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Electronic Ceramics Based on Polycrystalline SnO_2, TiO_2 and $(Sn_xTi_{1-x})O_2$ Solid Solution

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In the present text we discuss on electronic properties arising from polycrystalline semiconductor ceramics of SnO_2, TiO_2 and $(Sn_xTi_{1-x})O_2$ solid solution rutile-type structure. This is intended to be a short overview of the most recent papers in this area. One of the most important content discussed in this text is based on sinterability of these polycrystalline ceramics, which depends on the target application used to project porous or highly dense microstructure. The majority of discussion is focused in two main applications: varistor and sensor. In both applications there are similarities involved in the control of the sensor and varistor properties, which can mainly ascribed to the grain boundary structure and composition. The similarities found are consistently explained by the fact that all of these *n*-type semicondutor ceramics have the tendency to establish a grain boundary region with a "*p*-type semiconductor nature" (due to metal transition atoms segregated at the grain boundary region and then favors negative charged species to adsorb and enrich this region). This configuration enables electrons to become localized on the surfaces, giving rise to a negative surface and, as a result, electron depletion layers are formed, acting as potential barriers which control the properties of the mentioned devices.

Keywords: *varistor, sensor, polycrystalline system, tin dioxide and titanium dioxide*

1. Introduction

There are so many exciting ideas and new data and so many important technologies and devices developing based on SnO_2 and TiO_2 crystalline semiconductor that it would be impossible to discuss all of them here. Therefore, in the present text we will focus on the electronic properties arising from polycrystalline ceramics made of SnO_2, TiO_2 and $(Sn_x,Ti_{1-x})O_2$ compositions. SnO_2 and TiO_2 are ceramic materials that depend on its processing, microstructure and doping agents. These crystalline ceramic materials can be applied as component for communication, computation and control devices. More specifically they are used as insulator, as capacitor dielectrics, as conductors, which may be metallic, semiconductor, ionic, ohmic, or nonlinear. Pure or doped TiO_2, for instance as thin film configuration, can be used for their optical behavior or for some interactive combination of particular properties and behaviors.

The importance of interfaces to semiconductor technology is well known for electronic and ionic ceramics since they control the microstructure development. SnO_2 and TiO_2 as semiconductor oxides are used in a broad range of applications in which the defect chemistry of interfaces provides important chemical or electrical functionalities. The most well-known of these are perhaps grain boundary barrier-layer electroceramics such as varistors and positive-temperature-coefficient resistors, but interfacial defect properties also play a critical role in oxides used for a variety of other applications, including for example catalysts, heterojunctions-based gas and chemical sensors. The high temperature properties of grain boundaries and surfaces are clearly important in microstructure development processes such as creep, sintering, and grain growth as well. Consequently, the properties of SnO_2 and TiO_2 polycrystalline can be also dictated by physical chemistry of interfaces. The main goal of the present text is to discuss about SnO_2 and TiO_2 polycrystalline ceramics to applications as electronic devices such as sensor and varistor highlighting the similarity found in the operation mechanism of such devices and discussing on the promising applications of the solid state solution of these oxides. Besides, the control of the microstructure with specific dopants and processing in the pure oxides can be used to design different kinds of devices and applications as shall be also discussed here.

2. General Features of SnO_2 and TiO_2 Rutile-Type Structure

Tin oxide are known to display low densification during sintering, a characteristic that renders this typical *n*-type semiconductor appropriate for use in highly porous electronic ceramic devices, such as gas sensors, which can detect a variety of inflammable and oxidizing gases[1,2]. Like SnO_2, TiO_2 in the rutile phase is an electrically conductive ceramic (as well as an *n*-type semiconductor) material with a tetragonal crystalline structure. The electronic gap difference of stoichiometric SnO_2 (~ 3.6 eV) from that also stoichiometric TiO_2 (~ 3.2 eV) is around 0.4 eV. TiO_2 is being investigated for applications in electrocatalysis, photoelectrochemistry and as a counter electrode in smart windows[3]. Despite of the rutile crystalline structure, there are other similarities between SnO_2 and TiO_2 solid oxides. The Ti^{+4} ion has an ionic radius value of 0.68 Å while, in Sn^{+4}, the ionic radius value is 0.71 Å. Therefore, the substitution of Sn^{+4} by Ti^{+4} (or Ti^{+4} by Sn^{+4}) in the binary system lattice is not expected to generate oxygen vacancies or another kind of chemistry.

When fully dense, SnO_2 displays similar properties to those observed in TiO_2 for low voltage varistors[3] and humidity sensors[4]. However, the behavior of TiO_2 and SnO_2 differ greatly at high temperatures so that TiO_2 differs from SnO_2 during sintering because, unlike SnO_2, no dopants are required to densify it. Densities close to the theoretical[3] values are achieved by sintering at around 1300 °C.

One example of such differences are presented in Figure 1 which shows the microstructure obtained for pure SnO_2 and TiO_2 polycrystalline ceramics, both sintered at 1300 °C for 1 hour. The higher porosity and less densified microstructure observed for SnO_2 polycrystalline ceramics is consequence of nondensifying mass transport mechanism achieved during the sintering of the material. The electrical properties of low density SnO_2 polycrystalline ceramics depend on the non-stoichiometry of the oxide surface, the powder preparation methodology, the temperature, and atmosphere used during thermal treatment. This dependence on non-stoichiometry is related to poor densification[2-9]. Because of this poor SnO_2 densification, most of its applications are based on the high specific surface area. Low densification is believed to be caused by the predominance of non-densifying mechanisms,

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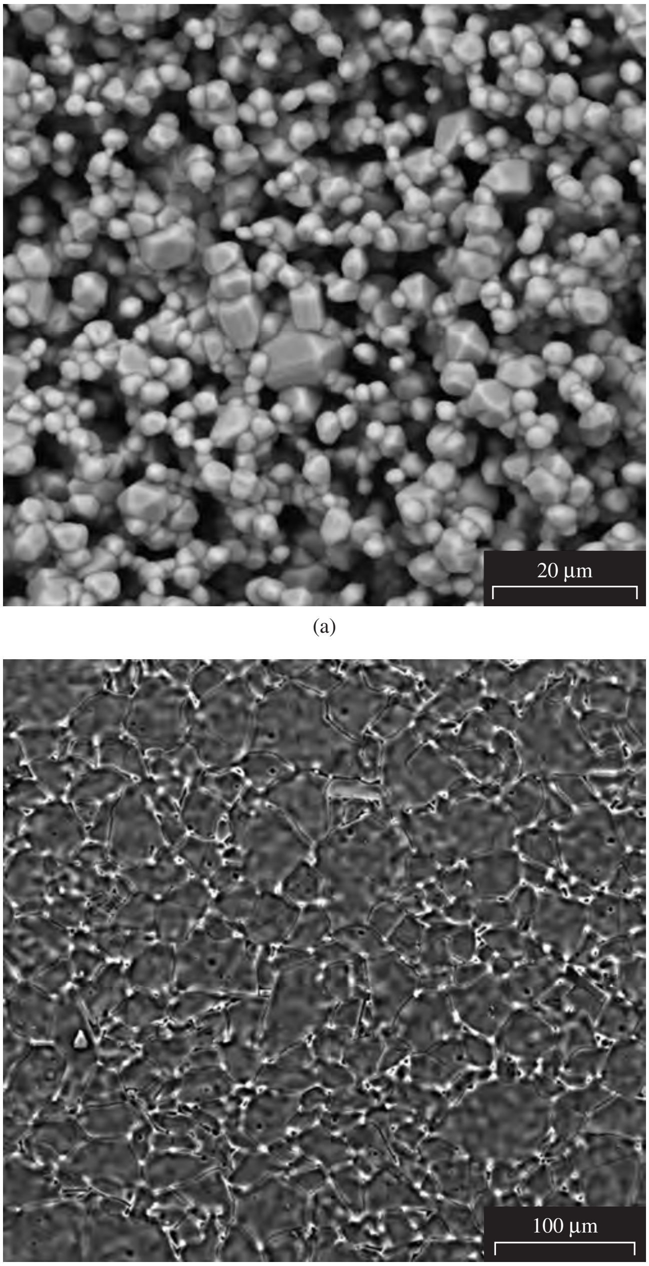

