X-ray crystallographic and conductance study of CuNiSnO₄ synthesized by two different methods

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Abstract. Two new ternary oxidic compositions of CuNiSnO₄ have been prepared. The ternary composition Cu²⁺Ni²⁺SnO₄ in orthorhombic symmetry with lattice dimensions \( a₀ = 5.773 \pm 0.01 \) Å, \( b₀ = 8.377 \pm 0.01 \) Å, \( c₀ = 10.094 \pm 0.01 \) Å, while Cu⁺Ni³⁺SnO₄ is also orthorhombic but with lattice dimensions \( a₀ = 5.737 \pm 0.01 \) Å, \( b₀ = 7.125 \pm 0.01 \) Å and \( c₀ = 10.071 \pm 0.01 \) 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; CuNiSnO₄; orthorhombic symmetry; lattice dimensions; \( p \)-type semiconduction.

1. Introduction

Stannates of O₄ stoichiometry have been studied for their formation and structural parameters. In comparison to stoichiometrically similar titanates the stannates show mixed behaviour, even though SnO₂ and TiO₂ both crystallize in a rutile lattice with comparable lattice dimensions (Swanson and Tatge 1953; Megaw 1973). Whereas ZnCuTiO₄ (Yamaguchi 1953) and LiFeTiO₄ (Kulshreshtha 1986) are reported as spinels, ZnCuSnO₄ (Deshpande et al 1977; Tare et al 1990) and LiFeSnO₄ (Watanabe et al 1982) are reported to be non-spinels. Binary stannates like Zn₂SnO₄ (Grigoryan et al 1975; Fujita et al 1988), CO₂SnO₄ (Glidewell 1976; Get'man et al 1986) and Mg₂SnO₄ (Tcheichvili 1972) are spinels, but Cd₂SnO₄ and Ca₂SnO₄ (Troemel 1969) are non-spinels. Ternary stannates studied include ZnNiSnO₄ (Chang and Kaldon 1976; Lee and Hwang 1977), ZnMgSnO₄ (Von Beckh et al 1981) and ZnCoSnO₄ (Ohtsuka 1972), and all of them crystallize in spinel symmetry. The stannate LiFeSnO₄ (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 Zn²⁺ (Miller 1959) has been found to greatly facilitate spinel formation (Ohtsuka 1972; Chang and Kaldon 1976) in ZnM₂⁺SnO₄ (M = Ni, Mg, Co) stannates. The non-formation of NiMgSnO₄ (Chang and Kaldon 1976) is attributed to the presence of Mg²⁺ 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$_2$SnO$_4$ 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$_3$SnO$_4$ in this system. It is noteworthy to mention here that Ni$_3$SnO$_4$ is a component of ZnNiSnO$_4$ (considering ZnNiSnO$_4$ as a solid solution of Zn$_2$SnO$_4$ and Ni$_2$SnO$_4$), 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$_x$Mg$_{2-x}$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$_2$SnO$_4$) 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$_2$O, Ni$_2$O$_3$, 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$_x$ radiation was used in XRD measurements. The resistivity measurements were determined with LCR (Markoni) bridge (for resistance ≤ $10^6$ ohms) and BPL megohmmeter (for resistance ≥ $10^6$ 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.