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# Synthesis of $SnO_2$ by chemical routes and its use in varistors production

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**Abstract**

Tin oxide, $SnO_2$, is a very used compound in industry and one of its uses is as varistor. For the current requirements of the technology is necessary a strict control of the chemical purity and the particle size of the raw material; for that reason the great interest that exists at the moment to develop synthesis methods that allow to get these requirements. In this work, ceramic powders of the Sn–Co–Nb–Ti–Al system using the controlled precipitation and polymeric precursor (Pechini) methods were synthesized. The raw material obtained was characterized using X-ray diffraction (XRD), thermal analysis (DTA/TG) and scanning electron microscopy (SEM).

The sintering samples shown a good varistor behavior with non-linear coefficient ($\alpha$) values ~22, and $E_r$ 2083 V/cm$^2$.


*Keywords:* Synthesis; Powders-chemical preparation; Electrical properties; Varistors

## 1. Introduction

Tin dioxide ($SnO_2$), is an n-type semiconductor with a crystalline structure of rutile type and has low densification rate due to its high surface diffusion at low temperatures and high partial pressure at high temperatures.[1] Dense $SnO_2$ based ceramics can be achieved by introducing dopants or by hot isostatic pressure processing.[2,3] Dopants with valence +2 can promote densification of $SnO_2$ ceramics due to the formation of solid solution with the creation of oxygen vacancies.[4] Therefore, interest in new $SnO_2$ based ceramic materials has grown in the last years due to their important technological applications.[5] $SnO_2$ is used in electro-optical equipments and glass industry,[6] also it is used as gas sensor, catalyst,[7] and varistor.[8] As varistor tin oxide presents electrical characteristics, highly non-linear, similar to ZnO varistor systems,[9] with the advantage that $SnO_2$ ceramics presents a single phase when the dopants concentration is low, facilitating the microstructural control of the material, and it possesses high resistance to degradation.[10]

Tin oxide have been synthesized through different chemical routes, such as precipitation,[11,12] hydrothermal,[13] sol–gel,[14] and polymeric precursor method (Pechini) among others.

In this work, $SnO_2$ ceramic powders were synthesized by coprecipitation and polymeric precursor methods to obtain Sn–Co–Nb–Ti–Al varistor systems.

## 2. Experimental procedure

The precursors used to obtain ceramic powders and shaping Sn–Co–Nb–Ti–Al varistor systems were $SnCl_2{\cdot}2H_2O$ (Mallinckrodt), $(CH_3CO_2)CO{\cdot}4H_2O$ (Aldrich), $Al(NO_3)_3{\cdot}9H_2O$ (Merck), $TiO_2$ (Aldrich), and $Nb_2O_5$ (Aldrich). The ceramic powders were synthesized using the controlled precipitation method (CPM) and polymeric precursor method, Pechini (PCH)[14,15]. The molar composition of the studied systems is indicated in Table 1. To obtain Tin oxide by CPM, an aqueous solution of $SnCl_2{\cdot}2H_2O$ 0.3 M was prepared; nitric acid ($HNO_3$) was added to increase the salt solubility. After complete dissolution of the salt, it was added $NH_4OH$ (Merck) with a Metrohm Dosimat 685 dosimeter in a controlled way to generate and favor the different hydrolysis and condensation system's reaction.

The pH evolution system was carried out with a Metrohm 744 pHmeter. The dissolution was taken until pH value reached 6.5. The obtained colloidal suspension was filtered and redispersed in 0.05 M diethylamine solution to eliminate chlorine ions. This washing step was made five times. After each washing step, the solution was aged during 24 h. Finally, the colloidal suspension solution was filtered and to this one was added Co, Al solutions and Ti, Nb suspensions. This mixture was homogenized with

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Table 1
Molar composition of Sn–Co–Nb–Ti–Al systems synthesized by CPM and PCH

| | $SnO_2$ | $Co_3O_4$ | $Nb_2O_5$ | $TiO_2$ | $Al_2O_3$ |
|---|---|---|---|---|---|
| SCNT05A | 97.9 | 1 | 0.05 | 1 | 0.05 |
| SCNT1A | 97.85 | 1 | 0.05 | 1 | 0.1 |
| SCNT2A | 97.75 | 1 | 0.05 | 1 | 0.2 |

an ultra-turrax T-50. Later, it was dried at 60 °C and milled in atritor mill during 2 h at 1000 rpm. A similar procedure to obtain the samples by Pechini method was fallowed.