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Figure 1. a) Typical microstructure found in pure SnO_2 sintering above 1250 °C. The porosity is around 40% and relative density around 60%; and b) Typical microstructure found in pure TiO_2 polycrystalline ceramics also sintering above 1250 °C. Here the porosity is lower than 3% and the relative density is higher than 97%. This figure illustrates how different mass transport mechanism influences the final microstructure of the ceramics.

such as the evaporation-condensation process and surface diffusion. These mechanisms are responsible for grain growth and the formation of necks between particles during sintering, but do not promote densification. Thus, the majority of devices based on SnO_2 have a porosity of up to 40%, which is very desirable for gas sensor applications, but is undesirable in applications requiring mechanical strength. On the other hand, densification higher than 97% is easier achieved during preparation of TiO_2 polycrystalline electronic devices.

An important feature of the highly porous SnO_2-based electronic ceramic devices is related to the existence of negatively charged oxygen adsorbates, such as O^-, O^{2-}, etc., on the surface of SnO_2 grain boundaries (and/or particles). This feature is known to play an important role in detecting inflammable gases[1,2,5,6]. For this reason, oxygen vacancies and electronic states on SnO_2 surfaces have been studied in great detail[1,2,5,6]. The most commonly accepted model for the operation of an *n*-type semiconductor gas sensor is based on the variation in the potential barrier height at the grain boundary, induced by the change in the amount of oxygen adsorbates by reaction with inflammable gases. However, nonlinear I-V characteristics in SnO_2 porous ceramics are observed only at temperatures above 250 °C, because oxygen adsorbates are favored and form a Schottky-like barrier between grains at temperatures exceeding 250 °C[6].

Highly porous SnO_2-based electronic ceramic are used also as solid-state NO_x sensors. Nitrogen oxides (mainly NO and NO_2) are produced in combustion furnaces and automobile engines, and are typical pollutants causing acid rain and photochemical smog. For effective control of both, the combustion conditions and the NO_x-eliminating systems, high performance porous SnO_2 chemical sensor has been developed[5,6]. The SnO_2 chemical sensor mechanism based on chemisorption of oxidizing gases such as NO_x competes with the traditional solid state electrolyte such as stabilized ZrO_2 equipped with oxide electrodes. It is important to emphasize that dense ZrO_2 is mainly applied as a bulk-type sensor material for pollutant gases such as NO_x or O_2, contrary to the SnO_2 or TiO_2 that are mainly used as thin-type sensor material. Both kind of devices are oxygen sensors, but the first one operates in a different mechanism based on Nernst effect, where an electrical potential is created in an oxygen pressure gradient.

In the resistive oxygen sensors based on TiO_2, a piece of TiO_2 dense ceramic material operates at the same temperature as a porous sensor of TiO_2. This is necessary to compensate the temperature-dependent effect. As the TiO_2 dense ceramics does not equilibrate quickly with the gas stream, a reference point to the conductivity can be established[7]. This is not necessary to oxygen sensor that operates based on Nernst effect.

In addition, SnO_2 porous semiconductor ceramic is being largely studied to be applied as sensor device in a new category of gas-sensor namely varistor-type gas sensor[5,6,8-14]. Traditional semiconductor gas sensors usually operate at very low electric field, e.g., less than few volts per mm of the thin-, thick- or bulk-type sensor materials. The resistance or conductance of material is capable to be changed so that it is used to detect changes induced by the gases of interest.

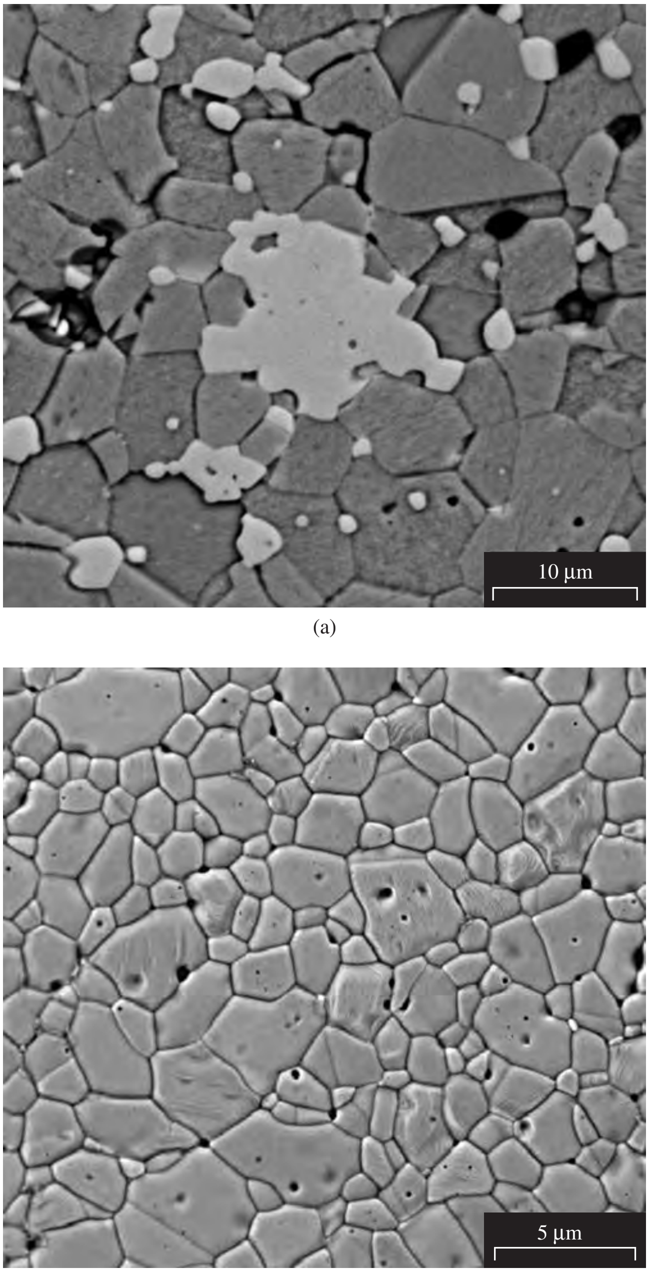
In case of varistor-type sensors, the breakdown voltage shift induced by the gases of interest is regarded as the measure of the gas sensitivity. In the present case, nonlinear current-voltage characteristics of the sensor materials is measured under relatively high electric fields, and then the magnitude of breakdown voltage shift induced by the gases of interest is regarded as a measure of the gas sensitivity.

