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SnO$_2$ Dense Ceramic Microwave Sintered with Low Resistivity

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ABSTRACT

The Hall-Héroult process is used for alumina reduction by the use of graphite anodes even though it involves a high emission of carbon dioxide (CO_2) and several other organic compounds. Proposals have been made aiming at substituting graphite for a single-phase SnO_2-based ceramic with low resistivity and chemical resistance to cryolite, which is characterized as an inconsumable anode, reducing pollutant emissions. To this end, a wide range of studies were carried out on SnO_2-based ceramics modified with ZnO as a densification aid doped with the promoters of electrical conductivity such as Nb_2O_5, Al_2O_3 and Sb_2O_3 through a mixture of oxides and hybrid sintering in a microwave oven. The pressed pellets were sintered in a microwave oven up to 1050°C under a constant heating rate of 10°C/min. After sintering, the density was determined by the Archimedes method, the phases were then characterized by X-ray diffraction, the microstructure and chemical composition resulting from the sintered SnO_2-based ceramics were also investigated by field emission scanning electron microscopy (FE-SEM) coupled with an energy-dispersive X-ray spectroscopy (EDS) and the electrical properties were determined by the measurements of the electric field × current density. A single-phase ceramic was obtained with a relative density of above 90% and electrical resistivity of 6.1 Ω·cm at room temperature. The ceramics obtained in this study could be a potential candidate as an inconsumable anode to replace the current fused coke used in the reduction of alumina.

Keywords: Tin Oxide; Anodic Electrode; Inconsumable Anode; Microwave Sintering; Electrical Resistivity

1. Introduction

To obtain the primary aluminum, the industries use the reduction process which is constituted by the extraction of metal (aluminum) from its oxide (alumina). The alumina is placed into an electrolytic vat (Hall-Héroult cell) basically formed by a carbon electrode and an electrolyte of cryolite (Na_3AlF_6-sodium hexafluoroaluminate), a melted mineral at a temperature of approximately 1000°C, which is used as a solvent for aluminum. However, the side effect has to do with the release of CO_2 in the atmosphere, one of the gases responsible for the greenhouse effect.
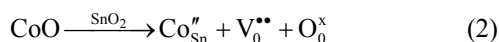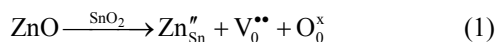
In order to reduce this effect, Clark [1], Alder [2,3] and Hansey [4] patented the inconsumable anodic SnO_2-based electrode which eliminates the consumption of graphite or coke. However, it was found out that these electrodes have a high concentration of additives, such as CuO and Sb_2O_3, which lead to the formation of segregates and/or precipitates at the grain boundaries, reducing their chemical resistance to cryolite. These precipi-

tated additives at the grain boundaries can lead to an increased rate of corrosion of the electrode, thereby reducing its useful life. In addition, SnO_2 electrodes are subject to corrosion by hydrogen from the molten cryolite bath and by ceramic compounds such as perovskite or spinel formed in the bath. Therefore, it is believed that the development of a single phase of SnO_2 ceramics would increase the corrosion resistance, leading to an improvement in the electrolytic process. Electrodes of similar composition to those proposed were patented by Citti *et al.* [5] and used for melting glass.

Tin oxide SnO_2 is an n-type semiconductor whose crystal structure is similar to the tetragonal rutile. The use of ceramic oxide, when pure, is found to be limited due to its low densification during sintering because of the high surface diffusion at low temperatures and the high partial pressure of this oxide at high temperatures [6]. So it was necessary to add densification agents to obtain densities greater than 90% during sintering.
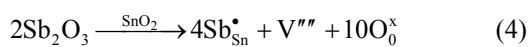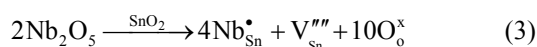
The densification of SnO_2 became feasible by the ad-

dition of densifying agents such as ZnO [7] and CoO [8] taking the process of oxygen vacancies generation into consideration, leading to diffusion when in solid solution, as shown in Equations (1) and (2):

$$ZnO \xrightarrow{SnO_2} Zn''_{Sn} + V_0^{\bullet\bullet} + O_0^x \qquad (1)$$

$$CoO \xrightarrow{SnO_2} Co''_{Sn} + V_0^{\bullet\bullet} + O_0^x \qquad (2)$$

The single-phase ceramic with high density greater than 95% becomes interesting to prevent aluminum infiltration, when dissolved in cryolite at 1000°C, this infiltration of both aluminum and cryolite can cause cracks in the electrode or the reaction of these materials with segregates and/or precipitates at the grain boundaries, thus weakening the electrode.

