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Advanced SnO₂-Based Ceramics: Synthesis, Structure, Properties

Mihaiu Maria Susana, Scarlat Oana,
Zuca Stefania and Zaharescu Maria

*"Ilie Murgulesc" Institute of Physical Chemistry of the Romanian Academy
Romania*

1. Introduction

Tin dioxide presents specific optical and electrical properties and a good chemical stability which confers special characteristics to the SnO₂ based materials.

SnO₂ belongs to the important class of transparent conductor oxide materials that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum. These properties are required for optoelectronic applications i.g light emitting diodes, electrode materials in solar cells flat panel displays, transparent field effect transistors [Wagner, 2003; Presley et al., 2004]. Tin dioxide is also an oxidation catalyst and its activity and selectivity can be substantially improved by incorporation of various additives [Mihaiu et al., 2002]. Another field in which tin dioxide plays a dominant role is in solid state gas sensors. A wide variety of oxides exhibit sensitivity towards oxidizing and reducing gases by a variation of their electrical properties, but SnO₂ was one of the first considered, and still is the most frequently used, material for these applications [Caldararu et al., 1999]. The sensor properties of SnO₂ depend not only on such factors as the oxide's surface stoichiometry, the methodology used to prepare the powder, temperature and atmosphere of calcination but also, and mainly, on the high specific area deriving from the low densification of this oxide. Nowadays, SnO₂ is certainly one of the main polycrystalline ceramic candidates to compete with the traditional multicomponent ZnO-based varistors (voltage-dependent resistor-VDR's), especially because of high electrical stability and its more simple microstructure [Bueno et al., 2007]. High density in polycrystalline ceramics is essential for high varistor properties, since the phenomena involved for good varistor properties occur in the region of the material's grain boundaries. The main restriction in a wider use of this type of material is related to poor sintering ability of the SnO₂-based compositions. This behaviour is related to the low diffusivity of the SnO₂ structure and predominance of the nondensifying mechanisms (surface diffusion and evaporation-condensation). The latter result in grain and pore growth, thus limiting the final density [Varela et al., 1990]. The sintering problem is further complicated by the formation of deleterious intermediate phases above 1273K and high vapor pressure of SnO [Dolet et al., 1992]. Dense SnO₂-based materials have been obtained either by using sintering additives (e.g., CuO) to promote densification by liquid-phase mechanism or by applying high pressures (e.g., in hot isostatic pressing technique).

In recent years, aluminium smelters have made great progress in reducing emissions of various gaseous and particulate compounds that may have a negative impact on the global, regional and local environment [Popescu et al., 2007]. The selection of a suitable anode material has proved to be very difficult task. It should be resistant to evolving oxygen and cryolite-alumina melt at $\sim 950^\circ\text{C}$, i.e., in the melt, which is used as solvent for oxides. The maximum allowable wear rate for a commercial use is evaluated as 1.0 cm/year at a current density of 0.8 A/cm^2 . The electric conductivity and electrocatalytic activity with respect to oxygen evolution should be high enough to prevent extra losses of electricity. The material should be resistant to mechanical and thermal stress, and its components should not be poisonous for the raw aluminum, to avoid further purification. The only materials that meet these requirements are a number of oxides. Over the years, many materials have been tested on a laboratory scale with mixed success. One such material is tin oxide (SnO_2) doped with different additives which is considered to be a promising material for manufacturing electrodes for melts electrolysis due to their excellent corrosion resistance and heat resistant properties. Studies on the electrical conductivity of SnO_2 -based ceramic materials revealed the major influence exerted by the nature of the dopants and the thermal treatment, i.e. the sintering conditions. The electrical resistance is claimed [Zuca et al., 1999] to be decreased drastically (by 4 to 5 orders of magnitude) by the addition of Sb_2O_3 as, following its limited solubility in the SnO_2 lattice, the concentration of charge carriers increases. On the other hand, the sintering capacity was found to be greatly improved by the addition of CuO [Dolet et al., 1995]. Although a list of various potential additives has been suggested by Varela, their influence on the sintering properties (namely densification) and electrical conductivity has not been systematically investigated so far [Varela et al., 1992]. The influence of a series of oxide additives (individual and various combinations), namely Sb_2O_3 , CuO , ZnO , Fe_2O_3 , Cr_2O_3 , TiO_2 , MnO_2 and MoO_3 on the sintering capacity and electrical conductivity of the SnO_2 -based ceramic materials has been investigated. From among various oxide additives tested, only CuO was found to promote the densification of the composite. The addition of Sb_2O_3 , which is claimed to increase the electrical conductivity, is only effective in the presence of CuO addition [Zuca et al., 1991].

During the electrochemical investigations some irregularities were found (it seemed that a small amount of oxygen was consumed on the anode). To understand the causes of these phenomena in order to diminish or remove them it is considered necessary to investigate the chemical processes between the three oxides (SnO_2 , Sb_2O_3 , and CuO) that take place during the thermal treatment of their mixture.

In this work we propose a review of chemical processes that occur in the SnO_2 - Sb_2O_3 - CuO system over the whole concentration range of the components. The obtaining of the sintered materials by conventional ceramic method and spark plasma sintering and the electrical behaviour of the oxide materials belonging to this system is also approached.

2. Phase formation in the SnO_2 - Sb_2O_3 - CuO ternary system

A summary of physical characteristics of individual SnO_2 , Sb_2O_3 , and CuO compound is given in the Table 1.

Based on the experimental data determined under non-isothermal conditions up to 1773K for pure components [Zaharescu et al., 1991], the following has been established:

1. no effects were observed for SnO_2 in the 293 - 1773 K temperature range;

2. the endothermal reduction of CuO to Cu₂O which starts at 1348 K, is followed by eutectic melting of the two copper oxides;
3. the oxidation of Sb₂O₃ to Sb₂O₄, which takes place within a wide temperature interval from 713 to 933 K is accompanied by a well marked exothermal effect and a mass increase; the endothermal effect observed at 1433 K indicates the vaporization of Sb₂O₄.

