pert[47] for the reaction of boron trichloride with alcohols to form the borate esters.

NEWARK, DELAWARE

(47) W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 2545 (1951).

[CONTRIBUTION FROM THE AMERICAN ELECTRO METAL CORPORATION]

Borides of Rare Earth Metals

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Until recently, hexaborides were the only binary compounds known to be formed between rare earth metals and boron. In this study, a series of tetragonal tetraborides of Pr, Sm, Gd and Yb isomorphous with CeB_4, ThB_4 and UB_4 were prepared and their lattice constants measured. The hexaborides of the above rare earth metals, as well as those of La and Th, were also prepared by carbon and boron reduction of their respective oxides. In addition, a group of isomorphous borides of a hitherto unreported structural type were found. The exact boron content of these compounds has not yet been determined.

I. Introduction

A wide variety of binary compounds are formed between boron and the transition metals of the 4th, 5th and 6th groups of the Periodic Table. These range in composition from M_2B to MB_{12}.[2] No such variety, however, characterizes the compounds formed between boron and the rare earth metals. Rare earth metal borides of the type MB_6 were prepared and described many years ago,[3,4] and, until recently, no other rare earth borides were known. Within the past few years, however, three compounds of the type MB_4 were prepared[5-8]; of these, one, CeB_4, is a rare earth metal boride and the other two (UB_4 and ThB_4) are closely related.

One of the objectives of the present investigation was the preparation and the study of hexaborides of various rare earth metals and of tetraborides of rare earth metals other than Ce. Efforts also have been made to prepare binary boride phases other than MB_6 or MB_4. In addition, procedures have been studied for the preparation of such binary borides by the direct reduction of the metal oxides by boron.

II. Raw Materials

Sm_2O_3, Gd_2O_3 and Yb_2O_3 were obtained from the Ames Laboratory of Iowa State College. The samarium and gadolinium oxides were of a purity greater than 99.9%, while the ytterbium oxide was 99.7% pure. The "Pr_4O_7" used was of a minimum purity of 93/94%, and contained about 5% La_2O_3. The La_2O_3 was of two grades, one of about 92% minimum purity, and the other approximately 99% pure. The boron powder used, purchased from Cooper Metallurgical Associates, was 96.3% pure, and contained 0.60% Fe and 0.26% C. The carbon used was Fisher carbon black "G" (gasblack).

III. Preparative Methods

Small amounts of rare earth oxide, boron and carbon black powders (totaling about 1 g.) were hand-mixed in the desired proportions until homogeneous and pressed at about 5 t.s.i. into thin wafers (1" × $^1/_2$" × $^1/_{16}$"). These were separately loaded into graphite crucibles about 1.5" high by $^5/_8$" in diameter. The latter were in turn placed in larger graphite crucibles (4" × 3") and heated by induction in a hydrogen atmosphere; specimens were heated either for 2 hours at 1500° or for 1 hour at 1800°.

After heating, the sintered compacts were crushed to a fine powder and analyzed chemically and by X-ray diffraction methods to determine the reaction products.

There were strong indications that, especially in reactions carried out at 1800°, the boron, rather than the carbon, acted as the reducing agent. When no carbon was added to the reaction mixtures (enough excess boron was added to reduce the oxide by forming the volatile B_2O_3), the borides readily were formed both at 1500 and 1800°. In the latter case, although no carbon was added to the reaction mixture, about 1 to 2% was picked up from the graphite crucibles. It was found that the borides were formed equally well in the absence of carbon, *i.e.*, where ZrB_2 crucibles were used as containers.

IV. Experimental Results

a. Hexaborides (MB_6).—The MB_6 phase appears to be by far the most stable of the rare earth borides. In all instances, when the appropriate amounts of boron and metal were caused to react, the MB_6 phase was formed. It was also detectable on most X-ray diagrams when other compositions were employed.