According to Pianaro et al. [9], doping with Nb₂O₅ causes an increase in the ceramic conductivity. The addition of metals with charges higher than that of Sn^{4+} leads to an excess of electrons or cations vacancies in the crystal structure. On the other hand, the addition of metals with charges lower than that of Sn^{4+} causes electron acceptor defects [10] as shown in Equations (3) and (4):

$$2Nb_2O_5 \xrightarrow{SnO_2} 4Nb_{Sn}^{\bullet} + V_{Sn}'''' + 10O_0^x \qquad (3)$$

$$2Sb_2O_3 \xrightarrow{SnO_2} 4Sb_{Sn}^{\bullet} + V'''' + 10O_0^x \qquad (4)$$

Oliveira et al. [11] found out that the antimony oxide acts as an electron donor, increasing the conductivity of the SnO₂-based ceramics. Although this oxide is trivalent and contains fewer valence electrons than tin, studies on SnO₂-based varistors indicate the coexistence of Sb^{5+} and Sb^{3+} and that the ratio between them depends on both the temperature as well as the oxygen concentration in the environment [12]. In order to explain the electrical behavior of SnO₂ doped with Sb₂O₃, Mishra et al. [13] carried out quantum-mechanical calculations for the SnO₂-Sb₂O₃ system and showed that antimony ions form an impurity band partially filled by free electrons within the band gap of tin oxide.

Coleto Júnior [14] studied the action of Al₂O₃, which decreases the resistivity of SnO₂ ceramics and this can be duly confirmed from the results obtained by Kovalevsky et al. [15]. Once Al₂O₃ is introduced in the SnO₂ lattice, the Al^{3+} replaces the Sn^{4+}, creating electron acceptors defects, as shown in Equation (5), with similar effect to that of Sb₂O₃:

$$Al_2O_3 \xrightarrow{SnO_2} 2Al'_{Sn} + V_0^{\bullet\bullet} + 3O_0^x \qquad (5)$$
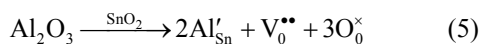
According to Ivanova et al. [16], working with ytria stabilized zirconia (YSZ), the addition of Al₂O₃ reduced the resistivity of the grain boundary of this ceramic, and thus removing the silica. This "cleaning effect" occurs because the Al₂O₃ forms a liquid phase (silicon aluminate) once it is in contact with silica, moving to the triple point and cleaning the grain boundary.

Clark [1] obtained a resistivity of 0.0025 Ω·cm at 975°C, while Citti et al. [5] obtained 0.1 Ω·cm at room temperature, these data were used as comparison parameters with the results obtained in the present work.

Gisane Gasparotto et al. [17] verified the possibility of obtaining low resistivity SnO₂-based ceramics using microwave sintering. The ceramics obtained showed uniform microstructure with little presence of intra or intergranular pores, and they neither observed the presence of precipitates and/or segregates at the grain boundaries nor triple points. In contrast, a different result was obtained when conventional sintering was used, for purposes of comparison, see **Figure 1**. The ceramic with 99.00% mol of SnO₂, 0.95% mol of ZnO and 0.05% mol of Nb₂O₅, sintered by microwave, showed an ohmic behavior with a resistivity of 1.3 ohm.cm and 93% of density.

Thus, the objective of this work was to investigate the influence of the Al₂O₃ and the Sb₂O₃ in different compositions on the electrical resisivity of SnO₂ doped with 0.95% mol of ZnO and 0.05% mol of Nb₂O₅, sintered in conventional oven and microwave, aiming at
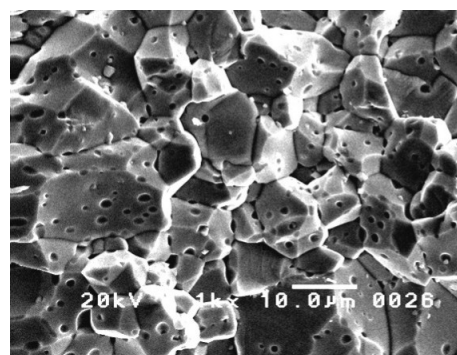
(a)
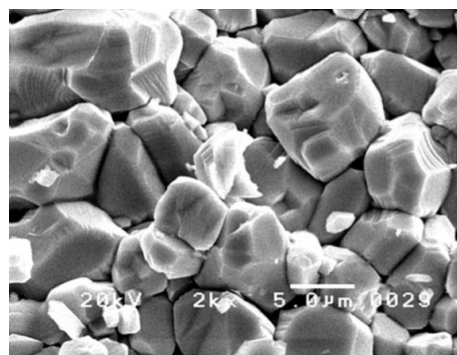
(b)

Figure 1. Micrographies of fractured samples of the composition of 99.00% mol SnO₂ + 0.95% mol de ZnO + 0.05% mol de Nb₂O₅, fractured obtained by conventional (a) microwave and (b) sintering [17].

obtaining a greater reduction in the resistivity of the SnO_2-based ceramics.

Heating with Electromagnetic Radiation of Microwave

The microwaves were first produced and studied by Hertz in 1886, but their practical application became possible with the development of appropriate generators such as Klystrons and magnetrons [18].

