

## ELECTRONIC CONDUCTION OF THE $\text{Sn}_{1-x}\text{Cu}_{x/3}\text{Sb}_{2x/3}\text{O}_2$ ( $x \leq 1/2$ ) RUTILE TYPE STRUCTURES

S. Mihaiu\*, O. Scarlat, G. Aldica<sup>a</sup>, M. Zaharescu

Romanian Academy, Institute of Physical Chemistry "I. G. Murgulescu", 202 Splaiul  
Independentei, 77208 Bucharest 6, Romania

<sup>a</sup>National Institute for Physics of Materials, PO Box MG-7, RO-76900 Bucharest, Magurele,  
Romania

The influence of the substituent quantity and the effect of CuO addition to the  $\text{SnO}_2$  based solid solutions belonging to the  $\text{SnO}_2 - \text{CuSb}_2\text{O}_6$  pseudobinary system and their electrical behaviour have been approached. The electrical properties were studied by electrical resistivity measurements in the 77 – 1100 K temperature range and by Seebeck coefficient measurements at the room temperature. All the studied samples present a high electrical  $n$  type conductivity over the whole investigated temperature range with activation energy within 0.08 – 0.78 eV interval. A decrease of the electrical conductivity with the increase of substituents quantity up to 500 K was observed. According to the morphology of the obtained samples, a distinctive linear dependence of  $\ln k$  against  $1000/T$  was obtained: 1) the dense  $\text{SnO}_2$  ss ceramics show a linear variation suggesting a direct dependence of electron mobility on temperature; 2) for the porous  $\text{SnO}_2$  ss ceramics, a visible modification of the slope takes place in the temperature range: 300 – 700 K. This was assigned to a change of the mechanism of the charge carrier motion due to the presence of the pores at the surface of the samples. The measured values for the Seebeck coefficient indicate that the main charge carriers are, for all studied samples, the electrons.

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### 1. Introduction

The study of the  $\text{SnO}_2 - \text{CuSb}_2\text{O}_6$  pseudobinary system, the most important subsystem of the Sn-Sb-Cu-O quaternary system, pointed out to the formation of the two types of solid solutions with *rutile* ( $\text{SnO}_2$  (SS)) and *trirutile* ( $\text{CuSb}_2\text{O}_6$  (SS)) structure. The highest solid solubility of  $\text{CuSb}_2\text{O}_6$  compound in the  $\text{SnO}_2$  lattice is 25 % (mol) and that of  $\text{SnO}_2$  into  $\text{CuSb}_2\text{O}_6$  lattice is 20% (mol). Between these two concentration limits, a mixture of  $\text{SnO}_2$  (SS) and  $\text{CuSb}_2\text{O}_6$  (SS) solid solutions was obtained [1].

One assumes that the formed solid solutions should essentially maintain the properties of the paragenesis terms, i. e. the semiconductive behavior of the  $\text{SnO}_2$  [2], and the paramagnetic properties of the  $\text{CuSb}_2\text{O}_6$  binary compound [3], respectively.

Our previous papers concerning the study of the dense ceramics from the  $\text{SnO}_2$ -CuO- $\text{Sb}_2\text{O}_3$  ternary system (CuO: $\text{Sb}_2\text{O}_3$  molar ratio = 1:1), pointed out, in the 77-1100 K temperature range, to an electroconductive behavior of the latter [4]. For these samples, the charge carriers were mainly identified as electrons [5]. It worth mention here, a better sintering capability of the samples obtained from the initial oxides ( $\text{SnO}_2$ , CuO and  $\text{Sb}_2\text{O}_3$ ), which proved a higher densification degree than the samples obtained from  $\text{SnO}_2$  and  $\text{CuSb}_2\text{O}_6$  binary compound (1373 K, 3 hours) [6]. This behavior may be assumed to be a result of an enhanced sintering process due to either the simultaneously phase

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\* Corresponding author: smihaiu@chimfiz.icf.ro

formation and sintering, or to the formation of a liquid phase between unreacted CuO (very small amount) and SnO<sub>2</sub>. This latter was previously evidenced for the SnO<sub>2</sub> based compositions [7].