Physical and structural characteristics	SnO ₂	Sb ₂ O ₃	Sb ₂ O ₄	CuO
Mineral	cassiterite	valentinite	cervantite	tenorite
Culour	white	colorless	white	black
Molecular weight	150,69	291,50	307,50	78,54
Symmetry	tetragonal	romboedric	orthorhombic	monoclinic
Space group	D _{4h} ¹⁴ (P4/mnm)	V _h ¹⁰ (P _{ccn})	Pna21	C _{dh} ^{6C} (c2/c)
Lattice parameters (Å)	a ₀ =b ₀ =4,7374 c ₀ =3,1864	a ₀ = 4,92 b ₀ =12, 46 c ₀ = 5,42	a = 5.43 b = 4.79 c = 11.73	a ₀ = 4,92 b ₀ =12, 46 c ₀ = 5,42 β =99°29′
Ionic radius (Å)	Sn ⁴⁺ = 0,71		Sb ³⁺ =0,76 Sb ⁵⁺ =0,62	Cu ²⁺ =0,72
Density (g/cm ³)	6,95	5,67	6.64	6,3- 6,49
Melting point (K)	-O;1800;>2200*		1433 sublimes	1599
Boiling point (K)	2073 sublimes			2273
Refraction index	2⊥ c 2,11// c	2,18 2,35 2,35	2,00	2,63

Table 1. Physical and structural characteristics of SnO₂, Sb₂O₃, CuO [Wyckoff, 1963, 1964]

2.1 Solid state reactions in the component subsystems

2.1.1 SnO₂-CuO binary system

The experimental data on the SnO₂-CuO binary system have been published in several papers [Zaharescu et al., 1991; Scarlat et al., 1999]. The thermal analysis of (1-x)SnO₂-xCuO compositions, in non-isothermal conditions, in air, up to 1773 K, underlined that the thermal effects registrated could be assigned exclusively to the presence of CuO in the reaction mixture. The reduction process of CuO to Cu₂O over 1273 K as well as the formation over 1373 K of the liquid phase have been evidenced. No binary compounds were formed.

The results obtained by isothermal treatments at 1173, 1273 and 1473 K of the (1-x)SnO₂-xCuO mixtures were also analyzed. Thus, for the samples with 1-10% content of CuO only SnO₂ was identified by X-ray diffraction, no matter of treatment temperature. Although the

ionic radii of the two ions are close ($0.71 \text{ \AA}$ for the Sn^{4+} and $0.72 \text{ \AA}$ for the Cu^{2+}) due to their different structures and especially their different valence, the formation of a solid solution between the two oxides is unlikely to occur. The disappearance of characteristic diffraction lines of copper oxide and the sharp contraction of these samples was assigned to its penetration into the liquid phase (eutectic melt), which facilitates rapid rearrangement of the ions [Zaharescu et al., 1991; Dolet et al., 1992]. It was observed that in isothermal condition the reaction of CuO reduction, namely: $\text{CuO} \rightarrow \text{Cu}_2\text{O}$ takes place at substantially lower temperature compared with the non-isothermal measurements. The phase composition of the binary mixtures with a content of CuO $>30\%$, thermally treated at 1273 K consists in a mixture of SnO_2 , CuO and Cu_2O . The samples with a CuO content exceeding 10% fused when thermally treated at 1473 K. The shrinkage of the tested samples increased with increasing temperature while the porosity decreased; at 1273 and 1473 K samples with a zero porosity were obtained, apparently owing to the presence of the liquid phase.

As a conclusions, at temperature over 1273 K the SnO_2 -CuO initial binary system transforms into the SnO_2 - CuO- Cu_2O pseudo-ternary system. In the presence of CuO the sintering ability of SnO_2 is promoted. Below 1173 K, the rate of densification can be explained in terms of viscous flow model [Zaharescu et al.,1993], while at higher temperature a copper-rich liquid is formed and rearrangement is occurring even for short sintering time.

2.1.2 SnO_2 - Sb_2O_3 binary system

Widely used as catalysts in catalytic oxidation reactions, the oxide powders belonging to the SnO_2 - Sb_2O_3 system are studied by many research groups in this field [Harrison et al., 1999; Park et al., 1999] especially in the subsolidus domain.

In accordance with the rules of formation of substitutional solid solutions (the sizes of two ions differ by less than 15%, have similar valency factor, chemical affinity and structure type) tin dioxide can form a limited solid solution with antimony oxides. Solid solubility limit depends on the method of preparation and treatment temperature. Volta obtained monophasic powders with rutile type structure by coprecipitation of tin (IV) and antimony (V) chlorides and heat treatment at 773 for 16 hours [Volta et al., 1985] of the resulted hydroxides. Similar results have been obtained by Vlasova for the powders with the antimony content of 40% and thermal treatment at 873 K temperature[Vlasova et al.,1990]. At 1273 K the amount of antimony atoms in solid solution decreases to 30% and at 1473 K to 4%. Orel et al. have found that regardless of the initial concentration of antimony, the maximum amount of Sb_2O_4 entered into the SnO_2 lattice is of 2.38 mol at 1473 K [Orel et al., 1995]. The interactions that occur between the two oxides in the whole concentration range in non isothermal (up to 1773 K) and isothermal conditions at 873, 1073, 1273 and 1473 K temperatures were investigated in paper [Zaharescu et al., 1991]. The temperature interval of the exothermal effect corresponding to the oxidation of Sb_2O_3 to Sb_2O_4 is substantially narrowed in the binary mixtures (695-716 K) compared to the pure Sb_2O_3 (713-933 K) which suggests the catalysing effect of SnO_2 in the oxidation process. It may be also assumed that in the reaction with SnO_2 , antimony participates as a heterovalent mixture of the Sb(III)Sb(V)O_4 type. The endothermal effect observed at high Sb_2O_3 concentrations at temperatures above 1423 K which is accompanied by a mass loss, is assigned to the vaporization of Sb_2O_4 . The exothermal effect indicates the oxidation of Sb_2O_3 to Sb_2O_4 at 873 K however, the latter oxide has not been identified by X-ray diffraction at concentrations up to 10% (all concentrations are given in mass %). This can be apparently assigned to the

formation of the solid solution owing to the substitution of antimony for tin in the SnO₂ crystal structure. Although the samples with a higher Sb₂O₄ concentration undergo deformation and peeling at higher temperatures which make them unsuited for the subsequent measurements. The concentration of Sb₂O₄ (up to 30%) in the solid solution apparently increases with increasing temperature (up 1273 K) and only SnO₂ is identified in the undeformed samples. The XRD results indicate the displacement of the pure SnO₂ diffraction peaks due to the formation of this rutile type of solid solution. All peaks were slightly shifted to the right after the solid solution was formed (larger angle or smaller both *a* and *c* lattice parameters) with respect to pure SnO₂.

Taking into account that Sb₂O₃ in the presence of SnO₂ over 773 K in air, completely turns into Sb₂O₄ and the oxidation state of tin ions do not change, the question is what form of antimony ions enter the tin dioxide lattice. Vlasova proposed the following "formula" [Vlasova et al., 1990]:

where e_x = free electrons

and V_k and V_a cation and anion vacancies, respectively

When contents of antimony atoms do not exceed 3% in the SnO₂ lattice, the following "compounds" were identified by EPR: $\text{Sn}^{4+}_{1-x}\text{Sb}^{3+}_x\text{O}^{2-}_{2-x}\text{V}_{ax}$; $\text{Sn}^{4+}_{1-x}\text{Sb}^{5+}_xe_x\text{O}^{2-}_2$;

In the case of higher concentration of antimony embedded in the SnO₂ lattice the most likely the resulted solid solution has the the following composition: $\text{Sn}^{4+}_{1-2x}\text{Sb}^{3+}_x\text{Sb}^{5+}_x\text{O}^{2-}_2$. By EXAFS it has been established that Sb dopants occupy Sn sites in the rutile structure [Chadwick et al.,1993; Rockenberger et al., 2000]. XANES measurements showed that the largest fraction of Sb has a valency of 5⁺, although 3⁺ was also observed in nanocrystalline SnO₂. The Sb³⁺ species may be due to a strong tendency of Sb to segregate to the surface [Dusastre et al., 1998; Slater et al., 1999].