During this type of sintering, the microwave energy is transformed into heat directly within the material through the interaction of molecules and atoms with the electromagnetic field, which enables internal and volumetric heating of the material, causing the formation of temperature gradients and reversed heat flow [19]. The cleaner grain boundaries obtained without pores, segregates and/or precipitates was attributed to microwave sintering as a result of the vibration mechanism caused by the microwaves, which favors the transfer of matter during the sintering process [17-22]. The advantages found for the microwave sintering include the reduction of heating time, energy savings, the volumetric heating, high heating rates and better control of sintering. However, the method has also some disadvantages, such as small microwave absorption at low temperatures for the SnO_2, requiring the use of hybrid sintering with silicon carbide, which may present the phenomenon of "thermal runaway" or leaking of temperature and thermal gradients during heating that can damage the ceramic device [19].

Figure 2 illustrates the loss tangent of some aluminas with different purities. The losses increase with increasing temperature, this behavior is a typical characteristic of the ionic solids such as Al_2O_3 and SnO_2, and of covalent solids as well, such as Si_3N_4 and AlN, and occurs at temperatures between 40% to 50% of the fusion tem-
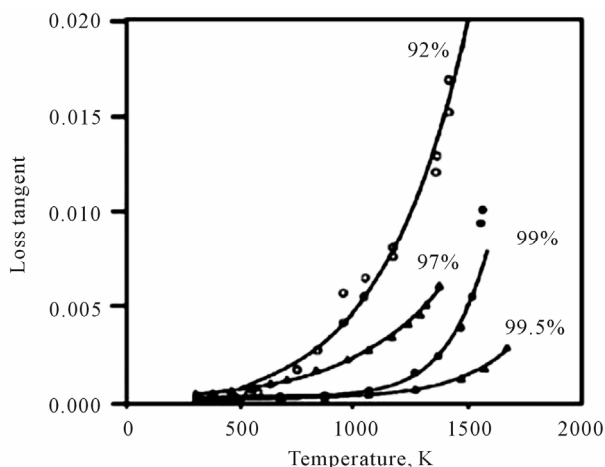
peratures. At these temperatures, the bonds between ions in the ionic crystals begin to break apart while the electrons in the covalent materials begin to migrate towards the conduction band, increasing the conductivity of the material. The softening of glassy and amorphous phases is also responsible for the sparking increases in the dielectric losses of the ceramic materials, being more significant in materials with low purity (<98%) [20].

In an attempt to solve these problems, the hybrid sintering was developed, which uses a silicon carbide as a susceptor that absorbs microwave radiation, causing the initial heating of the sample at low temperature until it reaches higher temperatures, beginning to absorb microwave energy more efficiently and heating up quickly.

2. Materials and Methods

The starting materials included the following commercial oxides: SnO_2 (Cesbra, 99.9%), ZnO (Unimaua, 99.9%), Nb_2O_5 (Alfa Aesar, 99.9%), Al_2O_3 (A300, 99.9%), and Sb_2O_3 (Vetec, 99.0%). The studied compositions were: 99.00% mol of SnO_2, 0.95% mol of ZnO, 0.05% mol of Nb_2O_5 modified with 0.05%; 0.10%; 0.25% and 0.50% mol of Al_2O_3 and Sb_2O_3. The oxides were mechanically mixed in isopropyl alcohol for 60 min., using zirconia balls as the medium. After drying, the powders passed through a 150 mesh (75 μm) sieve for de-agglomeration and were then compacted into 12 mm diameter with 2 mm thickness specimens and isostatically pressed at 210 MPa to a green density of 57% - 60% of the theoretical density (6.994 g/cm³). The pellets were sintered in two types of furnaces: conventional oven up to 1400°C, at a constant heating rate of 10°C/min and in a microwave oven up to 1050°C with a constant heating rate of 10°C/min, both in an oxygen sintering atmosphere. For the microwave sintering, a hybrid oven (CEM-Phoenix) was used, with magnetron of 770 W and frequency of 2.45 GHz, adapted in our laboratory to reach high temperatures. After measuring the sintered densities by the Archimedes method, the phases were then analyzed by XRD (RIGAKURINT2000 42 kV/120 mA). The resistivity was measured using the current source Keithley 2410-C 1100 V. In order to carry out the current × voltage measurements, the sintered samples were polished and metallized with gold by sputtering. The morphology of the ceramic compacts were analised by field emission scanning electron microscopy (FE-SEM—JEOL Model JSM 7500F) coupled with an energy-dispersive X-ray spectroscopy (Thermo Scientific, Noran System 7).

3. Results and Discussion

3.1. X-Ray Analyses

All X-ray diffraction patterns obtained in the present study indicated that there is no other phase formation

Figure 2. Loss tangent of some samples with alumina (the % indicates the purity) [19].

other than that of the SnO$_2$ (cassiterite) phase. Thus, even using the maximum amount of modifiers proposed in the compositions described above, it turns out that secondary phases were not formed during the microwave sintering, which could at least be detected by X-ray diffraction. **Figure 3** illustrates the results for the compositions with the highest amount of modifiers.

