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Development of metal oxide nanoparticles by soft chemical method

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Abstract

An extensive work for the study of SnO_2 samples doped with x-mol% of Sb (x = 0, 6, 10, 14 and 18) is reported. The materials were prepared by the polymeric precursor method (Pechini method), calcined for 4 h between 800 °C and 1200 °C. The Rietveld method with X-ray diffraction data (XRD) was used to analyze the unit cell dimensions, crystallite size and microstrain. It was observed the crystallite size increasing and decrease of the microstrain with the increase of the calcining temperature. The synthesis of tin oxide nanoparticles with high thermal stability against particle growth rate was achieved by doping SnO_2 particles with Sb_2O_3. All the phases tend to have the same dimension when the temperature increases, although its values varies with x and reaches the maximum value when fired at 1100 °C. These variations seem to be an indication that the oxidation state of the antimony changes with the amount of Sb added to the material.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. X-ray methods; SnO_2:Sb; Pigments

1. Introduction

Tin dioxide is a ceramic material with many interesting applications, for example catalysts, gas sensors, optoelectronic or photovoltaic devices [1–5], that requires specific characteristics like films, dense or porous materials for technological use and are directly related to the particles size.

It is known that the traditional source of blue color in currently known ceramic pigments contains Co [6]. In this work is presented an alternative to these systems with the antimony incorporation in the host lattice of SnO_2, which can decrease the environmental impact in the manufacturing process (Co is widely considered as toxic or hazardous), while also maintain an optical coloring performance in the desired glaze. The coloring performance of pigments depends very much on its thermal stability, chemical reactivity towards the glaze components, the coordination of host ions, and it was also noticed a great dependence on the methodology used to prepare it [7].

In this work were studied the Sb dopant and calcining temperature influences on the microstructure (size-strain), unit cell parameters and particles size of SnO_2 prepared by soft chemical route well known as Pechini method. The weighted size-strain method, described elsewhere [8], was applied for the microstructural analysis. The high resolution transmission electron microscopy (HRTEM) was used to observe the morphologic aspects and measure the size of the particles.

2. Experimental

SnO_2 samples doped with x-mol% of Sb (x = 0, 6, 10, 14 and 18) were prepared through Pechini method [9,10]. The process is based on metallic citrate polymerization using ethylene glycol. Citric acid was used to chelate cations in an aqueous solution. The addition of 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. Details of the sample preparation are described elsewhere [11].

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The treatment temperature ranged from 800 °C to 1200 °C, and the resulting powders were characterized by the Rietveld method with X-ray diffraction data. The XRD measurements were performed in a D5000 Siemens diffractometer, from 20 to 110° 2θ with $\Delta 2\theta = 0.02°$ 2θ, divergence slit = 2 mm, receiving slit = 0.6 mm, step time = 10 s, and copper radiation monochromatized by graphite crystal. The instrumental broadening was measured from a SiO_2 standard sample crashed from a single crystal. It was used a modified version the Rietveld refinement program DBWS 9807c [8], which is an upgraded version of the DBWS 9411 program [12].

In all samples it was observed only the SnO_2 phase. The initial FWHM parameters were that of the α-SiO_2 standard sample. At the beginning, it was refined the scale factor, sample displacement, cell parameters and background. After that, the FWHM parameters *U*, *Z*, *X* and *Y* were released to refine and then fixed again. Then the individual atom displacements parameters and the oxygen positional parameters were refined. It was observed small peaks at the low angle side of all SnO_2 peaks, which were caused by the L_α radiation of the tungsten. Then it was considered another SnO_2 phase with unit cell 4.48% greater than the first one, to fit that peaks caused by the W_{L_α} radiation. The refinement was considered complete when all parameters shifts were less than 10% of the standard deviations.

The HRTEM was used to observe the morphologic aspects of the particles and to measure its sizes.

3. Results and discussion

Fig. 1 shows the Rietveld plot for the sample calcined at 1000 °C/4 h for $x = 0.14$, where it is possible to observe the good agreement between the observed and calculated pattern. It is also shown there the Bragg peaks of the second supposed SnO_2 phase used to fit the tungsten L_α radiation.

