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SnO_2 electroceramics with various additives

Suzana Mihaiu [a,*], Oana Scarlat [a], Gh. Aldica [b], Maria Zaharescu [a]

[a] *Institute of Physical Chemistry, Romanian Academy, Bucharest, Splaiul Independentei 202, 77208 Bucharest, Romania*
[b] *National Institute for Physics of Materials, POB MG-7, RO-76900 Bucharest, Magurele, Romania*

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Abstract

The electrical properties of SnO_2 based ceramics are enhanced by the addition of different substituents into the SnO_2 lattice. For the composition containing 2.5 mol% Sb_2O_3 the highest value of the electrical conductivity was obtained. The mentioned composition has a SnO_2 solid solution structure and presents semiconducting properties. In the present work, the influence of Sb_2O_3, $CuSb_2O_6$, $CuO + Sb_2O_3$, In_2O_3, CeO_2 used in the same concentration as additives, on the structure and electrical properties of the SnO_2 was studied. The phase composition analyzed by XRD, pointed out the formation of the SnO_2 solid solution. When using In_2O_3, a mixture of phases is formed. The XRD results are confirmed by IR spectroscopy. The formation of *rutile* type structure is evidenced by the decreasing, up to disappearance, of SnO_2 bands. The Seebeck coefficient values and the resistivity measurements results showed a semiconductive behavior, with a *n*-type electrical conductivity for all the samples.

Keywords: SnO_2 ceramics

1. Introduction

Tin dioxide presents specific optical and electrical properties and good chemical stability, which confers special characteristics to the SnO_2 based materials.

Our previous papers have focused their interests on the study of the oxide materials from the Sn–Sb–Cu–O quaternary system. It is well known that in SnO_2 rich domain (SnO_2 content $\geqslant$ 90 wt.%) and in the presence of Sb_2O_3 and CuO acting as dopants, the semiconducting ceramics enjoy a great interest especially in manufacturing of the stable electrodes for the electrometallurgy of aluminium.[1,2]

Complementary studies were also done over the whole concentration range in the SnO_2–Sb_2O_3–CuO system, pointing out the complexity of the chemical processes occurring during the thermal treatments. At different temperatures the following chemical reactions take place:[3,4]

$$\approx 500^\circ C: \quad Sb_2O_3 + 1/2O_2 \rightarrow Sb_2O_4 \tag{1}$$

$$< 900^\circ C: \quad Sb_2O_4 + CuO + 1/2O_2 \rightarrow CuSb_2O_6 \tag{2}$$

$$940^\circ C: \quad CuSb_2O_6 + 7CuO \rightarrow 2Cu_4SbO_{4.5} + 2O_2 \tag{3}$$

$$1100^\circ C: \quad SnO_2 + Sb_2O_4 + CuSb_2O_6 \rightarrow SnO_{2(ss)} \tag{4}$$

Dense ceramics were obtained only in the compositions for which the CuO:Sb_2O_3 ratio $\geqslant$ 1.

The electrical behavior of the dense ceramics containing either $SnO_{2(ss)}$ or a material with $SnO_{2(ss)}$ as the main component was studied in the $-196^\circ C$ to $+850^\circ C$ temperature range using electrical resistivity and Seebeck coefficient measurements. The studied ceramics exhibited exclusively extrinsic *n*-type conductivity.[5]

This paper aims to present a comparative study of the SnO_2 based ceramics obtained in the presence of Sb_2O_3, $CuSb_2O_6$, $CuO + CuSb_2O_6$, CeO_2 and In_2O_3 used as additives. An additive concentration of 2.5 mol%. was used in the present work. It was previously established that SnO_2 doped with Sb_2O_3, at this additive concentration, exhibited the highest electrical conductivity value.[6] Orel and colab. indicated the obtaining by a different

* Corresponding author. Tel.: +40-1638-53-70-26; fax: +40-1-312-1147.
E-mail address: smilhaiu@chimfo2.icf.ro (S. Mihaiu).

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method of preparation,[7] of the highest electrical conductivity of the SnO_2 ceramics doped with 1.38 mol% Sb_2O_3.

