Publicado en *Anales de Física*. Tomo LXVI. Pág. 209. Núms. 5 y 6. Mayo-Junio 1970

THE CRYSTAL STRUCTURE OF ZINC DIBORATE, ZnB_4O_7

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RESUMEN

El diborato de cinc cristaliza en el sistema ortorrómbico, grupo espacial Pbca, con ocho moléculas en una celdilla de dimensiones $a=13.71_4$, $b=8.09_1$ y $c=8.63_1$ *A*. La estructura ha sido determinada por síntesis de Fourier tridimensional ,y refinada por el método de mínimos cuadrados, obteniéndose un factor de acuerdo final de 0.067 para 530 reflexiones observadas. La estructura cristalina del ZnB_4O_7 contiene triángulos de BO_3 y tetraedros de BO_4 compartiendo un vértice. Cada átomo de cinc está rodeado por cuatro átomos de oxígeno colocados en los vértices de un tetraedro distorsionado. Esta estructura es isomorfa de la del CdB_4O_7.

The binary system $ZnO\text{-}B_2O_3$ has been studied by several authors, (1), (2), (3), (4), (5). Recently, Fayos, García-Blanco and Rivoir (6), investigated the system by using calcined samples. In that case three compounds were reported: *a)* $Zn_3(BO_3)_2$ whose crystal structure was presented in the same paper, *b)* $Zn_4O(BO_2)_6$ (7), and *c)* a third compound having an approximate composition to $ZnO \cdot 2B_2O_3$.

The purpose of the present paper is to report on the crystal structure of the last compound. Single crystals were prepared by fusing a mixture of composition $ZnO \cdot 2B_2O_3$ with a small excess of boron oxide, and annealing the melt at 850 °C. Colourless crystals were extracted from the melt by treatment with ethanol. Chemical analysis of the ZnO content in the crystals led to the formula ZnB_4O_7. Oscillation and Weissenberg photographs showed orthorhombic symmetry, and the observed reflections led to the space group Pbca. The unit-cell dimensions were refined by using indexed powder lines from a diffractometer recording. The following dimensions were found: $a=13.71_4$ *A*, $b=8.09_1$ *A* and $c=8.63_1$ *A*. The calculated and observed densities with 8 formula units in the cell are 3.04 and 3.09 $gr \cdot cm^{-3}$ respectively. $CuK\alpha$ radiation and equi-inclination Weissenberg technique were used. The intensity data were collected from an untwinned crystal and measured photometrically. No absorption corrections were needed because of the small size of the crystal.

The crystal structure of zinc diborate has been determined by a three-dimensional Fourier synthesis. The atomic position parameters have been refined by a least-squares analysis including 530 reciprocal-lattice points. A residual index equal to 0.067 was obtained. A list of final positional parameters and temperature factors, together with standard deviations, is given in Table I. This crystal structure is isomorphous of that of cadmium diborate, (8). This type of

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boron-oxygen arrangement was found in the polyanion of borax, where 50% of the boron atoms are fourfold coordinated. The zinc atoms are surrounded by four close oxygens, arranged in a distorted tetrahedron. The average values of the boron-oxygen bond lengths are: 1.45 *A* (tetrahedra) and 1.37 *A* (triangles). The mean value of the zinc-oxygen bond lenghts is 2.00 *A*.

TABLE I

Fractional atomic coordinates and thermal parameters.

Atom	*X/a*	*Y/b*	*Z/c*	*B*
B(1)	0.0652 (7)	0.4221 (12)	0.2980 (19)	0.10
B(2)	0.2309 (8)	0.5297 (14)	0.3426 (24)	0.54
B(3)	0.1683 (8)	0.4709 (14)	0.0825 (22)	0.46
B(4)	0.0375 (8)	0.6656 (14)	0.1419 (22)	0.56
O(1)	0.0035 (5)	0.5649 (9)	0.2546 (12)	0.23
O(2)	0.0057 (5)	0.3151 (9)	0.3938 (12)	0.57
O(3)	0.1438 (5)	0.4764 (9)	0.4077 (12)	0.62
O(4)	0.2034 (5)	0.1036 (8)	0.4442 (15)	0.62
O(5)	0.2499 (5)	0.5193 (9)	0.1895 (15)	0.67
O(6)	0.1087 (4)	0.3499 (9)	0.1637 (13)	0.19
O(7)	0.1131 (5)	0.6157 (8)	0.0482 (16)	0.44
Zn	0.1176 (1)	0.1094 (1)	0.1203 (2)	0.85

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