

THERMAL AND STRUCTURAL INVESTIGATION OF SnO₂/Sb₂O₃ OBTAINED BY THE POLYMERIC PRECURSOR METHOD

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SnO₂-based materials are used as sensors, catalysts and in electro-optical devices. This work aims to synthesize and characterize the SnO₂/Sb₂O₃-based inorganic pigments, obtained by the polymeric precursor method, also known as Pechini method (based on the metallic citrate polymerization by means of ethylene glycol). The precursors were characterized by thermogravimetry (TG) and differential thermal analysis (DTA). After characterization, the precursors were heat-treated at different temperatures and characterized by X-ray diffraction. According to the TG/DTA curves basically two-step mass loss process was observed: the first one is related to the dehydration of the system; and the second one is representative to the combustion of the organic matter. Increase of the heat treatment temperature from 500 to 600°C and 700°C resulted higher crystallinity of the formed product.

Keywords: cassiterite, polymeric precursor method, thermal analysis

Introduction

Tin dioxide (SnO₂) is a *n*-type semiconductor, exhibiting a tetragonal crystalline structure which is similar to the rutile structure [1, 2]. The low densification of pure SnO₂ during the sintering processes results in a high porosity, allowing it to be used basically as high surface area and high sensitivity gas sensor. Such low sinterability of SnO₂ is related to the predominance of non densifying mechanisms in its mass transport, which is controlled by surface diffusion mechanism (at low temperatures) and evaporation–condensation processes (at high temperatures), that only promote coalescence and grain growth [1, 3].

Brazil is one of the greatest tin oxide producer countries paying growing interest to the tin oxide researches. Besides, the selection of SnO₂ in this work, is also due to its excellent electro-optical properties and low cost, as a national raw material.

SnO₂ is used in a great number of technological applications, as sensors, catalysts, electro-optical devices, photo-voltaic cells, smart windows, heating windows, electrodes for solar cells, liquid crystal displays (LCD's), electro-chromic displays (ECD's), transparent electrodes in electroluminescence [1–3]. SnO₂ can also be used in architecture as thermal mirror, in the automobile industry, in photothermal solar collectors and in electroluminescent lamps [4, 5]. Most of those applications involve porous ce-

ramic (sensor) or conductor and transparent dense thin films [6].

The electro-optical properties of tin dioxide are of great technological interest and, according to Jarsebski *et al.* [2], they are unique in two aspects: 1) SnO₂ is one of the few electrical conductors that are optically transparent in the visible wavelength region, when undoped; 2) SnO₂ is the simplest semiconductor oxide with rutile crystalline structure, with stable 'd' orbitals.

The use of Sb₂O₃ as a dopant, proposed in the present project, contributes to an increase in the conductivity, but does not result in a higher densification thus maintaining or improving the high surface area and sensitivity of the sensors. The SnO₂/Sb₂O₃ binary system is one of the most requested materials for application as conductive pigment and in systems that require special safety conditions for the deflagration prevention, as device that handle flammable gases and explosive substances [7].

Several synthesis methods to obtain oxides, such as SnO₂ or SnO₂/Sb₂O₃, with high degree of purity and high surface area are described in the literature. Among them the sol–gel method should be highlighted, since it is simple, operates at low processing temperature and does not require vacuum [6]. A variation of the sol–gel method is the polymeric precursor method, also known as Pechini method [6]. This

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method consists on the chelation of metallic cations (dissolved as salts in an aqueous solution) with a hydroxycarboxylic acid (preferentially citric acid) and the subsequent polymerization using a polyesterification reaction with a polyalcohol (preferentially ethylene glycol) [8]. The objective of this method is a random cation distribution, throughout the polymeric structure [9].

In the present study, undoped and Sb_2O_3 -doped SnO_2 were obtained, using the polymeric precursor method. These powders were heat-treated at three different temperatures, and their thermal, structural and morphological properties were investigated.

Experimental

Tin citrate preparation

Tin citrate was chosen as an intermediary compound for the synthesis of SnO_2 prepared according to [8]. SnCl_2 was slowly added to an aqueous solution, containing citric acid, followed by a dropwise addition of an ammonia solution for pH correction at room temperature. When the pH of the solution reached about 3 precipitation of tin citrate was observed. The precipitate was filtered and abundantly washed up to a negative chloride proof with silver nitrate. The white precipitate was dried for 24 h in an oven at 60°C .

For the preparation of the resins tin citrate was dissolved in an aqueous solution of citric acid. To help the complete dissolution of tin citrate, concentrated HNO_3 was used. Then Sb_2O_3 was added to the solution. After obtaining a homogeneous solution, ethylene glycol was added, leading to a polyesterification reaction. The mass ratio between citric acid and ethylene glycol was fixed at 60:40 and the molar ratio between citric acid and metal at 3:1. The final solution was kept under constant stirring in the $60\text{--}90^\circ\text{C}$ temperature range for NO_x elimination. Finally a transparent resin was obtained.