The crystalline phases of $SnO_2$ ceramic powders were determined by XRD (Siemens D-5000). The powder was pressed into pellets by uniaxial pressing followed by isostatic pressing at 210 MPa.

The samples of Sn–Co–Nb–Ti–Al systems were then sintered in an air atmosphere at 1350 °C for 1 h and slowly cooled to ambient temperature. Mean grain size was determined by analyzing the SEM micrographs (Topcom SM-300). Current–tension measurements were taken using a High Voltage Measure Unit (KEITHLEY Model 237). The non-linear coefficient ($\alpha$) was obtained by linear regression of the experimental points using a logarithmic scale around 1 mA/cm$^2$ and the breakdown electrical field ($E_b$) was obtained at this current density.

## 3. Results and discussion

Fig. 1 shows XRD pattern of samples of SCNT05A systems obtained by CPM and PCH and later on thermally treat at 600 °C during 1 h (CPM) and 2 h(PCH) to eliminate all the organic material present in them. Comparing with XRD data of pure $SnO_2$ no other phase besides cassiterite($SnO_2$) in the samples were observed. The amount of additives used was very low and other possible phases may not have been detected owing to the limit detection capacity of XRD.

The TG/DTA curves, Fig. 2b, shows a great loss of weight in the ceramic powders obtained by PCH due to the elimination of the organic material present in the system; the mass loss happens mainly between 80 and the 600 °C where the sample reaches a

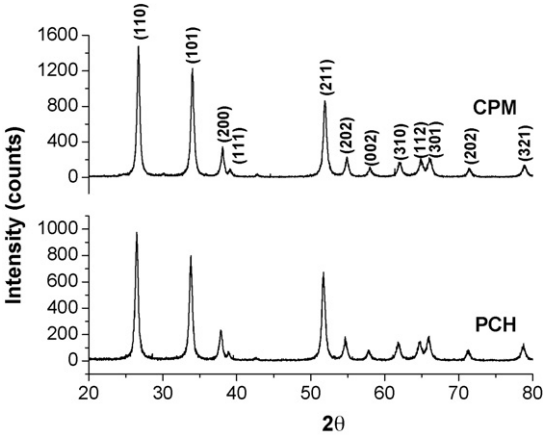


Fig. 1. X-ray diffraction data of the SCNT2A varistor system synthesized by CPM and PCH.

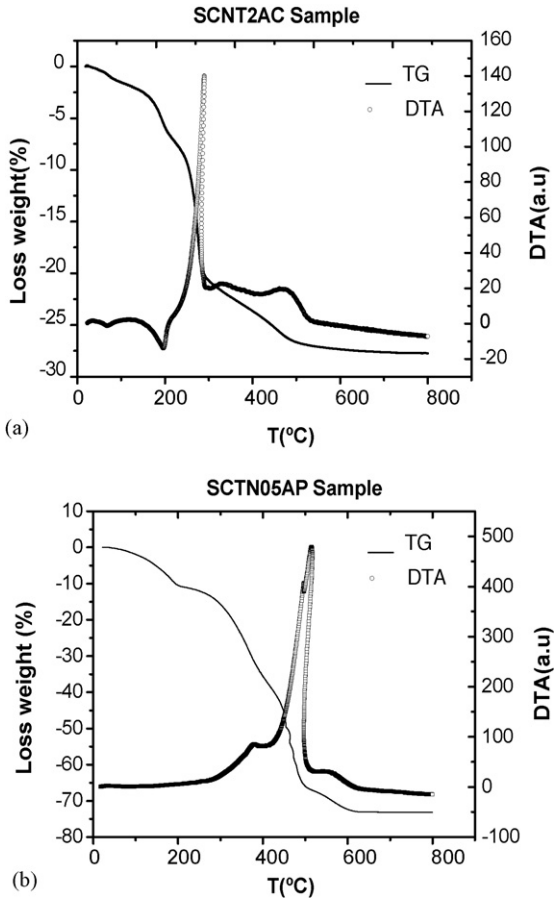


Fig. 2. TG/DTA curve for samples synthesized by CPM and Pechini method: (a) SCNT2AC and (b) SCNT05AP.

constant weight of 25% of the initial value, approximately. In the samples obtained by CPM, and tried thermally, the weight variation is considerably smaller, a weight loss of approximately 28% of the initial value can be mainly attributed to the acetates and nitrates elimination. The TG/DTA curves of the different studied samples present a similar behavior, indicating that the cation precursors concentration has little effect on the behavior of the studied systems in front of the thermal treatments. From Fig. 2 can be defined an optimal calcination temperature of 600 °C, with the purpose of eliminate all the organic material.