$CuSb_2O_6$ was chosen as additive, due to the fact that when CuO and Sb_2O_3 co-exist in the initial mixture its formation takes place previously to the formation of SnO_2 solid solution.

To improve the sintering capabilities of the samples CuO was supplementary introduced in some initial mixtures, besides $CuSb_2O_6$. A low amount of CuO was added, in the limit of its solid solubility in the SnO_2 lattice as indicated in the literature data.[8]

CeO_2 and In_2O_3 where chosen in order to establish the influence of the isovalent (Ce^{4+}), respectively heterovalent (In^{3+}) substitution of the SnO_2 lattice.

2. Experimental

Reagent grade oxides of SnO_2, Sb_2O_3, CuO (all Merck), In_2O_3 (Riedel de Haen), CeO_2 (Lobo Feinchemie) were used as starting materials for obtaining the initial mixtures. The $CuSb_2O_6$ compound was prepared in the laboratory from a $CuO:Sb_2O_3$ equimolecular mixture according to the literature data and our own previous results.[3,9]

To establish their thermal behavior, the mentioned oxides were analyzed by DTA/TG measurements up to 1350°C using a MOM-OD-3 Derivatograph with a heating rate of 7°C/min.

The ceramics samples were obtained by the classical ceramic method as cylindrical pellets with a diameter of 10 mm and variable heights.

After the thermal treatment at 1100°C for 3 or 10 h, respectively, the samples were analyzed by X-ray diffraction using a TUR M-62 apparatus equipped with a HZG-3 diffractometer operating with CoK_α radiation. The IR absorption measurements were performed between 1600 and 400 cm^{-1}, using an IR M-80 Carl-Zeiss spectrometer.

Table 1
DTA/TG analysis results

Sample	Thermal effects		Weight variation		Assignment
	Endo (°C)	Exo (°C)	Exp. (%)	Calc. (%)	
SnO_2	–	–	–	–	–
Sb_2O_3		440-660	+5.1	+5.5	$Sb_2O_3 + 1/2O_2 \rightarrow Sb_2O_4$
	1160				Sb_2O_4 evaporation
CeO_2	–	–	–	–	–
In_2O_3	–	–	–	–	–
CuO	1055	–	−9.6	−10.1	$2CuO \rightarrow Cu_2O + 1/2O_2$
	1130		+1.6	+1.9	$5Cu_2O + 1/2O_2 \rightarrow 4Cu_2O.2CuO$
$CuSb_2O_6$	1170	–	64.4	72.2	$8CuSb_2O_6 \rightarrow 2Cu_4SbO_{4.5} + 9O_2\uparrow + 7Sb_2O_3\uparrow$

The ceramic characteristics (porosity, P_a and linear shrinkage, $\Delta l/l$) of the samples were also determined.

To ensure a good electrical contact during Seebeck effect and electrical measurements the used pellets were gold coated by a special treatment. A direct current bridge, operating in four points scheme was used for electrical measurements in the −196 to +850°C temperature range. Depending on the investigated sample the control current varied within 0.1÷3 mA limits,. The accuracy of the measurements was ±0.01%.

The measurements of Seebeck effect were determined by the means of a special device built up by the authors.

3. Results and discussion

3.1. Structural characterization

Table 1 shows the results of the thermal analysis of the oxides used in this work. The thermal stability of the Sn(IV), In(III), Ce(IV) oxides and $CuSb_2O_6$ up to 1100°C was established. Only CuO presents the well known endothermal effect at 1055°C assigned to its reduction to Cu_2O. Based on DTA/TG results the thermal treatment was effected in isothermal conditions at 1100°C.

The initial compositions of the mixtures (column 2), the phase composition determined by X-ray diffraction (columns 3 and 6), and the ceramic properties (porosity columns 4,7 and linear shrinkage, columns 5,8) of the samples are presented in Table 2. Excepting P_4 sample (In_2O_3 additive), all the samples are formed from a *rutile* type solid solution ($SnO_{2(ss)}$). Only the samples doped with CuO (P_3 and P_6) present proper densification. The other samples exhibit high porosity and small relative shrinkage values.

