Finally, there seems to be a correlation of this structure with observed physical properties and reactions. The basic unit of 8 tetrahedra suggests rigidity and it was observed by means of X-ray diffraction photographs that a temperature of 800° is required for recrystallization. The X-ray diffraction pattern of the recrystallized material was the same as that of β-cristobalite which indicates that it may be a "stuffed" derivative of composition $(NaAlSiO_4)_4$ as discussed by Buerger.[14]

In highly alkaline solution, the sodium zeolite A converts irreversibly to a basic sodalite of composition $Na_6[(AlO_2)_6(SiO_2)_6]\cdot NaOH\cdot 8H_2O$, which has the same aluminosilicate framework as that surrounding the small cavity of the A zeolite structure.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Aluminum Diboride, AlB_2[1]

BY EDWARD J. FELTEN

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The purpose of the investigation was to find a relatively simple method for the preparation of aluminum diboride, AlB_2. The AlB_2 structure is the prototype of the structure of many of the transition metal diborides. The unit cell is hexagonal: $a_0 = 3.009 \pm 0.001$ Å., $c_0 = 3.262 \pm 0.001$ Å.

Introduction

The preparation of AlB_2 was first reported by Funk,[2] who heated an aluminum–boron mixture, rich in aluminum, at a temperature of about 1000°. Chemical analysis was cited as proof of the composition of the alloy. Steele and Mills[3] reported the preparation of an aluminum boride by the fusion of finely divided Al (3 parts) and finely powdered B_2O_3 (1 part) in an iron crucible. The composition of the boride formed was not specified. The first X-ray work on AlB_2 was done by Hofmann and Jäniche.[4] Using single crystals isolated by treatment of an aluminum–1% boron alloy with HCl, the structure of AlB_2 was established.

Recently the preparation of the aluminum borides has been critically reviewed by Lihl and Janitscheck.[5] The difficulties in the preparation of the aluminum borides by the various methods are discussed in detail. It is pointed out that the alloying of Al with elemental B yields AlB_{12} as well as AlB_2. The reaction of Al with sodium borate or B_2O_3 at temperatures above 1000° results in a product highly contaminated with Al_2O_3, while the reaction of the Al with gaseous boron compounds (ex. BCl_3) requires careful manipulation. The method preferred by the authors is a thermite reaction involving Al, B_2O_3, S and $KClO_3$, followed by treatment of the product with HNO_3 and HCl in order to isolate the AlB_{12} formed. The AlB_{12} is then made to react with Al at 1350–1450° to yield AlB_2.

In none of the above was AlB_2 prepared in good purity as a major reaction product. In the course of a study of various metal diborides, efforts were made to prepare AlB_2 by several methods; of these a simple procedure described below gave very satisfactory results.

Experimental

Powdered boron (99.5%; Cooper Metallurgical Associates, Cleveland, Ohio) and aluminum (Eimer and Amend A559) were mixed in the stoichiometric proportions. The mixture was placed in a graphite tube provided with a close-fitting graphite plunger. Veins had been milled lengthwise in the plunger to a depth of about 1/8″ in order to allow any trapped air or other gaseous products produced during the heating operation to escape. The assembly was then placed in a transparent fused silica tube. The silica tube was flushed several times with helium, then evacuated, placed in an electric furnace, allowing about a 12″ portion to protrude from the furnace and heated overnight at 800°. After cooling, the sample was removed and was found to be uniformly brown-grey in color. A representative sample was examined by X-ray diffraction methods using nickel-filtered Cu radiation. The principal component of the reaction was AlB_2, with Al, graphite and B_4C being present in small amounts. The amounts of graphite and B_4C may be kept at a minimum by careful removal of the reaction product from the graphite container as these compounds

TABLE I

DIFFRACTION DATA FOR AlB_2

hkl	*d* Spacings	Rel. intensity
001	3.264	4
100	2.608	39
101	2.307	100
002	1.631	13
110	1.505	28
102	1.383	7
111	1.367	3
200	1.303	4
201	1.210	12
112	1.106	11
202	1.018	2
210	0.9852	1
211	.9430	10
300	.8687	5
212	.8433	1
203	.8347	3
004	.8154	2

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] H. Funk, *Z. anorg. allgem. Chem.*, **142**, 269 (1925).

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probably are formed at the container walls. This technique also has been employed successfully for the preparation of magnesium diboride, MgB_2.

The AlB_2 structure is the prototype of the structure of many of the transition metal diborides which have been reported.[6] The space group of the hexagonal unit cell is C^6/mmm; $Z = 1$. The structure may be described in terms of close-packed layers of aluminum atoms separated by layers of boron atoms; both types of layers are perpendicular to the C axis. The unit cell dimensions of AlB_2, determined from Norelco geiger counter diffractometer measurements using Cu Kα radiation are: $a_0 = 3.009 \pm 0.001$ Å., $c_0 = 3.262 \pm 0.001$ Å. The X-ray diffraction pattern is given in Table I.

