CRYSTAL DATA AND CONDUCTANCE STUDY OF NiCuNbO₄

M. P. TARE and S. M. TARE
Department of Chemistry, Institute of Science,
Nagpur 440 010, India.

During our investigations of ternary oxides conforming to spinel formula (M⁺¹M⁺²M⁴O₄) hardly any work was noticed on NiCuNbO₄. A few analogous compounds have been reported in literature. The first, ZnCuNbO₄, which crystallizes in orthorhombic symmetry is not a spinel. The other NiLiNbO₄ (unpublished work) is also not a spinel but crystallizes again in orthorhombic symmetry. However, the lattice dimensions of ZnCuNbO₄ and NiLiNbO₄ differ considerably and the two structures are not strictly comparable. In these compounds Zn²⁺ and Li⁺ ions have maximum A site preference affecting the charge separation substantially which seems to be a contributing factor in deciding the structure and symmetry. On the other hand, due to large stabilization energy of Ni²⁺ ions in octahedral field (B site preference) NiCuNbO₄ is expected to show a structure different from that of the ZnCuNbO₄ and NiLiNbO₄. Hence it was considered worthwhile to synthesize NiCuNbO₄ and compare its structure with the other two similar compounds mentioned above.

NiCuNbO₄ has been synthesized for the first time by intimately mixing together the reacting oxides of A.R. grade in proper molar ratio under acetone till completely homogeneous. The mixture was heated in a platinum boat in air at 800°C for 40 hr and then at 1000°C for 30 hr. The sample was then cooled in furnace after switching it off. The formation of the compound was checked by x-ray diffraction pattern taken on Philips x-ray diffractometer using filtered CuKα radiation. The pattern indicated the formation of a single phase and total absence of lines due to reacting oxides.

The crystallographic result is given in table 1. All the observed reflections were indexed on a tetragonal unit cell with lattice parameters: a₀ = 7.75 Å and c₀ = 11.13 Å. It is evident from the observed combinations of h, k, l planes that the bravais lattice is primitive with c/a ratio = 1.436. The compound cannot be termed spinel. The orthorhombic structures of analogous compounds referred to above are not strictly comparable in the present case due to different site preferences of (i) Zn²⁺ and Ni²⁺ and (ii) Li⁺ and Cu⁺. Thus Ni²⁺ ions do not substitute for Zn²⁺, and Cu⁺ ions too do not substitute for Li⁺ ions. The observed tetragonal symmetry, however, may be attributed to large differences in ionic radius of Ni²⁺ (0.69 Å) as compared to that of Cu⁺ (0.96 Å) which is almost the same in Nb⁵⁺ (0.69 Å). This may bring about considerable lattice distortion of the otherwise spinel structure (axial ratio of a pseudo cell c₀/a₀ = 1.015).

The study of bulk resistivity of this compound supports the formation of a single phase on the basis of a linear dependence of log ρ vs 1/T observed with activation energy ΔE = 0.50 eV indicating that it is a semiconductor. It appears that different oxidation states of the constituent ions facilitate the charge hopping phenomenon responsible for the semiconducting nature (ρ RT = 2.207 x 10⁶ ohms-cm) of the compound. Work on similar compounds containing Ni²⁺ ions, viz NiCuTaO₄ and NiLiTaO₄ is in progress.

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