The IR spectra of thermally treated samples are presented in Fig. 1. As evidenced by X-ray diffraction for the samples $P_{1\text{-}3}$ and $P_{5\text{-}6}$, the IR spectra confirmed the formation of the SnO_2 based solid solutions, by the decreasing, up to disappearance of the characteristic bands of SnO_2 lattice positioned at 680 and 620 cm^{-1}. As compared with the samples obtained by isovalent substitution, the effect appear to be stronger in the case of the heterovalent substitution. Compared to the initial mixture, IR spectrum of P_2 sample, containing CeO_2 (isovalent substitution), shows a decrease of the intensity of the IR bands and the disappearance of the 680 cm^{-1} band. These could be assigned to the substitution of Sn^{4+} with Ce^{4+} into the SnO_2 lattice.

The IR spectra of P_1, P_3 and P_5 samples (heterovalent substitution), show an abnormal transmission decrease and the disappearance of both the characteristic bands at 680 and 620 cm^{-1}, belonging to SnO_2 lattice (the only phase identified by X-ray diffraction).

Table 2
Starting composition, phase composition and ceramic properties of the samples thermally treated at 1100°C

Sample	Additives (2.5 mol%)	3 h			10 h		
		Phase composition	P_a%	$\Delta l/l$%	Phase composition	P_a%	$\Delta l/l$%
P_1	Sb_2O_3	$SnO_{2(ss)}$	9.8	1	$SnO_{2(ss)}$	9.8	1
P_2	CeO_2	$SnO_{2(ss)}$	9.3	−1	$SnO_{2(ss)}$	9.0	1
P_3	$CuSb_2O_6$ + CuO 1.5% 1%	$SnO_{2(ss)}$	0	−16	$SnO_{2(ss)}$	0	−16
P_4	In_2O_3	$SnO_2 + In_2O_3$	9.1	−1	$SnO_2 + In_2O_3$	8.8	1
P_5	$CuSb_2O_6$	$SnO_{2(ss)}$	8.2	−3	$SnO_{2(ss)}$	7.2	−4
P_6	$CuO + CuSb_2O_6$ 0.45% 0.55%	$SnO_{2(ss)}$	0	−18	$SnO_{2(ss)}$	0	−18

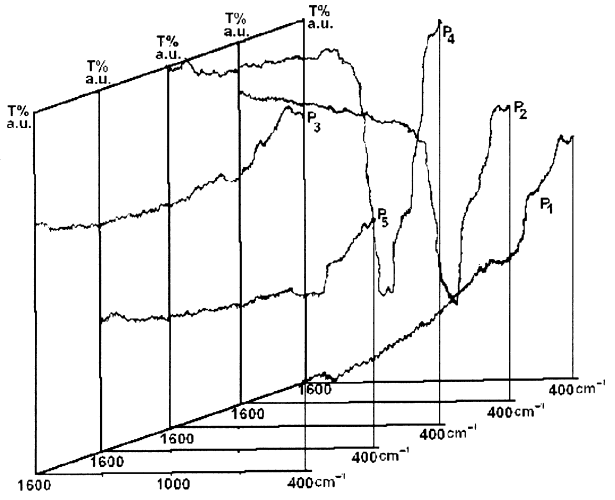

Fig. 1. IR spectra of the thermally treated samples at 1100°C for 10 h.

In previous studies[10,11] the behavior was attributed to the strong interaction between free charge carriers and the lattice phonons.

The IR spectrum of the P_4 sample, containing In_2O_3, in which by XRD no traces of $SnO_{2(ss)}$ but a mixture of phases was noticed, keeps the shape and the position of the characteristic bands of SnO_2. The weak and broad absorbtion band placed at 550 cm^{-1} was assigned to the presence of In_2O_3 crystalline phase.[12]

3.2. Electrical measurements

In Table 3 the results of the Seebeck effects measurements, determined for all prepared samples are presented. The negative values of the Seebeck coefficients indicate electrons as major charge carriers. The values obtained for the samples in which besides $CuSb_2O_6$, supplementary CuO was added, are similar to those previously reported[5] when the initial oxides SnO_2, CuO, Sb_2O_3 were used as starting components.