The DTA curve (Fig. 2b) corresponding to the samples synthesized by Pechini only presents exothermic picks, between 300 and 600 °C, that indicate the phase organic descomposition and the crystallization of the corresponding oxides present in the sample. On the other hand, the sample synthesized by CPM (Fig. 2a) two endothermic picks are observed at 80 and 200 °C indicating the water and $NH_3$ elimination of the system. The exothermic pick at 300 °C represents, mainly, the phase organic oxidation present in the solid; the other ones that appear between 300 and 500 °C correspond to the nitrates elimination and the oxides crystallization.

Fig. 3 shows that the microstructure of SCNTA bulk ceramics observed by SEM is highly dense, low porosity and apparently single phase, as indicated by the XRD in Fig. 1. The SCNTA systems grain size decreased with the increase in the Al content.

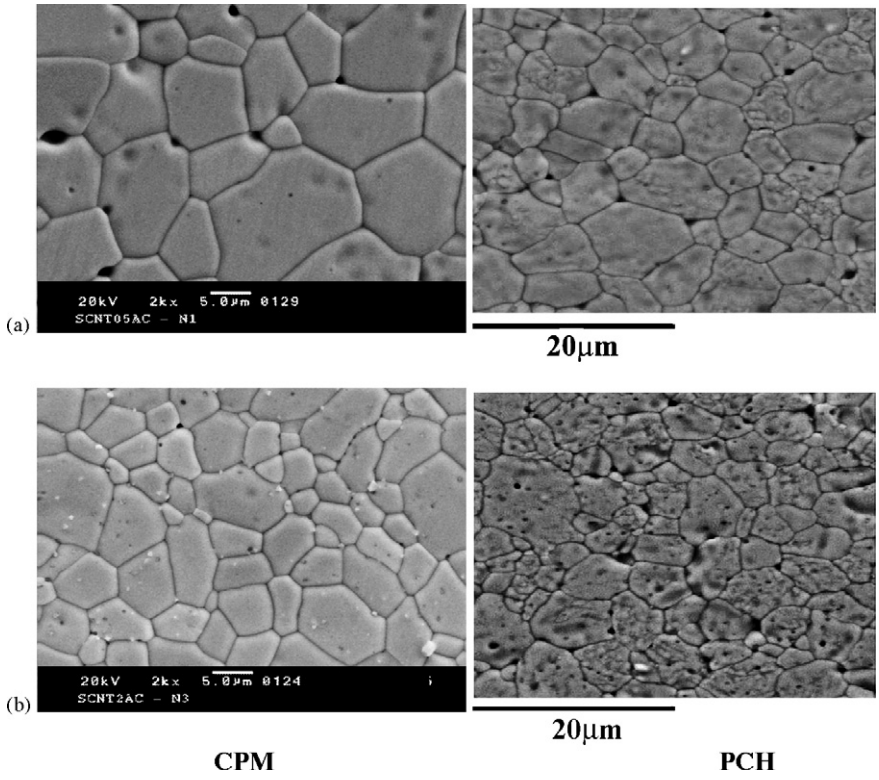


Fig. 3. SEM micrograph of sintered samples at 1350 °C, obtained by CPM and PCH with different $Al_2O_3$ concentration: (a) 0.05% and (b) 0.1%.

Therefore, one of the aluminium functions would be to control the grain growth. The CPM synthesized samples presents better microstructural characteristics that samples synthesized by PCH.

The curves of log $J$ versus log $E$ for the SCNTA systems with different $Al_2O_3$ concentration are shown in Fig. 4. It is observed in this picture that the samples synthesized by CPM increment its $E_r$ when increasing the $Al_2O_3$ concentration. When $Al_2O_3$ concentration was 0.2 mol% this relationship it was not fulfilled in spite of decreasing grain size. The optimum $Al_2O_3$ concentration of the SCNTAC varistor systems was around 0.1 mol%, for this value the best non-linear coefficient $\alpha$ was obtained (see Table 2).

