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X-ray crystallographic and conductance study of $CuNiSnO_4$ synthesized by two different methods

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Abstract. Two new ternary oxidic compositions of $CuNiSnO_4$ have been prepared. The ternary composition $Cu^{2+}Ni^{2+}SnO_4$ in orthorhombic symmetry with lattice dimensions $a_0 = 5{\cdot}773 \pm 0{\cdot}01$ Å; $b_0 = 8{\cdot}377 \pm 0{\cdot}01$ Å; $c_0 = 10{\cdot}094 \pm 0{\cdot}01$ Å, while $Cu^{+}Ni^{3+}SnO_4$ is also orthorhombic but with lattice dimensions $a_0 = 5{\cdot}737 \pm 0{\cdot}01$ Å; $b_0 = 7{\cdot}125 \pm 0{\cdot}01$ Å and $c_0 = 10{\cdot}071 \pm 0{\cdot}01$ Å. The variation of electrical conductance with temperature indicates the semiconducting nature of these compositions. Hot-probe method indicates *p*-type semiconduction in both the compositions.

Keywords. Oxidic composition; $CuNiSnO_4$; orthorhombic symmetry; lattice dimensions; *p*-type semiconduction.

1. Introduction

Stannates of O_4 stoichiometry have been studied for their formation and structural parameters. In comparison to stoichiometrically similar titanates the stannates show mixed behaviour, even though SnO_2 and TiO_2 both crystallize in a rutile lattice with comparable lattice dimensions (Swanson and Tatge 1953; Megaw 1973). Whereas $ZnCuTiO_4$ (Yamaguchi 1953) and $LiFeTiO_4$ (Kulshreshtha 1986) are reported as spinels, $ZnCuSnO_4$ (Deshpande *et al* 1977; Tare *et al* 1990) and $LiFeSnO_4$ (Watanabe *et al* 1982) are reported to be non-spinels. Binary stannates like Zn_2SnO_4 (Grigoryan *et al* 1975; Fujita *et al* 1988), CO_2SnO_4 (Glidewell 1976; Get'man *et al* 1986) and Mg_2SnO_4 (Tcheichvili 1972) are spinels, but Cd_2SnO_4 and Ca_2SnO_4 (Troemel 1969) are non-spinels. Ternary stannates studied include $ZnNiSnO_4$ (Chang and Kaldon 1976; Lee and Hwang 1977), $ZnMgSnO_4$ (Von Beckh *et al* 1981) and $ZnCoSnO_4$ (Ohtsuka 1972), and all of them crystallize in spinel symmetry. The stannate $LiFeSnO_4$ (Choisnet *et al* 1981; Watanabe *et al* 1982) is of great interest due to its temperature-based polymorphism.

Site preference of cations plays an important and decisive role in the formation and crystallization of ternary stannates. The presence of a strongly A-site-preferring ion like Zn^{2+} (Miller 1959) has been found to greatly facilitate spinel formation (Ohtsuka 1972; Chang and Kaldon 1976) in $ZnM^{2+}SnO_4$ (M = Ni, Mg, Co) stannates. The non-formation of $NiMgSnO_4$ (Chang and Kaldon 1976) is attributed to the presence of Mg^{2+} ions showing no strong preference for A-sites.

A thorough search of the literature on binary copper and nickel stannates indicated that very limited information is reported even regarding their existence. Though

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non-formation of Ni_2SnO_4 in the binary system $NiO–SnO_2$ (even after prolonged firing at 1100°C) is reported (Chang and Kaldon 1976), a more recent study (Panakh-Zade *et al* 1986) on the system $Ni_{2x}Cd_{2-2x}SnO_4$ indicates a probable separation of Ni_2SnO_4 in this system. It is noteworthy to mention here that Ni_2SnO_4 is a component of $ZnNiSnO_4$ (considering $ZnNiSnO_4$ as a solid solution of Zn_2SnO_4 and Ni_2SnO_4), which surprisingly, is reported to be cubic. This suggests that though one of the binary end members is unstable, a suitably derived ternary oxide may exist and also it may be stable.