2.1.3 Sb₂O₃-CuO binary system

Sb₂O₃-CuO binary system is the most complex subsystems of the SnO₂-Sb₂O₃-CuO ternary system. In this system, the formation of CuSb₂O₆ binary compound with pentavalent antimony has been reported. The compound has a tri-rutile structure, short-range and long range magnetic ordering. Under some special conditions, two other binary compounds, having a higher copper content, have been prepared: Cu₄SbO_{4.5} and Cu₉Sb₂O₁₉ [Bystrom et al.,1944; Shimada et al.,1982; 1985;1988]. Stan et al., have studied the (10-*n*)CuO + *n*Sb₂O₃mol (*n*=0;1;...10) mixtures belonging to the Sb₂O₃-CuO binary system at room temperature. According to the thermal analysis results, the following solid state reactions occur [Stan et al.,1998] :

Where $r \in (0,1)$ is the fraction of CuSb_2O_6 that transforms into $\text{Cu}_4\text{SbO}_{4.5}$.

In order to emphasize an intermediate stage in the compound formation, Fig. 1 shows the relative intensities of the X-ray characteristic lines for the mixtures thermally treated for only one hour.

The same compounds have been obtained in both isothermal treatment (one hour and three hours) and non-isothermal conditions. This points to the high reactivity of the oxides in this system. There is no evidence of $\text{Cu}_9\text{Sb}_2\text{O}_{19}$ compound formation. This compound as reported only for high pressures (see Table 2). Then, in the range of 293-1273 K at normal atmospheric pressure, the following compounds can be found in equilibrium: CuO , Cu_2O , Sb_2O_3 , Sb_2O_4 , CuSb_2O_6 and $\text{Cu}_4\text{SbO}_{4.5}$.

Fig. 1. Relative intensities of the X-ray characteristics lines for the binary mixtures thetmally treated at 773, 823 and 1273 K, one hour

All the experimental evidences show that equations (1), (2) and (3) are suficient to describe the reactions occuring in the $\text{Sb}_2\text{O}_3\text{-CuO}$ binary system with increasing temperature. If the

reactions are considered as completed, including $r=1$ in equation (3), then the quantity of oxygen that is gained or lost can be calculated for each sample.

The atomic composition modifications during the thermal treatments for the four representative samples is given Fig.2. At room temperature the compositions lay on the Sb₂O₃-CuO line as shown in Fig.2. The composition line moves to Sb₂O₄-CuO at 773 K and changes to Sb₂O₄-CuSb₂O₆-CuO over 823 K. Finally, if the reaction (3) is completed at 1273 K, the compositions lay on the CuO- Cu₄SbO_{4.5}-CuSb₂O₆ - Sb₂O₄ .

Fig. 2. Atomic compositions after the thermal treatment for the following initial mixtures: S₁ the mixture of 90 mol% of CuO and 10% mol of Sb₂O₃; S₃ the mixture of 70 mol% of CuO and 30% mol of Sb₂O₃; S₅ the mixture of 50 mol% of CuO and 50% mol of Sb₂O₃; S₇ the mixture of 30 mol% of CuO and 70% mol of Sb₂O₃ [Stan et al.,1998]

2.2 Solid state reactions in the SnO₂-Sb₂O₃-CuO ternary system

The SnO₂-Sb₂O₃-CuO ternary system have been investigated in the whole concentrations range isothermal and non-isothermal conditions in [Zaharescu et al.,1991;1993; Mihaie et al.,1995]. In the Fig.3 experimental ternary compositions are graphically presented.

Equimolecular mixture of CuO and Sb₂O₃ (which leads to CuSb₂O₆ formation) determine the next evolution of the mixtures in the system and this ratio affords the classification of sample in three categories:

- (I) CuO:Sb₂O₃=1 and the samples lie on SnO₂-equimolecular mixture;
- (II) CuO:Sb₂O₃ >1 and the samples are belonging to the CuO-CuO.Sb₂O₃-SnO₂ pseudo-ternary system;

Oxide compositions (%mol.)			Thermal effects (K)		Mass variation (%)		Assignment	Phase composition
SnO ₂	Sb ₂ O ₃	CuO	Endo	Exo	Exp.	Calc.		
93	3	4		695,728	+0.34	+0.34	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO ₂
80	10	10		713,733	+0.86	+1.01	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO ₂ , CuSb ₂ O ₆
					+0.47	+1.00	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
70	10	20		713	+0.96	+1.06	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO ₂ , CuSb ₂ O ₆ , Cu ₄ SbO _{4.5}
				1053	+0.96	+1.05	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
			1233		-0.41	-0.52	CuO → Cu ₂ O [-O]	
70	20	10		733	+1.65	+1.86	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO _{2ss} , Sb ₂ O ₄ , CuSb ₂ O ₆
					+0.76	+0.92	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
60	20	20		748	+1.66	+1.94	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO ₂ , CuSb ₂ O ₆
				1073	+1.63	+1.91	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
33.3	33.3	33.3		761	+3.07	+3.07	[O] Sb ₂ O ₃ → Sb ₂ O ₄	SnO ₂ , CuSb ₂ O ₆
				1112	+2.90	+2.89	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
10	45	45		713	+3.14	+3.96	[O] Sb ₂ O ₃ → Sb ₂ O ₄	CuSb ₂ O ₆ , SnO ₂
				1148	+3.14	+3.89	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
10	40	50		713,793	+3.44	+3.73	[O] Sb ₂ O ₃ → Sb ₂ O ₄	CuSb ₂ O ₆ , SnO ₂ , Cu ₄ SbO ₄
				1063	+3.55	+3.59	[O] Sb ₂ O ₄ → Sb ₂ O ₅	
			1223		-0.30	-0.43	CuO → Cu ₂ O [-O]	
10	50	40			+3.98	+4.15	[O] Sb ₂ O ₃ → Sb ₂ O ₄	CuSb ₂ O ₆ , SnO ₂ , Sb ₂ O ₄
					+3.12	+3.18	[O] Sb ₂ O ₄ → Sb ₂ O ₅	

Table 2. The results of differential thermal analysis and thermogravimetry of the ternary mixtures

