Effects of Synthesis and Processing on Supersaturated Rare Earth-Doped Nanometric SnO₂ Powders


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ABSTRACT

This paper presents and discusses some of the results of the effects of processing on rare earth-doped nanosize SnO₂. Several relevant factors that may influence the characteristics of the final product are studied. The influence of two preparation routes and two heat-treatment conditions on the incorporation of dopants is investigated. The route whereby a soluble salt is used as the dopant source is found to provide the highest degree of dopant incorporation, even under the least favorable heat-treatment conditions.

Tin oxide is used in a large range of technological applications, including varistors,¹ sensors,² catalytic ceramics,³ and conductive films.⁴ In the past few years, thin films and nanometric systems have been the main focus of several studies,⁵–⁷ because some of the characteristics of their properties still require improvement.

Based on the current state of the art of materials science, the production of nanostructured materials can be considered relatively simple. However, new challenges involving reproducible and controlled materials still have to be met. These challenges originate from the fact that nanosized materials are far removed from chemical equilibrium.⁸–¹⁰ Thus, very slight differences in processing or synthesis conditions are relevant factors that determine some of the characteristics of the material. In other words, the essence of the problem is that the processes to obtain these materials still involve a large number of variables. Hence, the study of these variables and their effects is very important.

We recently proposed that the grain growth of doped semiconductor oxides caused by heat treatments could be prevented by using a metastable solid solution.¹¹ This approach can be quite efficient, for the dopant is incorporated within the oxide matrix. However, the process of dopant incorporation into the matrix has been found to be highly deeply dependent on the material’s synthesis and processing conditions. Some of our findings on the effects of synthesis and processing on doped-SnO₂ nanopowders are presented herein, as are the influence of the dopant source and heat treatment conditions on the morphological characteristics and sintering behavior of these powders.

The polymeric precursor method¹² has been widely used to prepare thin films⁵ and nanoparticles.⁶,⁷ This method is based on the distribution of cations throughout the polymeric resin. Because this distribution occurs on an atomic scale, the method results in materials that are much more chemically homogeneous. Secondary phases are disfavored, and the temperature required for sintering is usually considerably lower than that used in conventional methods. Moreover, this sol–gel-like method uses water as solvent and usually requires only simple, stable, and inexpensive precursors.

In this study, two classes of samples of 5 mol % rare earth-doped (RE-Ce, -La, and -Y) tin oxide were prepared by a modified polymeric precursor route. This method has been employed quite frequently to synthesize nanoparticles because of its low cost and good stoichiometric control.¹³,¹⁴ The differences in the synthesis and heat treatment conditions are summarized in Table 1.

X-ray powder diffraction patterns were measured using a Siemens D-5000 instrument with a Bragg θ/2θ geometry, equipped with a graphite monochromator and Cu Kα radiation. TEM (transmission electron microscopy) observa-
tions were performed using a 200 kV Philips CM 200 microscope, and X-ray photoelectron spectra were taken using a commercial VG ESCA 3000 system. The spectra were collected using Mg Kα radiation, and the overall energy resolution was approximately 0.8 eV. These techniques were used to compare the influence of the synthesis procedure and processing conditions on the material. The results were analyzed by comparison of Samples A with Samples B.

Samples A and B were prepared very similarly; however, the dopant was added to Samples A in the form of a previously prepared citrate, while a soluble salt was used as the dopant source in Samples B. The sintering treatment involved another important difference between Samples A and B. While Samples A were placed in a furnace preheated to the heat treatment temperature, remained in the furnace for the scheduled sintering time (2 h), and then removed to room temperature, thus undergoing temperature quenching, Samples B were heated and cooled at a controlled rate of 10 °C/min.

The X-ray diffraction patterns, associated with the Rietveld refinement method, indicated the systems’ good crystallographic characteristics. The Rietveld refinement method was used to determine the crystallite size and microstrain values for Samples A and B, which were heat-treated at several temperatures. These results are illustrated in Figure 1. As can be seen, Samples A presented larger crystallite sizes, particularly at lower temperatures. Some segregation was detected only at temperatures above 1100 °C in the Ce-(CeO₂) and Y- (Y₂Sn₂O₇) doped systems. No segregation was observed in the La-doped Samples A, which were analyzed using both Rietveld refinements and electron diffraction patterns obtained by TEM. On the other hand, Samples B showed fairly intense phase segregation from 900 °C upward (Y₂Sn₂O₇, La₂Sn₂O₇, or CeO₂).

The strain values were very high for both Samples A and Samples B, indicating that the dopant acted as an Sn substitute in the inner part of the grain (core of the grain). Procedure B appears to be more effective in promoting dopant incorporation, since Samples B displayed a considerably higher strain and more distorted c/a ratio values. It should be noted that the heat-treatment to which Samples A (temperature quenching) were subjected should favor dopant incorporation. Nevertheless, the results presented by Samples B indicated better incorporation of the dopant. Thus, it can be concluded that the dopant source used in route B was far more efficient in keeping the dopant within the oxide matrix.

