

The Effect of Cr Concentration and Preparation Method on the Microstructure and Electrical Characterization of SnO₂-Based Ceramics

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Received: January 28, 2003; Revised: July 27, 2003

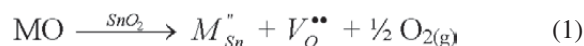
This paper reports a study of the influence of Cr concentration and preparation method in the electrical conductivity and microstructure of SnO₂-based powders doped with Mn and Nb, prepared by an organic route (Pechini method) and a mixture of oxides. All the samples were compacted into discs and sintered at 1300 °C for 3h, resulting in ceramics with relative density varying between 81 and 99%. The powders were morphologically characterized by X-ray diffraction and their specific surface area was determined by N₂ adsorption/desorption isotherms. Electrical conductivity characterization indicated that the conductivity decreases as Cr concentration increases, probably due to Cr segregation at grain boundaries, which reduces grain size, increasing the number of resistive boundaries, thus limiting the passage of current.

Keywords: SnO₂, conductivity, chromium

1. Introduction

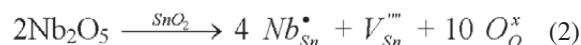
Tin dioxide (SnO₂) is a n-type semiconductor whose tetragonal crystalline structure is similar to the rutile one¹. This dioxide has many uses such as gas sensors, electrodes for electric glass melting furnaces, electrochromic devices, crystal displays, photo detectors, solar cells and protective coatings²⁻⁴. However the use of tin dioxide ceramics is limited due to poor densification during sintering caused by the dominance of non-densifying mechanisms for mass transport such as surface diffusion or evaporation condensation⁵. These mechanisms promote grain coarsening of SnO₂ leading to poor densification of this ceramics⁶.

Dense SnO₂-based ceramics can be achieved by introducing dopants such as MnO₂⁷ or by hot isostatic pressure processing⁸. Dopants with valence +2 can promote densification of SnO₂ ceramics due to the formation of solid solution with the creation of oxygen vacancies⁹, according to:

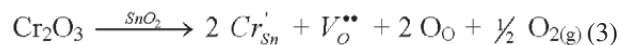


Dopants with valence +5, such as Nb₂O₅, are added to SnO₂ ceramics in small amounts to promote the substitu-

tion of Sn⁺⁴ for Nb⁺⁵, leading to an increase of electronic conductivity in the SnO₂ lattice¹⁰, according to:



The addition of Cr₂O₃ in SnO₂-based ceramics leads to a high non-linearity coefficient of $\alpha = 41$ due the introduction of defects in the crystal lattice that are responsible for the formation of Schottky type potential barriers at the grain boundaries, enabling its use in varistors¹¹. The introduction of Cr₂O₃ in the SnO₂ lattice leads to the substitution of Sn⁺⁴ by Cr⁺³, according to the reaction:



Due to the large influence of Cr⁺³ in the electrical properties of SnO₂-based ceramics, the effect of this ion on electrical conductivity in Sn-Mn-Nb systems, prepared by Pechini method and mixture of oxides, and its correlation with microstructural results were investigated in this work.

2. Experimental Procedure

The powders were prepared using the Pechini

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Trabalho apresentado no XV CBECIMAT, Natal - RN, Novembro de 2002.

method¹²⁻¹³ and mixture of oxides. The Pechini method consisted in the preparation of metallic citrates that were added to a solution of citric acid and ethylene glycol to form a polymeric resin. This resin was pre-calcined (400 °C/4 h) to eliminate organic material, de-aggregated by milling and calcined again (500 °C/15 h) to eliminate residual organic material.

The raw materials were ethylene glycol (Merck), citric acid (Synth), tin chloride (Merck), manganese carbonate (Carlo Erba), niobium oxide (Puratronic), chromium nitrate (Vetec), ammonia solution (Merck) and nitric acid (Merck), tin dioxide (Merck), manganese oxide (Aldrich), chromium oxide (Vetec).

The powders were ground by a ball mill process in an alcohol media. The composition of the molar system was (98.95–X)%Sn + 1.0% Mn + 0.03% Nb + X% Cr, with X equal to 0.0, 0.1, 0.5 and 0.7, all in mole% (see Table 1).

Morphological characterization of obtained powders was done by X-ray diffraction (XRD; SIEMENS D-5000) while the specific surface area was measured by N₂ adsorption/desorption isotherms (BET method; MICROMERITICS ASAP 2000).

