J Mater Sci (2006) 41:6256–6259
DOI 10.1007/s10853-006-0499-4

The effect of Sb and Nb on the electrical conductivity of tin dioxide based ceramics

**D. R. Leite · I. O. Mazali · E. C. Aguiar ·
W. C. Las · M. Cilense**

Received: 30 June 2004 / Accepted: 23 September 2005 / Published online: 12 August 2006

Abstract The electrical conductivity of Mn doped SnO_2 systems prepared by an organic route (Pechini's method) has been investigated as a function of antimony and niobium concentration. The conductivity increases with the increase of both concentration ions, however, in a different manner. While the conductivity of niobium doped ceramics increases with the power of 1.6 for the entire range of concentrations studied (0.01–0.7 mol%), the conductivity of antimony doped ceramics increases with the power of 1.9 in the range 0.01–0.05 mol% of Sb; 3.7 in the range 0.05–0.30 mol% and 1.8 in the range 0.30–0.70 mol%. This behavior is attributed to the existence of two stable oxidation states for antimony: Sb^{3+} and Sb^{5+}, while for niobium there is only one: Nb^{5+}. The power of 3.7 for Sb would be related to the segregation of this ion on the grain boundary accompanied by an additional contribution coming from the substitution of Sn^{2+} by Sb^{3+} on the grain surface.

Introduction

Tin dioxide (SnO_2) is a n-type semiconductor which presents a tetragonal structure similar to rutile [1], and has been utilized in a large number of technological applications such as furnace electrodes in the glass industry, conductive films for transparent electrodes and gas sensors [2–4]. Sensor properties are related to the large superficial area resultant from the low densification of this oxide in a pure state (without intensional dopants), due to the predominance of non-densifying mass transport mechanisms such as evaporation–condensation [5].

Another characteristic of great interest presented by SnO_2 is its varistor behavior. One of the prerequisites for developing a varistor system is a high level of ceramics densification [6–8], since the phenomena involved to obtain the non-linear properties occur in the grain boundary region of the material. Thus, the addition of dopants with valence +2, such as MnO, to SnO_2 can promote densification of this oxide [5] due to a solid solution formation with the creation of oxygen vacancies, which lead to an increase in the diffusion process through the SnO_2 lattice.

It is known that the addition of antimony oxide to SnO_2-based ceramics is responsible for a large increase in its electrical conductivity [9]. The addition of niobium oxide also increases conductivity, but in a lesser extent [10, 11]. This increase in conductivity is attributed to the fact that a pentavalent ion is an electron donor in the SnO_2 lattice, according to the equation [12]:

$$M_2O_5 \xrightarrow{SnO_2} 2M^{\cdot}_{Sn} + 2e' + 4O^{x}_{O} + 12O_2(g) \qquad (1)$$

in which M is Nb or Sb. Equation 1 is obtained by considering that tin vacancies are created when a pentavalent ion substitutes Sn^{4+}, as represented by the following equation [11]:

$$2M_2O_5 \xrightarrow{SnO_2} 4M^{\cdot}_{Sn} + 10O^{x}_{O} + V^{4'}_{Sn} \qquad (2)$$

D. R. Leite (✉) · I. O. Mazali · E. C. Aguiar ·
W. C. Las · M. Cilense
Departamento de Físico-Química,
Instituto de Química – UNESP, C.P.355, Araraquara,
SP, Brazil 14801-970
e-mail: danirussoleite@hotmail.com

and by considering the equilibria represented in the equations:

$$2\,O_O^x \Leftrightarrow O_{2(g)} + 4\,e' + 2\,V_O^{\cdot\cdot} \tag{3}$$

and

$$V_{Sn}^{4'} + 2\,V_O^{\cdot\cdot} \Leftrightarrow O_O^x \tag{4}$$

Equation 1 is obtained by substituting Eqs. 3 and 4 in Eq. 2. Therefore, if pentavalent ions substitute Sn^{4+} in Eq. 1, tin vacancies are created as in Eq. 2 and the concentration of oxygen vacancies decreases, as shown in Eq. 4; if the number of oxygen vacancies decreases, the number of electrons increases, as shown in Eq. 3, resulting in the increased conductivity.

Few authors show resistivity or conductivity data as a function of Sb or Nb concentration. Szczuko et al. [10], for example, present resistivity data as a function of Nb and Sb concentration, showing that up to 1 mol% the resistivity decreases with increasing ion concentration. There are, however, only few data in the 0.01–0.5 mol% range.

