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## PREPARATION AND CHEMICAL PROPERTIES OF CUBIC BORON ARSENIDE, BAs

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## Introduction

J. A. Perri<sup>1)</sup> and F. V. Williams *et al.*<sup>2)</sup> prepared cubic boron arsenide by making boron or boron halides react on arsenic or arsine in sealed silica tubes. When unreacting boron and arsenic and rhombohedral boron arsenide  $B_{13}As_2$  coexist with cubic BAs, the isolation of BAs by chemical method is not easy to make since BAs is more changeable than boron and  $B_{13}As_2$  in the chemical treatment (oxidation with nitric acid).

The zone melting method is also useless because BAs has not a definite melting point but it decomposes to  $B_{13}As_2$  at about 1100°C releasing arsenic under atmospheric pressure.

The authors have reported<sup>4)</sup> that the reaction of boron and arsenic (B : As = 1 : 1 and 13 : 2 atomic ratio samples) at high temperature and high pressure finished within about an hour at 1200–1300°C under 2–30 kb and yielded BAs and/or  $B_{13}As_2$ . Now, in the reaction system of boron and arsenic, boron reacts completely to prepare cubic BAs within 3 hours at about 1200°C under 4–5 kb in the case of mixed powder samples of atomic ratio B : As = 1 : 2–2.5, while  $B_{13}As_2$  is not prepared in this condition. Therefore BAs is isolated from unreacting arsenic and arsenic trioxide\* by oxidizing with 4.5 N aqueous nitric acid heated at about 85°C.

## Experimentals and Results

Extra pure grade boron and arsenic were obtained commercially and mixed in the atomic ratio of 1 : 2–2.5 in an agate mortar. High pressure technique was described previously<sup>3,4)</sup>.

**Isolation and analysis** After the reaction the sample was powdered and it was confirmed by X-ray diffraction that the sample consisted of cubic BAs, unreacting arsenic and arsenic trioxide, but not

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- \* Some parts of unreacting arsenic were oxidized to arsenic trioxide in the air.
- 1) J. A. Perri, S. LaPlaca and B. Post, *Acta Cryst.*, **11**, 310 (1958)
  - 2) F. V. Williams and R. A. Ruehrwein, *J. Am. Chem. Soc.*, **82**, 1330 (1960)
  - 3) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **40**, 105 (1964)
  - 4) J. Osugi, K. Shimizu and Y. Tanaka, *ibid.*, **42**, 48 (1966)

$B_{13}As_2$  as shown in Fig. 1a. It was treated with 30 ml of 4.5 N aqueous nitric acid for 75 seconds at about 85°C. The unreacting arsenic and arsenic trioxide and some part of BAs were oxidized to boric acid and arsenic acid in solution. BAs was filtered and dried. Removal of As and  $As_2O_3$  was confirmed by X-ray diffraction (Fig. 1b). Very small amount of graphite intermixed in the isolated BAs, which came

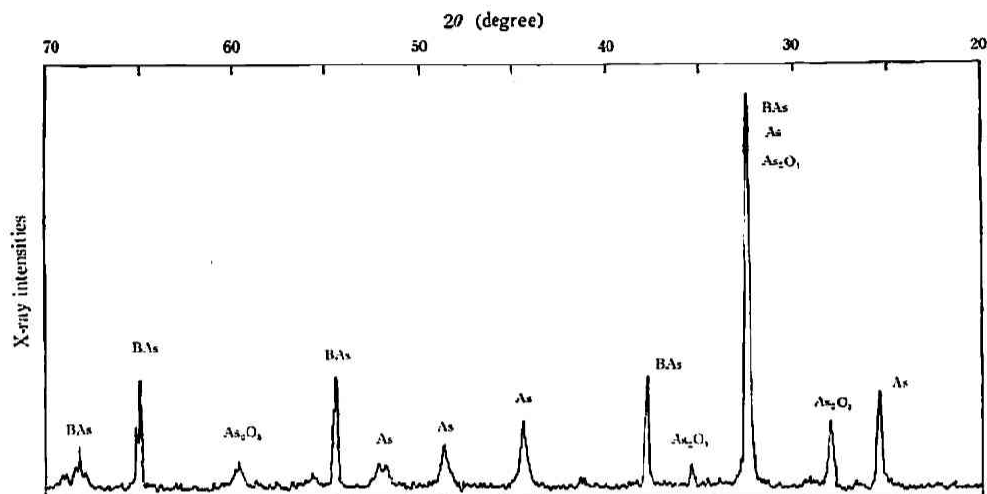


Fig. 1 a X-ray diffraction patterns of the sample before the chemical treatment with nitric acid