3.2. Sintering and Densities

After sintering, the relative densities of pellets were calculated by the Archimedes method and the results are illustrated in **Table 1**.

It is observed from this table that given an increase in the amount of modifiers, the relative density of the samples decreases. Densities close to the proposed density of 95% for the modified ceramic with 0.05% mol of Al$_2$O$_3$ and 0.05% mol of Sb$_2$O$_3$ were obtained. For the composition modified with 0.05% mol of Al$_2$O$_3$ the
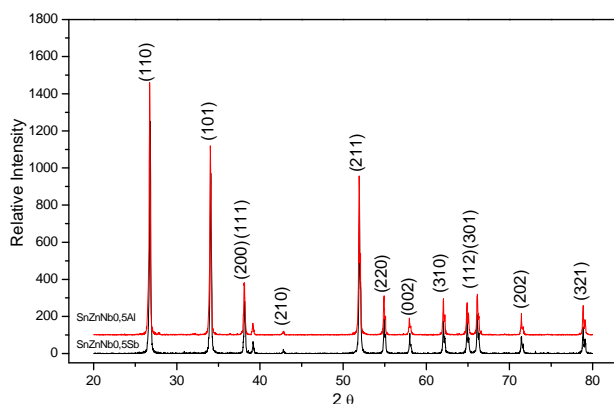

Figure 3. X-Ray diffraction patterns of powders of the systems modified with 0.5% mol of Al$_2$O$_3$ and 0.5% mol of Sb$_2$O$_3$.

Table 1. Results of relative density for the pellets sintered in a conventional oven (1400˙C/4h - 10˙C/min) and microwave (1050˙C/30min - 10˙C/min).

Composition: SnO₂ + 0.95 mol% of ZnO + 0.05 mol% of Nb₂O₅ (mol%)+ x% Al2O3	Density (g/cm³)	
	Conventional Oven	Microwave Oven
0.05 Al₂O₃	95.5%	94.5%
0.10 Al₂O₃	94.5%	92.1%
0.25 Al₂O₃	94.0%	90.6%
0.50 Al₂O₃	91.3%	90.0%
0.05 Sb₂O₃	93.8%	92.0 %
0.10 Sb₂O₃	91.6%	91.0%
0.25 Sb₂O₃	88.1%	90.1%
0.50 Sb₂O₃	84.7%	86.6%

relative density was 95.5% for the conventional sintering and 94.5% for the microwave sintering and for the composition modified with 0.05% mol of Sb$_2$O$_3$, 93.8% was obtained for the conventional sintering and 92.0% for the microwave sintering. These values are very close to our goals, indicating that it is possible to obtain these ceramics with high densities. Increasing the concentration of modifiers leads to a decrease in density, probably due to segregation of phases formed by Al and Sb at the grain boundaries. This was observed in the previous work by Perazolli *et al.* [21], where they found out that the addition of more than 1.00% mol of ZnO forms SnZnO$_3$ phase, hindering densification. Thus, the maximum amount of modifiers added to the SnO$_2$ system in this study did not exceed 1.00% mol.

3.3. Electrical Properties

The electrical properties of these systems were analysed by the current × voltage measurements at room temperature. The results are shown in **Table 2**.

Figure 4 illustrates the plots of electric field × current density calculated by the current × voltage measurements at room temperature with the results listed in **Table 2**. From this Table, it can be observed that the samples sintered in conventional oven showed a non-ohmic behavior except for the samples modified with 0.25% and 0.50% mol of Sb$_2$O$_3$, indicating that this oxide also decreases the resistivity of the ceramic. A resistivity of 6.1 Ω·cm was obtained for the sample with 0.10% mol of Sb$_2$O$_3$. However, during the microanalysis of this system, segregations and precipitations were found at the grain boundaries in the form of grains smaller than those of the matrix (**Figure 5(b)**).

The decrease of matrix resistivity was attributed to

Table 2. Results of the electrical characterization for the pellets sintered in conventional oven (1400˙C/4h - 10˙C/min) and microwave (1050˙C/30min - 10˙C/min).