3. Highly Dense SnO_2 Polycrystalline Ceramics

Dense SnO_2 based ceramics can be achieved by introducing dopants[15,16] or by hot isostatic pressure processing[17,18]. Dopants with valence +2 can promote densification of SnO_2 ceramics due to formation of solid solution with creation of oxygen vacancies and is an easier method to achieve highly non-ohmic electronic properties at room temperature. Therefore, the addition of CoO and MnO (or MnO_2) to SnO_2 produces high densification[15,16,19], allowing for the development of other electronic devices, such as varistors[19-41], presenting highly non-ohmic behavior at room temperature.

When SnO_2-based polycrystalline ceramics are densified by the presence of CoO, the non-ohmic behavior observed in SnO_2.CoO-based systems can be as good as that achieved in $ZnO.Bi_2O_3$-based varistor systems, and is related to a Schottky-type barrier at the grain boundary, as was demonstrated using the complex plane analysis technique and the Mott-Schottky approach[23]. However, the microstructure is very different as can be seen in the Figure 2.

It is important to emphasize that porous ZnO-based materials can also be used as varistor-type sensor. The breakdown voltage of porous ZnO-based varistors shifted to a lower electric field upon exposure to reducing gases, such as H_2 [10,14], in the temperature range of 300-500 °C. In contrast, the breakdown voltage of the ZnO-based varistor-type sensor shifted to a higher eletric field upon exposure to oxidizing gases, such as O_3 and NO_2 [6]. Nonohmic behavior of dense ZnO-based and SnO_2-based varistor is very sensitive to thermal treatments in oxygen- and nitrogen-rich atmospheres and certain similarities arises here between dense and porous SnO_2-based ceramics or ZnO-based ceramics[24].



(a)

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Figure 2. a) Typical microstructure of $ZnO.Bi_2O_3$-based traditional polycrystalline ceramics used as commercial varistor devices; and b) Typical microstructure of SnO_2.CoO-based varistor system, candidate to commercial applications.

Concerning dense ceramic materials it was proposed that the grain boundary region has a "*p*-type semiconductor nature" (due to metal transition atoms segregated at the grain boundary), while the bulk has an "*n*-type semiconductor nature" (SnO_2-, ZnO-based varistor matrix). This configuration enables electrons to become localized on the surfaces, giving rise to a negative surface (negative interfacial states) and as a result, electron depletion layers are formed and act as potential barriers. The potential barriers have a Schottky-like nature due to negative interfacial states, the selfsame nature often found in all metal oxide varistors and in most metal oxide gas sensors at higher temperatures[5,6,8-11,13,14,42]. It is important to note here that for varistor-type sensor the mechanism is very similar, however, the formation of the Schottky-type barrier and density states values are temperature-dependent being used as a probe for gas sensing, while in the dense traditional varistor applications, the parameters of the barrier are fixed at low temperature and are changed only during a re-sintering or thermal treatment at high temperatures in different atmospheres[23-27]. The influence of oxidizing gases during thermal treatments for dense SnO_2-based varistors system is illustrated in Figure 3. In the first case (Figure 3a), the La segregated metals at grain boundary region is already saturated with negative species, i.e., oxygen species so that thermal treatment at O_2-rich atmosphere does

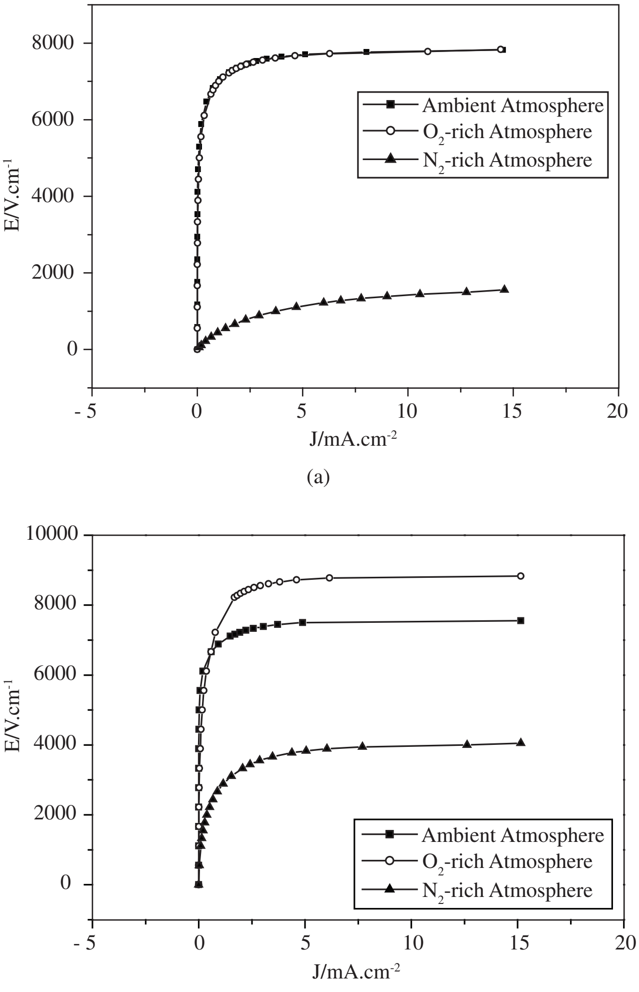

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Figure 3. Influences of thermal treatment at 900 °C in current-tension features of two distinct SnO_2.CoO-based polycrystalline ceramics.

not change the nonohmic behavior of the device. However, when the material is submmited to a N_2-rich atmosphere the nonohmic behavior is greatly degradated. Therefore, in second case (Figure 3b), there is no saturation of negative species in the grain boundary region so that a thermal treatment at O_2-rich atmosphere is able to improve the nonohmic behavior of the material with an increase of the breakdown voltage[23-25, 27].

Considering that Schottky-type barrier formed at grain boundary are dependent of the density of metal atoms segregated at grain boundary and also of oxygen species density at this region[23-25,27,34,43,44], annealing under a reducing atmosphere (N_2, air or vacuum) eliminates excess oxygen, thereby, decreasing the nonlinear electrical properties of the material. The process is reversible so that an annealing under an oxidizing atmosphere (O_2-rich atmosphere) at high temperature may increase again the content of oxygen at grain boundary, recovering the previous nonohmic behavior. Figure 4 shows the tendency to reversible behavior of the Schottky-type barrier for SnO_2-based varistor after thermal treatment at reducing and oxidizing atmosphere.