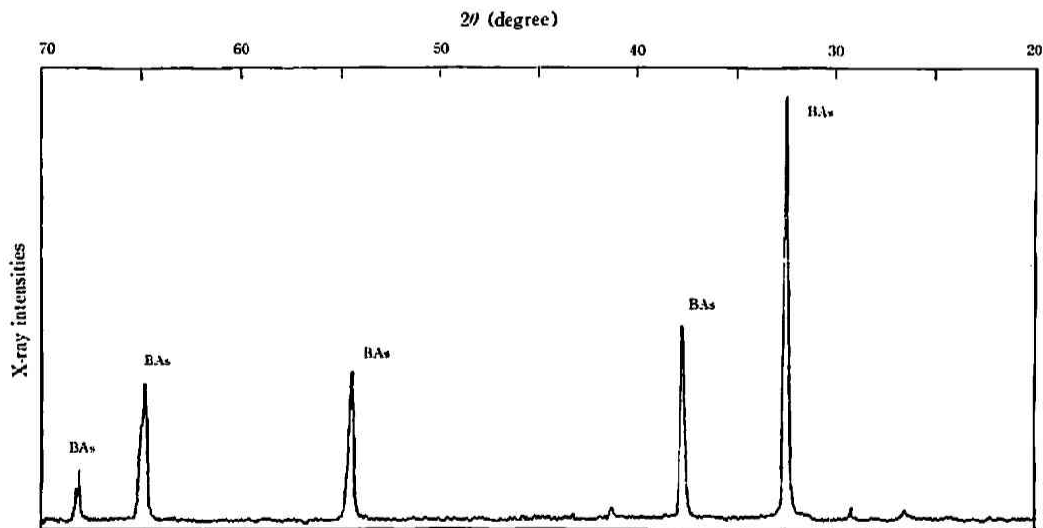


Fig. 1 b X-ray diffraction patterns of the sample after the chemical treatment with nitric acid

from the graphite high pressure reaction vessel, was removed by the floatation method with a heavy solution of stannic bromide and carbon tetrachloride, of which density at room temperature is 2.9–3.3  $g/cm^3$ , since the density of graphite is 2.25  $g/cm^3$  and that of BAs is about 5.2  $g/cm^3$ , respectively. A certain amount of isolated BAs was heated for 2 hours with 20 ml of concentrated nitric acid in a flask

Table 1. Results of the chemical analysis of the isolated BAs

Expt. No	BAs (mg)	B in BAs (mg) experimented	B in BAs (mg) calculated	Atomic ratio B/As
1	162.0	22.0	20.4	1.09
2	246.8	31.8	31.2	1.02
3	246.8	30.6	31.2	0.975

equipped with a reflux condenser and decomposed to boric acid and arsenic acid. Boric acid in the solution was determined colorimetrically by the carminic acid method<sup>5)</sup>. Thus, as shown in Table 1, it was confirmed that the isolated BAs did not contain unreacting boron and was stoichiometrical.

**Chemical properties of BAs** As described in the previous paper,  $B_{13}As_2$  is not attacked by hot concentrated nitric acid and isolated from boron, arsenic and BAs, while BAs reacts rapidly and vigorously with nitric acid.

Now, the order of reactivities of these reagents with nitric acid is as follows:



Therefore the next two conditions should be satisfied in order to isolate BAs with nitric acid.

1.  $B_{13}As_2$  must not be prepared together with BAs.
2. Boron in the mixed powder sample should be consumed completely to prepare BAs.

The reaction of boron and arsenic under high pressure is greatly influenced by temperature. But there are always some proper conditions in which only BAs is prepared but not  $B_{13}As_2$  independently of the atomic ratio of boron and arsenic in the sample, since  $B_{13}As_2$  is prepared in higher temperature and pressure range than in the case of BAs through the following reaction process under high pressure:



When the reaction was undertaken at about 1200°C and 4–6 kb in use of B : As = 1 : 2–2.5 powder sample, only BAs was prepared with a very high reaction yield. Excess arsenic in this sample suppresses effectively the preparation of  $B_{13}As_2$  stoichiometrically. In this condition the reaction was completed in 3 hours.

Arsenic and arsenic trioxide are oxidized completely to arsenic acid within about 45 seconds by the treatment with 4.5 N aqueous nitric acid heated at 85°C. BAs decomposes partly in this treatment, but great part is not attacked and isolated. In the treatments with hot concentrated nitric acid or very dilute nitric acid (about 0.7 N) there was no distinct difference between the reactivity of BAs and those of arsenic and arsenic trioxide.

Isolated BAs is brown colored powder and one of III–V compound semiconductors. It is attacked

5) E. B. Sandell, "Colorimetric Determination of Traces of Non-Metals," Interscience publishers, Inc. New York (1958)

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vigorously by aqua regia, rather rapidly by heated  $\text{H}_2\text{O}_2$  (30%), and slowly by hot concentrated  $\text{H}_2\text{SO}_4$ . Concentrated  $\text{HCl}$ ,  $\text{HClO}_4$  (60%),  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$  (28%) do not react on BAs.

Physical properties of BAs will be investigated in the future.

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