

The Structure of Dinickel Niobium(V) Boron Oxide Ni_2NbBO_6

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(Received 5 May 1981; accepted 14 September 1981)

Abstract. Ni_2NbBO_6 , orthorhombic, $Pnma$, $a = 10.057$ (4), $b = 8.618$ (1), $c = 4.490$ (2) Å, $D_c = 5.41$ Mg m⁻³, $V_c = 389.2$ Å³. 1285 independent reflections have been used to refine a structure giving an R value of 0.050. The compound has a layer structure consisting of distorted hexagonally close-packed O atoms and contains zig-zag chains of NiO_6 and NbO_6 octahedra that are linked together by corner-shared BO_4 tetrahedra. The material is isostructural with Fe_3BO_6 and the mineral norbergite.

Introduction. During the course of flux-growth experiments in which various proportions of NiO , Nb_2O_5 and $\text{Na}_2\text{B}_4\text{O}_7$ were cooled from 1523 K at 2 K h⁻¹ in platinum crucibles (Wanklyn, Wondre & Davison, 1976), a new phase was prepared that consisted of emerald-green platelets with composition determined by electron probe microanalysis of 37.0% Ni and 29.3% Nb (calc.: 37.03, Ni; 29.30, Nb for Ni_2NbBO_6) and which displayed an antiferromagnetic transition near 298 K. A single crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was mounted on an Enraf–Nonius CAD-4 single-crystal diffractometer and lattice constants were determined from setting angles of 25 accurately centered reflections. Intensities were measured out to $2\theta = 45^\circ$ with graphite-monochromatized $\text{Mo } K\alpha$ ($\lambda = 0.71073$ Å) radiation using

an ω - 2θ scanning technique with the scan rates varied between 4 and 20° (2θ) min⁻¹. ψ scans indicated that any absorption correction would be negligible. The Ni- and Nb-atom positions were located by interpreting a Patterson function computed using 1285 observed reflections with $I > 3\sigma(I)$. The remaining atoms were found by standard Fourier and least-squares techniques. As frequently occurs when refining structures of high-melting-point mixed heavy-metal oxides, refining all the thermal factors isotropically resulted in Nb, O(3) and B assuming small negative values. However, when anisotropic values were assigned and refined for the other three atoms, Nb, O(3) and B maintained small but realistic positive B values. An extinction correction of the form $|F_c|(1 + gI_c)^{-1}$ (Stout & Jensen, 1968) was applied to F_o where the parameter g was refined in the least squares and converged to a value of 0.63364×10^{-5} . Anomalous-dispersion corrections were applied to Ni and Nb scattering factors. With unit weights, the refinement converged when the values $R = 0.050$ and $R_w = 0.059$ were obtained.* Positional coordinates are given in Table 1 and major bond lengths in Fig. 1.†

* All computer programs were provided by Enraf–Nonius (1980).

† Lists of bond angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36374 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and thermal parameters with *e.s.d.*'s in parentheses

Atomic coordinates and β_{ij} values $\times 10^5$, $B \times 10^3$.										
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (Å ²)
Ni	13554 (5)	7020 (6)	48139 (13)	40 (3)	12 (4)	244 (15)	-17 (6)	-15 (12)	-57 (14)	
Nb	41866 (4)	‡	47239 (11)	—	—	—	—	—	—	26 (5)
O(1)	22711 (43)	‡	23020 (101)	9 (24)	71 (32)	209 (120)	—	-6 (91)	—	
O(2)	8431 (47)	‡	78263 (99)	59 (25)	59 (25)	260 (123)	—	-43 (102)	—	
O(3)	29239 (30)	38483 (34)	76158 (68)	—	—	—	—	—	—	130 (30)
O(4)	-3806 (31)	41537 (36)	25840 (79)	33 (17)	50 (22)	671 (96)	9 (36)	-42 (71)	-153 (87)	
B	22646 (63)	‡	91063 (145)	—	—	—	—	—	—	144 (63)

The form of the anisotropic thermal factor is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