Copper stannate, on the other hand, is reported as the end member of the spinel series $Cu_xMg_{2-x}SnO_4$ (Schmitz-Dumont *et al* 1966). In this spinel series the stannate $CuMgSnO_4$ has Cu^{2+} occupying both the sites, probably due to the very weak A-site preference of Mg^{2+}. A close comparison of $CuMgSnO_4$ (Mg^{2+} having weak preference of A-site) and $CuNiSnO_4$ (Ni^{2+} preferring B-site strongly) indicates that probably $CuNiSnO_4$ may exist and crystallize in a symmetry other than that of $CuMgSnO_4$. Again, literature points to the fact that $MgNiSnO_4$ does not form in spite of prolonged firing (Chang and Kaldon 1976). Since the site preferences of Cu^{2+} and Mg^{2+} are similar, it was considered worth while to compare $Cu^{2+}Ni^{2+}SnO_4$ with $MgNiSnO_4$. Hence to study the ternary composition $Cu^{2+}Ni^{2+}SnO_4$ in which one end member is unstable (viz. Ni_2SnO_4) and to have a better understanding of the nature of other ions in association with Sn^{4+} in influencing its symmetry, the above composition was synthesized.

Since it was not possible to know which of the starting oxides may be more conducive to lattice formation, and also to evaluate the possibility of existence of mixed valence states of Cu and Ni, a second composition having Cu and Ni in the relatively less stable oxidation state, viz. $Cu^{+}Ni^{3+}SnO_4$, was also synthesized. The mode of synthesis was the same (ceramic method), but the study was planned with two different combinations of starting oxides. The oxidation states of Cu and Ni in planned oxides have only been indicated to understand the starting oxide used in $Cu^{2+}Ni^{2+}SnO_4$ (hereafter referred to as composition I) and $Cu^{+}Ni^{3+}SnO_4$ (composition II). These two compositions have been studied for their formation, X-ray crystallographic and electrical studies and compared.

2. Experimental

The compositions were synthesized using the standard ceramic technique (Economos 1955). Compositions I and II were prepared by mixing equimolar proportions of CuO, NiO, SnO_2 and Cu_2O, Ni_2O_3, SnO_2 respectively. AR acetone was used as the mixing medium. Polyvinyl acetate was used as binder to prepare the pellets. The firing of the pellets was carried out in steps of 400, 600 and 800°C for 20 h each and in a final phase at 1100°C for 45 h. Ni-filtered CuK_α radiation was used in XRD measurements. The resistivity measurements were determined with LCR (Markoni) bridge (for resistance $\leqslant 10^6$ ohms) and BPL megohmmeter (for resistance $\geqslant 10^6$ ohms). The energy of activation was determined for the linear part of the logarithm of resistivity vs temperature curve. Hot-probe method (Dunlop 1957) was employed to know the type of charge carriers.

3. Results and discussion

3.1 *Structural aspects*

A detailed examination of XRD patterns of compositions I and II revealed the non-existence of lines due to constituent oxides and oxidic phases (CuO, Cu_2O, NiO, Ni_2O_3, $NiSnO_3$). Surprisingly, however, the pattern was similar and somewhat consistent with that of SnO_2. Such a phenomenon was observed earlier in the ASTM data of $ZnSnO_3$ (Coffeen 1953), which also was somewhat consistent with that of SnO_2. From the literature, it seems that SnO_2 has a capacity to act as a solvent for certain oxides like Fe_2O_3 (Wali 1971) and oxidic phases (Kikuchi *et al* 1983). The existence of SnO_2 lines as well as somewhat consistent patterns of the compositions studied suggested solvent action (Tare *et al* 1990) of SnO_2. Both the compositions crystallized in orthorhombic symmetry (table 1) with comparable lattice

Table 1. X-ray crystallographic data of $Cu^{2+}Ni^{2+}SnO_4$ (I) and $Cu^{+}Ni^{3+}SnO_4$ (II) (radiation: CuK_α).