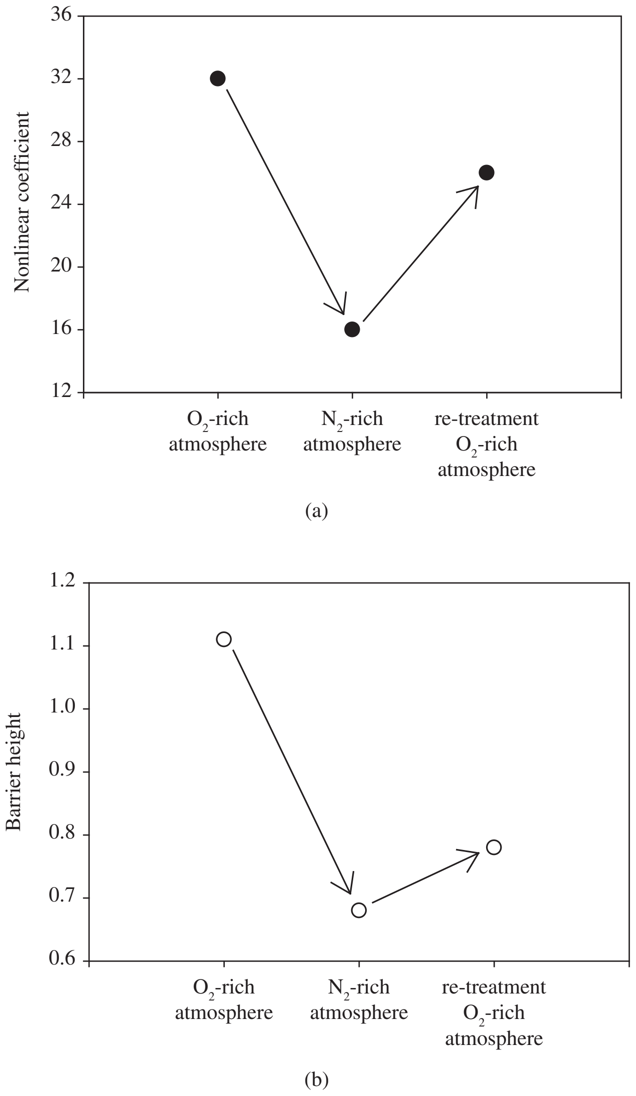

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Figure 4. Exemplification of the influence of thermal treatment in different atmospheres to the dense SnO_2-based polycrystalline ceramics. a) Here, it can be shown the reversibility of the nonlinear coefficient obtained from I-V curves after thermal treatment at oxidizing atmosphere, N_2-rich atmosphere and again at oxidizing atmosphere; and b) The same behavior is obtained concerning barrier height values of the potential barrier formed at grain boundaries.

Thermal treatment in reducing/oxidizing atmospheres at higher temperature for dense SnO_2-based polycrystalline ceramics compared to SnO_2 varistor-type sensor is necessary to alter their nonohmic behavior due to the fact that an oxygen diffusion throughout the grain boundary is likely necessary. In other words, this is probably a temperuture activated process which might be controlled by O^{-2} ions diffusion and interfacial reaction. Therefore, once the transport mechanism is activated following by O^{-2} interface reaction. The content of oxygen species at the grain boundary can be controlled by the concentration of oxygen in the gas-phase and also by the content of metal segregated at grain boundary[24]. On the other hand, in varistor-type sensor based on SnO_2 the Schottky-type barrier, parameters can be altered by a physical adsorption process because in this case, the surface of the SnO_2 crystal is exposed directly to the gases of interest whose molecules adsorbate on the crystal surface and boundaries. In other words, this is not a chemical reaction as in the previous case, but it is a physical and reversible reaction in the conditions of the experiment or temperature operation of the device.

Going back to the dense SnO_2 polycrystalline ceramics, as already pointed out in the beginning of this section, SnO_2 can also be densified by the addition of MnO besides ZnO or CoO. Like, SnO_2.CoO-based system, SnO_2.MnO-based system presents high relative density (higher than 97%) when MnO is added in concentrations equivalent to or higher than 0.5 mol %. Such as SnO_2.CoO-based system, SnO_2.MnO-based system is single phase under X ray diffraction resolution. However, when analytical electron microscopy is applied to study differences in the microstructure and to proceed with a deep analysis of the distribution of dopants in microstructure, important differences arise.

Typical microstructures of dense SnO_2.CoO- and SnO_2.MnO-based devices are presented in Figure 2 and Figure 5. Despite both SnO_2.CoO- and SnO_2.MnO-based polycrystalline ceramics are dense

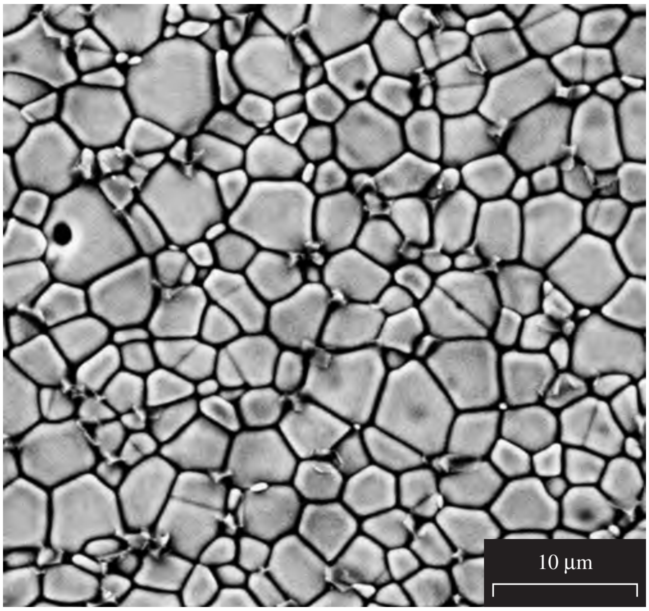


Figure 5. Microstructure of SnO_2.MnO-based polycrystalline ceramics. Compared to the SnO_2.CoO-based polycrystalline ceramics (which is illustrated in Figure 2b) it can be noted the presence of precipitates at grain boundary triple-point so that heterogeneity junctions arises. Longer sintering times increase the precipitation of Mn_2SnO_4 and the heterogeneity of junctions[45,46].

there are important difference on the microstructure sufficiently to alter electronic behavior of the system, as a consequence of differences in defect segregation at grain boundaries and surfaces controlling the interfacial properties in these electroceramic devices[45].

High resolution analytical electron microscopy was recently used for a detailed characterization of the microstructure and grain boundary chemistry of the dense polycrystalline SnO_2 compositions containing MnO, revealing that SnO_2-MnO dense ceramics consist of two phases, SnO_2 grains and Mn_2SnO_4, the latter is found precipitated mainly at triple grain points[45]. In addition, two types of SnO_2-SnO_2 grain boundary were identified: type I, Mn-rich and thin, and type II, Mn-poor and thick. Changes in Mn concentrations at the grain boundaries are ascribed to both grain misorientation and Mn diffusivity along the grain boundary[45,46]. The identification of two kinds of junctions in SnO_2-MnO has significant implications in the material's nonohmic behavior[45,46], and it is important in understanding the sintering mechanism and microstructure developing in SnO_2 ceramics. Longer sintering times increase the precipitation of Mn_2SnO_4 and the heterogeneity of junctions[45]. The specific and most significant conclusions obtained about SnO_2.MnO-based polycrystalline ceramics are listed as: a) The SnO_2.MnO system consists of two phases, SnO_2 grains and Mn_2SnO_4, precipitated along multiple grain junctions; b) Two types of SnO_2-SnO_2 grain boundaries were identified; type I – thin and rich in Mn and type II – thick and poor in Mn; and c) Changes in the concentration of Mn along the grain boundary are associated not only to grain misorientation but also to Mn diffusivity along the grain boundary, which controls the junctions' heterogeneities[45,46].