The phase composition consists in SnO_{2ss}, Sb₂O₄, CuSb₂O₆ mixtures. In isothermal conditions the ternary mixtures have been themally treated at 873, 1073, 1273, 1373 and 1473 K. Samples thermally treated at lower temperatures (873,1073,1273 K) showed no linear

shrinkage but linear dilatation and high porosity pointing out an inadequate sintering [Zaharescu et al., 1999]. Besides oxide composition in Table 3 the phase components and the ceramic characteristics of studied mixtures thermally treated at 1373 K are given. In the categorie (I) ($\text{CuO}:\text{Sb}_2\text{O}_3=1$) the solid solutions with SnO_2 crystal structure (rutile) includes CuSb_2O_6 (tri-rutile structure) up to a limit of about 50 mol%. Below this limit a mixture of SnO_2 and CuSb_2O_6 is detected. A similar behaviour has been reported by Kikuchi in the $\text{SnO}_2\text{-MSb}_2\text{O}_6$ system ($\text{M}=\text{Zn},\text{Mg}$) [Kikuchi et al., 1983]. As claimed by the author, ZnSb_2O_6 is solved in SnO_2 up to 50 mol% as $\text{Zn}_{1/3}\text{Sb}_{2/3}\text{O}_2$ at 1473K whereas SnO_2 is dissolved in ZnSb_2O_6 up to 20 mol% at the same temperature. The lattice parameters decrease with decreasing SnO_2 contents. Similarly, MgSb_2O_6 dissolved in SnO_2 up to 50 mol% at 1523 K but SnO_2 was sparingly solved into MgSb_2O_6 . In the categorie (II) ($\text{CuO}:\text{Sb}_2\text{O}_3 > 1$) the same type of solid solubility has been observed. The compounds CuSb_2O_6 and $\text{Cu}_4\text{SbO}_{4.5}$ have been also identified by XRD for a large range of concentrations. For the mixture containing 10 mol% SnO_2 , this compound was not identified. One can assume that SnO_2 dissolves in CuSb_2O_6 forming a solid solution with tri-rutile structure. In the categorie (III) ($\text{CuO}:\text{Sb}_2\text{O}_3 < 1$) SnO_2 -based solid solution and CuSb_2O_6 compound have been observed. Although in this system Sb_2O_3 is exceeding the necessary amount required by CuSb_2O_6 stoichiometry, it was not identified by XRD. This result suggests that the unreacted Sb_2O_4 dissolves preferentially in SnO_2 and hinders the dissolutions of CuSb_2O_6 in the SnO_2 crystal network.

Based on the experimental data, the authors [Stan et al.1997] reported that in $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-CuO}$ ternary system besides the solid state reactions represented by 1-3 equations (section 2.1.3.), at temperature above 1273 K, the following reactions take place:

Evolution of the phase composition of the $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-CuO}$ ternary system with thermal treatment at 873, 1073, 1273, 1373 K could be better visualized in a quaternary representation (Figure 4).

Fig. 4. Evolution of phase composition with thermal treatment temperature

In these representations the experimental ternary mixtures belonging to $\text{SnO}_2\text{-Sb}_2\text{O}_4\text{-CuO}$ ternary subsystem at 773K, $\text{SnO}_2\text{-Sb}_2\text{O}_4\text{-CuO-CuSb}_2\text{O}_6$ pseudo-quaternary system at 1073 K and $\text{SnO}_2\text{-Sb}_2\text{O}_4\text{-CuSb}_2\text{O}_6\text{-Cu}_4\text{SbO}_{4.5}$ pseudo-quaternary system at temperatures $>1273 \text{ K}$.

Crt. No.	Composition (mol.%)			Phase composition	Shrinkage %	Porosity %	Density g/cm ³
	SnO ₂	Sb ₂ O ₃	CuO				
(I) CuO: Sb ₂ O ₃ =1							
1.	80	10	10	SnO ₂ (ss)	10	-	5.815
2.	60	20	20	SnO ₂ (ss)	10	0.16	5.9237
3.	40	30	30	SnO ₂ + CuSb ₂ O ₆	2	3.56	
4.	33.3	33.3	33.3	SnO ₂ + CuSb ₂ O ₆	+5	6.25	
5.	20	40	40	CuSb ₂ O ₆ + SnO ₂	+1	4.92	
(II) CuO: Sb ₂ O ₃ >1							
1.	70	10	20	SnO ₂ (ss)	12	0.73	
2.	60	10	30	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	12	0.77	
3.	50	10	40	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	15	0.79	
4.	50	20	30	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	13	0.35	
5.	40	10	50	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	20	0.43	6.3018
6.	40	20	40	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	12	0.38	
7.	30	10	60	SnO ₂ (ss)+ Cu ₄ SbO _{4.5}	12	0.58	
8.	30	20	50	CuSb ₂ O ₆ + SnO ₂ + Cu ₄ SbO _{4.5}	9	0.33	5.9820
9.	30	30	40	CuSb ₂ O ₆ + SnO ₂ + Cu ₄ SbO _{4.5}	6	0.92	
10.	20	10	70	CuSb ₂ O ₆ (ss) + Cu ₄ SbO _{4.5}	11	0.31	5.8785
11.	20	20	60	CuSb ₂ O ₆ (ss)+ Cu ₄ SbO _{4.5}	6	0.11	6.0248
12.	20	30	50	CuSb ₂ O ₆ (ss) + Cu ₄ SbO _{4.5}	7	0	5.6297
13.	10	10	80	Cu ₄ SbO _{4.5} + SnO ₂ (ss)	12	1.45	
14.	10	20	70	CuSb ₂ O ₆ (ss) + Cu ₄ SbO _{4.5}	10	0	5.8088
15.	10	30	60	CuSb ₂ O ₆ (ss) + Cu ₄ SbO _{4.5}	7	0	5.7790
16.	10	40	50	CuSb ₂ O ₆ (ss)	+5	5.29	
(III) (CuO: Sb ₂ O ₃ <1							
1.	70	20	10	SnO ₂ (ss)	1		
2.	60	30	10	SnO ₂ (ss) + CuSb ₂ O ₆	+2		
3.	20	50	30	CuSb ₂ O ₆ + SnO ₂ (ss)	+3		
4.	10	50	40	CuSb ₂ O ₆ (ss)	-		

Table 3. Oxide composition, phase composition, ceramic characteristics of the ternary mixtures thermally treated at 1373 K, 1 h

2.2.1 SnO₂–CuSb₂O₆ binary system

In the subsolidus domain, the formation of the CuSb₂O₆ binary compound was found to be a basic stage in the SnO₂-Sb₂O₃-CuO ternary sistem evolution and, consenquently, SnO₂-CuSb₂O₆ binary system was considered to be representative for the study of Sn-Sb-Cu-O quaternary system. In the work [Scarlat et.al., .2002], the high temperature interactions between SnO₂ and CuSb₂O₆ have been investigated both in non-isothermal and isothermal conditions. The experimental compositions are expressed as (1-*x*)SnO₂-*x* CuSb₂O₆, with *x*= 0, 0.025, 0.04, 0.06, 0.08, 0.1, 0.2, 0.25,0.75, 0.8...1, covering the whole concentration range. The thermal treatments in the non-isothermal conditions pointed out that more than one chemical process developed between 1398 - 1723 K which are exclusively a result of the presence in the initial mixture of CuSb₂O₆ (see Table 2, section 2.1.3.) according to the following equations:

This observation suggests that no solid state interactions have occurred between SnO₂ and CuSb₂O₆ in non-isothermal conditions.

