

Acta Cryst. (1953). **6**, 870

An X-ray study of the magnesium borides. By VIRGINIA RUSSELL, ROBERT HIRST, F. A. KANDA and A. J. KING, *Department of Chemistry, Syracuse University, Syracuse, N. Y., U. S. A.*

(Received 13 July 1953 and in revised form 27 July 1953)

Introduction

A complete investigation of the magnesium-boron system has not been reported in the literature although a number of different compositions have been suggested for intermediate phases which may occur in the system. Winkler (1890) proposed Mg_3B_2 as one of the products of the reaction between magnesium and boron trioxide, and Mg_2B_3 as a product of the action of magnesium on sodium tetra-borate. Moissan (1892) believed that Mg_3B_2 as well as other borides may be formed. Travers & Ray (1912) studied the mechanism of the reaction between magnesium boride and water and found their results were not in accord with those expected for the compound Mg_3B_2 . They pointed out, however, that the boride Mg_4B_2 would account satisfactorily for the results which they obtained. Ray (1914) investigated the products of the reaction of magnesium with boron trioxide and with boron, and concluded that Mg_3B_2 is the only compound formed. He stated that Mg_3B_2 decomposes at elevated temperatures into magnesium and a mixture of crystalline and amorphous boron. Stock (1933) has considered Mg_3B_2 as the compound which reacts with acids to yield the boranes.

Experimental

Because of the volatility of magnesium and the high melting point of the phases involved, conventional methods of thermal analysis were impracticable. Identification of the intermediate phases was made principally by X-ray diffraction methods.

Commercially available amorphous boron is too impure to be used in a study of this kind and attempts to purify it were not successful. A number of methods have been reviewed by Laubengayer, Newkirk & Brandour (1942) for the preparation of pure boron, but the yield of most of these is too small to be of practical value. A method described by Kiessling (1948), with slight modifications to improve the yield and purity, was adopted for this study. Samples from various runs showed a purity of over 99% and a spectroscopic analysis showed the presence of less than 0.1% Si and 0.01% Fe.

Cylindrical samples were prepared for this study by pressing pure boron and freshly prepared magnesium wool, in the desired ratio, in a steel die at 10,000 Lb.in.⁻². These were heated in cylindrical crucibles, turned from steel, which could be sealed by forcing a polished steel plug into the open end in a hydraulic press. The crucibles were lined with magnesium oxide or with sheet tantalum. The crucibles and contents, with the plug lightly pressed in place, were degassed in vacuum at 200° C. and flushed with argon before sealing under pressure. The final heating was conducted in a quartz system in an atmosphere of argon. Powdered samples for the X-ray diffraction studies were ground under dry mineral oil. Filtered $Cu K\alpha$ radiation was used. Intensities of the reflections were estimated visually by the triple-film technique applied to two sets of film with exposure times of 1½ and 3 hr. respectively.

Experimental results

A series of preparations with decreasing magnesium content gave diffraction patterns which contained the lines of magnesium and a second crystalline phase. The intensities of the lines of the new phase increased to a maximum while those of magnesium decreased to the vanishing point as the series approached a composition corresponding to the compound MgB_2 . Samples of this composition dissolved almost completely in dilute hydrochloric acid. Compositions richer in boron than that corresponding to MgB_2 were progressively less soluble in dilute acid. The acid insoluble residue was found by analysis to agree in all instances with the compound MgB_4 and gave a diffraction pattern which was distinctly different from that of the soluble phase. The patterns of the two phases appeared simultaneously for all compositions between MgB_2 and MgB_4 . Two other crystalline phases with characteristic diffraction patterns appear in the system. The identity of these and the structure of MgB_4 is being studied.

All lines of the diffraction pattern of the acid-soluble phase could be accounted for by a primitive hexagonal cell with

$$a = 3.084 \pm 0.001 \text{ \AA}, c = 3.522 \pm 0.002 \text{ \AA}.$$

On the basis of the composition, MgB_2 , the observed density, 2.667 g.cm.⁻³, requires one molecule per unit cell.

Observed intensities were in complete agreement with those calculated for a structure isomorphous with AlB_2 (Hofmann & Jäniche, 1935, 1936) and a number of other diborides which have been investigated by Kiessling (1949) and by Norton, Blumenthal & Sindeband (1949). The B-B distance in the hexagonal net of boron atoms is $1.780 \pm 0.001 \text{ \AA}$.

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