After obtaining the polymeric precursors (resins), they were heat-treated for 2 h in air at 300°C to obtain the powder precursor. The powder precursors were de-agglomerated and ground in agate mortar until no grains were retained in a 200-mesh sieve. After that, they were analyzed by thermal analysis.

Instrumentation

TG/DTG curves were obtained in a TGA-50 Shimadzu thermobalance, and the DTA curves were recorded using a Shimadzu DTA-50 analyzer. Flowing air (flow rate: 100 mL min^{-1}), dynamic heating (heating rate: 10 K min^{-1}), small alumina crucibles and about 5 mg initial sample masses were used. Both TG

and DSC runs were carried out between room temperature and 800°C .

The powder precursors were heat-treated at different temperatures (500 , 600 and 700°C) for 4 h. The evolution of crystalline phase as a function of the heat treatment temperature and antimony amount was studied by X-ray diffraction (XRD), in Siemens D-5000 equipment, using a monochromatic $\text{CuK}\alpha$ radiation. The average crystallite size was calculated using the Scherrer equation. Morphological analysis of the $\text{SnO}_2/\text{Sb}_2\text{O}_3$ system was performed in a DSM 940 A ZEISS scanning electron microscope (SEM).

Results and discussion

The thermogravimetric results of the different powder precursors are presented in Figs 1 and 2.

The results related to the thermal decomposition of the powder precursors are summarized in Table 1. Two thermal decomposition steps were observed. The first one is related to the loss of H_2O and the second one is due to the elimination of the organic material [9, 10]. A decrease in the mass loss and peak temperature was observed upon dopant addition.

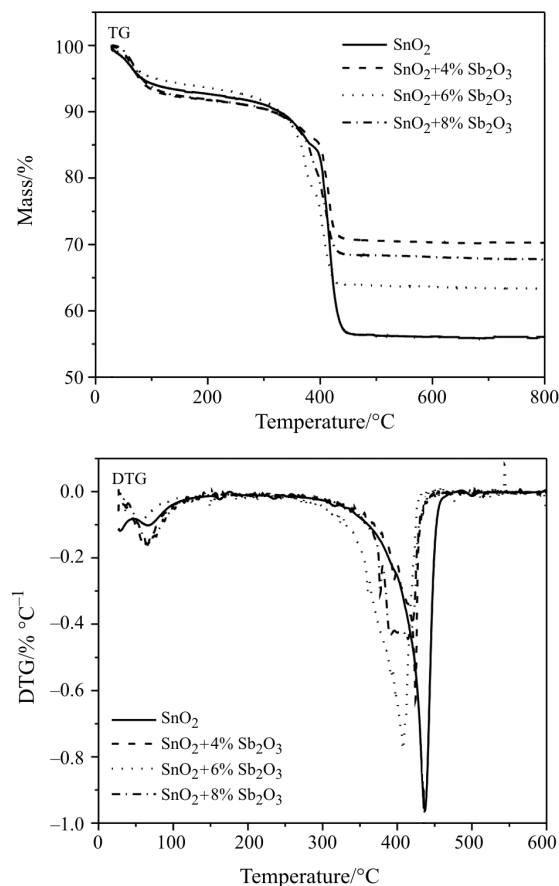
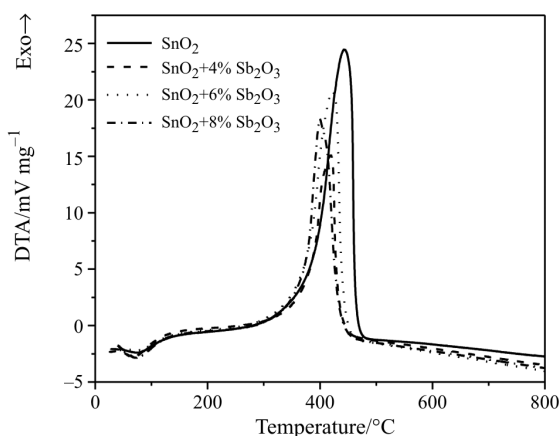