This paper aims to a comparative study of the electrical properties of the *rutile* type solid solutions from the SnO<sub>2</sub> – CuSb<sub>2</sub>O<sub>6</sub> pseudobinary system, and of the same compositions for which a small amount of copper oxide (II) was selectively added.

## 2. Experimental

SnO<sub>2</sub> (Merck, Co) and CuSb<sub>2</sub>O<sub>6</sub> (prepared in our laboratory [8]) were used as starting materials for the preparation, by classical ceramic method [5,8], of the (1-x) SnO<sub>2</sub> - x CuSb<sub>2</sub>O<sub>6</sub> (x = 0.025 -0.25) studied compositions (*series a*). For the same compositions supplementary CuO was added in the range of 0.5-1.0% mol, to the SnO<sub>2</sub> content in the samples (*series b*).

Uniaxially pressed pellets (30 MPa, Φ = 10 mm) were thermally treated at 1373 K – 10 h (4 deg/min) [6]. For phase determination, a Scintag Automated Diffractometer (CuK<sub>α</sub> radiation - λ<sub>Kα1</sub>=1.54059 Å), was used over the range of 10 to 80° 2θ. X-ray step scans (0.01° step size, 2.5 s counting time) were performed to measure the unit cell parameters.

For the obtained pellets, the densification degree was evaluated by: linear shrinkage (Δl/l - %) by the measuring the variation of the sample diameter before and after the thermal treatment, apparent porosity (P<sub>a</sub> %) by weighing the thermally treated samples before and after 24 hrs of toluene immersion. The experimental density (d<sub>exp</sub>) was measured in methanol by the Archimede method.

To investigate the internal morphology of the samples, the surfaces and fracture of the sintered ceramics was observed by Scanning Electron Microscopy (SEM JEOL 32 type).

A direct current bridge was used for electrical resistivity measurements (four points scheme) on the gold - coated pellet [9], in the 77 to 1123 K temperature range. The Seebeck coefficient was measured at room temperature (warm point method, platinum reference).

## 3. Results and discussion

### 3. 1. X-ray diffraction results

All the investigated samples consist after the thermal treatment at 1373 K from a SnO<sub>2</sub> – based solid solution, i. e. *rutile* type structure (Table 1). For these solid solutions, the unit cell volumes (V<sub>RX</sub>) and theoretical density (d<sub>th</sub>) data - calculated from X-ray diffraction - as well as the measured ceramic properties: linear shrinkage (Δl/l %), apparent porosity (P<sub>a</sub> %) and archimedic density (d<sub>exp</sub>) are also presented (Table 1). The samples obtained from the SnO<sub>2</sub> and CuSb<sub>2</sub>O<sub>6</sub> initial mixtures were nominated by (1-4)a and those with CuO supplementary added by (1 - 4)b.

From the data presented in Table 1, one finds out a linear decrease of the SnO<sub>2</sub> unit cell volume, with the increase of CuSb<sub>2</sub>O<sub>6</sub> content incorporated in the base matrix. In the same direction points the results obtained for the variation of the theoretical density of the studied samples (column 7 of Table 1).

### 3. 2. Ceramic Properties

Concerning the experimentally determined ceramic properties, one may notice a good agreement of the results obtained for the linear shrinkage (Table 1 - column 8), apparent porosity (Table 1 - column 9) and the experimental density (Table 1 - column 10) almost for all the studied samples; for the Sn<sub>0.75</sub>Cu<sub>0.083</sub>Sb<sub>0.167</sub>O<sub>2</sub> (2a) and Sn<sub>0.745</sub>Cu<sub>0.087</sub>Sb<sub>0.167</sub>O<sub>1.996</sub> (2b) solid solutions, even if they present an almost null apparent porosity, the measured values of the densities are lower than the calculated ones.