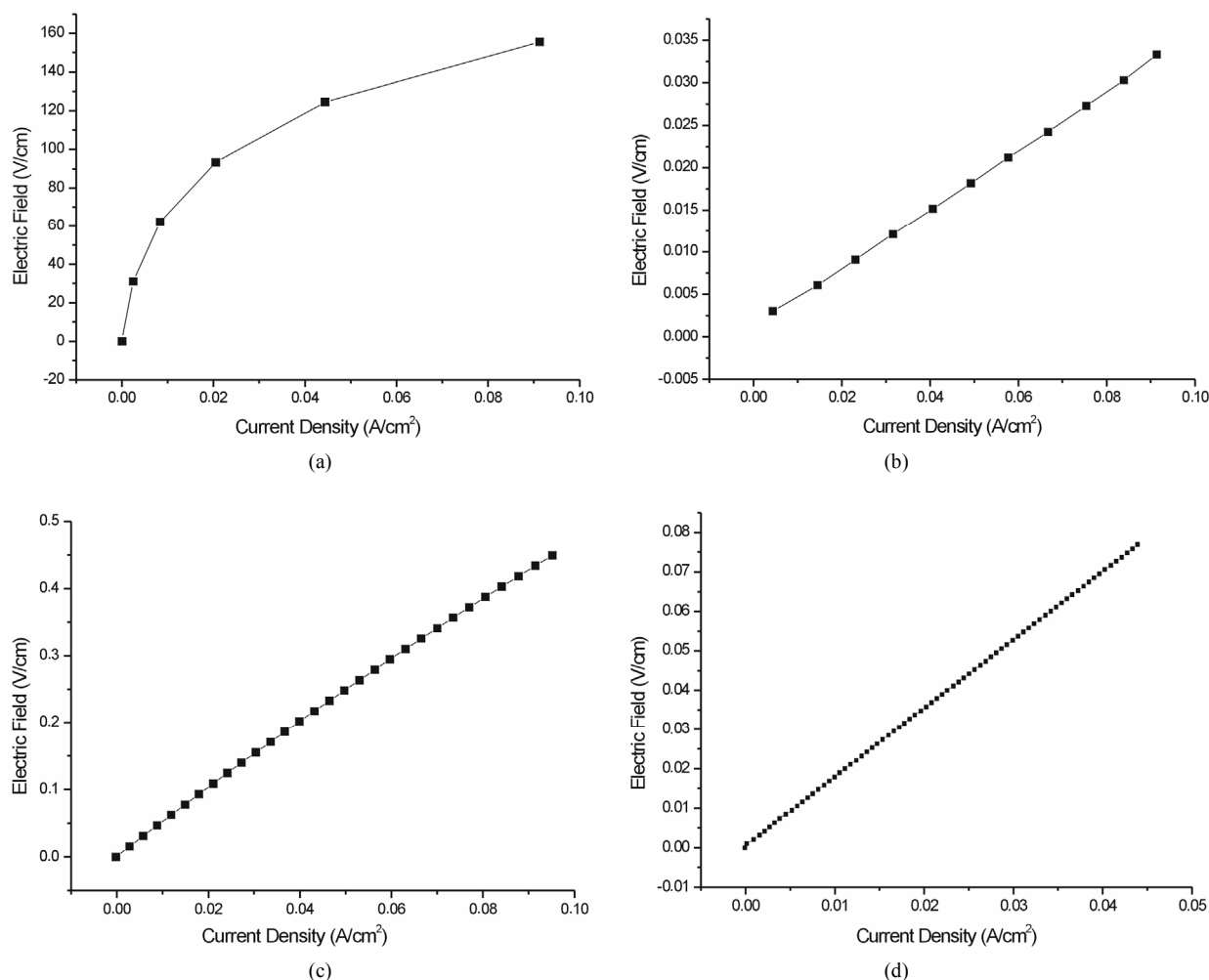| Composition: SnO₂ + 0.95 mol% of ZnO + 0.05 mol% of Nb₂O₅ (mol%)	Nonlinearity coefficient α or Resistivity (Ω·cm)	
	Conventional Oven	Microwave Oven
0.05 Al₂O₃	1.8	55.5
0.10 Al₂O₃	2.5	10.1
0.25 Al₂O₃	3.9	26.1
0.50 Al₂O₃	4.5	25.9
0.05 Sb₂O₃	1.8	8.1
0.10 Sb₂O₃	1.2	6.1
0.25 Sb₂O₃	51.7	9.8
0.50 Sb₂O₃	3.8	9.3

Figure 4. Electric field × current density measurements at room temperature of the samples sintered in conventional oven: (a) modified with 0.05% mol of Sb$_2$O$_3$; (b) modified with 0.50% mol of Sb$_2$O$_3$ in microwave oven; (c) modified with 0.05% mol of Al$_2$O$_3$ and (d) modified with 0.50% mol of Al$_2$O$_3$.

these formations, which consist of conductive phases, and also to the formation of Sb^{5+} during heating, leading to the formation of free electrons by the generation of metal vacancies as shown in Equation (6).

3.4. Scanning Electronic Microscopy

In order to verify the action of the modifiers (Sb and Al) on the crystal structure of SnO$_2$, samples with large excess of cations were produced. From **Figure 5**, it can be observed as expected that the Al formed a liquid phase and was segregated at the grain boundaries. The triple point is formed at the grain boundaries by the joining together of three grains with three dimensions instead of 2 as seen on the grain boundary. This action may be positive provided the goal is to eliminate contaminations, responsible for increasing the ceramic resistivity at the grain boundaries (**Figure 5(a)**). Further addition of Sb resulted in segregated phases at the grain boundaries forming precipitates

in the form of small grains observable in **Figure 5(b)**.