The final unit cell parameters are in Table 1, the unit cell volume variation can be observed in Fig. 2; the crystallite size and microstrain are in Fig. 3.

The final Rietveld refinement indexes, defined by Young and Wiles (1982) [13] had been the maximum value of 1.42 of the goodness of fit index (*S*) indicates that the profile agreement was of good quality for all samples. The Bragg intensity index

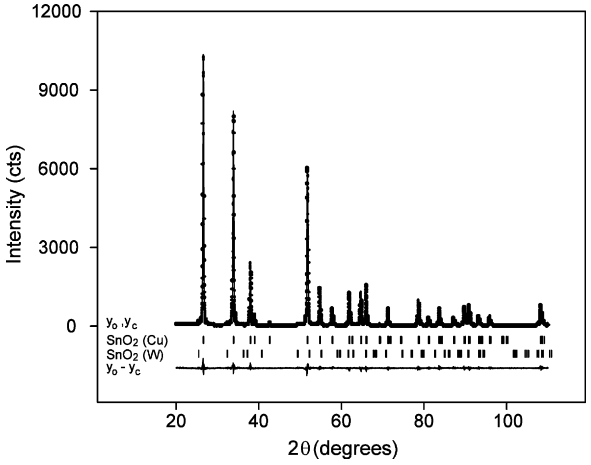

Fig. 1. Rietveld plot for the sample calcined at 1000 °C/4 h for $x = 0.14$.

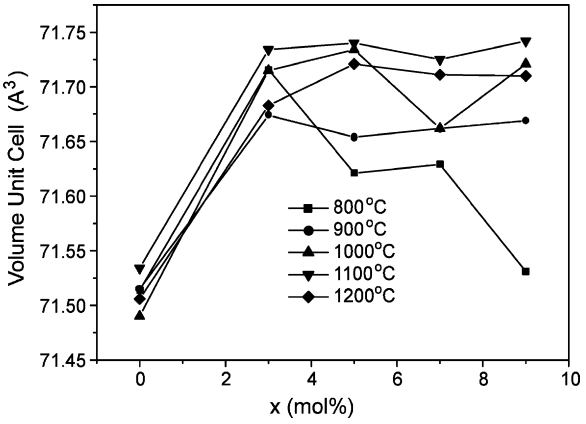

Fig. 2. Unit cell volume variation in function of the Sb_2O_3 concentration.

(R_B) for all refinements are very low, indicating that the crystal structure model refined is in good agreement with the observed data.

One can note in Figs. 2 and 3:

(a) The unit cell is larger for the doped materials.
(b) The largest unit cell is reached for the material heated at 1100 °C.

Table 1
Unit cell parameters of the SnO_2 for the different systems

	Unit cell (Å)	800 °C	900 °C	1000 °C	1100 °C	1200 °C
$x = 0$	*a* (Å)	4.73742(8)	4.73745(7)	4.73690(5)	4.73791(6)	4.73718(4)
	c (Å)	3.18648(6)	3.18648(5)	3.18610(4)	3.18670(5)	3.18644(3)
$x = 3$	*a* (Å)	4.74118(2)	4.74036(1)	4.74101(5)	4.74138(4)	4.74037(4)
	c (Å)	3.19038(1)	3.18962(1)	3.19057(4)	3.19089(3)	3.19000(3)
$x = 5$	*a* (Å)	4.73926(2)	4.73989(1)	4.74134(5)	4.74149(4)	4.74111(4)
	c (Å)	3.18873(2)	3.18937(9)	3.19097(4)	3.19105(3)	3.19068(3)
$x = 7$	*a* (Å)	4.73907(2)	4.73989(1)	4.74120(5)	4.74160(4)	4.74098(4)
	c (Å)	3.18934(2)	3.18978(7)	3.19077(4)	3.19107(3)	3.19046(3)
$x = 9$	*a* (Å)	4.73755(2)	4.74021(1)	4.74118(5)	4.74155(5)	4.74090(4)
	c (Å)	3.18701(2)	3.18963(7)	3.19062(4)	3.19102(4)	3.19049(3)