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Growth of $7\,ZnO.Sb_2O_5$ spinel crystals.

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The composition $7\,ZnO.Sb_2O_5$ 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. Sb_2O_3 and 200 g. PbF_2 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 $\frac{1}{4}''$ on an edge have been grown in this manner. The crystals are colored pale yellow and exhibit no birefringence.

In the PbF_2 solvent ZnO to Sb_2O_3 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 PbF_2 that they can be leached away from the crystals with hot water or hot ammonium hydroxide.

The lattice constant of $7\,ZnO.Sb_2O_5$ was determined by X-ray powder diffraction using a Straumanis type Norelco camera (114·6 mm. diameter) and Cr $K\alpha$ 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.

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Matkovich (1961*a*) reported the unit cell, space group and composition of $B_{13}P_2$. In the course of studies on boron phosphide in this laboratory, additional data on $B_{13}P_2$ have been determined. $B_{13}P_2$ was prepared by heating BP, prepared by the reaction of BCl_3 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, NHO_3, H_2SO_4 and to aqua regia. The product composition was proved to be $B_{13}P_2$ by a study of weight losses during decomposition, chemical analysis, density and X-ray diffraction patterns.

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

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