The hexaborides of the rare earth metals have been investigated extensively. The structure is of the CsCl type, *i.e.*, the unit cell is primitive cubic, with boron octahedra at the corners and a metal

TABLE I

LATTICE CONSTANTS (IN Å.) OF THE CUBIC UNIT CELLS OF THE HEXABORIDES OF VARIOUS METALS

Metal	(1)[a]	(2)[b]	(3)[c]
Ba	4.29	4.268	
Sr	4.20	4.198	
Ca	4.153	4.145	
Y	4.08	4.113	
La	4.153	4.157	4.153
Ce	4.137	4.141	
Pr	4.129		4.130
Nd	4.126	4.128	
Sm			4.129
Eu			
Gd	4.13	4.112	4.110
Tb			
Dy			
Ho			
Er	4.11		
Tm			
Yb	4.14	4.144	4.140
Lu			
Th	4.16	4.113	4.110

[a] Various authors quoted in Kiessling.[2] [b] Blum and Bertaut.[6] [c] The present work.

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(1) To whom inquiries may be addressed.

(2) R. Kiessling, *Acta Chem. Scand.*, **4**, 209 (1950).

(3) G. Allard, *Bull. soc. chim. France*, **51**, 1213 (1932).

(4) L. Andrieux, *Ann. Chim.*, **12**, 423 (1929).

(5) L. Brewer, *et al.*, *J. Am. Cer. Soc.*, **34**, 173 (1951).

(6) P. Blum and F. Bertaut, *Acta Cryst.*, **7**, 81 (1954).

(7) A. Zalkin and D. H. Templeton, *ibid.*, **6**, 269 (1953).

(8) F. Bertaut and P. Blum, *Compt. rend.*, **234**, 2621 (1952).

atom at the body center of each unit cell. The lattice constants of the unit cells of hexaborides and related metals, as determined by various investigators, are listed in Table I.

In general, results obtained in the course of the present investigation agree well with those reported by Blum and Bertaut.[6] It is clear that the value of 3.16 Å. reported by Allard[3] for ThB_6 is considerably in error; Blum and Bertaut found the lattice dimension to be 4.113 Å.; in the present investigation it was found to be 4.110 Å.

The preparation of SmB_6 had not been reported prior to the present work; the lattice dimensions of this compound are of the expected magnitude.

b. Dodecaborides (MB_{12}).—Dodecaborides of uranium[9] and zirconium[10] recently have been prepared and described. Efforts were made to prepare rare earth borides with this interesting crystal structure. In all cases, no phase richer in boron than MB_6 was detected in the X-ray diagrams when mixtures of composition MB_{12} were prepared. Nor was any evidence of unreacted boron detected in the X-ray patterns. This did not necessarily imply that free boron was absent from the reaction products. The scattering power of boron is extremely low relative to that of the rare earth metals; some free boron might very well, therefore, have gone undetected.

In the case of Yb and La, when excess boron was used in the reaction (*i.e.*, when sufficient boron was used to form MB_{12}), the MB_6 unit cell which was formed was very slightly smaller than in instances where the MB_6 phase was prepared using stoichiometric quantities of boron. It appears likely that the MB_6 structures in these cases contained large numbers of metal atom vacancies, since the actual composition was close to MB_{12}, resulting in a diminution of the lattice constant. The absence of boron lines from the X-ray diagram of the reaction products is less puzzling in terms of this hypothesis.

In this connection, we may note that, in his detailed study of the thermionic properties of various metal hexaborides, Lafferty[11] has discussed the effects of migration of metal atoms through the boron lattice to cathode surfaces. He concluded that in the case of LaB_6, "lanthanum diffuses out through the boron framework and evaporates, while the boron structure remains intact. After prolonged operation at high temperatures, the LaB_6 will become so depleted in lanthanum that the boron framework will collapse, leaving a boron coating on the cathode." The effect noted in the present study, if real, is quite consistent with Lafferty's hypothesis.

c. Tetraborides (MB_4).—Brewer, *et al.*,[5] have described the preparation of UB_4, ThB_4 and CeB_4. The isomorphous structures of these compounds were determined by Zalkin and Templeton[7]; the unit cells are tetragonal with four formula weights per cell. Bertaut and Blum[8] have also prepared UB_4 and described its structure.

