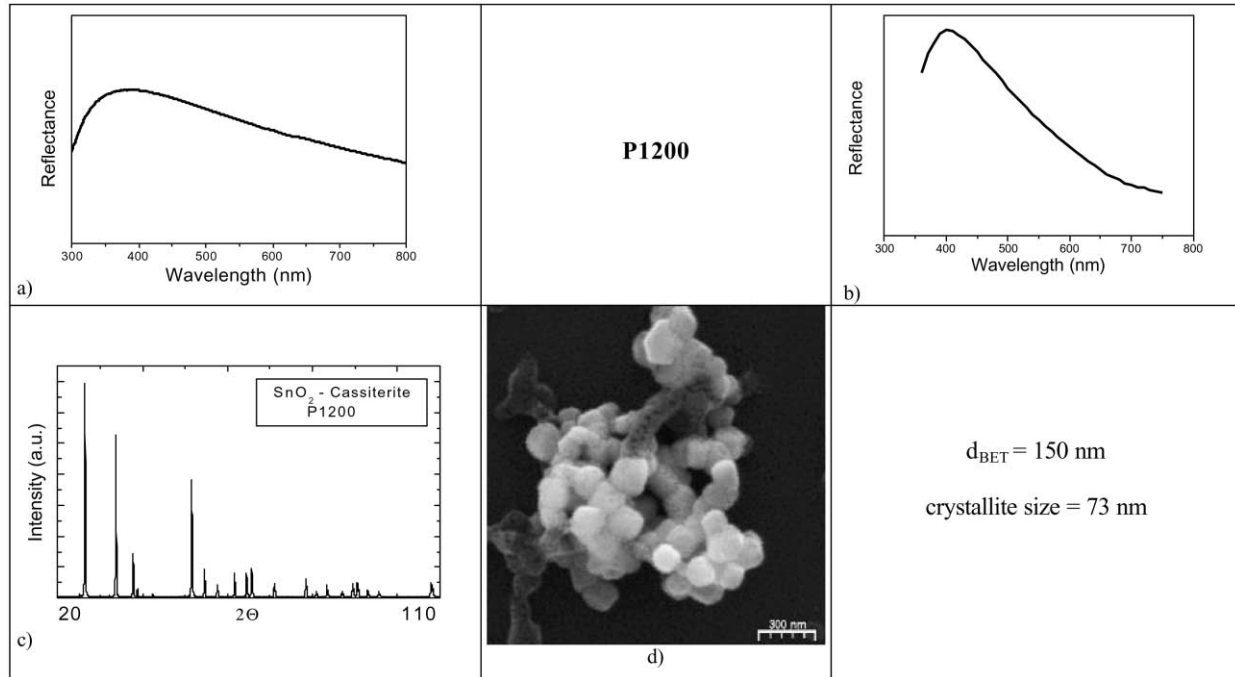


Fig. 10. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1200 °C, by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