In the varistors obtained by PCH (Fig. 4b) it is clearly observed the aluminium influence since breakdown field $E_r$ behavior can be related very well with decreasing grain size of the ceramics when increasing the $Al_2O_3$ concentration: a non-

Table 2
Microstructural and electrical characteristics more important of SCNTA varistor systems sintered at 1350 °C during 1 h, synthesized by CPM, SCNTAC, and PCH, SCNTAP, with different $Al_2O_3$ concentrations

| Samples | $\alpha$ | $E_b$ (V/cm) | Grain size (µm) | Relative density (%) |
|---|---|---|---|---|
| SCNT05AC | 8.1 | 2809 | 13.4 | 99.85 |
| SCNT1AC | 14.3 | 5304 | 10.3 | 99.71 |
| SCNT2AC | 10.2 | 3217 | 8.3 | 99.56 |
| SCNT05AP | 14.7 | 3410 | 12.4 | 98.05 |
| SCNT1AP | 17.9 | 5087 | 10.5 | 97.12 |
| SCNT2AP | 21.7 | 6330 | 7.4 | 97.89 |

Theoretical density of $SnO_2$ ($d_t = 6.95$ g/cm$^2$).

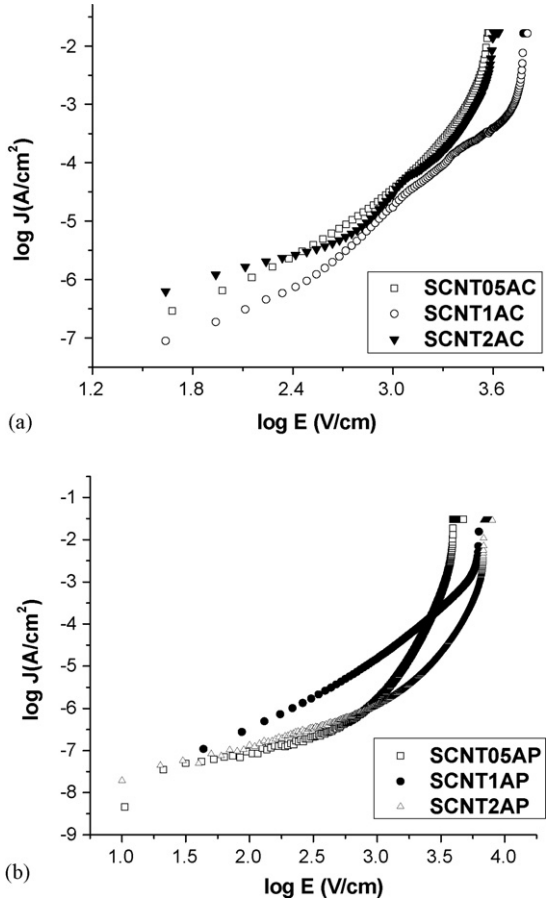


Fig. 4. *I–V* characteristics of samples with different $Al_2O_3$ concentration sintered at 1350 °C.

linear coefficient maximum value was obtained ($\alpha = 21.7$) for the SCNT2AP varistor systems that had a 0.2 mol% alumina concentration; the value of the other electric parameters are indicated in Table 2. Therefore, the optimum $Al_2O_3$ concentration to the studied SCNTAP varistor systems was 0.2 mol%.

## 4. Conclusions

Based on the experimental data, the following conclusions can be drawn:

1. The CPM and PCH chemical methods allow to obtain ceramic powder based on $SnO_2$, where independent of the synthesized method used, second phase does not exist in the systems. This systems presented a good varistor behavior with optimum electrical and microstructure properties.
2. Addition of $Al_2O_3$ inhibits the grain growth and increases the breakdown field of the SCNTA varistor ceramics. The breakdown field is about inversely proportional to the grain size.
3. The ideal $Al_2O_3$ concentration for which it was obtained the best electric characteristics in the SCNTA varistor systems depend of the synthesized method used. In the CPM synthesized systems, the ideal aluminium oxide concentration was 0.1 mol%, while for the ones synthesized by PCH was 0.2 mol%.

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