$Cu^{2+}Ni^{2+}SnO_4$				$Cu^{+}Ni^{3+}SnO_4$			
d(obs) (A)	1/1	*d*(cal) (A)	*hkl*	*d*(obs) (A)	1/1	*d*(cal) (A)	*hkl*
5·973	4	5·774	100	7·130	5	7·125	010
4·152	4	4·188	020	5·700	4	5·737	100
3·361*	100	3·364	003	3·578	5	3·562	020
2·756	5	2·775	201	3·344*	95	3·357	003
2·641*	89	2·635	211	2·750	6	2·762	201
2·608	17	2·621	023	2·705	4	2·684	113
2·527	13	2·523	004	2·651*	100	2·663	210
2·419	26	2·416	014	2·521	22	2·518	004
2·373*	20	2·377	220	2·440	10	2·443	023
2·324	12	2·314	221	2·367*	26	2·375	030
2·310*	10	2·312	104	2·362	15	2·356	212
2·096*	40	2·094	040	2·324	21	2·311	031
1·770*	70	1·778	043	2·306*	14	2·306	104
1·693	6	1·695	240	2·091*	40	2·092	213
1·680*	16	1·682	006	1·858	8	1·854	310
1·596*	10	1·590	052	1·759*	73	1·756	025
1·562	5	1·565	331	1·704	5	1·702	140
1·501*	16	1·500	053	1·675*	17	1·670	006
1·442*	17	1·443	400	1·670	10	1·667	320
1·416*	25	1·417	340	1·498*	17	1·498	225
				1·495	11	1·497	241, 330
				1·477	13	1·477	331
				1·439*	23	1·439	400
				1·435	13	1·437	007
				1·427	4	1·425	050
				1·414*	23	1·411	410
Symmetry; orthorhombic				Symmetry; orthorhombic			
$a = 5·773 \pm 0·01$ Å; $b = 8·377 \pm 0·01$ Å;				$a = 5·737 \pm 0·01$ Å; $b = 7·125 \pm 0·01$ Å;			
$c = 10·094 \pm 0·01$ Å				$c = 10·071 \pm 0·01$ Å			
*Lines similar to those of SnO_2							

dimensions, viz. for composition I $a_0 = 5{\cdot}773$ Å, $b_0 = 8{\cdot}377$ Å and $c_0 = 10{\cdot}094$ Å, and for composition II, $a_0 = 5{\cdot}737$ Å, $b_0 = 7{\cdot}125$ Å and $c_0 = 10{\cdot}071$ Å. Comparison of the unit cell dimensions revealed that composition I had a larger unit cell volume compared to composition II. This phenomenon may be attributed to the difference in size, the site preferences and distortive influence of cations involved, which in turn influences the packing. The existence of J–T ions (Dunitz and Orgel 1957) may also be responsible for the larger unit cell volume of composition I. This composition is isostructural with the earlier reported analogous stannate, $Co^{2+}Cu^{2+}SnO_4$ (Sampath *et al* 1989) in which the role of Sn^{4+} to act as a cooperative J–T ion was discussed. In the present study also the nature of Sn^{4+} ion to act as a cooperative J–T ion (Tare *et al* 1990) was evidenced in both the compositions. The unit cells are quite comparable as the a_0 and c_0 values are almost identical. However, the different oxidation states of Cu and Ni in the two compositions profoundly influences the crystal morphology, resulting in different internal arrangement of atoms, as reflected in different *hkl* values.