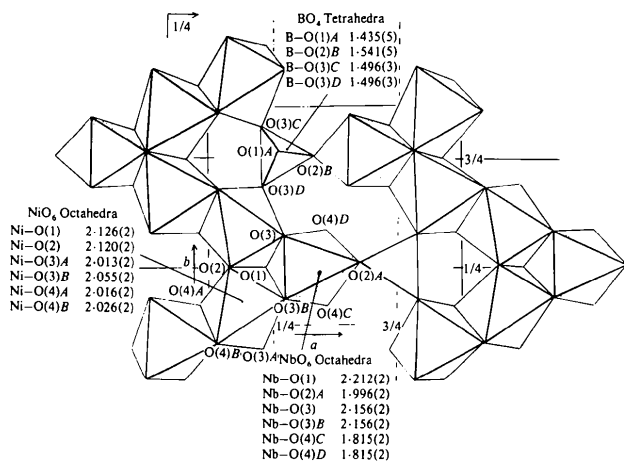


Fig. 1. One layer of the structure as viewed down the c axis.

Discussion. The structure contains layers that consist of zig-zag chains of edge-shared distorted NiO_6 and NbO_6 octahedra, and these metal-oxide chains are cross-linked within the layer through corner-shared BO_4 tetrahedra. As can be seen in the one-layer projection (Fig. 1), these chains fold at each NbO_6 octahedron and the intervening spaces between the metal-oxide chains constitute a set of analogous zig-zag chains of vacant octahedra, with BO_4 tetrahedra occupying selected sites. Each corner-shared BO_4 tetrahedron links one NbO_6 octahedron to two NiO_6 octahedra in another chain within the layer; the fourth BO_4 oxygen is then corner-shared with the unique oxygen of a triangular array (see below) of NbO_6 and NiO_6 octahedra in the next layer. The stacking direction of the layers coincides with the c axis of the lattice and each unit cell contains two layers that are

related by an a glide. The position of the metal-oxide chains in one layer is directly over the vacant octahedra chains in the layer below it in the c direction.

This structure also may be described as possessing distorted hexagonal close-packed O atoms with the metal and B atoms occupying certain octahedral and tetrahedral interstices respectively. This ionic packing restricts the Ni^{2+} and Nb^{5+} ions to within ± 0.28 Å of the planes $z = 0.0, 0.5$ of the unit cell and the O atoms to within ± 0.30 Å of the planes $z = 0.25, 0.75$, with the B atoms sandwiched between these at $z = \pm 0.09163$. The average Ni—O (2.059) and Nb—O (2.024 Å) bond lengths are in excellent agreement with those calculated (2.06, 2.01 Å) using the ionic radii for Ni^{2+} , Nb^{5+} and O^{2-} suggested by Shannon (1976). B—O distances range from 1.435 to 1.541 Å and are similar to those found in the isostructural compound Fe_3BO_6 (1.439 to 1.504 Å) described by Diehl & Brandt (1975) and by White, Miller & Neilsen (1965). The compound is also isostructural with the mineral norbergite $[\text{Mg}_2\text{SiO}_4\text{Mg}(\text{OH},\text{F})_2]$ (Taylor & West, 1929).

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Acta Cryst. (1982). B38, 893–895

Structure of a Basic Cancrinite

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(Received 18 April 1981; accepted 21 September 1981)

Abstract. Basic cancrinite, $(\text{Na}_2\text{O})_{1.24}\text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{2.01} \cdot 1.87\text{H}_2\text{O}$, from electron microprobe analysis, hexagonal, $P6_3$, $a = 12.678$ (8), $c = 5.179$ (6) Å, $V = 720.9$ Å³, $Z = 3$; Mo $K\alpha$ radiation; final $R = 0.034$ for 648 independent reflections. According to the framework interatomic distances [mean

Al—O 1.742 (5), Si—O 1.615 (5) Å] the ordered distribution of Si and Al atoms is maintained as in the natural $(\text{Ca},\text{Na})\text{CO}_3$ cancrinite, as well as the oxygen framework and cation sites. However, significant differences with respect to the structure analysis of another synthetic basic cancrinite are found.