For the Sn<sub>0.75</sub>Cu<sub>0.083</sub>Sb<sub>0.167</sub>O<sub>2</sub> (2a) solid solution the SEM micrographs show the presence of uniform grains (Fig. 1a) and of the pores with a size dimension less than 0.50 μm. By prolonged thermal treatment the sintering process is enhanced, but some pores are still enclosed in the obtained dense ceramics (Fig. 1b).

The supplementary addition of CuO - (1 - 4)*b* series of the samples - improves the sintering abilities especially in the case of the samples with higher  $\text{SnO}_2$  content (Table 1). Apparently, only in the case of  $\text{Sn}_{0.947}\text{Cu}_{0.024}\text{Sb}_{0.029}\text{O}_{1.990}$  - (1*b*) sample, the quantity of the formed liquid phase is enough to adequately densify the studied sample, for which a 94 % relative density was calculated.

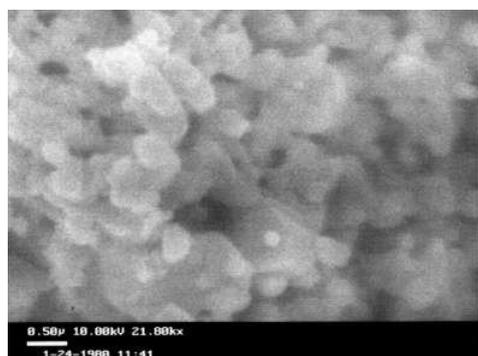
### 3. 3. Electrical properties

For the both category of the samples, i. e. *a* and *b* series, the conductivity values were calculated from resistivity data measured in the 77 - 1100 K temperature range and plotted in the form of  $\ln k$  against  $1000/T$  in Fig. 2 - (2 - 4)*a* and Fig. 3 (1*a*). As seen in Fig. 2 the  $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$  (2*a*) sample - which presented the smallest value for the apparent porosity (see data in Table 1) - also exhibit a distinct behavior comparatively with other samples. For this latter sample, the variation of  $\ln k$  against  $1000/T$  suggests a direct dependence of electron mobility on temperature  $T$  (Fig. 2).

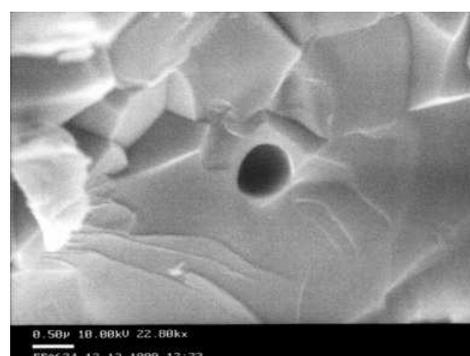
The rest of the samples (3 - 4), belonging to the same *a* series, exhibit a similar electrical behavior with a visible modification of the slope in the 300 - 700 K temperature range, probably due to the presence of the open pores. This behavior is common for *n*-type semiconductors and it is caused by the partial blockage of the electrons from the conduction band by chemisorption accompanied in air by dissociation and ionization of oxygen [9].

Table 1. Initial composition, unit cell volumes and ceramic properties of the samples thermally treated at 1373 K, 10 hours.