3.2 *Electrical conductance studies*

The electrical study (table 2) indicates the absence of mixed valence states (Verwey 1951) of Cu and Ni in both the compositions, as room temperature resistivity $\geqslant 10^6$ ohm. Both the compositions are good semiconductors in the temperature range (400–800°K) studied. Composition I has activation energy of 0·43 eV, while that of composition II 0·62 eV. The existence of cationic vacancies seems probable in view of the *p*-type semiconduction in both the compositions. The linearity of graph in the temperature range studied indicates that the stoichiometry is almost constant for both compositions.

4. Conclusions

(i) Both the new compositions form and crystallize in orthorhombic symmetry which may be considered to be a highly distorted cubic symmetry (e.g. other than that of $ZnNiSnO_4$). This distortion may be attributed to the cooperative J–T influence of Sn^{4+} ions.

(ii) The coincidence of some of the lines of both the patterns (though not in proper intensity ratios) with that of SnO_2 strongly suggests possible solvent type action of SnO_2.

Table 2. Summary of electrical parameters of compositions I and II.

Electrical parameter	Composition I	Composition II
ρ_{RT} (room temp. resistivity)	$1{\cdot}64 \times 10^6$ ohm-cm	$1{\cdot}72 \times 10^7$ ohm-cm
Energy of activation	0·43 eV	0·62 eV
Type of charge carriers	*p*-type	*p*-type

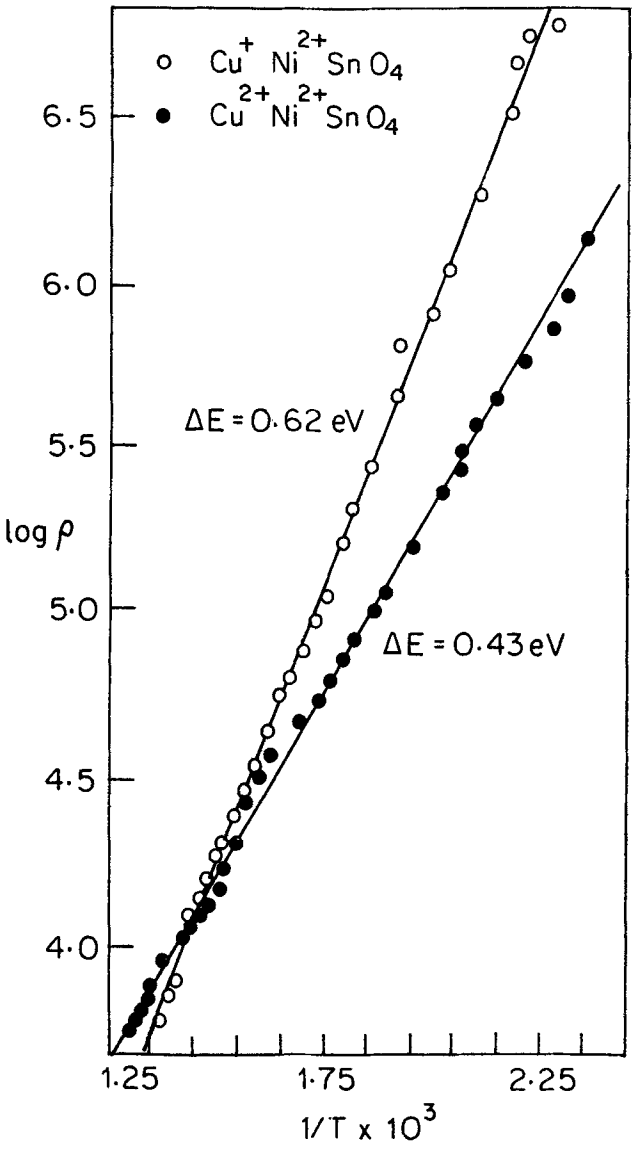

Figure 1.

(iii) The composition $Cu^{2+}Ni^{2+}SnO_4$ is isostructural with the earlier reported stannate $Co^{2+}Cu^{2+}SnO_4$.

(iv) Electrical studies indicate the absence of mixed valence states of Cu and Ni in both compositions.

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