Although most nonlinear behaviors of SnO_2 ceramics have appeared in SnO_2.CoO-based systems[19,21,23-26,37,38,47], non-ohmic properties have also been reported in other systems[24,28,41] by different authors. Yongjun et al.[41] demonstrated that ZnO can substitute CoO without significantly altering the nonlinear coefficient (α) when compared to the previous SnO_2.CoO-based system, which was the first of such SnO_2-based systems reported on in the literature[19]. Yongjun et al.[41] also obtained non-ohmic properties in SnO_2.Bi_2O_3-based systems. Castro et al.[28] showed how dopants such as Co_3O_4, CuO, MnO_2, Bi_2O_3 and Sb_2O_3 can influence the dielectric properties, microstructure and densification of SnO_2-based ceramics.

It has recently been found that the nature of potential barriers in SnO_2-based varistors is Schottky-like, as that observed in ZnO-based systems. Furthermore, as discussed in earlier reports[19-21,23-27,37, 38,43,48], dense SnO_2-based systems present values of nonlinear coefficient (α), breakdown voltage (E_b) and barrier voltage per grain (ν_b) equivalent to those of the traditional ZnO varistor. However, non-ohmic ZnO systems have a complex microstructure consisting of several crystalline phases, such as the Bi_2O_3 rich phases, spinel (nominally $Zn_7Sb_2O_{12}$) and pyrochlore (nominally $Zn_2Bi_3Sb_3O_{14}$), as illustrated in Figure 2. The presence of these crystalline phases in these systems is easily verified by X ray diffraction patterns (XRD) and scanning electronic microscopy (SEM)[16,36]. Unlike the ZnO.Bi_2O_3-based system in SnO_2.CoO, a secondary phase is not detectable by XRD. This technique only allows for the detection of the SnO_2 cassiterite phase in SnO_2-based varistor systems. SEM analysis shows non-ohmic SnO_2.CoO[19-21,23-27,37,38,43,48] polycrystalline systems to have a homogeneous microstructure that is simpler than that of ZnO.Bi_2O_3 [49].

CoO in a SnO_2 matrix forms a solid solution by substituting Sn^{+4} ions for Co^{+2} or Co^{+3} ions, as reported and discussed in previous articles[15,19,23-27,37,38,43,48]. A Co_2SnO_4-precipitated phase at the grain boundary can only be determined when the EDS stage attached to the high resolution STEM and electron diffraction is used[16]. The success of CoO in achieve high non-ohmic properties, in SnO_2 varistors is related to the fact that this component is one of the responsible for barrier formation[24,25] in SnO_2-based varistors, according to the model for barrier formation[23-25]. The influence of cooling rates on the nonlinear behavior is attributed to CoO oxidation during cooling. The change in cobalt valence states occurs according to the reactions represented by Equations 1 to 3:

$$2CoO + \frac{1}{2}O_2 \xrightarrow{600\ °C} Co_2O_3 \tag{1}$$

$$Co_2O_3 + CoO \xrightarrow{800\ °C} Co_3O_4 \tag{2}$$

$$Co_3O_4 + CoO \xrightarrow{1000\ °C} 4CoO + \frac{1}{2}O_2 \tag{3}$$

Cobalt oxide can, thus, affect the trapping state at the grain boundary and modify the potential barrier, according to the cooling rate and atmosphere employed during sintering of the material[23-25]. As Co atoms are segregated in the grain boundary[24], depending on the cooling rate, the grain boundaries segregates can became richer in oxygen by oxidation of the Co atom (CoO to Co_2O_3, for example) below 1000 °C, thereby affecting the trapping state at the interface of the grain boundary region and, consequently, the nonlinear behavior of SnO_2-based varistors. This picture is in agreement with the potential barrier formation mechanism presented in reference 24.

Similar effect is observed due to Cr_2O_3 addition. The defects generated by the presence of small amount of Cr metal atoms segregated in grain boundary in analogy with SnO_2 based varistor system are fundamental to create the potential barrier at grain boundary interface, improving non-ohmic properties. The defects generated by these dopants are necessary condition to obtain a varistor behavior according to the approach presented in reference 24. These negative charge lead to the formation of the depletion layers at grain boundaries, forming barrier voltage at grain boundary. However, if the Cr metal atoms are segregated in excess, the nonohmic behavior is not observed likely due to the fact that grain boundaries became much more resistive[43].

4. Dense $(Sn_x,Ti_{1-x})O_2$ Polycrystalline Ceramics

As SnO_2, TiO_2 as matrix can also be designed to surge arrester applications, possessing nonohmic behavior without the needs of a densifying agents because TiO_2 is easier densified as discussed previously. Yan and Rhodes first reported that (Nb,Ba) doped TiO_2 ceramics have an useful varistor property[50] to be used as low voltage surge arresters, with a low non-linearity coefficient of (α = 3-4), with an oxidizing atmosphere during cooling necessary to achieve better results. The effect of oxidizing atmosphere on the electrical properties of TiO_2 doped with a small quantity of Al was investigated by Pennewiss and Hoffmann[51]. The best non-linear coefficient (α = 7) was obtained when the voltage-dependent resistivity was caused by opposite surface oxidation layers of the pellets, rather than grain boundary effects within the pellets. The processing of a single phase TiO_2 doped with the same concentration of Cr_2O_3 and Nb_2O_5 found in highly nonohmic SnO_2.CoO-based polycrystalline system is also capable of activate nonohmic behavior in TiO_2 [43].

The addition of Nb_2O_5 in small amounts to the TiO_2 or SnO_2 ceramics leads to an increase of the electronic conductivity in the TiO_2/SnO_2 lattice, due to substitution of Ti^{4+}/Sn^{4+} by Nb^{5+}, according to the solid state reaction:

$$Nb_2O_5 \xrightarrow{TiO_2} 2Nb^{\bullet}_{Ti} + 2e' + 4O_O^X + \frac{1}{2}O_2 \tag{4}$$

However, due to the grain growth in TiO_2 polycrystalline ceramics, the varistor has a low breakdown voltage, which is desirable to applications as low voltage surge arresters.