Sample	Initial composition (mol%)			$\text{SnO}_{2(\text{ss})}$ composition	$V_{\text{RX}}$ ( $\text{\AA}$ )	$d_{\text{th}}$ ( $\text{g/cm}^3$ )	$\Delta l/l$ %	$P_a$ %	$d_{\text{exp}}$ ( $\text{g/cm}^3$ )
	$\text{SnO}_2$	$\text{CuSb}_2\text{O}_6$	$\text{CuO}$						
1 <i>a</i>	97.5	2.5	-	$\text{Sn}_{0.928}\text{Cu}_{0.024}\text{Sb}_{0.048}\text{O}_2$	71.06	6.99	+1.0	8.0	4.63
1 <i>b</i>	97.5	1.5	1.0	$\text{Sn}_{0.947}\text{Cu}_{0.024}\text{Sb}_{0.029}\text{O}_{1.990}$	-	-	-16	0	6.58
2 <i>a</i>	90.0	10.0	-	$\text{Sn}_{0.750}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$	70.78	6.88	-9.5	0.2	5.60
2 <i>b</i>	89.5	10.0	0.5	$\text{Sn}_{0.746}\text{Cu}_{0.087}\text{Sb}_{0.167}\text{O}_{1.996}$	-	-	-9.0	0.0	5.83
3 <i>a</i>	80.0	20.0	-	$\text{Sn}_{0.571}\text{Cu}_{0.143}\text{Sb}_{0.286}\text{O}_2$	69.80	6.84	-0.9	6.5	4.74
3 <i>b</i>	79.6	20.0	0.4	$\text{Sn}_{0.569}\text{Cu}_{0.146}\text{Sb}_{0.286}\text{O}_{1.997}$	-	-	-3.4	5.2	5.18
4 <i>a</i>	75.0	25.0	-	$\text{Sn}_{0.5}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$	69.42	6.82	0	6.8	4.54
4 <i>b</i>	74.6	25.0	0.4	$\text{Sn}_{0.498}\text{Cu}_{0.169}\text{Sb}_{0.333}\text{O}_{1.998}$	-	-	-5.1	4.5	5.40



a) 1373 K - 3h



b) 1373 - 10 h

Fig. 1. SEM microphotographs of the  $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$  sample

Moreover, when the measurements for the  $\text{Sn}_{0.928}\text{Cu}_{0.024}\text{Sb}_{0.048}\text{O}_2$  (1a) sample, are performed in argon (see Fig. 3) the plot for the  $\ln k$  vs.  $1000/T$  is almost identical with those obtained for samples (3 - 4)a.

In the Table 2 the electrical characteristics of the samples thermally treated at 1373 K, 10 hours, are presented. The activation energy was calculated for several temperature ranges, while the Seebeck coefficient was determined at room temperature.

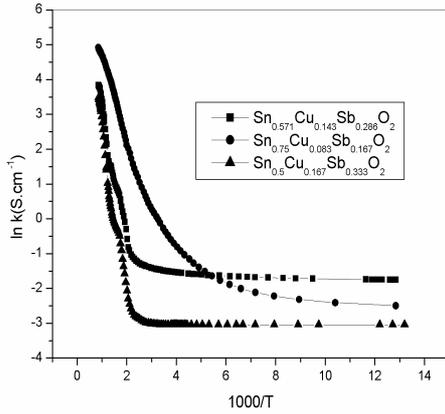


Fig. 2. Arrhenius behavior in the 77 – 1100 K temperature range of selected samples; —■— (3a), —●— (2a), —▲— (4a).

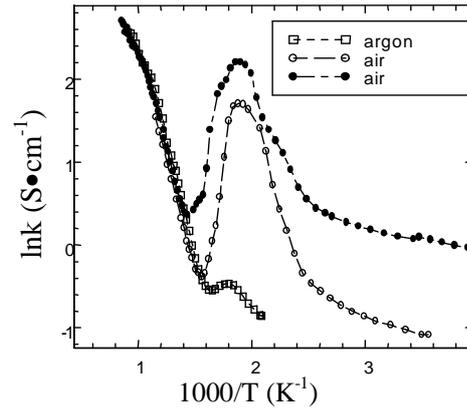


Fig. 3. Arrhenius behavior (air and argon) of  $\text{Sn}_{0.928}\text{Cu}_{0.024}\text{Sb}_{0.048}\text{O}_2$  (1a) sample; —●— measured on as-sintered sample, —○— measured after one year.

Table 2. Electrical characteristics of the samples thermally treated at 1373 K, 10 hours.

