Publicado en *Anales de Física*. Vol. 67. Pág. 399. Núms. 9 y 10. Septbre.-Octubre 1971

NOTAS

THE CRYSTAL STRUCTURE OF NICKEL ORTHOBORATE, $Ni_3(BO_3)_2$

BY

J. PARDO, M. MARTÍNEZ-RIPOLL and S. GARCÍA-BLANCO

Instituto de Química-Física «Rocasolano», C.S.I.C., Serrano, 119. Madrid

(Recibido el 12 de mayo de 1971)

RESUMEN

El ortoborato de níquel, $Ni_3(BO_3)_2$, cristaliza en el sistema ortorrómbico, grupo espacial *Pnnm*, con dos moléculas en una celdilla de dimensiones $a=5.396\pm0.001$, $b=4.459\pm\pm0.001$ y $c=8.297\pm0.002$ Å. La estructura cristalina ha sido determinada por síntesis de Patterson tridimensional, y refinada por el método de mínimos cuadrados, obteniéndose un factor de acuerdo final de 0.086 para 177 reflexiones observadas. La estructura cristalina del $Ni_3(BO_3)_2$ consiste en octaedros de $(NiO_6)^{10-}$ unidos entre sí a través de todos los átomos de oxígeno de los mismos. Cada átomo de oxígeno está coordinado a tres átomos metálicos y a un átomo de boro. Como es usual en los ortoboratos, la unidad borato característica la forman los triángulos de BO_3. Esta estructura cristalina es isomorfa de las de los ortoboratos de cobalto y magnesio.

Nickel orthoborate, $Ni_3(BO_3)_2$, has been reported (1) to be isomorphous with cobalt and magnesium orthoborates (2). However, as far as we know, its crystal structure has not yet been determined. As a part of a programme in progress aimed at achieving a better understanding of the structural principles of anhydrous borates, and in order to obtain its own interatomic distances, the crystal structure of nickel orthoborate was therefore undertaken.

Single crystals were prepared by fusing a mixture of composition $3NiCO_3 \cdot B_2O_3$ with a small excess of boron oxide and annealing the melt at 1200 °C. Deep green crystals were extracted from the melt by treatment with acids. Chemical analysis of the Ni content in the crystals led to the formula $Ni_3(BO_3)_2$.

Nickel orthoborate shows orthorhombic symmetry and belongs to the space group *Pnnm* (D_{2h}^{12}). Precise lattice parameters were obtained by least-squares refinement of the 2θ values for several reflexions from the powder pattern. The following dimensions were found: $a=5.396\pm0.001$, $b=4.459\pm0.001$ and $c=8.297\pm0.002$ Å. These parameters compare well with 5.398, 4.462 and 8.305 Å given by Perloff and Shumate (3). However they differ slightly from the parameters 5.395, 4.490 and 8.391 Å reported by Götz (1). The calculated density with two formula units in the cell is 4.885 $g \cdot cm^{-3}$. Cu K_α radiation and an integrating equi-inclination Weissenberg technique were used. The intensity data from five reciprocal layers along *a* axis and four along *b* axis were measured photometrically.

The crystal structure of nickel orthoborate has been determined by a three-

---

(1) GÖTZ, W.; *Naturwissenschaften*, **50**, 567 (1963).
(2) BERGER, S. V.; *Acta Chem. Scand.*, **3**, 660 (1949).
(3) PERLOFF, A. and SHUMATE, P.; Private communication in the paper from WEIR, C. E. and SCHROEDER, R. A.; *J. Res. Nat. Bur. Stand.*, **68A**, 471 (1964).

TABLE I

Fractional atomic coordinates and thermal parameters

Atom	*x/a*	*y/b*	*z/c*	B (Å²)
Ni (1)	0.0000 (0)	0.0000 (0)	0.0000 (0)	1.38
Ni (2)	0.0000 (0)	0.5000 (0)	0.3154 (2)	1.23
O (1)	0.3254 (16)	0.2464 (19)	0.0000 (0)	0.01
O (2)	0.2015 (10)	0.7002 (14)	0.1402 (7)	0.03
B	0.2555 (26)	0.5480 (33)	0.0000 (0)	0.13

(Estimated standard deviations, multiplied by 0.0001, in parentheses.)

TABLE II

Interatomic distances and their standard deviations

BO_3 - triangle

B - O (1)	1.39 (1) Å	
- O (2)	1.38 (1)	(×2)
Average	1.38	

Ni (1) - octahedron

Ni (1) - O (1)	2.071 (8) Å	(×2)
- O (2)	2.079 (6)	(×4)
Average	2.076	

Ni (2) - octahedron

Ni (2) - O (1)	2.107 (8) Å	(×2)
- O (2)	2.125 (8)	(×2)
- O (2′)	2.023 (8)	(×2)
Average	2.085	

dimensional Patterson synthesis. The positional and thermal parameters have been refined by least-squares analysis including 177 observed reflexions, yielding a final R value of 0.086. A list of positional and thermal parameters is shown in Table I. There are two types of Ni atoms, both octahedratlly coordinated. These $(NiO_6)^{10-}$ groups are linked together by oxygen sharing to form a three-dimensional network. The coordination number of the oxygen atoms is four; each is surrounded by three nickel atoms and one boron atom arranged in an irregular tetrahedron. The oxygen atoms form layers, at right angles to the a axis, where the boron atoms are located to form the well known BO_3 triangles. All interatomic distances are of the usual order of magnitude and are reported in Table II together with their standard deviations.