Growth of 7ZnO.Sb₂O₅ spinel crystals. By R. C. Linares and A. D. Mills, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

The composition 7 ZnO.Sb₂O₅ has been synthesized in single crystal form by the flux growth technique. This compound as reported by Bayer (1961) from a study of ceramic compositions, has a spinel structure.

To prepare the crystals, 22 g. ZnO, 3·9 g. Sb₂O₃ and 200 g. PbF₂ are melted together in a 100 ml. platinum crucible at 1150 °C. After holding this temperature for a period of five hr., the temperature is cooled slowly (1 to 5°/hr.) to 800 °C. Next, the crucible is removed from the furnace and air cooled to room temperature. The crystals thus formed are then mechanically broken from the frozen melt. Octahedral shaped crystals up to ¼″ on an edge have been grown in this manner. The crystals are colored pale yellow and exhibit no birefringence.

In the PbF₂ solvent ZnO to Sb₂O₃ ratios of 2·5:1 to 8·5:1 will yield the spinel. Higher amounts of ZnO will cause crystallization of ZnO and lesser amounts cause crystallization of a lead antimony compound identified as bindheimite (Mason & Vitaliano, 1953). The spinel can also be grown from molten sodium tetraborate or molten zinc orthophosphate. These two solvents offer the advantage over PbF₂ that they can be leached away from the crystals with hot water or hot ammonium hydroxide.

The lattice constant of 7 ZnO.Sb₂O₅ was determined by X-ray powder diffraction using a Straumanis type Norelco camera (114·6 mm. diameter) and Cr *Kα* radiation for a two hr. exposure. The *d* spacings for crystals grown from lead fluoride are given in Table 1. These spacings measured were identical on samples from three separate runs made with varied antimony contents. Other than having two additional spacings, these *d* spacings show only slight deviations from those determined by Bayer. The lattice constant of the single crystals was found to be 8·594 Å (±0·003) as compared to

8·585 Å (±0·005) for the ceramic. This small difference in lattice constant between the crystals and the ceramic may be due to a slight loss of antimony by evaporation in the ceramic. Spectrochemical analysis of the single crystals showed no impurities present in high enough concentrations to effect the lattice constant.

Table 1. *X-ray data*

hkl	d_o	Int_o	hkl	d_o	Int_o
111	4·92	w	440	1·519	ms
220	3·027	mw	531	1·452	vw
311	2·585	s	620	1·358	vw
222	2·475	mw	533	1·310	m
400	2·145	m	622	1·295	mw
331	1·969	vvw	444	1·240	w
422	1·752	w	551	1·203	w
511	1·653	m	642	1·1486	ms

Attempts have been made to grow single crystals having substitutions of chromium and rare earths. Chromium does substitute up to at least 1% giving a green crystal, but rare earths apparently do not substitute. Attempts were also made to grow analogous compounds substituting beryllium, magnesium, calcium, and barium for zinc, and substituting niobium, molybdenum, tungsten, and vanadium for antimony. These attempts were all unsuccessful.

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The crystal structure of tridecaboron diphosphide. By Leo H. Spinar* and C. C. Wang†, *Department of Chemistry, Colorado State University, Fort Collins, Colorado, U.S.A.*

Matkovich (1961a) reported the unit cell, space group and composition of B₁₃P₂. In the course of studies on boron phosphide in this laboratory, additional data on B₁₃P₂ have been determined. B₁₃P₂ was prepared by heating BP, prepared by the reaction of BCl₃ and AlP at 1000 °C., in a new porcelain boat to 1100–1400 °C. in vacuum or under an argon atmosphere until decomposition was apparently complete. The decomposition product is a grayish white crystalline powder, inert to concentrated HCl, NHO₃, H₂SO₄ and to aqua regia. The product composition was proved to be B₁₃P₂ by a study of weight losses during decomposition, chemical analysis, density and X-ray diffraction patterns.

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Assuming that the decomposition reaction to be

$$13\ BP \rightarrow B_{13}P_2 + 11/2\ P_2$$
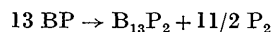
the calculated ratio of original sample weight to product weight is 2·68 which compares to an experimentally observed ratio of 2·62 ± 0·05.

The product was decomposed by sodium peroxide fusion. The phosphorus was precipitated from aqueous solution as ammonium phosphomolybdate, dissolved in ammonium hydroxide, reprecipitated as magnesium ammonium phosphate, dried and weighed. The boron was determined volumetrically by titration of the boric acid with sodium hydroxide to a pH of 11. These chemical analyses gave a B to P atom ratio of 6·3.

The pycnometric density, using dinonyl phthalate as the fluid, was found to be 2·72 ± 0·02 g.cm.⁻³ which compares with a density of 2·76 g.cm.⁻³ calculated from

the X-ray data based on one $B_{13}P_2$ per unit cell. Matkovich (1961a) reported a density of 2·74 g.cm.$^{-3}$.

X-ray powder diffraction studies were carried out using Cu $K\alpha$ ($\lambda = 1·5418$ Å) radiation in a General Electric XRD-5 unit with spectrogoniometer. A rhombohedral (trigonal) unit cell for $B_{13}P_2$ was deduced from the wide angle extrapolation of the data in Table 1. The lattice parameters of $a = 5·231$ Å and $\alpha = 69·50°$ were calculated from the standard rhombohedral crystal geometry equation.