In this work, we were interested mainly in the conductivity behavior as a function of Sb and Nb concentrations. Apparently, the conductivity curves should be similar in behavior, for both ions, since Eq. 1 holds for both cases, if we consider only pentavalent ions. After results for Sb-doped ceramics were obtained, Nb was chosen to confirm a hypothesis about oxidation states of these ions. Concentrations smaller than 1% mol were utilized since values larger than this cause a saturation effect in the conductivity behavior.

Experimental procedure

Chemical powder synthesis was carried out by employing Pechini's method, applied to the case of SnO_2, as described with more detail by Gouvêa et al. [13]. It consists in the preparation of metallic citrates, which were added to a solution of citric acid and ethyleneglycol in order to form a polymeric resin. This polymer was pre-calcined at 400 °C for 4 h to eliminate part of the organic matter, milled in a mortar for particle desaggregation and calcined at 500 °C for 15 h. This chemical synthesis allows doping with small quantities as opposed to the mixture oxide method. The powders were ball-milled in an alkoholic medium. The molar composition of the systems was: $(0.99 - x)\%Sn + 1.0\%Mn + x\%$ Sb or Nb, with x varying from 0.01 to 0.7.

The resulting powders were uniaxially pressed to 20 MPa in disc shape with 8 mm diameter and 1.5 mm thickness, followed by an isostatic pressing of 210 MPa. The compacts were sintered at 1300 °C for 4 h in air, in a tubular furnace, with heating and cooling rates of 10 °C/min. The electrical conductivity was obtained as a function of temperature by measuring the four point resistance in a HP 3457 A multimeter. The ceramics were polished and had their parallel surfaces painted with platinum paste before being introduced in a kanthal resistance furnace, which was heated to 900 °C for 15 h in a static ambient atmosphere. Measurements were taken during furnace cooling.

Results and discussion

The conductivity behavior as a function of temperature for the systems prepared with various Sb and Nb concentrations is illustrated in Figs. 1 and 2. It is observed that the conductivity increases with the increase of both concentration ions.

Figure 3 shows the conductivity as a function of Sb and Nb concentrations in a log–log scale, for data taken from Figs. 1 and 2 at 162 °C. It is noted that $\log(\sigma)$ increases with log[Nb] in a linear manner, while in the case of Sb, the curve can be divided in three segments. Also, the conductivity of the ceramics with Sb is always larger than that of the ceramics with Nb. Considering a function of the type $\sigma = \sigma_o\,[M]^a$, fitting the data of Fig. 3 resulted in values for a presented in Table 1.

It is cited in the literature that Sb segregates on the Sb-doped SnO_2 powder particles [14] and also on the grain surface of dense ceramics [11]. Considering that Sb is in the form Sb_2O_4, which consists in a mixture of Sb^{3+} and Sb^{5+}, the segregation is mainly attributed to the Sb^{3+} ions [10, 14, 15], because they have ionic radius (0.76 Å) larger than Sn^{4+} (0.69 Å), while Sb^{5+} (0.60 Å) would be in solid solution with SnO_2.

According to Cox et al. [14] and also to Cox et al. [16], the electrostatic neutrality of the non-stechiometric SnO_2 would be maintained by the presence of Sn^{2+} adjacent to oxygen vacancies at the surface. In principle, reduced species such as Sn^{2+} should appear only in vacuum treated samples, as the monocrystals used by Cox et al. [16]. However, Cox et al. [14] used ceramics apparently sintered in air. We also sintered our ceramics in air, but the presence of the reduced Sn^{2+} is expected because of the highly reducing atmosphere developed during powder preparation, which involves the decomposition of a large quantity of organic matter, during burning of the resin. After sintering, some Sn^{4+} would remain on the grain surface,

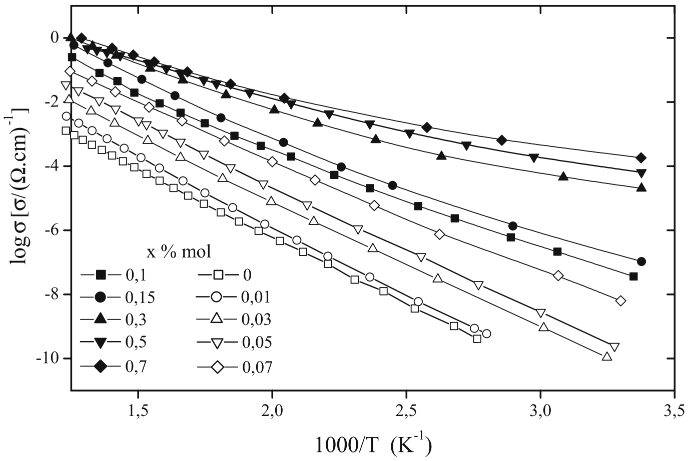

Fig. 1 Conductivity as a funcuion of temperature to SnO_2 + 1.0% Mn + *x*% Sb, with *x* varying from 0.01 to 0.7

