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Unit cell, space group and composition of a lower boron phosphide.

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Although preparations of a boron phosphide were reported very early (Moissan, 1891; Besson, 1891) there was very little interest in the compound. Interest increased recently when it was shown (Welker, 1952) that the compound has interesting semiconducting properties. A few methods of preparation were since discovered and crystallographic structure was established (Peri, LaPlaca & Post, 1958).

Decomposition of BP into a lower phosphide at high temperatures was first reported by Williams (1959). On basis of weight loss and chemical analysis the decomposition product was believed to have the approximate formula of B_6P.

The study of boron–phosphorus system has been conducted in this Laboratory for some time. The lower boron phosphide was prepared by the decomposition of BP in graphite crucibles in a neutral gas atmosphere at temperatures of 1400–1700 °C. It was also prepared directly under similar conditions by reacting aluminum phosphide and amorphous boron powder. The remaining aluminum phosphide and aluminum can be easily removed by dilute hydrochloric acid. Some alumina impurities from the AlP should be expected.

The resulting lower phosphide is invariably a very fine powder and only a few very small crystals were obtained. The unit cell data was obtained from single crystal rotation photographs and powder photographs (Table 1).

Table 1. *X-ray diffraction powder data for* $B_{13}P_2$ (Cr $K\alpha$ radiation)

hkl	*d*	I/I_1	*hkl*	*d*	I/I_1
101	4·74 Å	1	220	1·495	50
012	3·88	60	018 }	1·426	50
110	2·978	60	131 }		
104	2·569	80	027	1·4173	30
021	2·522	100	223 }	1·3970	50
015	2·149	40	312 }		
006	1·971	5	306	1·2999	60
024	1·946	5	134	1·2930	20
211	1·927	50	401 }	1·2867	30
122	1·854	1	208 }		
300	1·722	5	042	1·2650	1
116	1·645	70	315	1·2288	60
214	1·632	20	119	1·2054	20
107	1·607	10	226	1·1926	20
303	1·582	10	232	1·1656	10
125	1·509	90	1,0,10	1·1552	20

The unit cell was found to be rhombohedral with the following hexagonal dimensions.

$$a = 5{\cdot}984,\ c = 11{\cdot}850\ \text{Å}\ .$$

Systematic absences place it within the following space groups: $R\bar{3}m$, $R\bar{3}$, $R3m$, $R3$, $R32$. However, since the compound appears to be isomorphous with B_4C and B_4Si (Matkovich, 1960), the $R\bar{3}m$ space group is assigned.

The density of crystals measured by heavy liquids method was found to be $2{\cdot}74 \pm 0{\cdot}02$ g.cm.$^{-3}$. On basis of unit-cell sizes and density the molecular weight (per unit cell) is 202 ± 1 which is in excellent agreement with the theoretical molecular weight of $B_{13}B_2$. The rhombohedral unit cell contains, therefore, one molecule. Comparing $B_{13}P_2$ with B_4Si ($B_{12}Si_3$), the three silicon atoms contained in the unit cell appear to be replaced by two phosphorus and one boron atom. The B_6P formula appears, therefore, incompatible with the above data. The boron to phosphorus ratio determined by the weight loss during the decomposition of BP at 1600 °C. was found to be about 6·3 and chemical analyses of samples resulted invariably in ratios of 6·4–6·5. Following is a chemical analysis of a $B_{13}P_2$ sample.

P	29·2%	Al	1·0%
B	65·5	Fe	0·1
C	1·0	Si	0·2
N	0·6	Cu	0·1
Mg	0·1		

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The crystal and molecular structure of *dl*-alphaprodine hydrochloride. *Addendum.*

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Dr R. E. Marsh (1960) has kindly drawn our attention to an oversight, and its implications, in our paper on *dl*-alphaprodine hydrochloride (Kartha, Ahmed & Barnes, 1960, p. 530) in which it is stated that the chlorine ion is 4·02 Å from the *nearest* nitrogen atom. This distance is from Cl to N(1) with both atoms in the positions represented by the fractional co-ordinates x, y, z given in our Table 2. In point of fact, however, the chlorine atom (Cl′) at $x, \frac{1}{2}-y, z-\frac{1}{2}$ is appreciably closer to the nitrogen atom, i.e., N(1)–Cl′ = 3·02$_6$ Å. Taking 1·48 Å for the radius