The isothermal treatements of the binary mixtures at 1273 K (one, three and ten hours) and at 1373 and 1473 K respectively (three hours) have been done. An increase of the temperature value over 1473 K was not possible due to reactions (7) and (8), resulting in the decomposition and partial melting of pure CuSb₂O₆ and solid solutions.

Based on the experimental results, the subsolidus phase relations of SnO₂-CuSb₂O₆ system are presented in Fig.5.

Fig. 5. Subsolidus phase relations in the SnO₂ -CuSb₂O₆ system

Accordingly, the system was divided at 1373 K into the following three subsolidus domain:

Due to the CuSb₂O₆ decomposition and to the presence of the liquid phase extending from the Cu-O system [Scarlat et al., 20020], the phase relationships establishing becomes more difficult over 1473 K.

One has established that SnO₂-CuSb₂O₆ is a pseudobinary system with solid solubility limit of the end members.

2.2.2 Solid state solutions

The results previously presented evidenced the formation of large domains of unique phase with rutile as well as tri-rutile structure. The mechanism of their formation was approached in the papers [Mihaie et al., 1995; Scarlat et al., 2002]. It considers framing the initial ternary mixtures from which the unique phase is formed in the subsystems component of the Sn-Sb-Cu-O quaternary system: (1) SnO₂-CuO.Sb₂O₅ pseudobinary system (the ratio CuO:Sb₂O₃ =1), (2) SnO₂-CuO.Sb₂O₅-CuO pseudoternary subsystem (the ratio CuO: Sb₂O₃ ≥1) and (3) SnO₂ -CuO.Sb₂O₅-Sb₂O pseudoternary subsystem (the ratio CuO: Sb₂O₃ ≤1). As has been stated previously, in all cases the formation of the CuSb₂O₆ binary compound, which precedes the formation of the SnO₂ solid solution as unique phase, was found to be a basic stage in the interactions at high temperature of the initial components.

In the following, the formation of solid solutions from the ternary mixtures belonging to the SnO₂-Sb₂O₃-CuO system as well as from the SnO₂ and CuSb₂O₆ binary mixtures will be presented. The rutile type solid solution unique phase was formed from the ternary mixtures with a SnO₂ molar content of over 70% and a ratio CuO:Sb₂O₃ ≥1, and was thermally treated at 1273K for 3 h. The lattice parameters calculated from X-ray diffraction data decrease due to the inclusion of CuSb₂O₆ in the SnO₂ lattice [Mihaie et al., 1995]. The solid solution which was formed is of Sn⁴⁺_{1-x}Cu²⁺_{x/3}Sb⁵⁺_{2x/3}O₂ (0 < x < 1/2) type. The excess of copper oxide forms with SnO₂ a liquid phase which is responsible for the sample densification at 1273K. In case of the ternary mixtures with the ratio CuO: Sb₂O₃ ≤1 (molar content of SnO₂ ≥70%) the formation of the rutile type solid solution as a unique phase takes place in two steps. In the first step, Sb₂O₄ dissolves in the SnO₂ lattice (1273 K), and in the second step CuSb₂O₆ is included in the SnO₂ lattice (1273K). The decrease of the parameters is more important than previously mentioned [Mihaie et al., 1995].

The following formula was proposed: Sn⁴⁺_{1-x}Cu²⁺_{x/5}Sb³⁺_{x/5}Sb⁵⁺_{3x/5}O₂, in which 0 < x < 1/2

In case of the ternary mixtures with the ratio CuO: Sb₂O₃ =1, the unique phase of rutile type solid solution was obtained up to the composition domain with over 60 mol% SnO₂.

The development of phase composition of the ternary mixture with 60 mol% of SnO₂, 20 mol% of Sb₂O₃ and 20mol% of CuO at different temperature is presented in the Fig.6. [Zaharescu et al., 2001] At 1373 K temperature only SnO_{2ss} solid solution with Sn_{0.5}Cu_{0.17}Sb_{0.33}O₂ formula should be observed. To clarify the way CuSb₂O₆ is dissolved into SnO₂ lattice to form a solid solution, IR absorption spectra (Fig.7) for the same samples utilized to identify by XRD the formation of SnO₂-based solid solution were recorded.

One can draw the following conclusions:

After thermal treatment, one hour at 873 K the presence of SnO₂ by the 635 cm⁻¹ strongest band was identified. One can assume that CuO bands overlap those of SnO₂, whose presence is predicted from the shoulder located at 580 cm⁻¹. The bands group that comes up at 735, 480 and 377 cm⁻¹ may be assigned to the presence of α- Sb₂O₄. At 1073 K the SnO₂ typical band (650 cm⁻¹) does not change its position but becomes less clear. The bands of α- Sb₂O₄ come out less outlined in the same wave number domain as at 873 K. The authors

Fig. 6. XRD patterns of the mixture with initial composition: 60mol% of SnO_2 , 20 mol% of Sb_2O_3 and 20 mol% of CuO , thermally treated one hour at 873, 1073, 1273, 1373 and 1473 K.

noted the presence of two extra-bands (located at 575 cm^{-1} and 815 cm^{-1}) and a shoulder at 680 cm^{-1} assigned to CuSb_2O_6 presence whose formation started at about 1023K. At 1273 K the SnO_2 - based solid solution besides SnO_2 and CuSb_2O_6 presence was identified by X-ray diffraction. IR measurements have shown an intensity decrease for the SnO_2 strongest absorption band and its splitting into 682 cm^{-1} and 630 cm^{-1} bands. At this temperature better conditions are offered to CuSb_2O_6 formation which can be noticed from its typical bands (575 cm^{-1} and 815 cm^{-1}) those bands intensify and an extra-band at 680 cm^{-1} appears. At $>1273\text{ K}$ the typical pure oxides and CuSb_2O_6 compound bands disappear and one can note an abnormal decrease of transmission, assigned to the dissolution of CuSb_2O_6 into the SnO_2 lattice.

The typical IR bands disappearance of the SnO_2 - based solid solution may be explained by the strong interaction between the lattice phonons and a higher charge carrier concentration determined by the solid solution formation. The assumption is sustained by semimetallic behaviour of the sample [Ionescu et al., 1997].