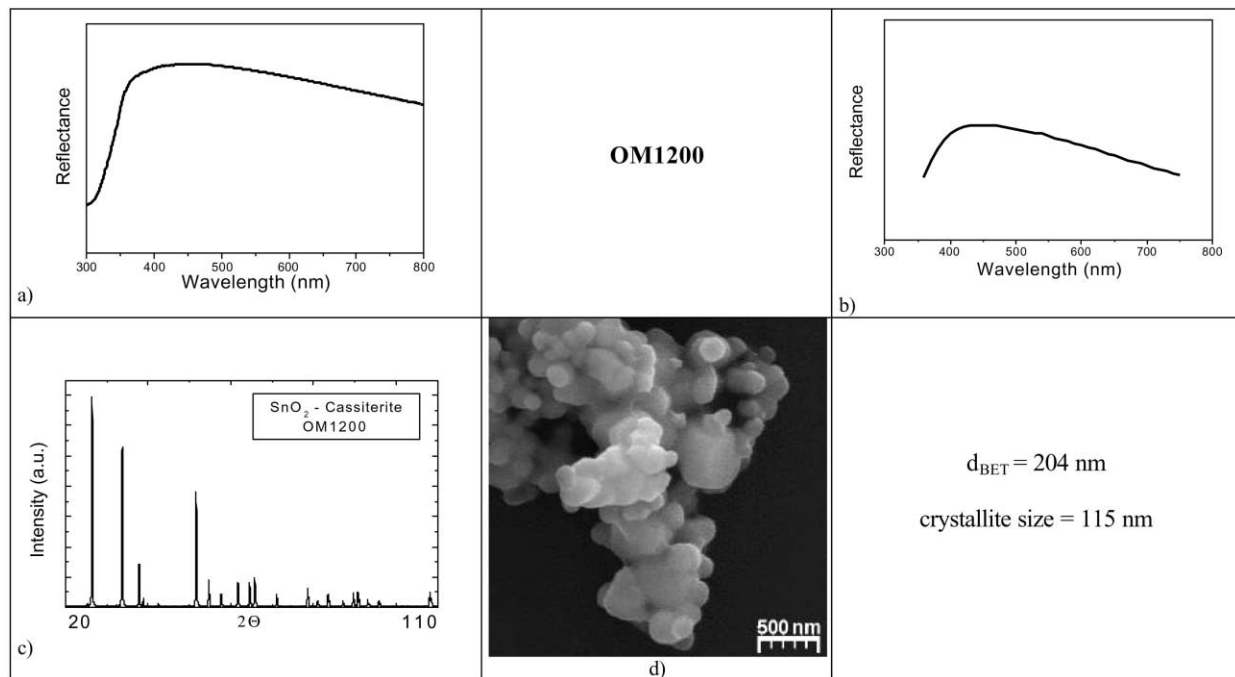


Fig. 11. Spectra of the $\text{SnO}_2:7\%\text{Sb}_2\text{O}_3$ system obtained, after a heat treatment at 1200 °C, by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

and glasses at temperatures of 800 and 900 °C was observed due to the non-homogeneity of the method. It is observed from the X-ray diffractograms that at these temperatures the system is not a monophasic system. Only from 1000 °C on it becomes a monophasic system

(structure: cassiterite). For the system obtained by the Pechini method there is an increase in the reflectance along with the increase in the temperature. The contrary occurs for the system obtained by the oxide mixture method. Hue variations due to heat treatment temperatures are