The powders obtained were pressed into 8.0 × 1.5 mm discs by uniaxial pressing (20 MPa), followed by isostatic pressing at 210 MPa. The discs were sintered at 1300 °C for 3 h and slowly cooled down to room temperature. The relative densities were determined by the Archimedes method. Mean grain size was determined by analyzing the Scanning electron microscopy micrographies (SEM, TOPCOM SM – 300), using the intercept method¹⁴. The discs for electrical conductivity measurements were subjected to a thermal treatment at 900 °C for 10 h and, after cooling, the plate surfaces were polished and platinum plated to insure a good electrical contact with the platinum tape of the disc holder. Four ohmic contacts were made at the sample using platinum paste. Values of resistance as a function of temperature were collected using a Hewlett-Packard 3457A multimeter connected to a computer.

3. Results and Discussion

The X-ray diffraction patterns of the compositions studied are shown in Fig. 1 for powders prepared by Pechini

method and in Fig. 2 for mixture of oxides. It can be seen that the X-ray diffraction analysis indicates a single phase, the cassiterite, in all systems, as already observed in other reports^{1,5,9-11}.

The values of specific surface area (S_{BET}) and mean particle size (D_{BET}) are given in Table 2. An analysis of these data leads us to conclude that powders prepared by Pechini

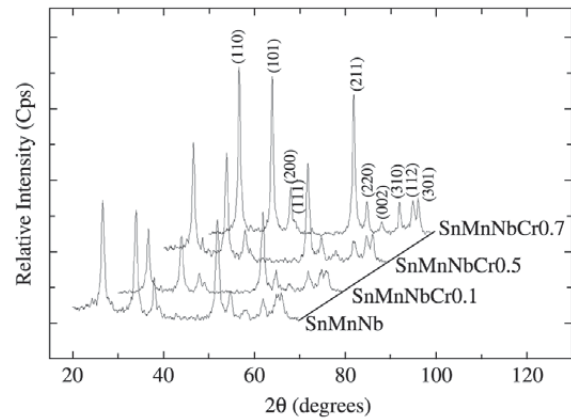


Figure 1. X-ray diffraction patterns of powders prepared by Pechini method, calcined at 500 °C for 15 h.

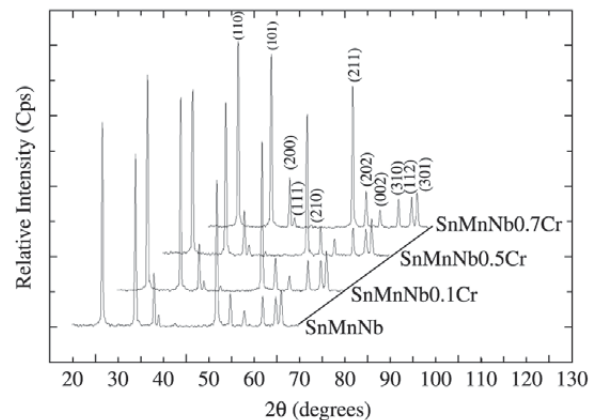


Figure 2. X-ray diffraction patterns of powders prepared by mixture of oxides.

Table 1. Molar system composition and nomenclature used for each system (Pch indicate Pechini method and Mox, mixture of oxides).

Composition of System				Nomenclature	
%Sn	%Mn	%Nb	%Cr		
98.7	1.00	0.03	-	SnMnNbPch	SnMnNbMox
98.6	1.00	0.03	0.10	SnMnNbCr0.1Pch	SnMnNbCr0.1Mox
98.2	1.00	0.03	0.50	SnMnNbCr0.5Pch	SnMnNbCr0.5Mox
98.0	1.00	0.03	0.70	SnMnNbCr0.7Pch	SnMnNbCr0.7Mox

method showed to be finer and more reactive than those prepared by the mixing oxide method and that milling reduces the particle size of powders prepared by Pechini method. The particle size increases with Cr addition for both preparation methods, excepting the system without Cr prepared by mixture of oxides, probably due to a problem in milling. Table 3 presents the relative density of systems before and after sintering. According to this table, addition of 0.1 mole% of Cr presented better densification for both preparation methods. However, by increasing the Cr con-

centration to 0.7 mole%, the final density of the ceramics decreases substantially, which could be associated to the decrease of oxygen vacancy formation at the grain boundary¹¹.

The scanning electron microscopy micrographs are presented in Fig. 3a, 3b, 3c and 3d for ceramics prepared by Pechini method and in Fig. 3e, 3f, 3g and 3h for mixture of oxides. In agreement with the relative density values shown in Table 3, it was found that the ceramics porosity increased with Cr concentration for both preparation methods. This

Table 2. Characterization of powders obtained by Pechini method and mixture of oxides, before and after milling: theoretical density, BET surface area and mean particle size.