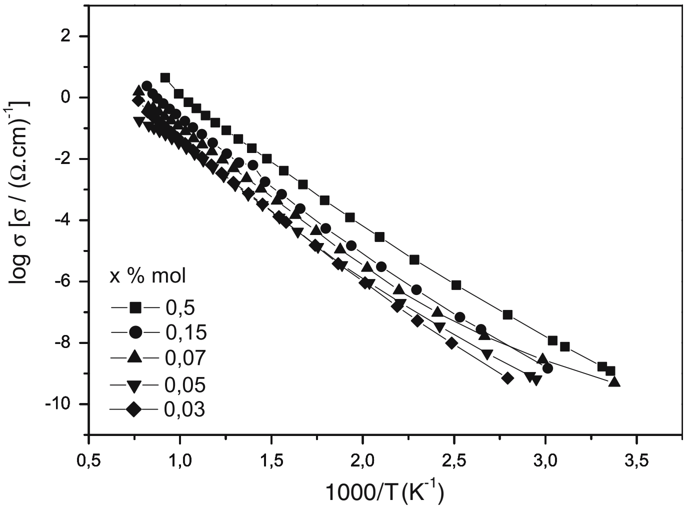

Fig. 2 Conductivity as a funcion of temperature to SnO_2 + 1.0% Mn + *x*% Nb, with *x* varying from 0.01 to 0.5

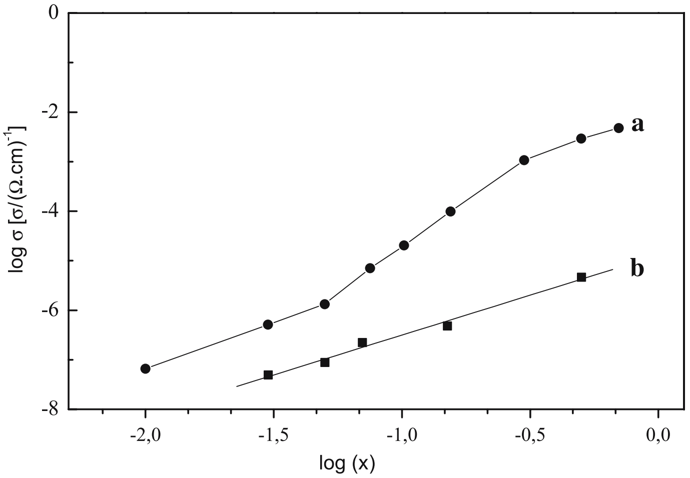

Fig. 3 Conductivity of SnO_2 ceramics as a funcion of dopants concentrations: (**a**) Sb and (**b**) Nb, (for data taken from Figs. 1 and 2 at 162 °C)

just on the regions where there is porosity, therefore in contact with the outer atmosphere. In the regions where grains touch each other, there would be the presence of Sn^{2+}. Our ceramics have around 95% of theoretical density.

The same reasoning applies to the reduced Sb^{3+}. Besides, we must remember that Vincent [17] said that although Sb_2O_5 is more stable than Sb_2O_5 below 1340 K, this result holds for pure antimony oxides, which is not our case. He said that it is not possible to

Table 1 Parameter a in $\sigma = \sigma_o\,[M]^a$ (M = Nb or Sb)

Concentration interval mol%	Sn–Mn–Nb	Sn–Mn–Sb
0.01–0.05	1.6	1.9
0.05–0.30	1.6	3.7
0.30–0.70	1.6	1.8

conclude that Sb^{3+} is never stable in oxygen below this temperature.

Considering the presence of SnO on the surface, Sb^{3+} would substitute Sn^{2+}, contributing to the increase of the conductivity on the segregation layer as represented in the following equation:

$$Sb_2O_3 \xrightarrow{SnO_2} 2Sb_{Sn}^{\cdot} + 3O_O^x + 2\,e' \tag{5}$$

However, since Nb^{3+} is not stable, it is not expected that this ion segregates on the grain boundary and, therefore, it is not expected that the behavior of log(σ) vs. log[x] for ceramics containing Nb is the same as for those containing Sb.