All the compositions with modifiers sintered in microwave oven presented an ohmic behavior, however the behavior was opposite to that presented by the samples sintered in conventional oven. For samples modified with Sb$_2$O$_3$, it was found out that the amount of Sb did not significantly affect the value of resistivity, with the results obtained being equivalent to the lowest value obtained by conventional sintering 6.1 Ω·cm. Thus, it can be concluded that during the microwave sintering, Sb tends to reduce the resistivity of the system regardless of the concentration, due to a larger extent to a greater diffusion of Sb in SnO$_2$. The influence of the segregated phases at the grain boundaries, in this case, should not be considered once the microwave sintering produces ceramic with cleaner grain boundaries.

The addition of Al$_2$O$_3$ in the samples sintered in conventional oven leads to an increase in non-ohmic behavior with the increase in the value of α, or an increase in
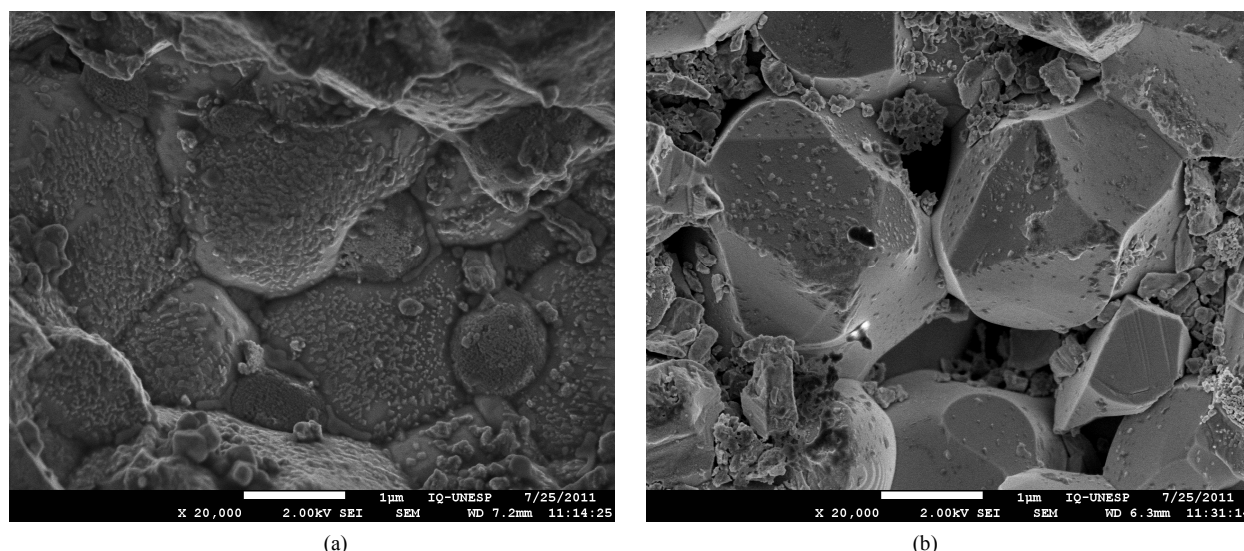

(a)

(b)

Figure 5. Micrographs of the ceramics with large amounts of modifiers (1.00% mol): (a) Al and (b) Sb.

resistivity, due to the probable segregation of phases formed with aluminum excess at the grain boundaries, as can be observed by FE-SEM, **Figures 5** and **6**.

The addition of Al did not contribute to the decrease in resistivity. Indeed for a further addition of modifiers, the obtained resistivity 10.1 $\Omega \cdot$cm is found to be equivalent to the resistivity obtained for ceramics without Al [17] 1.3 $\Omega \cdot$cm. The aluminum has only the cationic form Al^{3+} with a tendency to form aluminates and segregates at the grain boundaries, moving to the triple points [15,16], cleaning the boundaries (**Figure 5(a)**) and thus justifying the observed decrease in resistivity with the increase in the addition of Al.

The effect of sintering on the microstructure can be seen in **Figure 6**, which presents the microstructure of samples with the same composition sintered in conventional oven as well as in microwave oven. The micrographs illustrate that the samples sintered in microwave oven showed little or no pore formation and segregations at the grain boundaries as compared to the samples sintered in conventional oven, leading to the formation of a cleaner microstructure as a result of the diffusion caused by the microwave heating.

3.5. Cations Diffusion

During the microwave sintering, there is a greater diffusion of cations and anions of the SnO₂-based ceramics, due to the vibrational characteristics of the microwave heating. Hence, Sb diffuses in the SnO₂ matrix, leading to a decrease in resistivity, as shown in **Table 2**. However, as the concentration of Sb increases the value of the resistivity does not decrease, this could be attributed to another mechanism. Further investigation is therefore being conducted in order to arrive at a flawless explanation.