The Y-doped system was found to present a particular behavior, reinforcing the fact that samples prepared by different procedures may display considerably distinct characteristics. In Samples A, Y doping produced almost no change in crystallite size and strain compared to that in the pure system up to 950 °C (i.e., while the dopant was not segregated). In contrast, the Y-doped system in Samples B exerted a markedly dopant effect. In Samples B, Y doping proved to be considerably more effective in reducing crystallite sizes and increasing strains. These results indicate that, as a result of the method by which Samples A were prepared, the dopant was not incorporated within the matrix, whereas the method used in the preparation of Samples B allowed for the efficient incorporation of the dopant within the matrix. This effect suggests that some of the characteristics or properties of a material can be controlled only by selecting the proper synthesis conditions. On the other hand, it was found that nanostructured ceramics are sensitive to small variations in the preparation route, a fact that should be noted by those who work with this kind of material, i.e., reliability and reproducibility are not that simple.

Another relevant fact is that the nature of the dopant strongly influences the behavior of dopant incorporation. As pointed out above, Y can be well incorporated by procedure B, but not by procedure A. On the other hand, in the case of the samples containing Ce, the influence of the procedure was hardly perceptible, as Samples A and B showed very similar characteristics (crystallite size, strain, and c/a ratio). The La-doped samples displayed an intermediate behavior, with smaller strains and larger crystallite sizes in Samples A than in Samples B, although the dopant effect was not negligible, as it was in the Y-doped system. At higher temperatures, the strain in Sample-B decreased due to dopant segregation. A similar trend was observed in crystallite size, indicating that, in Samples B, La was more strongly incorporated in the Sn–O matrix than it was in Samples A.

The results found for the 3d Sn spectra obtained for all the doped samples (not shown) indicated that there was a slight displacement in the position of the 3d Sn peak in relation to the pure system. This is in agreement with the Rietveld refinement results and suggests that the dopants were strongly incorporated into the Sn–O matrix, since XPS
peak displacement relates to the chemical environment. No significant differences between the peak position of Samples A and B were observed, suggesting that the incorporated fraction of dopant was dissolved in a similar manner in both Samples A and B.

Figure 2 shows the Ce3d and La3d XPS spectra, comparing the results obtained for Samples A and B, and the corresponding oxide, while Figure 2a reveals that no significant signal of oxide was observed on the grain surface of Sample A. In contrast, Sample B shows visible evidence of oxide. Both the La-doped samples shown in Figure 2b present the 3d La profile, indicating the presence of a secondary phase, possibly $\text{La}_2\text{Sn}_2\text{O}_7$, which was detected in the XRD measurements.

Figure 2c depicts the surface concentration, measured by XPS, versus the heat-treatment temperature. An analysis of the peak areas allows one to find the ratio between the concentration of dopant and tin. To obtain these data, the ratio $[\text{dopant}] / [\text{Sn}]$ was calculated based on the total peak area of 3d La and 3d Sn, with the background already subtracted. The same procedure was followed for the Ce-doped samples. The results revealed that, in Samples B, the ratio between [La] and [Sn] increased with the heat treatment temperatures, indicating that the dopant migrated toward the
surface. On the other hand, the ratio between [Ce] and [Sn] decreased from 900 °C upward, suggesting that the dopant was expelled from the matrix. In Samples A, the relation between [dopant] and [Sn] remained almost constant, reinforcing the assumption that this preparation route enhances the dopant’s stability in the tin matrix.

Finally, TEM images (Figure 3) were used to compare the two sample preparation procedures. The crystallite size values obtained by XRD and the values obtained by TEM (Table 2) were in good agreement. The electron diffraction pattern of Ce-doped samples heat-treated at 1100°C confirmed the phase segregation, demonstrating that, under Procedure A, there is the presence not only of the cassiterite phase (SnO₂) but also cerium(IV) oxide (Figure 3c). In the La-doped samples, only the cassiterite phase was detected. On the other hand, in Samples B, phase segregation was observed in all the doped systems. The second phase detected by electron diffraction was CeO₂ in the Ce-doped sample, La₂Sn₂O₇ in the La-doped sample, and Y₂Sn₂O₇ in the Y-doped sample.

In conclusion, this study consisted of an investigation of the influence of the synthesis and processing conditions on undoped SnO₂ and rare earth-doped nanoparticles. Our analysis of the results obtained by XRD associated with Rietveld refinement, XPS spectra, and TEM images led us to conclude that modifications in the synthesis and heat treatment conditions can affect the characteristics of the samples. The use of different synthesis routes may be responsible for the incorporation (or nonincorporation) of the dopant within the matrix. Moreover, the use of oxygen during the elimination of residual organic matter and the use of temperature quenching produces powders with different morphological characteristics.

In addition to the processing effects, it is important to point out that the nature of the dopant is also responsible for the characteristics and behaviors of the samples. Each dopant interacts differently with the SnO₂ lattice, as shown in our XPS results for Ce and La doping, and these differences are critical in determining the final product. We stress the fact
that, when dealing with a form of material as far removed from chemical equilibrium as nanoparticles are, all the variables of the preparation process must be very carefully controlled.

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