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OXIDE MATERIALS WITH MAGNETIC PROPERTIES IN THE SnO_2-$CuSb_2O_6$ PSEUDOBINARY SYSTEM

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SnO_2-Sb_2O_3-CuO ternary system contains ceramics with specific electrical and magnetic properties, used as sensors, electrodes and catalysts. Previous studies over the whole concentration range of the system have shown the presence of a large domain of SnO_2-based solid solution. The formation of $CuSb_2O_6$ is an intermediate step of both type of solid solution formation. According to the literature data $CuSb_2O_6$ has paramagnetic properties, with magnetic susceptibility value $\chi_{g,}293K=3,7\cdot10^{-6}cm^3/g$, while SnO_2-based solid solutions presents a semimetallic or semiconducting behavior in the temperature range 77-1100 K. Based on our preliminary results, in the present work the magnetic properties of the ceramics in the SnO_2-$CuSb_2O_6$ pseudo-binary system were investigated. In the SnO_2-$CuSb_2O_6$ pseudo-binary system the domain of the SnO_2-based solid solutions extends to 75% mol. SnO_2 and the domain of $CuSb_2O_6$ is situated at a $CuSb_2O_6$ content higher than 80% mol. Between these two limits a mixture of mentioned solid solution was noticed. A decrease of the lattice parameters, for both type of solid solution was established. The measured magnetic susceptibility value ranged within 2.5×10^{-6} - $3.7 \times 10^{-6}\cdot cm^3/g$ showing a paramagnetic behavior for all investigated samples. Excepting the sample containing more than 80 mol % SnO_2, the magnetic moment (μ_p) values calculated from the magnetic susceptibility data are in the range corresponding for Cu^{2+} ($3d^9$) ion.

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1. Introduction

Previous studies over the whole concentration range of the SnO_2-$CuSb_2O_6$ pseudobinary system have established that, depending on the composition of the mixtures $(1\text{-}x)SnO_2 + xCuSb_2O_6$ the following reactions take place in the 1273–1373 K temperature range [1]:

$$\text{when } x = 0 \div 25 \qquad (1\text{-}x)SnO_2 + xCuSb_2O_6 \rightarrow SnO_{2\,ss} \qquad (1)$$

$$\text{when } x = 25 \div 80 \qquad (1\text{-}x)SnO_2 + xCuSb_2O_6 \rightarrow SnO_{2\,ss} + CuSb_2O_{6\,ss} \qquad (2)$$

$$\text{when } x = 80 \div 100 \qquad (1\text{-}x)SnO_2 + xCuSb_2O_6 \rightarrow CuSb_2O_{6\,ss} \qquad (3)$$

It must emphasis that SnO_2 based solid solutions presents a semimetallic or semiconducting behavior in the 77–1100 K temperature range. Hitherto, the properties of the $CuSb_2O_6$ based solid solutions were lesser studied. It is known that $CuSb_2O_6$ compound crystallizes in a distorted monoclinic trirutile structure in space group $P2_{1/c}$ or $P2_{1/n}$ [2]. 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-dimensional antiferomagnet. Nakua et al. [2] 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·$10^{-6}cm^3/g$. Paramagnetic moment values of 1.5, respectively, 1.9 (B.M.) was determinated by Donaldson et al. [3] in the 90-950 K temperature range.

In the present work the magnetic properties of the ceramics in the SnO_2-$CuSb_2O_6$ pseudo-binary system were investigated.

2.Experimental

2.1. Samples preparation

The samples were prepared from SnO_2 reagent grade and $CuSbO_6$, previously obtained [4] by classical ceramic method presented elsewhere. In the Table 1 the starting compositions, the average molecular mass (M) and the conditions of the thermal treatment are presented.

Table 1. The starting compositions and thermal treatment conditions.

Sample	Composition (mol. %)		M	Thermal treatment	
	SnO_2	$CuSb_2O_6$		temperature (K)	Time(h)
S_0	100	-	150.69	1373	3
S_1	90	10	175.93	1273; 1373	3; 10
S_2	80	20	201.16	1273; 1523	3; 3
S_3	75	25	213.78	1373	3; 10
S_4	50	50	276.87	1373	3
S_5	30	70	327.34	1373	3
S_6	20	80	352.58	1373	3
S_7	10	90	377.81	1373	3
S_8	-	100	403.05	1373	3

2.2. Samples characterization

The phase composition was analyzed by X-ray and IR spectroscopy.

Ceramic properties, porosity (P_a) and linear shrinkage (Δ l/l), were investigated by means of conventional procedures.

Magnetic measurements were carried out with a Faraday-type magnetometer. The magnetic susceptibility was measured on powder samples. For each sample, the independence of susceptibility from the applied magnetic field was checked. Additionally to the calibration of the susceptibility constant of the instrument, one must also calibrate the thermometer for accurate measurements of the temperature of the sample.

3. Results

The phase composition, ceramic properties and magnetic parameters are presented in Table 2.

The lattice parameters for $SnO_{2\,ss}$ and $CuSb_2O_{6\,ss}$ were calculated from diffraction data using a computer program [5]. The variation of the lattice parameters for the composition which consists from SnO_{2ss} is shown in Figure 1(a, b).

The lattice parameters of the $CuSbO_6$ compound (S_8) and of S_6 sample are presented in Table 3.

Table 2. The phase compositions ceramics, properties and magnetic parameters of the studied samples.