Nonetheless, due to the shorter time and lower temperature for the microwave sintering, it can be observed that the average size of the grains obtained is smaller to that obtained by conventional sintering. Moreover, given an increase in the sintering temperature coupled with a reduction in the heating rate and/or an increase in the isothermal sintering, it is possible to increase the average size of the grains with a probable reduction in resistivity.

The analysis of the compositions at the grain boundaries was performed by means of FE-SEM/EDS and the presence of Al (**Figure 7**) and Sb (**Figure 8**) modifiers can be observed at the grain boundaries of SnO₂-based ceramics. However, as can be seen on the micrographs of the ceramics containing Sb, the peaks in keV for the Sn have values close to those of the Sb and the presence of Sb was determined by the change in the peaks, which showed the formation of an irregularity in the form of shoulders. After analyzing all the points shown in **Figure 7**, only points 1, 3, and 5 showed peaks of Al in 1.52 keV. In **Figure 8(b)**, the vertical bars that are clearly observed indicate the position of the peaks in keV for Sb, the formation of irregularities can also be seen in the peaks in the form of shoulders, which are attributed to the presence of Sb at the grain boundaries.

4. Conclusions

Single-phase SnO₂ based-ceramics were obtained with high density and low resistivity by the conventional mixed oxide method, doped with Zn^{+2}, Nb^{5+}, Al^{3+} and Sb^{3+} using microwave sintering. The addition of modifiers in SnO₂, with total concentrations above 1.00% mol leads to the formation of segregates at the grain boundaries in both sintering methods.

The microwave sintering is indicated for the production
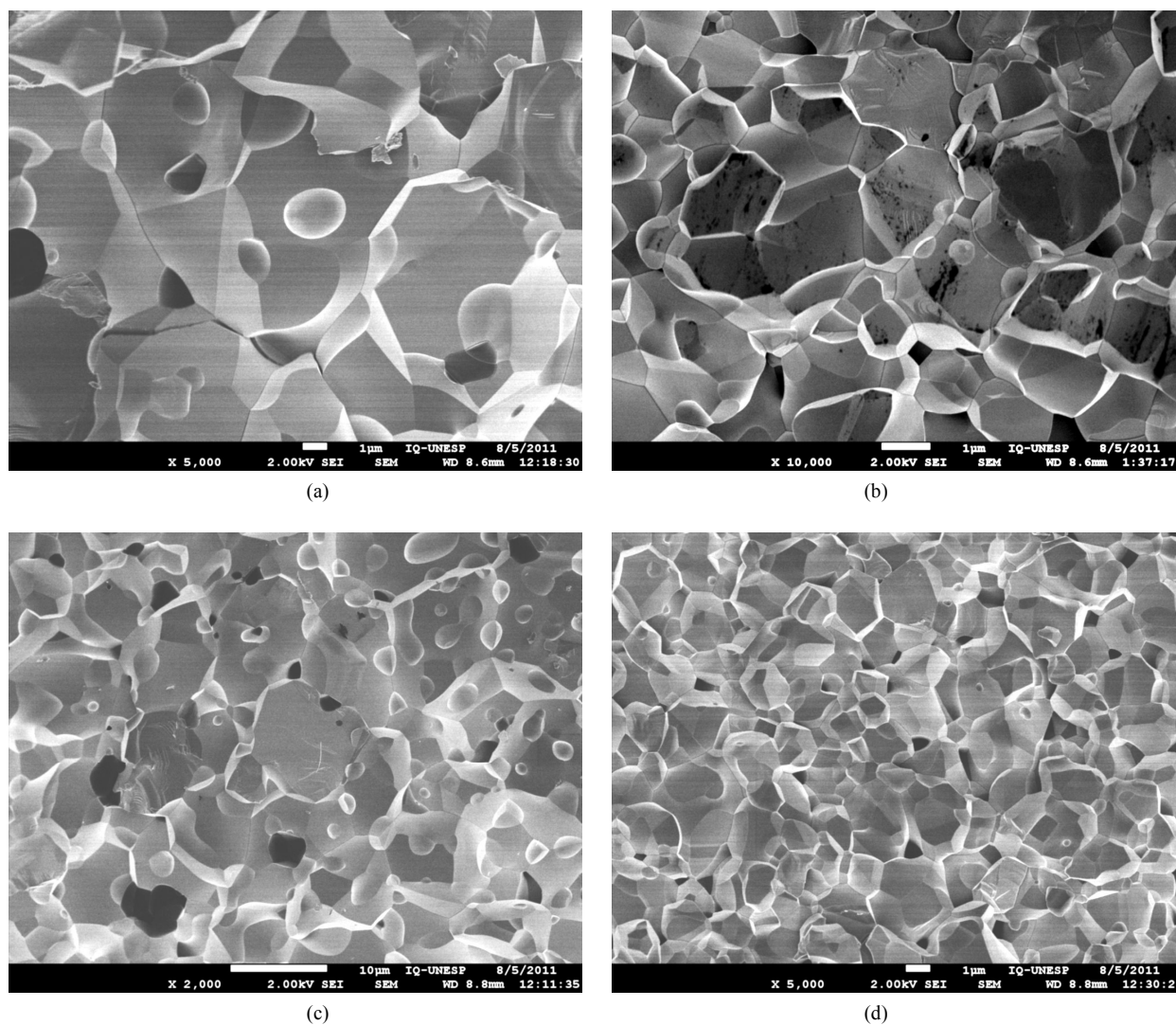
(a)