System	d _{theoretical} (g/cm ³)	Pechini method				Mixture of oxides	
		S _{BET} (m ² /g)		D _{BET} (μm)		S _{BET} (m ² /g) M8 h	D _{BET} (μm) M8 h
		WM*	M8 h**	WM	M8 h		
SnMnNb	6.919	36.6	44.1	0.024	0.020	8.50	0.102
SnMnNbCr0.1	6.916	37.7	42.9	0.023	0.020	12.1	0.072
SnMnNbCr0.5	6.902	36.1	38.6	0.024	0.023	9.92	0.088
SnMnNbCr0.7	6.897	22.0	28.6	0.040	0.030	9.38	0.093

* WM = without milling;

** M8 h = grinding for 8 h in a ball milling.

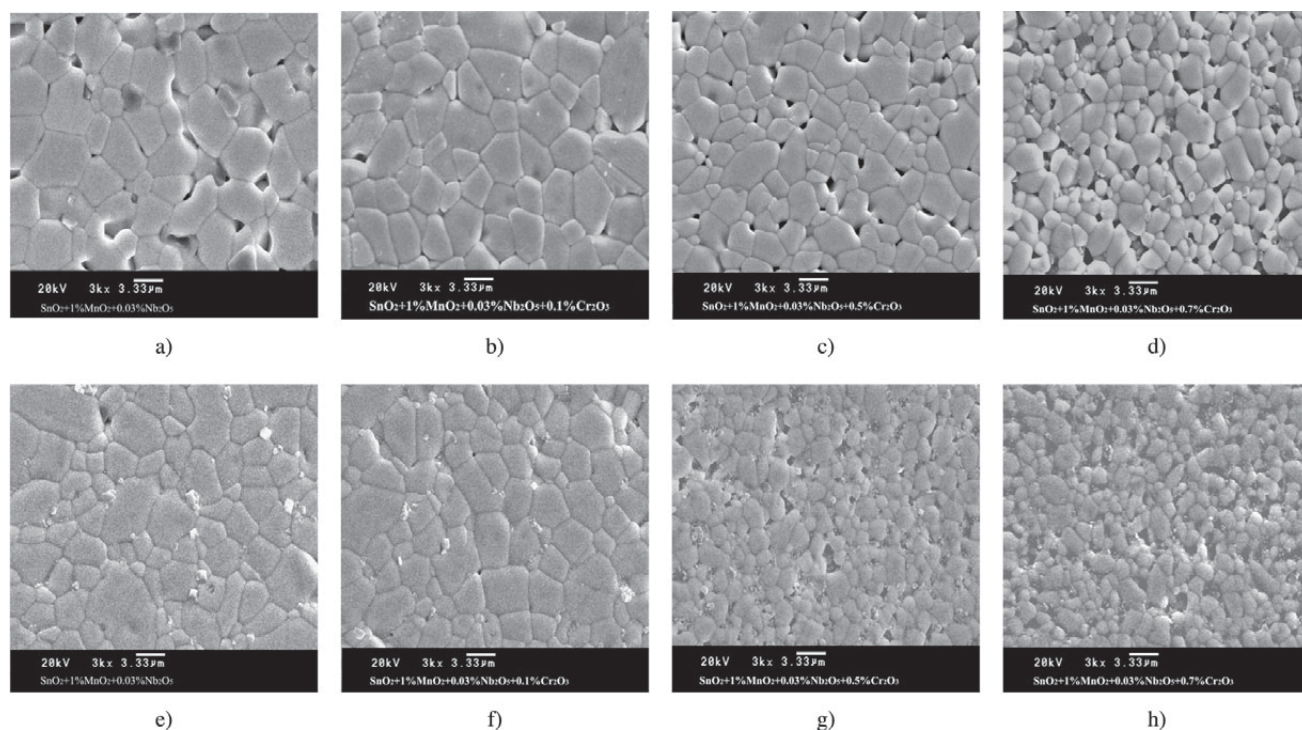


Figure 3. a) SEM micrographs of sintered compacts at 1300 °C for 3 h, prepared by Pechini method, with: (a) 0.0% mol of Cr; b) 0.1% mol of Cr; c) 0.5% mol of Cr; d) 0.7% mol of Cr; and prepared by mixture of oxides, with: e) 0.0% mol of Cr; f) 0.1% mol of Cr; g) 0.5% mol of Cr; h) 0.7% mol of Cr.

increase in porosity is probably due to the segregation of Cr at the grain boundary region, impairing mass transport during sintering. The ceramics systems are characterized by heterogeneous grain size distribution.