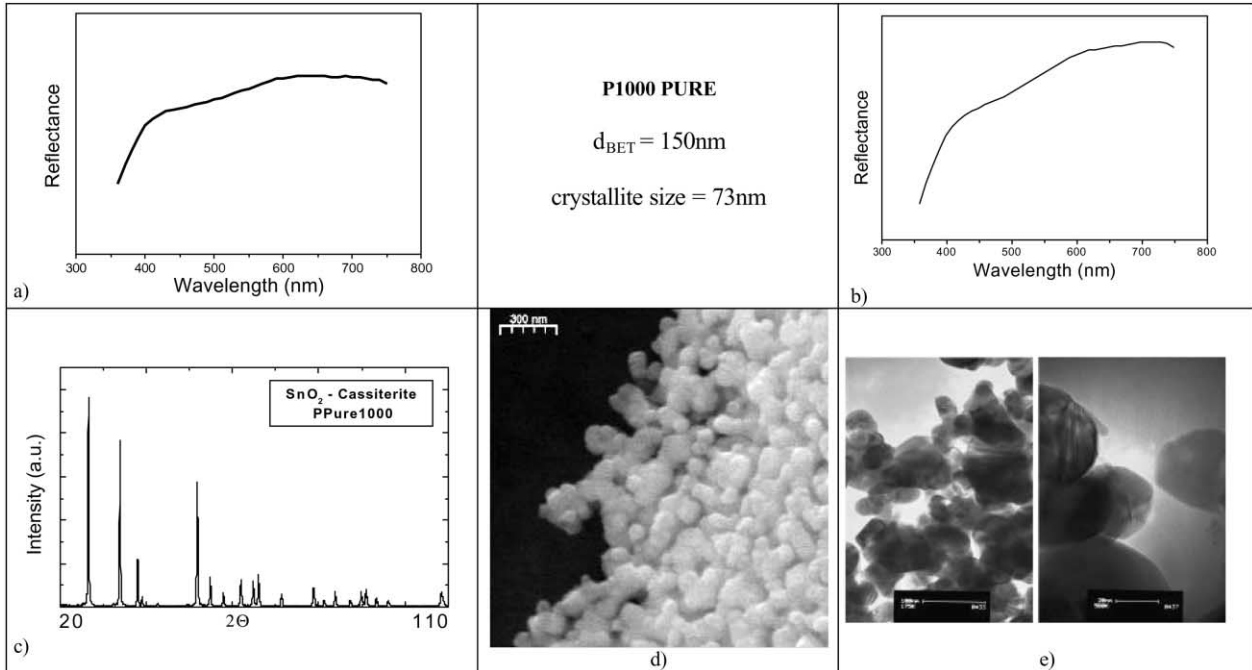


Fig. 12. Spectra of the pure SnO_2 system obtained, after a heat treatment at 1000 °C, by the Pechini method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder, (d) SEM micrograph for the powder and (e) TEM micrograph of the powder.