As was mentioned before by Vlasova and Berry[13,14] the value of Seebeck coefficient obtained for P_1 sample, prepared using Sb_2O_3 as additive, can be considered as a proof for the formation of $Sn^{4+}_{1-x}Sb^{5+}_x e_x O_2$ compound. The value of the Seebeck coefficient of P_4 sample (with In_2O_3 as additive) confirms the XRD results, which have shown the presence of the mixture of phases. It is well known that in the rich In_2O_3 domain of the In_2O_3–SnO_2 system, the so-called ITO materials are obtained by the incorporation of SnO_2 into the In_2O_3 lattice, generating the formation of a n-type electroconductive cubic solid solution. In our case the ITO type solid solution might be the phase allowing the electroconductive behavior. Further research will elucidate the assumption. It is well known that even at very low concentration of the host oxide, electroconductive solid solutions are formed. For example, at 1% SnO_2 and 99% Sb_2O_3 content the presence of the SnO_2 solid solution was evidenced by using SEM.[15]

Table 3
Seebeck coefficent values

Sample	P_1	P_2	P_3	P_4	P_5	P_6
Seebeck coefficient (μV/°C)	−12.3	−13.4	−3.3	−4.6	−25.8	−1.8

The conductivity values were calculated from the electrical resistivity measurements determined on dense samples (0% porosity, shrinkage >15%). Fig. 2 shows the variation of ln$k$ versus $10^3/T$ in −196 to +850°C temperature range. An Arrhenius type behavior was established and high values of the electrical conductivity were obtained for the whole investigated temperature range. The calculation of the activation energies was done using the formula:

$$k = k_0.e^{-\Delta E/RT} \quad (5)$$

The calculated values for the each sample were obtained in the temperature range where a marked change of slope is recorded, respectively 227–257°C for the sample P_6 and 237–497°C for the sample P_3. The obtained values of (E_d) 0.25 and 0.5 eV were similar to

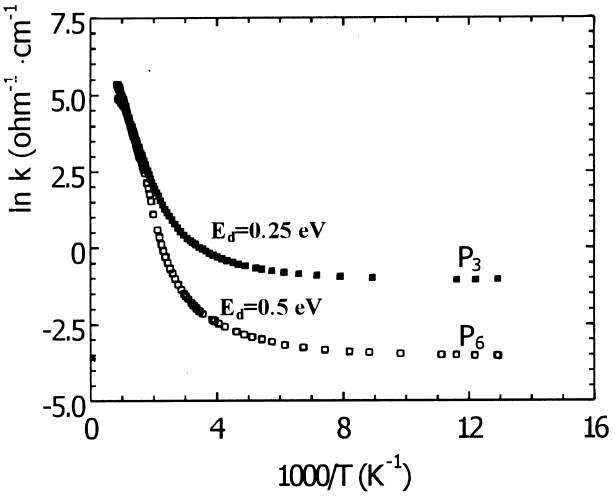

Fig. 2. Arrhenius behavior for the temperature range (−196–850°C) for dense ceramics.

those previously reported[5] for the samples from the SnO_2–CuO–Sb_2O_3 system.

4. Conclusions

The influence of Sb_2O_3, $CuSb_2O_6$, $CuO + CuSb_2O_6$, CeO_2, In_2O_3 used as additives (2.5 mol%) on the structural an electrical properties of the SnO_2 based ceramics was studied.

The phase composition analyzed by XRD, pointed out the formation of the SnO_2 solid solutions with *rutile* type structure. When using In_2O_3 as additive for a similar composition, a mixture of phases is formed.

IR spectroscopy confirmed the formation of the SnO_2 based solid solutions by the decreasing, up to disappearance, of the characteristic vibration bands of the SnO_2 lattice. The effect is stronger in the case of the heterovalent substitution.

Dense ceramics were obtained only when CuO was added in the initial mixture.

The negative values of the Seebeck coefficient for all studied samples indicate electrons as major charge carriers.

The conductivity values of the dense samples are high over the investigate temperature range and present a semiconducting behavior.

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