Table 1. *X-ray diffraction powder data for* $B_{13}P_2$

Cu $K\alpha$ *radiation,* $\lambda = 1·5418$ Å

d	hkl	I_o	I_c	a
3·897 Å	110	35	32	5·242 Å
2·976	10$\bar{1}$	40	60	5·222
2·533	11$\bar{1}$	100	100	5·253
2·154	221	16	13	5·240
1·932	20$\bar{1}$	18	12	5·249
1·641	321	25	54	5·221
1·507	320	30	61	5·237
1·428	332/21$\bar{2}$	14	20	5·255
1·397	31$\bar{1}$/30$\bar{1}$	12	10	5·246
1·297	411	10	6	5·233
1·225	410	7	2	.5·231

On the basis of the agreement between calculated and observed intensities, the space group for $B_{13}P_2$ was found to be $R\bar{3}m$, which is the same space group reported for B_4C, $B_{13}C_2$, $B_{13}As_2$, and $B_{13}Si_2$. The atomic positions were determined using the IBM 1620 computer by calculating the relative integrated intensities resulting from several trial combinations of atomic coordinates. The set of atomic positions which gave intensities that were of the same relative ordering as the observed intensities as shown in Table 1, have the following coordinates expressed in terms of the related-hexagonal axes:

B(1): (*b*) $0, 0, \frac{1}{2}$;
P(2): (*c*) $0, 0, u$; $0, 0, \bar{u}$,
  where $u = 0·342$;
B(1): (*h*) $\bar{v}, \bar{v}, w$; $v, 2v, w$; $2\bar{v}, \bar{v}, w$; $\bar{v}, v, \bar{w}$;
  $v, 2\bar{v}, w$; $2v, v, w$,
  where $v = 1/6$ and $w = 0·253$;
B(2): (*h*) $v', \bar{v}', w'$; $v', 2v', w'$; $2\bar{v}', \bar{v}', w'$; $\bar{v}', v', w'$;
  $\bar{v}', 2\bar{v}', \bar{w}'$; $2v', v', w'$,
  where $v' = 0·106$ and $w' = 0·113$.

A similar set of points are around (1/3, 2/3, 1/3) and (2/3, 1/3, 2/3).

The observed relative integrated intensities of the lines, I_o, were measured with the spectrogoniometer and integrated by use of a planimeter. The calculated relative integrated intensity, I_c, depends primarily upon Lorentz polarization factor, the Bragg angle, the Miller indices, the atomic coordinates and the atomic scattering factors.

This work confirms the suggestion by Matkovich (1961b) that $B_{13}P_2$ is an interstitial compound consisting of B_{12} icosahedra with linear BP_2 units as the interstitialites.

The bond lengths calculated from the atomic positions are: icosahedral B–B: 1·75 Å, P–icosahedral B: 2·03 Å and P–interstitial B: 1·87 Å. The interstitial axis length is 11·85 Å and the unit cell volume, 121·8 Å^3.

A comparison of the X-ray diffraction data in Table 1 and that reported by Matkovich (1961a) shows good agreement for the d values of the stronger lines. The weaker lines reported by Matkovich are not detectable in this work. Two strong lines at 2·569 Å and 1·495 Å were not observed in our patterns although they have been observed in the isostructural compounds, B_4C, $B_{13}O_2$, B_4Si and $B_{12}S$. The absence of these lines in our patterns is due to the higher purity of our samples. Singlets in the pattern for the higher purity material become doublets in the lower purity material. This effect for a slight change in unit-cell size has been ob-

Table 2. *Comparison of X-ray powder diffraction lines observed in this work with d values calculated from corrected hexagonal parameters.* (Matkovich)

Hexagonal parameters $a = 6·01$, $c = 11·72$ Å

Hexagonal		Observed in this work	
hkl	d	d	hkl
003	3·90 Å	3·90 Å	110
012	3·89		
110	3·00	2·98	10$\bar{1}$
104	2·55	2·53	11$\bar{1}$
021	2·54		
015	2·14	2·15	221
211	1·936	1·932	20$\bar{1}$
116	1·639	1·641	32$\bar{1}$
214	1·634		
125	1·506	1·507	320
220	1·502		
131	1·431	1·428	332/21$\bar{2}$
223	1·4C1	1·397	33$\bar{1}$/30$\bar{1}$
312	1·400		
306	1·297	1·297	411
315	1·227	1·225	410

served by Laplaca & Post (1961) for $B_{13}As_2$. Spectrographic analysis of the material used in this work showed the major impurities to be:

Si	50–500 p.p.m.	Cu	5–50 p.p.m.
Fe	10–100 p.p.m.	Al	5–50 p.p.m.

A direct comparison of the line intensities in these two papers is difficult because Cu $K\alpha$ radiation was used in this work while Cr $K\alpha$ radiation was used in the previous work. The difference in hkl assignments in the two papers is due to the fact that this work is based on a rhombohedral unit cell while the previous work was based on a related hexagonal cell.

Matkovich (1962) has shown that an increase of the a axis to 6·01 Å and a decrease of the c axis to 11·72 Å in the hexagonal dimension of his unit cell lead to better agreement between the two papers as shown in Table 2.

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