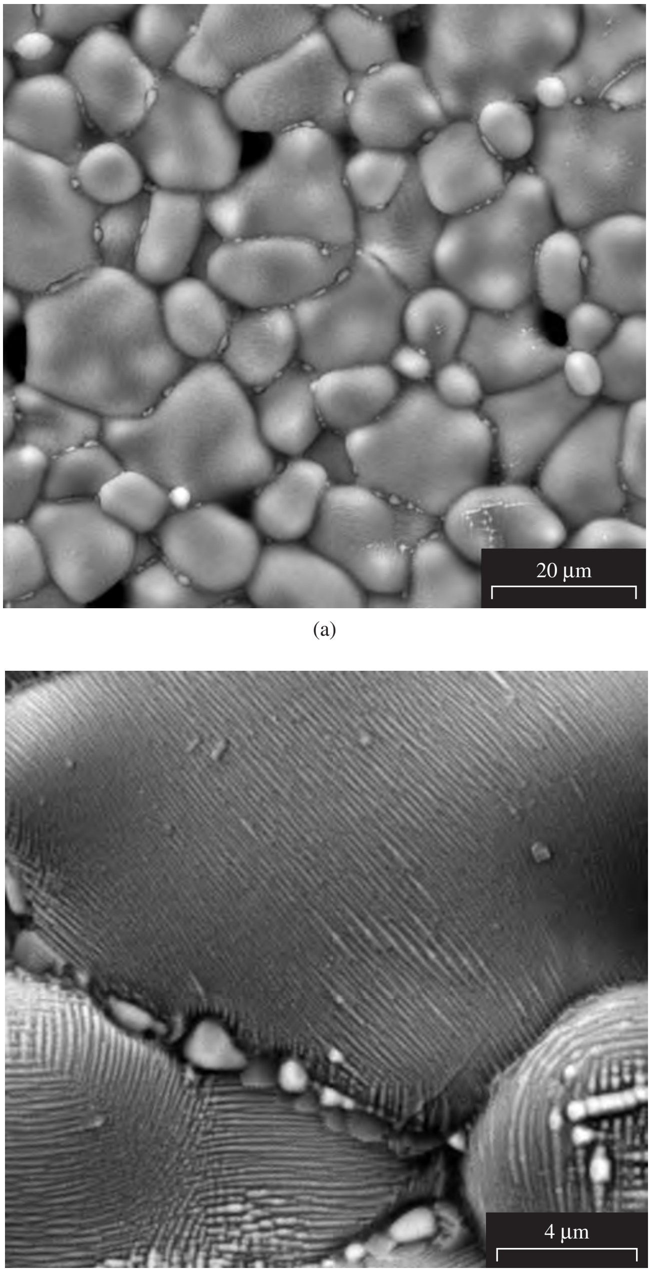
In analogy, it was demonstrated that similar description can be given in $(Sn_x,Ti_{1-x})O_2$-based systems. A matrix found in $(Sn_x,Ti_{1-x})O_2$-

based systems doped with Nb_2O_5 leads to a low voltage-based varistor system with nonlinear coefficient values of approximately 9. The presence of the back-to-back Schottky-type barrier is observed based on the voltage dependence of the capacitance. When doped with CoO, the $(Sn_x,Ti_{1-x})O_2$-based system presents higher nonlinear coefficient values ($\alpha > 30$) which is comparable to the values found in SnO_2-based varistor system. Therefore, it can be inferred that Co atoms act as oxidant agents in the grain boundary region increasing the barrier height and nonohmic properties. However, in this situation, the grain growth decreases and breakdown voltage greatly increases.

In $(Sn_x,Ti_{1-x})O_2$-based systems we have the advantage of control the Ti atoms content so that the microstructure can be designed as desired. Therefore, this varistor matrix may give rise to low or high voltage varistor applications, depending on the composition of the matrix and the nature of the dopant[52,53]. The non-ohmic properties of this system derive from the presence of Nb_2O_5, which is probably responsible for the grain (bulk) conductivity, analogous to that of the SnO_2-based varistor system. The presence of Schottky-like barriers was inferred from capacitance-voltage characteristics. These Schottky-like barriers are ascribed to the presence of a precipitated phase in the grain boundary region and relate to the typical spinodal decomposition frequently observed in these $(Sn,Ti)O_2$ systems[52].

At this point it is important to mention little about $(Sn,Ti)O_2$ systems as matrix ceramic. The thermodynamic and kinetic properties of isostructural solid solutions between SnO_2 and TiO_2 have been quite extensively studied. However, more general properties relevant to applications of SnO_2-TiO_2 binary compositions have not yet been investigated in depth. The crystallographic and thermodynamic properties of the SnO_2-TiO_2 system have been exhaustively investigated to determine the phase diagram[54-58] and to study the extent of spinodal decomposition. This system shows a miscibility gap, such as that proposed by Schultz and Stubican[54], Gupta and Cooper[59], and Park et al.[55]. Interest in spinodal decomposition began with Cahn's[60] classic work about the kinetics of spinodal decomposition in metallic binary systems. Since that time, experimental evidence of the occurrence of this type of phase separation has been published in the literature for a large number of systems, including metallic alloys of Al-Zn[61], Au-Ni[62] and, later, in glasses and ceramics. In crystalline materials, the characteristics of spinodal decomposition are modified by the elastic strain energy accompanying compositional separation. Due to the anisotropy of crystal elastic constants, composition waves tend to propagate in the interfaces parallel to elastically soft directions of the crystal, often resulting in lamellar structures. The SnO_2-TiO_2 system possesses a nearly symmetric miscibility gap[52]. Upon cooling a solid solution from a high temperature in the miscibility gap, a structure consisting of finely divided lamellae alternatively rich in Sn and Ti, is formed within each polycrystalline grain[55-58,63].

Therefore, there are several processing variables to be exploited to design different properties of $(Sn,Ti)O_2$ systems (see Figure 6). As expected, this system is also promising matrix to application in gas sensor devices[64,65]. Particularly in gas sensor applications[64,65], Radecka et al.[65] have studied the SnO_2-TiO_2 compositions[64] and have explored the transport properties[65] of polycrystalline ceramics and thin films. However, apart from this, little is known about the basic optical and electrical features of the $(Sn,Ti)O_2$ system and the answers to questions regarding mass transport, charge carriers and the sintering mechanism have not yet been found in detail. Some sintering studies are given in reference 52 where the authors investigate the sintering parameters and some aspects of mass transport in $(Sn,Ti)O_2$ polycrystalline ceramics with different compositions prepared by a mechanical mixture of oxides, correlating them to the chemical bonding nature and the intrinsic structural defects of these polycrystalline ceramics.



(a)

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Figure 6. These SEM micrographies illustrate the spinodal decomposition of the solid solution between TiO_2 and SnO_2. Both crystallize in the rutile strutucture, and form a complete solid solution above 1400 °C. However, at lower temperatures there is nearly symmetric immiscibility gap centered at ~50% of each component. As a result, spinodal decomposition can occur upon cooling TiO_2 and SnO_2 solid solutions, the early stages of which are characterized by separation into Ti-rich and Sn-rich, lathe-like regions oriented in specific crystallographic directions[52,54,55].

5. Conclusion

SnO_2, TiO_2 and $(Sn_xTi_{1-x})O_2$ semiconductor polycrystalline structures are promising materials to be used as sensor and varistor devices, offering an enormous range of opportunities based on control of grain boundary characteristics and of barrier layers. Despite of great improvements in achieving selectivity and better non-ohmic properties, many aspects involving control of the properties need to be studied. Control of oxygen pressure, cooling and heating cycles used in devices fabrication is essential. At the same time, polycrystalline materials discussed here could be exploited for new applications involving thin film ceramic insulators, positive coefficient resistors and barrier layer capacitors, since these properties are as well boundary phenomena controlled. Therefore, a deep study of grain boundary structure in such electronic ceramics is a field in which have both great need for more extensive understanding and opportunities for further devices development.