(b)

(c)

(d)

Figure 6. Comparison of the microstructure through FE-SEM micrographs: (a) ceramics modified with 0.05% mol of Al₂O₃ sintered in conventional oven; (b) in microwave oven; (c) ceramic modified with 0.05% mol of Sb₂O₃ sintered in conventional oven and (d) in microwave oven.
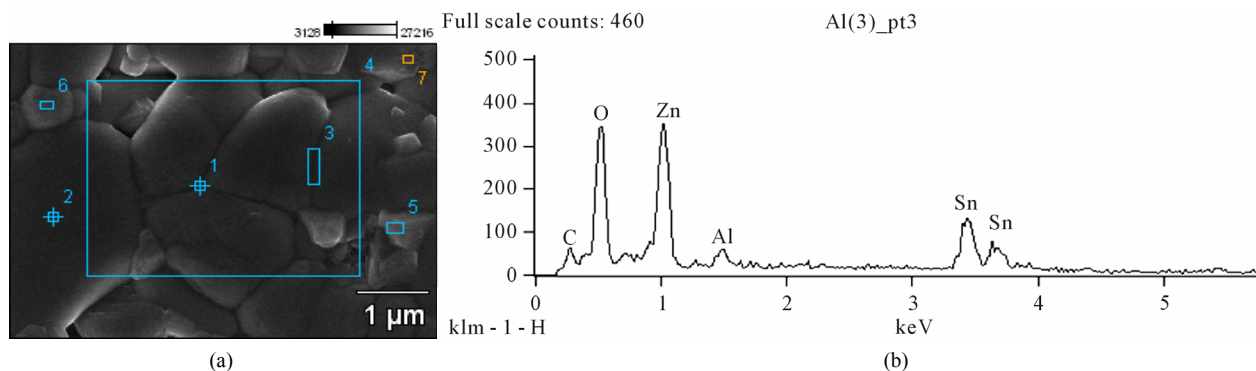

(a)

(b)

Figure 7. Analysis of the composition of grain boundaries for the sample modified with 0.5% mol of Al₂O₃: (a) micrograph showing the points of analysis and (b) results obtained by EDS for the grain boundary in position 3.

of conductive ceramics due to the improvement of cations diffusion during the sintering and the formation of cleaner

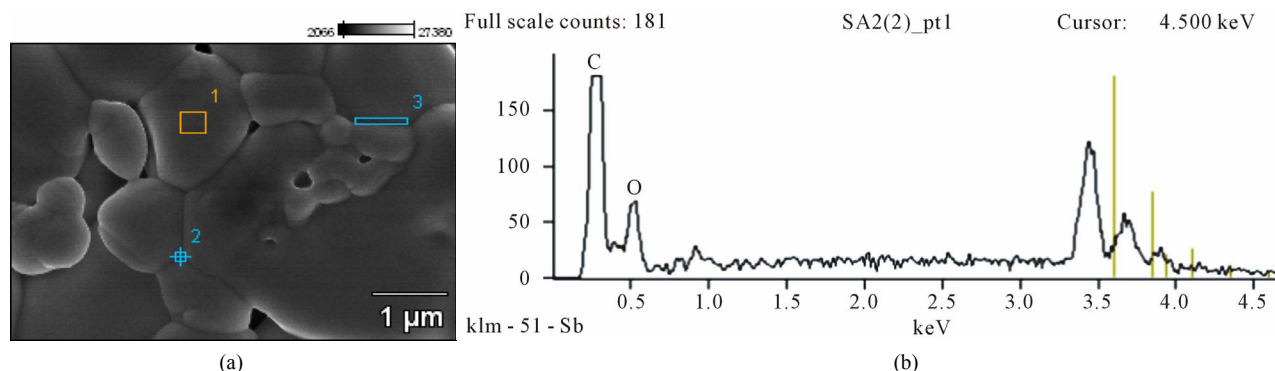grain boundaries without pores, segregates and/or precipitates.

Figure 8. Analysis of the composition of grain boundaries for the sample modified with 0.5% mol of Sb$_2$O$_3$: (a) micrograph showing the points of analysis and (b) results obtained by EDS for the grain boundary in position 3.

The addition of Sb decreased the resistivity of the ceramic and the increasing of Sb concentration resulted in no further reduction in resistivity for the microwave sintering method. The addition of Al did not lead to the reduction of resistivity.

5. Acknowledgements

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