

CRYSTAL DATA AND CONDUCTANCE STUDY OF NiCuNbO₄

M. P. TARE and S. M. TARE

Department of Chemistry, Institute of Science,
Nagpur 440010, India.

DURING our investigations of ternary oxides conforming to spinel formula ($M^I M^{II} M^V O_4$) hardly any work was noticed on NiCuNbO₄. A few analogous compounds have been reported in literature. The first, ZnCuNbO₄¹ 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 The other NiLiNbO₄ (unpublished work) is also not a spinel but crystallizes again in orthorhombic symmetry.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 CuK α 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: $a_0 = 7.75 \text{ \AA}$ and $C_0 = 11.13 \text{ \AA}$. 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

Table 1 Crystal data of NiCuNbO₄ Radiation CuK α

I/I_0	$d(\text{Å})$ observed	hkl	$d(\text{Å})$ calculated
26	4.467	102	4.519
37	3.631	201	3.638
40	3.478	210	3.465
35	3.077	113	3.071
100	2.939	212	2.941
10	2.777	004	2.779
35	2.741	220	2.739
46	2.577	300	3.579
56	2.530	301	2.516
21	2.478	114	2.480
10	2.329	302	2.342
10	2.229	005	2.231
10	2.134	105	2.138
11	2.063	115	2.063
17	1.789	106	1.803
22	1.698	324	1.700
10	1.659	422	1.654
10	1.645	315	1.647
7	1.518	510	1.519
10	1.507	511	1.505
17	1.441	217	1.444

Symmetry - Tetragonal $a_0 = 7.75 \text{ \AA}$, $C_0 = 11.13 \text{ \AA}$.

observed tetragonal symmetry, however, may be attributed to large differences in ionic radius² of Ni²⁺ (0.69 Å) as compared to that of Cu¹⁺ (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 $c_0/a'_0 = 1.0155$).

The study of bulk resistivity of this compound supports the formation of a single phase on the basis of a linear dependence of $\log \rho$ vs $1/T$ observed with activation energy $\Delta E = 0.50 \text{ eV}$ 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 ($\rho RT = 2.207 \times 10^6 \text{ ohms-cm}$) of the compound. Work on similar compounds containing Ni²⁺ ions, viz NiCuTaO₄ and NiLiTaO₄ is in progress.

22 January 1986

1. Deshpande, P. D., Kulkarni, D. K. and Khandekar, P. V., *Curr. Sci.*, 1976, 45, 447.
2. Bloss, F. D., *Crystallography and crystal chemistry*, Holt, Rinehard and Winston Inc., New York, 1971, p. 210.