Sample	Activation energy ( $E_a$ )		Seebeck coefficient ( $\mu\text{V/K}$ )
	Temperature (K)	Values (eV)	
1.a	450 - 480	0.25	-25.8
	960 - 1180	0.36	
b	500 - 830	0.25	-3.3
2.a	490 - 660	0.25	-3.4
	540 - 590	0.37	
3.a	480 - 570	0.35	-30.0
	690 - 725	0.32	
	805 - 925	0.63	
b	524 - 555	0.28	-3.86
	655 - 735	0.19	
	860 - 950	0.66	
4.a	234 - 245	0.08	-54.0
	490 - 580	0.48	
	840 - 940	0.71	
b	520 - 575	0.16	-4.2
	615 - 720	0.26	
	800 - 910	0.78	

#### 4. Discussion

From the data presented above one may conclude that in the studied compositional range rutile type solid solutions are obtained with the general formula of  $\text{Sn}_{1-x}\text{Cu}_{0.33x}\text{Sb}_{0.67x}\text{O}_7$  and  $\text{Sn}_{1-(x+y)}\text{Cu}_{0.33x+y}\text{Sb}_{0.67x}\text{O}_{2-y}$ , respectively, depending on the presence or absence of the supplementary added CuO. Their electrical properties are strongly influenced by the morphology of the samples.

The different values of the electrical conductivity obtained up to 700 K for the three discussed samples (1a, 3 - 4a), are rather due to the different quantity of  $\text{CuSb}_2\text{O}_6$  incorporated in  $\text{SnO}_2$  lattice, since a decrease of conductivity with the increase of its content may be noticed. However, the conductivity values are almost identical at high temperatures, for all the studied samples. The studied samples also presented high porosity values (see Table 1), pointing out to a great amount of open and closed pores. Still, considering their similar electrical behavior this might indicate the uniform distribution of these pores and a good connectivity of the electroconductive phases [10].

Data obtained for *b* series, with CuO supplementary added, are nearly similar to the electrical resistivity values previously presented for *a* series, except the  $\text{Sn}_{0.928}\text{Cu}_{0.024}\text{Sb}_{0.048}\text{O}_2$  (1b) sample. For this latter sample the electrical behavior seems to be very similar to that of (2a) sample and in good agreement with ceramic properties previously discussed.

Considering an Arrhenius type behavior, the activation energies were calculated for the studied samples and are listed in Table 2. Two or three separate activation energies may be noticed in Table 2 - for the samples that presented a significant apparent porosity, the higher activation energies being predominated at high temperatures, while the lower ones at lower temperatures.

It is our basic conclusion that in the 300 - 700 K temperature range, the obtained values for the activation energies, may be assigned to a different conduction mechanism, due to the migration of charge carriers in the presence of pores.

As seen from the data presented in Table 2, negative values for the Seebeck coefficient were obtained for all the studied samples, pointing out to electronic type conduction - with electrons as major charge carriers. The Seebeck coefficient values obtained for the dense samples as well as those for the samples with CuO supplementary added, are close to the values reported for metals [11,12], confirming the uniform distribution of the pores and a better connectivity of the electroconductive phases in the ceramic body.

#### 5. Conclusions

Solid solution with formula  $\text{Sn}_{1-x}\text{Cu}_{0.33x}\text{Sb}_{0.67x}\text{O}_7$  and  $\text{Sn}_{1-(x+y)}\text{Cu}_{0.33x+y}\text{Sb}_{0.67x}\text{O}_{2-y}$ , when CuO was supplementary added, were characterized from structural, morphological and electrical points of view.

All the studied samples present a *n*-type semiconducting behaviour.

The electrical properties are strongly influenced by the morphology of the samples:

- 1) the dense  $\text{SnO}_2$  ss ceramics show a linear variation suggesting a direct dependence of electron mobility on temperature;
- 2) for the porous  $\text{SnO}_2$  ss ceramics, a visible modification of the slope takes place in 300 - 700 K temperature range. This was assigned to a change of the mechanism of the charge carrier motion due to the presence of the pores at the surface of the samples.

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