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References

1. Jarzebski ZM, Marton JP. Physical properties of SnO_2 materials. I - Preparation and defect structure. *Journal of Electrochemical Society*. 1976; 123(7):199C-205C.
2. Jarzebski ZM, Marton JP. Physical properties of SnO_2 materials. II - Electrical properties. *Journal of Electrochemical Society*. 1976; 123(9):299C-310C.
3. Finklea HO. *Semiconductor Electrodes*. Amsterdam: Elsevier; 1988.
4. Gopel W, Shierbaum KD. SnO_2 sensor: current status and future prospects. *Sensor and Actuators B*. 1995; 26-27:1-12.
5. Egashira M, Shimizu Y, Takao Y, Fukuyama Y. Hydrogen-sensitive breakdown voltage in the I-V characteristics of tin dioxide-based semiconductors. *Sensors and Actuators B*. 1996; 33(1-3):89-95.
6. Egashira M, Shimizu Y, Takao Y, Sako S. Variations in I-V characteristics of oxide semiconductors induced by oxidizing gases. *Sensors and Actuators B*. 1996; 35-36:62-7.
7. Chiang Y-M, Birnie III D, Kingery WD. Physical Ceramics. *Principles for Ceramics Science and Engineering*. New York: John Wiley & Sons, Inc.; 1997.
8. Shimizu Y, Kanazawa E, Takao Y, Egashira M. Modification of H-2-sensitive breakdown voltages of SnO_2 varistors with noble metals. *Sensor and Actuators B*. 1998; 52(1-2):38.
9. Shimizu Y, Kanazawa E, Takao Y, Egashira M. Modification of H_2-sensitive breakdown voltages of SnO_2 varistors with noble metals. *Sensors and Actuators B*. 1998; 52:38-44.
10. Shimizu Y, Kanazawa E, Takao Y, Egashira M. Zinc oxide varistor gas sensors: II, effect of chromium(III) oxide and yttrium oxide additives on the hydrogen-sensing properties. *Journal of American Ceramic Society*. 1998; 81(6):1633.
11. Egashira M, Shimizu Y, Takao Y, Fukuyama Y. *Sensor and Actuators B*. 1996; 33:89.
12. Lin F-C, Takao Y, Shimizu Y, Egashira M. Zinc oxide varistor gas sensor: I, Effect of Bi_2O_3 content on the H_2-sensing properties. *Journal of American Ceramic Society*. 1995; 78(9):2301-6.
13. Lin F, Takao Y, Shimizu Y, Egashira M. Hydrogen-Sensing mechanism of Zinc-oxide varistor gas sensosrs. *Sensor and Actuators B*. 1995; 25(1-3):843.
14. Lin CF, Takao Y, Shimizu Y, Egashira M. Zinc-oxide varistor gas sensors 1. Effect of Bi_2O_3 content on the H_2-sensing properties. *Journal of American Ceramic Society*. 1995; 78(9):2301.
15. Cerri JA, Leite ER, Gouvea D, Longo E. Effect of cobalt(II) oxide and manganese(IV) oxide on sintering of tin(IV) oxide. *Journal of American Ceramic Society*. 1996; 79(3):799-804.
16. Varela JA, Cerri JA, Leite ER, Longo E, Shamsuzzoha M, Bradt RC. Microstructural evolution during sintering of CoO doped SnO_2 ceramics. *Ceramics International*. 1999; 25:(253-256).
17. Paria MK, Maiti HS. Electrical-conductivity of polycrystalline tin dioxide and its solid-solution with ZnO. *Journal of Material Science*. 1983; 18(7):2101.
18. Kimura T, Inada S, Yamaguch T. Microstructure development in SnO_2 with and without additives. *Journal of Materials Science*. 1989; 24(1):220.
19. Pianaro SA, Bueno PR, Longo E, Varela JA. A new SnO_2-based varistor system. *Journal of Materials Science Letters*. 1995; 14(10):692-4.
20. Antunes AC, Antunes SRM, Pianaro SA, Longo E, Leite ER, Varela JA. Effect of La_2O_3 doping on the microstructure and electrical properties of a SnO_2-based varistor. *Journal of Material Science: Materials in Electronics*. 2001; 12(1):69-74.
21. Antunes AC, Antunes SRM, Pianaro SA, Rocha MR, Longo E, Varela JA. Nonlinear electrical behaviour of the SnO_2.CoO.Ta_2O_5 system. *Journal of Materials Science Letters*. 1998; 17:577-9.
22. Bernik S, Daneu N. Characteristics of SnO_2-doped ZnO-based varistor ceramics. *Journal of European Ceramic Society*. 2001; 21(10-11): 1879-82.
23. Bueno PR, Cassia-Santos MR, Leite ER, Longo E, Bisquert J, Garcia-Belmonte G, et al. Nature of the Schottky type barrier of highly dense SnO_2 systems displaying nonohmic behaviour. *Journal of Applied Physics*. 2000; 88(11):6545-8.
24. Bueno PR, Leite ER, Oliveira MM, Orlandi MO, Longo E. Role of oxygen at the grain boundary of metal oxide varistors: A potential barrier formation mechanism. *Applied Physics Letters*. 2001; 79(1):48-50.
25. Bueno PR, Oliveira MM, Bacelar-Junior WK, Leite ER, Longo E, Garcia-Belmonte G, et al. Analysis of the admittance-frequency and capacitance-voltage of dense SnO_2.CoO-based varistor ceramics. *Journal of Applied Physics*. 2002; 91(9):6007-14.
26. Bueno PR, Oliveira MM, Cassia-Santos MR, Longo E, Tebcherani SM, Varela JA. Varistores à base de SnO_2: estado da arte e perspectivas. *Cerâmica*. 2000; 46(299):124-9.
27. Cassia-Santos MR. Effect of oxidizing and reducing atmospheres on the electrical properties of dense SnO_2-based varistor. *Journal of the European Ceramic Society*. 2000.
28. Castro MS, Aldao CM. Characterization of SnO_2-varistors with different additives. *Journal of the European Ceramic Society*. 1998; 18(14):2233-9.
29. Dhage SR, Ravi V, Date SK. Influence of lanthanum on the nonlinear I-V characteristics of SnO_2: Co, Nb. *Materials Letters*. 2002; 57:727-9.
30. Dibb A, Tebcherani SM, Lacerda Jr. W, Santos MRC, Cilense M, Varela JA, et al. Influence of simultaneous addition on MnO_2 and CoO on properties of SnO_2-based ceramics. *Materials Letters*. 2000; 46(1):39-43.
31. Li C, Wang J, Su W, Chen H, Zhong W, Zhang P. Effect of Mn^{+2} on the electrical nonlinearity of (Ni, Nb)-doped SnO_2 varistor. *Ceramic International*. 2001; 27:655-9.
32. Li CP, Wang JF, Su WB, Chen HC, Wang WX, Zang GZ, et al. Influence of La_2O_3, Pr_2O_3 and CeO_2 on the nonlinear properties of SnO_2 multicomponent varistor. *Ceramics International*. 2002; 28:521-6.
33. Li CP, Wang JF, Su WB, Chen HC, Wang WX, Zang GZ, et al. Nonlinear electrical properties of SnO_2.Li_2O.Ta_2O_5 varistors. *Ceramics International*. 2002; 28:521-6.
34. Oliveira MM, Bueno PR, Cassia-Santos MR, Longo E, Varela JA. Sensitivity of SnO_2 non-ohmic behavior to the sintering process and to the addition of La_2O_3. *Journal of European Ceramic Society*. 2001; 21:1179-85.
35. Oliveira MM, Bueno PR, Longo E, Varela JA. Influence of La_2O_3, Pr_2O_3 and CeO_2 on the nonlinear properties of SnO_2 multicomponent varistor. *Material Chemistry and Physics*. 2002; 74:150-3.
36. Oliveira MM, Soares Jr PC, Bueno PR, Leite ER, Longo E, Varela JA. Grain-boundary segregation and precipitates in La_2O_3 and Pr_2O_3 doped SnO_2.CoO-based varistors. *Journal of the European Ceramic Society*. 2003; 23:1875-80.
37. Pianaro SA, Bueno PR, Longo E, Varela JA. Microstructure and electric properties of a SnO_2 based varistor. *Ceramic International*. 1999; 25:1-6.
38. Pianaro SA, Bueno PR, Olivi P, Longo E, Varela JA. Electrical properties of the SnO_2-based varistor. *Journal of Materials Science: Materials in Electronics*. 1998; 9:158-65.