Fig. 1 TG and DTG curves of the pure and doped SnO_2 powder precursors

Table 1 Temperature and mass loss values determined by TG

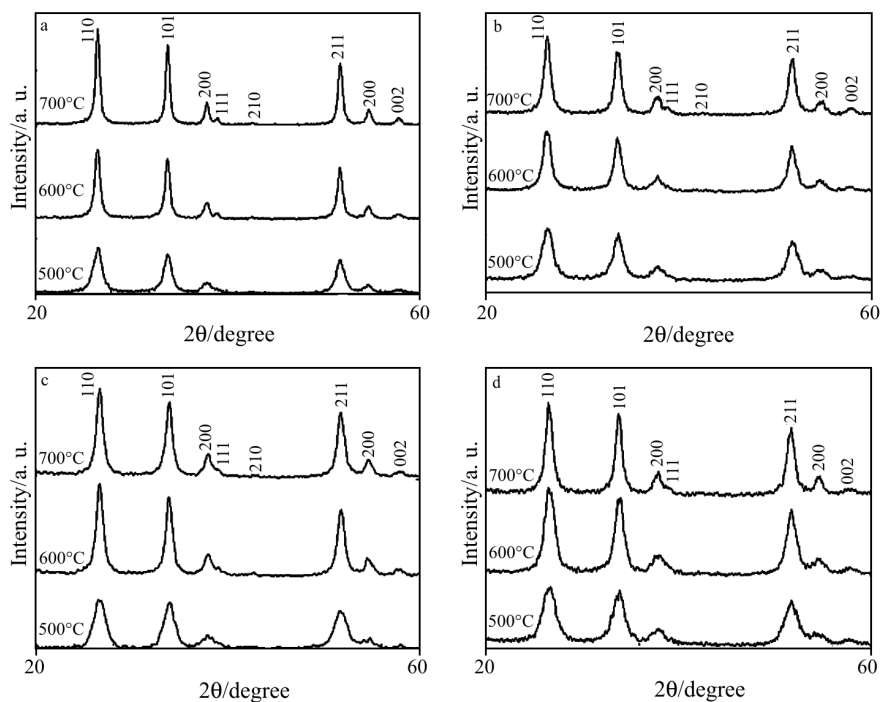
Material	Step	T _p /DTG/°C	Mass loss/%
Pure SnO ₂	1	73	6
	2	443	35
SnO ₂ +4% Sb ₂ O ₃	1	66	7
	2	419	20
SnO ₂ +6% Sb ₂ O ₃	1	74	5
	2	423	29
SnO ₂ +8% Sb ₂ O ₃	1	74	7
	2	398	23

**Fig. 2** DTA curves of the powder precursors

DTA curves are presented in Fig. 2. It can be observed that the second and more intense exothermic peak is related to the thermal decomposition of the organic matter, just as observed in the TG curves. This peak is attributed to the combustion of the organic material yielding basically CO₂ and H₂O. A peak temperature decrease was observed upon the dopant addition, corroborating the thermogravimetry results.

The XRD patterns of the powders heat-treated at different temperatures are presented in Fig. 3. In undoped SnO₂ (Fig. 3a), the formation of the cassiterite is observed, at 500°C. The increase of the heat treatment temperature results the formation of narrower and more intense diffraction peaks, due to the increase of the crystallinity. For the Sb₂O₃-doped SnO₂ powders, small displacements in the diffraction peaks were noticed compared to the undoped SnO₂, which can be ascribed to the distortions promoted by the dopant within the SnO₂ lattice. All the XRD patterns (Fig. 4) presented diffraction peaks are characteristic to single phase systems, since peaks from secondary phases were not detected.

In Fig. 4, the crystallite sizes and the crystallinity of degree of the SnO₂ powders, with different dopant amounts are presented. The increase in the heat treatment temperature leads to an increase in the crystallite size and in the crystallinity of all samples. This increase is due to the absorption of a large amount of energy, leading to the ordering of the amorphous

**Fig. 3** XRD patterns of SnO₂ powders a – undoped and doped with: b – 4, c – 6 and d – 8 mol% of Sb₂O₃, heat-treated at different temperatures

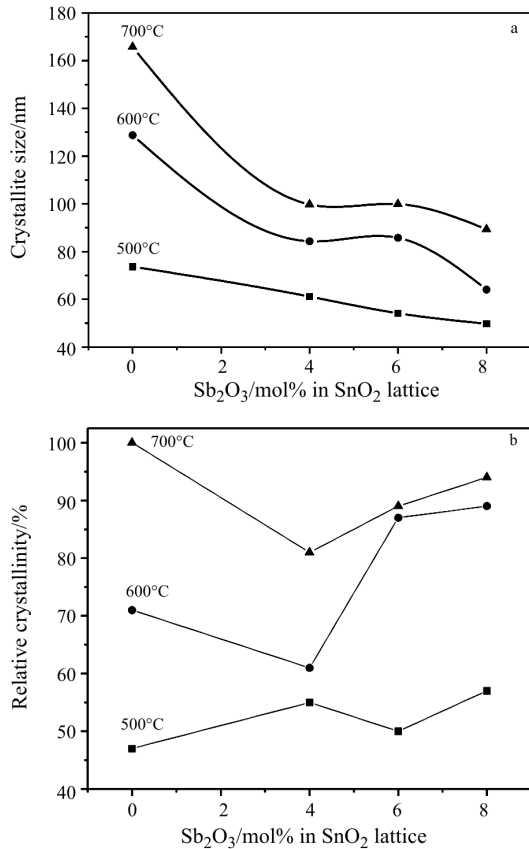


Fig. 4 Crystallite size and degree of crystallinity curves as a function of the heat treatment temperature and of the Sb₂O₃ doping level in the SnO₂ lattice