BROOKLYN, N. Y.

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[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY, UNION CARBIDE NUCLEAR COMPANY]

Studies in the Carbonate–Uranium System

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Portions of the phase diagram for the four component system UO_3–Na_2O–CO_2–H_2O have been investigated at 26°. Solubilities have been determined for UO_2CO_3 in sodium carbonate solutions and for $Na_4UO_2(CO_3)_3$ in sodium carbonate and other salt solutions as a function of the concentration of co-solute. A solubility of 320 g. U/l. was obtained at molar ratio CO_2:Na:U close to 2:2:1 and *p*H close to 7. From solubilities and spectrophotometric measurements, evidence has been obtained for the existence of $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$, with an estimate of the stability of the latter, and also for an additional complex ion having the molar ratio $CO_2:U = 0.5$.

It has long been known that uranyl compounds show considerable solubility in sodium carbonate solutions, indicating the formation of stable complex ions. This rather unique property of uranium has been useful in analytical separation procedures and in industrial uranium separation processes. Prior to the time that the present investigation was made[1–3] no thorough study of the carbonate–uranium system had been published although the particular compound sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$, had been prepared and identified[4] and its solubility had been measured.[5] In addition Haldar[6] observed discontinuities in conductometric titrations of uranyl nitrate with carbonate solutions at points corresponding to carbonate:uranium mole ratios of 3:1 and 2:1. Bachelet, Cheylon, Davis and Goulette[7] have studied the preparation and properties of some alkali and alkaline earth carbonates and Bullwinkel[8] has confirmed the existence of two of the aqueous complexes described in this paper, discussing some of the chemical properties of these complexes and of uranyl carbonate.

Experimental

The uranium trioxide used in this investigation was prepared by precipitating uranium peroxide ($UO_4 \cdot xH_2O$) from uranyl nitrate solution (*p*H held at 2.5) with subsequent decomposition of the precipitate at a temperature of 325°. The uranium trioxide thus produced is a fluffy, reactive material, free from peroxide.

In the preparation of uranyl carbonate (UO_2CO_3), 20 g. of uranium trioxide, 10 ml. of water and a considerable excess of crushed Dry Ice were loaded into a small stainless steel bomb. Consistently good results (U:CO_3 mole ratios ranging from 1.01 to 1.03) were obtained by agitation of the bomb for 5 hr. at temperatures between 90–105° and pressures between 2500 and 3000 p.s.i. The product was very pale yellow and is stable at 109°.[9]

Sodium uranyl tricarbonate was prepared according to a general method proposed previously.[5] In this method sodium polyuranates are first prepared by precipitation from uranyl nitrate solution with sodium hydroxide. This precipitate is washed thoroughly and dissolved in a solution of sodium bicarbonate. The solid tricarbonate is obtained by evaporating to a low volume while passing carbon dioxide through the solution. A recrystallization from water was made to purify the material, which was bright yellow and stable at 240°. Carbonate:uranium mole ratios in the product varied from 3 to 3.2.

Reagent grade sodium carbonate, sodium bicarbonate and tank carbon dioxide were used in making the experimental mixtures.

Solubility equilibrations were made in Pyrex or in plastic (polyfluoroethylene) bottles. The solids and solutions were shaken for sufficient time (at least 10 days, usually 3 weeks or more) to ensure equilibrium. The agitation was carried out in a constant temperature room at 26 ± 2°. The contents of a bottle were then centrifuged, and usually both solid and solution were analyzed for uranium, sodium and carbonate. Solution densities were measured and the solubilities were calculated in weight per cent. The solid residues were complex in tests in the high solubility region near the invariant point, in tests in basic solutions and in tests starting with uranium trioxide. Application of Schreinemakers'[10] method of wet residues to the analyses of the wet solids permitted the calculation of the solid phase in only a few cases.

Concentrated solutions resulting from the dissolution of uranyl carbonate in aqueous sodium carbonate were very viscous and difficult to centrifuge. The solutions were also in equilibrium with appreciable carbon dioxide pressure. Equilibrium concentrations in these particular solutions, therefore, could not definitely be established.

Analyses of high level uranium samples were obtained by reducing the uranium and titrating potentiometrically with ferric sulfate solution.[11] On low level samples the ascorbic acid colorimetric procedure[12] was used. Sodium was determined with the flame photometer and the usual absorption–gravimetric method was used for carbonate.

For the spectrophotometric investigations, it was neces-

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