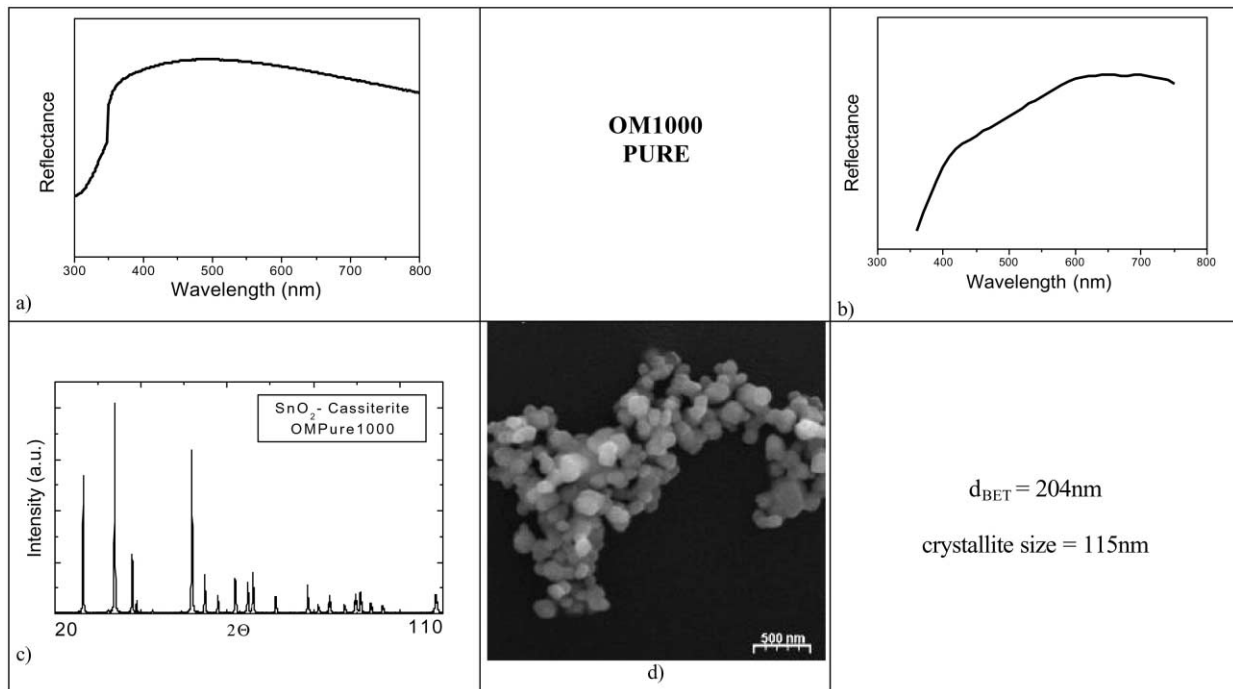


Fig. 13. Spectra of the pure SnO_2 system obtained, after a heat treatment at 1000 °C, by the OM method: (a) UV-vis reflectance of the powder, (b) UV-vis reflectance of the ceramic piece, (c) XRD pattern of the powder and (d) SEM micrograph of the powder.

Table 1
Lattice parameters of SnO₂ in the SnO₂:7%Sb₂O₃ system (Pechini)

Temperature (°C)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
800	4.7391 (2)	3.1893 (2)	71.629 (7)
900	4.7399 (1)	3.1898 (7)	71.662 (3)
1000	4.7412 (5)	3.1908 (4)	71.725 (1)
1100	4.7416 (4)	3.1911 (3)	71.744 (1)
1200	4.7410 (4)	3.1905 (3)	71.711 (1)

Table 2
Lattice parameters of SnO₂ in the SnO₂:7%Sb₂O₃ system (MO)

Temperature (°C)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
800	4.7380 (5)	3.1869 (4)	71.540 (1)
900	4.7382 (4)	3.1871 (3)	71.550 (1)
1000	4.7383 (4)	3.1871 (3)	71.555 (1)
1100	4.7387 (3)	3.1874 (2)	71.575 (1)
1200	4.7381 (5)	3.1872 (4)	71.549 (1)

Table 3
Chromatic coordinates of SnO₂:7%Sb₂O₃ pigments obtained by the Pechini method as a function of the heat treatment temperature

Temperature (°C)	<i>L</i> *	<i>a</i> *	<i>b</i> *	Δ <i>E</i>
800	27.65	−4.14	−7.05	28.84
900	28.51	−4.12	−8.27	29.97
1000	28.09	−7.19	−15.93	33.08
1100	29.29	−7.34	−14.89	33.67
1200	32.44	−8.17	−15.42	36.84

Table 4
Chromatic coordinates of SnO₂:7%Sb₂O₃ pigments obtained by the oxide mixture, as a function of the heat treatment temperature

Temperature (°C)	<i>L</i> *	<i>a</i> *	<i>b</i> *	Δ <i>E</i>
800	82.45	4.92	10.35	83.24
900	81.30	2.68	6.30	81.59
1000	80.45	4.00	9.20	81.07
1100	76.59	−2.05	−1.32	76.63
1200	70.65	−4.13	−5.16	70.96

presented in Tables 3 and 4. Opposite behaviors for both studied systems are observed, reinforcing that the homogeneity degree of the pigment has a direct influence on the color response. So does the particle size, which directly depends on the preparation method used.

4. Conclusion

The SnO₂:*x*Sb system pigments obtained by Pechini method developed a bluer color hue than the pigments prepared by the mixture of the oxide method.

The temperature needed to obtain a monophasic structure for the pigment system was 800 °C by the Pechini method and 1000 °C by OM. As for the powders obtained by the Pechini method, both the crystallite size and the particle size increased with temperature. On the other hand, as for the powders obtained by OM, the crystallite size was approximately constant and the particle size increased with temperature, although at a smaller rate than in the case of Pechini method.

For the system obtained by the Pechini method there is an increase in the reflectance along with the increase in the temperature. The contrary occurs for the system obtained by the oxide mixture method. Regarding the effect of hue variations due to the heat temperature, opposite behaviors for both studied systems are observed, reinforcing that the fact the homogeneity degree of the pigment has a direct influence on the color. So does the particle size, which directly depends on the preparation method used.

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