phase (increase of crystallinity) and consequently the crystallite growth. It was also observed that the dopant addition leads to a decrease in the crystallite size. This decrease of the average crystallite size suggests that Sb₂O₃ acts as an inhibitor of the crystallite growth of the SnO₂-based system. This may be due to the formation of secondary phase in the grain boundary, making crystallite growth more difficult. Another possibility is the distortion in the crystalline lattice, making the diffusion processes more difficult. The crystallinity degree also indicates that a distortion in the crystalline lattice is occurring, making crystallization more difficult, when a small amount of dopant is added to the lattice.

Figures 5–7 depict the SEM images presenting the morphology of the undoped and Sb₂O₃-doped SnO₂ powders.

Antimony addition led to changes in the particle size and morphology. The presence of antimony seems to promote the increase in the formation of ag-

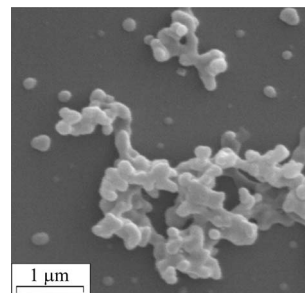


Fig. 5 SEM image of the undoped SnO₂ powder, heat-treated at 500°C for 4 h

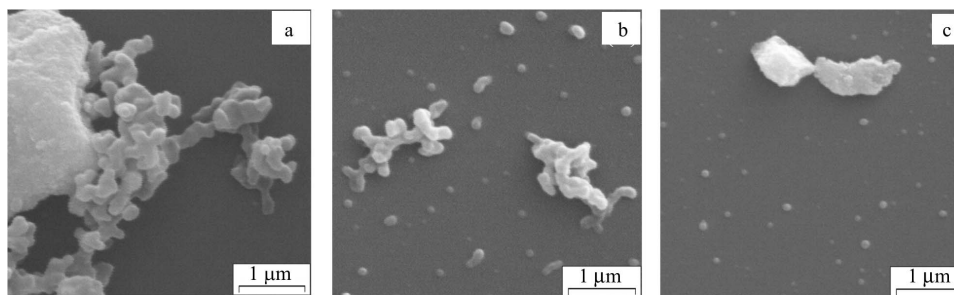


Fig. 6 SEM images of the SnO₂ powder doped with 4% of Sb₂O₃, heat-treated at: a – 500, b – 600 and c – 700°C for 4 h

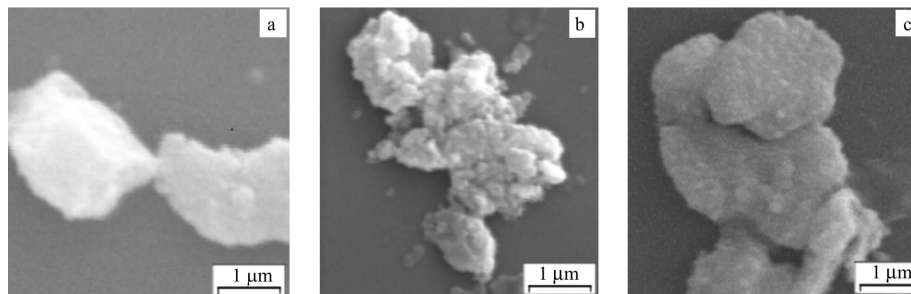


Fig. 7 SEM images of SnO₂ powders heat-treated at 700°C for 4 h with varying Sb₂O₃ doping levels: a – 4, b – 6 and c – 8 mol%

gregates. The increase in the heat treatment temperature led to an increase in the relative crystallinity, according to the XRD results.

Conclusions

The SnO₂ powder precursors obtained by the polymeric precursor method presented two well defined mass loss steps. The first one is related to elimination of water and adsorbed gases; the second one is related to the combustion of the organic material. After calcination, a single phase material was detected by XRD, with cassiterite structure, characteristic of SnO₂. The average crystallite sizes of the powders increase with the increase of the heat treatment temperature and decrease with the addition of the dopant. The degree of crystallinity is also affected by the addition of dopant. The SEM images evidenced the modifications occurred in the morphology and in the average particle size due to Sb₂O₃ addition into the SnO₂ lattice, as well as the formation of aggregates.

Acknowledgements

The authors acknowledge CNPq and CAPES for the financial support.

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DOI: 10.1007/s10973-006-7778-9