Fig. 7. IR Spectra of the mixture with initial composition:60 mol% of SnO₂, 20 mol% of Sb₂O₃ and 20 mol% of CuO, thermally treated one hour at 873, 1073,1273,1343,1373 and 1473 K

The scanning electron micrograph(SEM) of the Sn_{0.5}Cu_{0.17}Sb_{0.33}O₂ solid solution thermally treated at 1373 K (Fig.8) show homogeneous textures with mono-sized grains. No vitreous phase is noticed. According with the results of the chemical microanalysis obtained from SEM a good agreement between initial composition of the mixture and Sn_{0.5}Cu_{0.17}Sb_{0.33}O₂ (SS) should be observed.

Tri-rutil type solid solutions occur at concentration below 20 mol% of SnO₂ at 1273. The cell parameters calculated from the diffraction data show a small variation of the elementary cell as compared to those of CuSb₂O₆.

In the papers following [Mihaie et al., 1999; 2001; Scarlat et al., 2002] the formation of *rutil* (SnO₂) and *tri-rutil* type (CuSb₂O₆) solid solutions was studied starting not with the three component oxides (SnO₂, Sb₂O₃, CuO) but with SnO₂ and CuSb₂O₆ thermally treated at 1373 K, 3 hours.

The lattice parameters for SnO₂_{ss} and CuSb₂O₆ ss were calculated from diffraction data. For the tin rich-end members of the series, which crystallise with the *rutil* type lattice, the measured a_0 [Å] and c_0 [Å] lattice parameters obey Vegard's Rule:

$$a_0 = 4.736 - 0.0016 \cdot x_{\text{CuSb}_2\text{O}_6} \pm 0.002 \text{ \AA}$$
$$c_0 = 3.1865 + 0.016 \cdot x_{\text{CuSb}_2\text{O}_6} \pm 0.002 \text{ \AA}$$

The chemical microanalysis from Scanning electron micrographs (SEM) data for the $\text{Sn}_{0.5}\text{Cu}_{0.17}\text{Sb}_{0.33}\text{O}_2$ solid solution thermally treated at 1373 K:

% at.	Exp.	Calc.
Sn	18.23	16.67
Cu	6.77	5.55
Sb	11.11	

Fig. 8. SEM image of the $\text{Sn}_{0.5}\text{Cu}_{0.17}\text{Sb}_{0.33}\text{O}_2$ solid solution thermally treated at 1373 K

The solid solubility limit of CuSb_2O_6 in SnO_2 was estimated to be at $x_{\text{CuSb}_2\text{O}_6} = 0.25$, in accordance with previous results obtained using the mixture with 60mol% of SnO_2 , 20 mol% of Sb_2O_3 and 20 mol% of CuO . The variation of the lattice parameters for the composition which consists from $\text{SnO}_{2\text{ss}}$ is shown in Fig. 1(a, b)

For the SnO_2 based solid solutions (Fig. 9), a linear decrease of the lattice parameters a and c was noticed up to a 25% mol. CuSb_2O_6 content in the initial mixture. At higher amount of CuSb_2O_6 in the mixture, the lattice parameters remain constant, confirming the assumption that the dissolution of CuSb_2O_6 in the SnO_2 matrix take place until half of the Sn^{4+} were substituted with Cu^{2+} and Sb^{5+} in the 1:2 ratio.

In this way the composition of the higher limit of the solid solution formed corresponds to the $\text{Sn}_{1/2}\text{Cu}_{1/6}\text{Sb}_{2/3}\text{O}_2$ compound (the same value as when starting with individual tin, antimony, copper oxides). In the case of the sample which contains the highest quantity of CuSb_2O_6 incorporated in the SnO_2 matrix, the magnetic susceptibility ($\chi_{g,293\text{K}}$) value of $2.5 \times 10^{-6}\text{cm}^3/\text{g}$ is very close to those obtained in the case of mixture of phases ($\chi_{g,293\text{K}} = 2.9 \times 10^{-6}\text{cm}^3/\text{g}$). That could be a confirmation of the inclusion of the CuSb_2O_6 compound in the rutile type structure as a $\text{Cu}_{1/3}\text{Sb}_{2/3}\text{O}_{6/3}$ moiety [Mihaiu et al., 2001].

The CuSb_2O_6 based solid solutions were lesser studied [Mihaiu et al., 2001; Scarlat et al., 2002]. It is known that CuSb_2O_6 compound crystallizes in a distorted monoclinic trirutile structure in space group $\text{P}2_1/\text{c}$ or $\text{P}2_1/\text{n}$ [2] with folllowing unit cell parameters: $a=4.6324\text{\AA}$, $b=4.6359\text{\AA}$, $c=9.2967\text{\AA}$ and $\beta^\circ=91.12$. The trirutile type structure can be generated from the rutile structure by tripling the c -axis due to the chemical ordering of the divalent and pentavalent cations. The structure consists of a network of edge and corner sharing CuO_6 and SbO_6 octahedra. The Cu^{2+} and Sb^{5+} cation position are such that the magnetic Cu^{2+} ions are separated from each other by two sheets of diamagnetic ions. In fact, the magnetic cation sublattice is the same as that of the K_2NiF_4 structure, which is the canonical example of a square lattice two-two-dimensional antiferromagnet. Nakua established that CuSb_2O_6 compound shows the clearest evidence for the dominance of one-dimensional correlations

in the short range ordered regime with the magnetic susceptibility value $\chi_{g,293K}=3,7.10^{-6}\text{cm}^3/\text{g}$ [Nakua et al., 1991].

Fig. 9. Variation of the lattice parameters (a , c) for the solid solution $\text{SnO}_2\text{-CuSb}_2\text{O}_6$

Paramagnetic moment values of 1.5, respectively, 1.9 (B.M.) was determined by Donaldson in the 90-950 K temperature range [Donaldson et al., 1975]. Based upon the cell parameters vs. composition dependence, the solubility limit of SnO_2 in CuSb_2O_6 at 1373 K was estimated to be $x_{\text{SnO}_2} \leq 0.20$. Similarly, for the *trirutile* type solid solution in accordance with Vegard's rule, the lattice parameters varied with the decreasing of SnO_2 content:

$$a_o = 4.679 + 0.0005 \cdot x_{\text{SnO}_2} \pm 0.002 \text{ \AA}$$

$$c_o = 11.065736 + 0.017544 \cdot x_{\text{SnO}_2} \pm 0.002 \text{ \AA}$$

In the case of the CuSb_2O_6 solid solution formation, the volume of the unit cell lattice decrease with the decreasing of SnO_2 content. In the same time the β angle value indicates a stabilization of the tetragonal structure of the CuSb_2O_6 compound even at room temperature. The magnetic susceptibility ($\chi_{g,293K}$) values of about $3.6 \times 10^{-6} \text{cm}^3/\text{g}$ obtained for CuSb_2O_6 solid solutions was found to lie within the reported limits typical for Cu^{2+} ions. It is suggested that the Sn^{4+} incorporation into *trirutile* lattice take place preferentially on Sb^{5+} sites [Scarlat et al., 2002].