Table 4 shows the variation of Cr concentration on mean grain size. Increasing Cr concentration leads to microstruc-

Table 3. Relative density (d_R) of green compacts and sintered compacts at 1300 °C for 3 h.

System	Pechini method		Mixture of oxides	
	Green d_R (%)*	Sintered d_R (%)	Green d_R (%)	Sintered d_R (%)
SnMnNb	50.6	91.8	53.5	98.6
SnMnNbCr0.1	49.5	98.3	54.1	99.4
SnMnNbCr0.5	50.6	94.6	54.0	87.2
SnMnNbCr0.7	51.9	88.5	53.7	81.0

* The relative density was calculated considering the theoretical density of the system.

** $P = 100 - d_R$

Table 4. Mean grain size ($S_{\text{grain}}/\mu\text{m}$) of systems sintered at 1300 °C for 3 h.

System	$S_{\text{grain}} \pm \text{standart deviation } (\mu\text{m})$	
	Pechini Method	Mixture of Oxides
SnMnNb	4.5 ± 1.4	3.7 ± 1.6
SnMnNbCr0.1	4.4 ± 1.6	3.6 ± 1.5
SnMnNbCr0.5	2.8 ± 1.2	1.8 ± 0.6
SnMnNbCr0.7	2.1 ± 0.8	1.8 ± 0.6

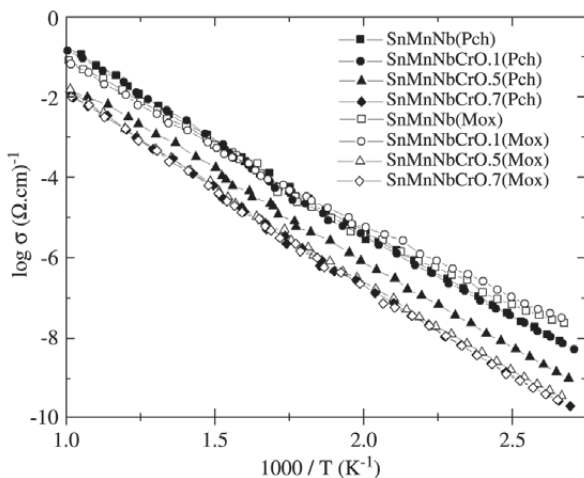


Figure 4. Electrical conductivity as a function of temperature of system SnMnNbCr_x, with $0 \leq x \leq 0.7\%$ mol, sintered at 1300 °C for 3 h.

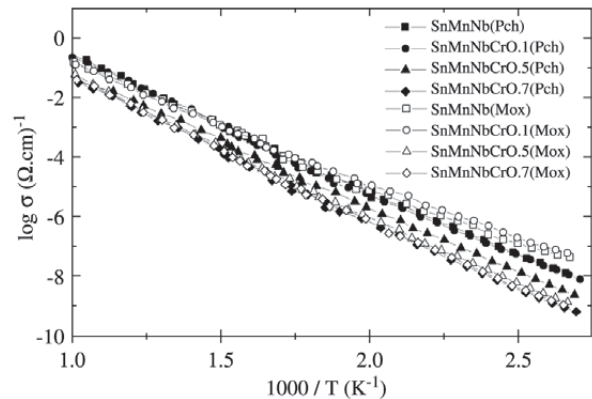


Figure 5. Electrical conductivity normalized to grain size as a function of temperature of system SnMnNbCr_x, with $0 \leq x \leq 0.7\%$ mol, sintered at 1300 °C for 3 h.

tures with decreasing mean grain size for both preparation methods. The decrease in mean grain size could be associated to segregation in the grain boundaries.

The dependence of the conductivity on the temperature is shown in Fig. 4. The conductivity decreases with decreasing temperature, what is expected for this semiconductor oxide. Normalizing these curves to grain size (Fig. 5), a significant decrease in conductivity for ceramics doped with Cr concentration higher or equal than 0.5 mole% was observed. Also, this is probably due to Cr segregation at the grain boundaries, which reduces mean grain size, so that the number of resistive boundaries increases, limiting the passage of current.

4. Conclusion

The relative density results agree with the scanning electron microscopy micrographs. The ceramic microstructure is strongly dependent on the Cr concentration. The Cr forms a phase segregated at the grain boundary and appears to control the sintering and grain growth rates. Thus, excess of it in the chemical composition leads to the formation of porous microstructure, deleterious for electrical conductivity.

Acknowledgments

The financial support of this research by FAPESP, CNPq and CAPES is gratefully acknowledged.

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