It is observed in Table 1 that, for low Nb or Sb concentrations, between 0.01% mol and 0.05% mol, the conductivity increases with the power of 1.6 for Nb and almost 2 for Sb. This may be due to the contribution of the solid solution of Nb^{5+} or Sb^{5+} in SnO_2, according to Eq. 1. Between 0.05% mol and 0.3% mol, the conductivity increases with the power of almost 4, only for Sb; the segregation of this ion would occur on the grain boundary and there would be an additional contribution, which would come from the substitution of Sn^{2+} by Sb^{3+}, according to Eq. 5. However, the curve for the ceramics with Nb has the same inclination for concentrations up to 0.5% mol, what can be attributed to the fact that there is no stable Nb^{3+}. Between 0.3% mol and 0.7% mol, the conductivity for ceramics with Sb increases again with the power of almost 2, situation in which practically all the Sn^{2+} would be substituted by Sb^{3+}, and the behavior would be a function only of the Sb^{5+} in solid solution. The changes in the Sb oxidation state as a function of Sb concentration just described were also suggested by Terrier et al. [18].

We believe that oxidation state changes appear at Sb concentrations lower than 1 mol% in our work because of the method preparation, which produces a very fine precursor powder, with particle sizes of 0.042 µm [19] for SnO_2 and 0.023 µm for SnO_2 doped with 1 mol% Mn and 0.5 mol % Sb, derived from BET measurements. Therefore, in finer powders, Sb^{3+} ions would travel smaller distances from bulk to surface and segregation would occur at lower dopant concentrations, as compared to other works [10, 14].

The higher conductivity of the ceramics with Sb as compared to those with Nb must be the result of Sb segregation on the grain boundary, which decreases the potential barrier. It is also the result of the fact that Sb introduces electrons directly in the conduction band [14], what seems not to occur with Nb.

Conclusion

It is concluded that the model of surface Sn^{2+} substituted by Sb^{3+}, as proposed by Cox et al. [14], in addition to the assumption of Sb^{3+} and Sb^{5+} oxidation states for antimony and only Nb^{5+} for niobium, is consistent with our conductivity results.

References

1. Jarzebski ZM, Marton JP (1976) J Electrochem Soc 123:299C
2. Chopra KL, Major S, Pandya PK (1983) Thin Solid Films 102:1
3. Fagan JG, Amarakoon VRW (1993) Am Ceram Soc Bull 72:119
4. Olivi P, Souza ECP, Longo E, Varela JA, Bulhões LOS (1993) J Electrochem Soc 140:L81
5. Cerri JA, Leite ER, Gouvêa D, Longo E, Varela JA (1996) J Am Ceram Soc 79:799
6. Clarke DR (1999) J Am Ceram Soc 82:485
7. Bacelar WR, Oliveira MM, Souza VC, Longo E, Leite ER, Varela JA (2002) J Mater Sci: Mater Electron 13:409
8. Bueno PR, Cassia-Santos MR, Simões LGP, Gomes JW, Longo E, Varela JA (2002) J Am Ceram Soc 85:282
9. Uematsu K, Kato Z, Uchida N, Saito K (1987) J Am Ceram Soc 70:142C
10. Szczuko D, Werner J, Oswald S, Behr G, Wetzig K (2001) Appl Surface Sci 179:301
11. Las WC, Dolet N, Dordor P, Bonnet JP (1993) J Appl Phys 74:6191
12. Pianaro SA, Bueno PR, Longo E, Varela JA (1995) J Mater Sci Lett 14:692
13. Gouvêa D, Varela JA, Longo E, Smith A, Bonnet JP (1993) Eur J Solid State Inorg Chem 30:915
14. Cox PA, Egdell RG, Harding C, Patterson WR, Tavener PJ (1982) Surf Sci 123:179
15. Dyshel DE (1996) Inorg Mat 32:51
16. Cox DF, Fryberger TB, Semancik S (1988) Phys Rev B 38:2072
17. Vincent CA (1972) J Eletrochem Soc Solid State Sci Technol 119:515
18. Terrier C, Chatelon JP, Roger JA (1997) J Sol–Gel Sci Technol 10:75
19. Mazali IO, Las WC, Cilense M (2003) J Mater Sci 38:3325