3. Sintered ceramics

For improving properties as thermal and electrical conductivity, translucency and strength it is desirable to eliminate as much of the porosity as possible. For some other application it may be desirable to increase the strength without decreasing the gas permeability.

The conventional ceramic method, the hot isostatic pressing technique and spark plasma sintering technique are some of the techniques used for the obtaining sintered compacts. The flow chart of the whole experimental procedure is given in Fig.10.

Fig. 10. The flow chart of the whole experimental procedure

3.1 Conventional ceramic method

The usual processing of ceramics, polycrystalline powders are compacted and then thermally treated at temperature sufficient to develop useful properties. During the thermal treatments for the obtaining ceramic compact three major changes commonly occur: (a) an increase in grain size; (b) a change in pore shape; (c) change in pore size and number, usually to give a decreased porosity.

Ceramics belonging to the $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-CuO}$ ternary system thermally treated at lower than 1273K temperatures showed no linear shrinkage but linear dilatation and high porosity pointing out an inadequate sintering[Mihaiu et al., 1999]. The oxide composition that lead to dense ceramics were obtained starting with mixtures with $\text{CuO}:\text{Sb}_2\text{O}_3 \geq 1$ and the SnO_2 content >40 mol% at 1373 K.

Dense ceramics with zero porosity and relative density $>94\%$ ($d_r = d_{\text{exp}}/d_c$).have been reported only in the compositional range with $>85\text{mol}\%$ SnO_2 and thermal treatment at 1473 K, four hours[Popescu et al.,2002]. For the theoretical density authors [Mihaiu et al., 2005]used the following relation:

$$d_c = \frac{2(1-x)A_{Sn} + 2\frac{x}{3}A_{Cu} + 2\frac{2x}{3}A_{Sb} + 4A_O}{N_A \cdot V_{SnO_2(ss)}} \quad (7)$$

in which : A_{Sn} , A_{Cu} , A_{Sb} and A_O are the atomic weights of tin, copper, antimony and oxygen, N_A is Avogadro's number and $V_{SnO_2(ss)}$ unit cell volume of the solid solution calculated from the X-ray measured lattice parameters. At 1373 K ceramics formed by the incorporation of the $CuSb_2O_6$ in SnO_2 matrix have not the ability to sinter by conventional sintering method authors [Mihaiu et al., 2005]. Thus, for the $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition after thermal treatment three hours, 8.45 % porosity and a relative density of 64.53% have been reported [Mihaiu et al., 2005]. A better sintering capability of the samples with the same compositions was observed from the initial oxides (SnO_2 , CuO and Sb_2O_3) mixtures (72,12% relative density). This difference in the obtained relative density values may be related only to the better sintering capabilities of the sample prepared starting from the initial oxides; as a result of the simultaneously proceeding of the sintering and the formation process of the SnO_2 based solid solution, the latter taking place in stages and thus increasing the whole reactivity of the system. On the other hand, the presence of some un-reacted CuO may develop the formation of a liquid phase at high temperatures. Such a liquid phase rich in CuO was evidenced in the SnO_2 - Sb_2O_3 - CuO based compositions even for short sintering times⁷ and its presence may thus significantly improve the densification properties of the latter sample. The microstructure developed is vizualized by SEM in the Fig.11 (a and b) [Scarlat et al., 2003]

a) starting with ternary mixture of 80 mol% of SnO_2 , 10 mol% of Sb_2O_3 and 10 mol% of CuO
b) starting with binary mixture 90 mol% of SnO_2 and 10 mol% of $CuSb_2O_6$

Fig. 11. SEM micrographs of the sintered $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$ composition at 1373 K, 3 hours

The presence of grains of about the same shape and size with some local and occasional inhomogeneties and a high amount of voids are evidenced.

The SEM images of the $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ composition (binary mixtures) thermally treated at 1373 K, ten hours and at 1473 K three hour are presented in Fig.12(a and b). By prolonged thermal treatment the sintering process is enhanced, but some pores (about 0.5 μm) are still enclosed in the obtained dense ceramics (Fig. 12. a). For the sample Thermally treated at 1473 K (Fig.12 b) the presence both of the primary phase composed of the relative uniform grains with the sizes more of 10 μ , and of the secondary phase with smaller size grains can be observed. However, the supplementary addition of CuO to the $\text{Sn}_{1-x}\text{Cu}_x/3 \text{ Sb}_{2x/3}\text{O}_2$ solid solutions did not improve essentially the sintering abilities of the sample [Mihaiu et al., 2003]

3.2 Spark plasma sintering technique (SPS)

The spark plasma sintering technique (SPS) is a nonconventional densification method, which has been succesfully applied to difficult-to-sinter materials. A pulsed low-voltage high current is applied to loose powder loaded into a graphite punch and die unit. The pulsed current promotes electrical discharges at powder particle surfaces, thus activating them for subsequent bonding. A modest pressure (<100MPa) is applied throughout the sintering cycle. Densities in excess of 99% have been reported by SPS sintering of ceramics powders, such as AlN, Al_2TiO_5 or TiN without any sintering additives [Scarlat et al., 2003].

Fig. 12. SEM micrographs of the sintered $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ composition starting with binary mixture 90 mol% of SnO_2 and 10 mol% of CuSb_2O_6 : a) thermally treated at at 1373 K, 10 hours ; and thermally treated at at 1473 K, 3 hours.

The sintering modulus of the SPS machine is presented in Fig.13.

The solid solutions of the $\text{Sn}_{0.82}\text{Sb}_{0.18}\text{O}_2$ composition (prepared after thermal treatment at 1273 K, 3 hour of the tin and antimony oxide mixture) and of $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ composition have been densified by Spark plasma sintering technique. The sintered compacts with high relative density of 92.44% in the case of $\text{Sn}_{0.82}\text{Sb}_{0.18}\text{O}_2$ composition and 99.6% for $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ composition have been reported by [Scarlat et al., 2003; Mihaiu et al., 2005]. The SEM photographs of the samples $\text{Sn}_{0.82}\text{Sb}_{0.18}\text{O}_2$ and $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ illustrated in Figs.13 (a and b) indicate the obtaining of the consolidated microstructure with the grain sizes lower than 1 μ . However, the very fine homogeneous grains of the sample $\text{Sn}_{0.82}\text{Sb}_{0.18}\text{O}_2$ in comparison with the sample $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ could be notice.