39. Wang JF, Wang YJ, Su WB, Chen HC, Wang WX. Novel (Zn, Nb)-doped SnO_2 varistors. *Materials Science and Engineering B*. 2002; 96:8-13.
40. Wang YJ, Wang JF, Li CP, Chen HC, Su WB, Zhong WL, et al. Improved varistor nonlinearity via sintering and acceptor impurity doping. *Eur Phys J AP*. 2000; 11:155-8.
41. Yongjun W, Jinfeng W, Hongcun C, Weilie Z, Peilin Z, Huomin D, et al. Electrical properties of SnO_2-ZnO-Nb_2O_5 varistor system. *Journal Physical D: Applied Physics*. 2000; 33:96-9.
42. Edelman F, Hahn H, Seifried S, Alof C, Hoche H, Balogh A, et al. Structural evolution of SnO_2-TiO_2 nanocrystalline films for gas sensors. *Materials Science and Engineering B*. 2000; 69-70:386-91.
43. Bueno PR, Camargo E, Longo E, Leite E, Pianaro SA, Varela JA. Effect of Cr_2O_3 in the varistor behaviour of TiO_2. *Journal of Materials Science Letters*. 1996; 15:2048-50.
44. Leite ER, Nascimento AM, Bueno PR, Longo E, Varela JA. The influence of sintering process and atmosphere on the non-ohmic properties of SnO_2-based varistor. *Journal of Material Science: Materials in Electronics*. 1999; 10:321-7.
45. Bueno PR, Orlandi MO, Simões LGP, Leite ER, Longo E, Cerri J. Non-ohmic behavior of SnO_2-MnO Polycrystalline Ceramics. Part I - Correlations between microstructural morphology and non-ohmic features. *Journal of Applied Physics*; 2004.
46. Orlandi MO, Bueno PR, Bomio MRD, Longo E, Leite ER. Non-ohmic behavior of SnO_2-MnO Polycrystalline Ceramics. Part II - Analysis of Admittance and Dielectric Spectroscopy. *Journal of Applied Physics*; 2004.
47. Themlin JM, Sporken R, Darville J, Caudano R, Gilles JM. Resonant-photoemission study of SnO_2: cationic origin of the defect band-gap states. *Physical Review B*. 1990; 42(18).
48. Pianaro SA, Pereira EC, Bulhoes LOS, Longo E, Varela JA. Effect of Cr_2O_3 on the electrical properties of multicomponent ZnO varistors at the pre-breakdown region. *Journal of Materials Science*. 1995; 30:133-41.
49. Clarke DR. Varistor ceramics. *Journal of American Ceramic Society*. 1999; 82(3):485-502.
50. Yan MF, Rhodes WW. Preparation and properties of TiO_2 varistors. *Applied Physics Letters*. 1982; 40(6):536-7.
51. Pennewiss J, Hoffmann B. Varistor made from TiO_2 - practicability and limits. *Matterials Letters*. 1990; 9(5,6):219-26.
52. Bueno PR, Leite ER, Bulhões LOS, Longo E, Santos COP. Sintering and mass transport features of $(Sn,Ti)O_2$ polycrystalline ceramics. *Journal of the European Ceramic Society*. 2003; 23(6):887-97.
53. Bueno PR, Santos MRdC, Simões LGP, Gomes JW, Longo E, Varela JA. A low voltage varistor based on $(Sn,Ti)O_2$ ceramics. *Journal of the American Ceramic Society*. 2002; 85:282-4.
54. Schultz AH, Stubican V. S. *Modulated structures in* TiO_2*-*SnO_2. 1968; 929-37.
55. Park M, Mitchell TE, Heuer AH. Subsolidus equilibria in the TiO_2-SnO_2 system. *Journal of the American Ceramic Society*. 1975; 58:43-7.
56. Yuan TC, Virkar AV. Kinetics of the spinoidal decomposition in the TiO_2-SnO_2 system: the effect of aliovalent dopants. *Journal of the American Ceramic Society*. 1988; 71:12-21.
57. Nambu S, Sato A, Sagala DA. Computer simulation of kinetics of spinoidal decomposition in the tetragonal TiO_2-SnO_2 system. *Journal of the American Ceramic Society*. 1992; 75:1906-13.
58. Flevaris NK. Spinoidal decomposition in tetragonal systems: SnO_2-TiO_2. *Journal of the American Ceramic Society*. 1987; 70:301-4.
59. Gupta PK, Cooper AR. *On phase separation in the* TiO_2*-*SnO_2 *system*. 1969: 611-7.
60. Cahn JW. *Acta Metallurgica*. 2001; 9:795-801.
61. Rundman KB, Hilliard JE. Early stages of spinodal decomposition in an aluminum-zins alloy. *Acta Metallurgica*. 1967; 15:1025-33.
62. Woodilla JE, Acverbach BL. Modulated structures in Au-Ni alloyds. *Acta Metallurgica*. 1968; 16:255-63.
63. Wu N-L, Wang S-Y, Rusakova IA. Inhibition of crystallite growth in the sol-gel synthesis of nanocrystalline metal oxide. *Science*. 1999; 285:1375-7.
64. Radecka M, Zakrzewska K, Rekas M. SnO_2-TiO_2 solid solutions for gas sensors. *Sensors and Actuators B*. 1998; 47:194-204.
65. Radecka M, Pasierb P, Zakrzewska K, Rekas M. Transport properties of $(Sn,Ti)O_2$ polycrystalline ceramics and thin films. *Solid State Ionics*. 1999; 119:43-8.