Sample	Phase composition	Ceramic properties		Magnetic parameters	
		P_a	Δ l/l	$\chi_{g,293K}$ ($10^6 cm^3.g^{-1}$)	μ_p (B.M.)
S_0	SnO_2	-	-	-	-
S_1	$SnO_{2\ ss}$	6.25; 0.28	-4.3; -0.86	0.8; 0.4	-
S_2	$SnO_{2\ ss}$	6.75; 6.26	-1; -2.59	1.1; 0.9	-
S_3	$SnO_{2\ ss}$	7.49; 7.25	0; -1.72	2.5	1.5
S_4	$SnO_{2\ ss}$ + $CuSb_2O_{6\ ss}$	9.13;	0	2.9	1.6
S_5	$SnO_{2\ ss}$ + $CuSb_2O_{6\ ss}$	9.17	0	3.2	1.7
S_6	$CuSb_2O_{6\ ss}$	9.23	+0.1	3.6	1.75
S_7	$CuSb_2O_{6\ ss}$	10.63	+0.1	3.7	1.85
S_8	$CuSb_2O_6$	-	-	3.7	1.9

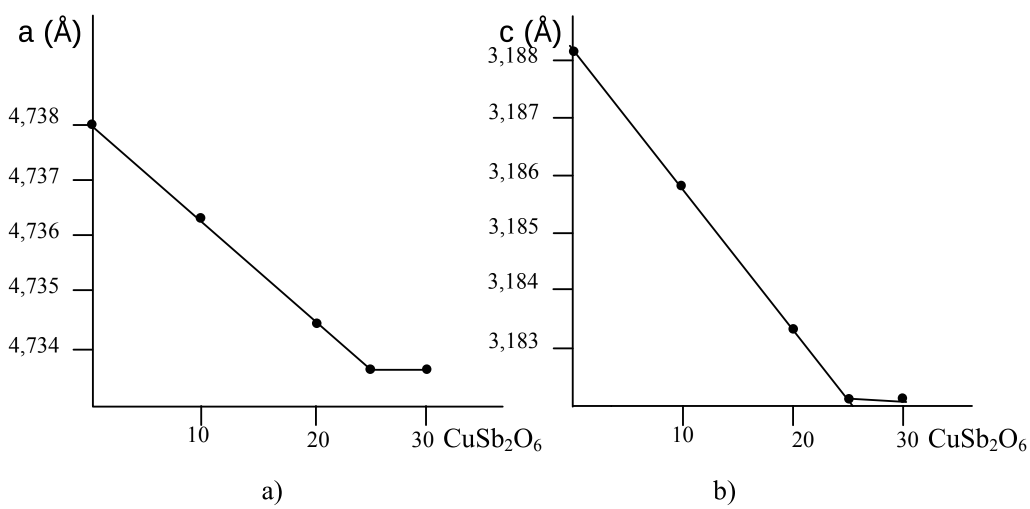

Fig. 1. Variation of the lattice parameters (a, c) for the solid solution SnO_2-$CuSb_2O_6$.

Table 3. Lattice parameters of the sample with trirutile type structure.

Sample	Lattice parameters			
	a (Å)	b (Å)	c (Å)	β (°)
$CuSb_2O_6$ ASTM File	4.6359	4.6339	9.2640	91.14
S_8	4.6292	4.6288	9.2868	91.17
S_6	4.6256	4.6305	9.2650	90.99

4. Discussion

The X-ray diffraction data presented in the Table 2 (column 2) confirm the results obtained before [1] (see reactions 1-3).

For the SnO_2 based solid solutions (Fig. 1), 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 $Sn_{1/2}Cu_{1/6}Sb_{2/3}O_2$ compound.

As results from the Table 2, the lattice parameters decrease in the case of the $CuSb_2O_6$ solid solution formation, as well. 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.

Ceramic properties presented in the Table 2 (columns 3 and 4) confirm the low sintering ability of the compositions in the studied system, that was previously established.

The magnetic susceptibility of the $CuSb_2O_6$ compound determined in our work has the same value as that mentioned by Nakua et al. [2], underlying the accuracy of our magnetic measurements. The measured magnetic susceptibility value ranged within 2.5×10^{-6} - $3.7 \times 10^{-6} cm^3/g$ showing a paramagnetic behavior for all investigated samples.

The decrease of the magnetic susceptibility was noticed with the increase of SnO_2 content (diamagnetic compound). The very low values of magnetic susceptibility of the samples S_1- S_2 (solid solutions with SnO_2 structure) requires supplimentary investigation in order to clarify their magnetic characteristics. It must be noticed that in the case of the sample S_3 which contains the highest quantity of $CuSb_2O_6$ incorporated in the SnO_2 matrix, the magnetic susceptibility value is very close to those obtained in the case of mixture of phases (Samples S_4-S_5). That could be a confirmation of the inclusion of the $CuSb_2O_6$ compound in the rutile type structure as a $Cu_{1/3}Sb_{2/3}O_{6/3}$ moiety, as was mentioned before by Kikuki [6].

Excepting the samples containing more than 80 mol. % SnO_2, the magnetic moment (μ_p) calculated from the magnetic susceptibility data are in the range corresponding to Cu^{2+} ($3d^9$) ion.

5. Conclusions

Preliminary magnetic investigations on the ceramics in the SnO_2-$CuSb_2O_6$ system have been carried out.

The obtained data bring supplementary information on the structure and properties of these materials. The magnetic moment (μ_p) values calculated from the magnetic susceptibility data are in the range corresponding to Cu^{2+} ($3d^9$) ion.

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