Fig. 13. Sintering modulus of the SPS machine

Fig. 14. SEM micrograph of the compacts sintered by Spark plasma sintering technique (SPS): a.) solid solution of $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$ composition obtained after thermal treatment at 1373 K, 3 hours [Scarlat et al., 2004]; b.) solid solution of $\text{Sn}_{0.82}\text{Sb}_{0.18}\text{O}_2$ composition obtained after thermal treatment at 1273 K, 3 hours [Scarlat et al., 2003]

Even though the exact mechanism of the enhanced SPS densification is not yet known, it is assumed that the pulsed electrical current creates favorable conditions for the removal of impurities and activation of powder particle surfaces. Some arcing or electrical discharge phenomena at particle-to-particle contacts may be responsible for adsorbate elimination or surface “cleaning”, thus creating favorable conditions for subsequent particle bonding. This activation explained the high densities obtained in ceramics without additives and direct grain-to-grain contact at atom scale observed by HREM in ceramics and metals. In addition to the little coarsening due to a very short time at high temperatures, the final nanometer grain sizes by SPS sintering also reflect a minimal coarsening during the heating up stage.

4. Electrical behaviour of the SnO₂-based ceramics

The electrical behaviour of the dense ceramic masses in the system was approached in Sn-Sb-Cu-O papers [Zuca et al., 1995, 1999; Mihaiu et al., 200; Scarlat et al., 2003, 2004; Popescu

et al., 2002] Electrical conductivity measurements were effected in the 77-1100 K temperature range on two types of materials with distinct structure:

- SnO_2 monophasic ceramics with rutile type structure
- ceramics consisting of phase mixtures: $\text{SnO}_2 + \text{Cu}_4\text{SbO}_{4.5}$ or

Measurements in the 300-1100 K temperature range were accomplished in the cell presented in Fig.15

1, 2 refractory steel threaded bodies; 3 boron nitride ring; 4 four channel insulator; 5 Pt-PtRh thermocouple; 6 platinum wire; 7 platinum electrodes; 8 semiconductor pellet; 9 boron nitride support; 10 stainless steel screw; 11 platinum ring.

Fig. 15. The pellet holder for conductivity measurements.

An other serie of measurements were realized in the low temperature range between 77-300 K .The dependence of the resistivity on the temperature and the values of Seebeck coefficient for some selected samples is shown in Fig. 16(a) and Tables 4. A small variation of the samples consisting of SnO_2 ss with the temperature was found. The samples consisting of phase mixtures show an important decrease of three orders of magnitude of the resistivity up to 800K. Over this temperature, all the samples have a similar behaviour.

A graphical analysis of the linear of $\ln k$ vs. $1/T$ dependence in the two temperature ranges studied(Fig. 16. b) brings about new additional information. According to these data all samples exhibit a n-extrinsic conductivity whose activation energy ranges within 0.04-0.3 eV. As it could be seen in Fig.16 (b-inserted) for the samples composed from a unique phase single Arrhenius line was obtained over the whole 300-1100 K, similar behavoiur of the sample where Sb_2O_3 and CuO act as dopant [Zuca et al., 1991]. However some distinctive tendencies were recorded in Fig.17 for samples consisting of a mixture of phases. As seen a marked change of slope takes place at temperatures exceeding 600K which suggests a possible modification of charge carriers involved in conduction process. Indeed Shimada and Mackenzie identified in the temperature range under discussion, the following chemical reaction [Shimada & Mackenzie, 1982]:

Sample	Oxide composition			Phase Composition	Seebeck Coefficient (μV/K)
	SnO ₂	Sb ₂ O ₃	CuO		
t ₁	95	1	4	SnO _{2ss}	-1.7
A ₁	80	10	10	SnO _{2ss}	-1.6
A ₂	60	20	20	SnO _{2ss}	-1.7
B ₃	50	10	40	SnO _{2ss} +Cu ₄ SbO _{4.5}	-
B ₄	50	20	30	SnO _{2ss}	-3
B ₅	40	20	40	SnO _{2ss}	-1.8
B ₉	30	10	60	SnO _{2ss} +Cu ₄ SbO _{4.5}	+10
B ₁₀	20	30	50	CuSb ₂ O ₆ + SnO ₂ +Cu ₄ SbO _{4.5}	-

Table 4. Oxide composition and phase composition

Fig. 16. Electrical behavior: a) Dependence ρ plotted against temperature; b) Arrhenius behaviour in 300-1100K temperature range for various samples; solid solutions of $\text{Sn}_{0.75}\text{Sb}_{0.17}\text{Cu}_{0.08}\text{O}_2$ and $\text{Sn}_{0.5}\text{Sb}_{0.33}\text{Cu}_{0.17}\text{O}_2$ composition are inserted in b.)

Which could generate the behaviour shown in Fig17.b By an additional incorporation of CuSb_2O_6 in the SnO_2 labilized lattice with increasing temperature[Zuca et al., 1999] The small negative values of the Seebeck coefficient confirm the electronic conduction in all samples except the sample which consists of a phase mixture. In this case the existence of $\text{Cu}_4\text{SbO}_{4.5}$ compound even at 300K temperature can favour a different mechanism of carrier motion (a possible p-type conductivity), which accounts for the Seebeck coefficient which take comparatively high positive value.

5. Conclusions

Discussion on the high-temperature interactions of components in the binary $\text{SnO}_2\text{-Sb}_2\text{O}_3$, $\text{SnO}_2\text{-CuO}$, $\text{Sb}_2\text{O}_3\text{-CuO}$, $\text{SnO}_2\text{-CuSb}_2\text{O}_6$ systems and in the ternary $\text{SnO}_2\text{-Sb}_2\text{O}_3\text{-CuO}$ system was presented. The complexity of phase formation and phase composition evolution with thermal treatment temperature was established.

Results on the sintering capacity and consequently the densification using conventional and spark plasma sintering were presented. The powders sintering behavior depends on the method used. Highly densified ceramics were obtained only by using SPS sintering.

According to the electrical data all samples exhibit n-extrinsic conductivity whose activation energy ranges within 0.04-0.3 eV.

6. References

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**Advances in Ceramics - Synthesis and Characterization,
Processing and Specific Applications**

Edited by Prof. Costas Sikalidis

ISBN 978-953-307-505-1

Hard cover, 520 pages

Publisher InTech

Published online 09, August, 2011

Published in print edition August, 2011

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How to reference

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Mihaiu Maria Susana, Scarlat Oana, Zuca Stefania and Zaharescu Maria (2011). Advanced SnO₂-Based Ceramics: Synthesis, Structure, Properties, Advances in Ceramics - Synthesis and Characterization, Processing and Specific Applications, Prof. Costas Sikalidis (Ed.), ISBN: 978-953-307-505-1, InTech, Available from: <http://www.intechopen.com/books/advances-in-ceramics-synthesis-and-characterization-processing-and-specific-applications/advanced-sno2-based-ceramics-synthesis-structure-properties>

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