It appeared probable that other rare earth metals, in addition to Ce, form MB_4 phases, and that the failure of previous investigators to detect this phase might very well have been due to the relatively low reaction temperatures employed in their preparation.

This expectation was realized. MB_4 phases, isomorphous with the structure reported by Zalkin and Templeton, and by Bertaut and Blum, were readily prepared. In no case, however, could a "pure" MB_4 phase be prepared; the X-ray diagrams always showed the presence in the reaction products of either MB_6 or a phase tentatively labelled MB_x, in addition to the MB_4 compound. For reasons which are not at all clear, La, which readily formed LaB_6, did not form detectable amounts of LaB_4.

Lattice constances of CeB_4, ThB_4 and UB_4, as determined by Zalkin and Templeton,[7] are listed in Table II together with corresponding values for PrB_4, SmB_4, GdB_4 and YbB_4, determined in the present investigation.

TABLE II

LATTICE DIMENSIONS OF MB_4 COMPOUNDS (Å.) (TETRAGONAL)

	a	*c*
CeB_4[a]	7.205	4.090
ThB_4[a]	7.256	4.113
UB_4[a]	7.075	3.975
PrB_4[b]	7.20	4.11
SmB_4[b]	7.12	4.07
GdB_4[b]	7.12	4.05
YbB_4[b]	7.01	4.00

[a] Zalkin and Templeton.[7] [b] The present work.

d. MB_x Phase.—In addition to MB_6 and MB_4 phases, lines of another, hitherto unreported, boride phase appeared in the X-ray diagrams, usually in addition to those of the other two phases (MB_6 and MB_4). Although there were some indications of the presence of this "MB_x" phase in patterns of borides of samarium, a definite identification could not be made in that case. In the cases of lanthanum, praesodymium, gadolinium and ytterbium, the additional phase could be identified readily. Each of these MB_x phases contains one metal atom per unit cell; their unit cell dimensions are listed in Table III.

TABLE III

LATTICE DIMENSIONS OF MB_x (Å.)

	a	*c*	Crystal system
LaB_x	3.82	3.96	Tetragonal
PrB_x	3.81	..	Cubic or pseudo-cubic
GdB_x	3.79	3.63	Tetragonal
YbB_x	3.77	3.56	Tetragonal

It was not possible to identify the compositions of these phases unequivocally by the usual analytical means. These compounds could be prepared reproducibly, and the constancy of the lattice dimensions—despite a variety of preparative methods—indicated that they possessed narrow ranges of homogeneity. The value of *x* is probably either 3 or 4. The possibility of stabilization of this phase by carbon could not be excluded, although the amount of carbon contained in the structure would have to be rather small. This was shown by

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(9) F. Bertaut and P. Blum, *Compt. rend.*, **229**, 666 (1949).

(10) B. Post and F. W. Glaser, *J. Metals*, **4**, 631 (1952).

(11) J. M. Lafferty, *J. Appl. Phys.*, **22**, 299 (1951).

the value of the lattice parameters which fit very well the atomic size of boron, and by chemical analysis.

A closer study of the dimensions of the MB_x compounds (LaB_x, PrB_x, GdB_x, YbB_x) reveals an interesting variation with atomic number. LaB_x is tetragonal, with "c" greater than "a" (3.96 *versus* 3.82 Å.). PrB_x is "cubic" with $a_0 = 3.81$ Å. GdB_x and YbB_x are both tetragonal, but in their unit cells "a" is greater than "c." It is believed that all four compounds are really tetragonal and that they differ primarily with respect to axial ratios. c/a decreases from 1.036 in the case of LaB_x, to 1.000 in the case of PrB_x, to 0.962 for GdB_x, and 0.943 for YbB_x. If this view is valid, then PrB_x is only pseudo-cubic and should manifest its non-cubic character by splitting of lines on X-ray diagrams at elevated temperatures. This would result from differences in coefficients of expansion in the "a" and "c" directions, if the compound is really tetragonal.

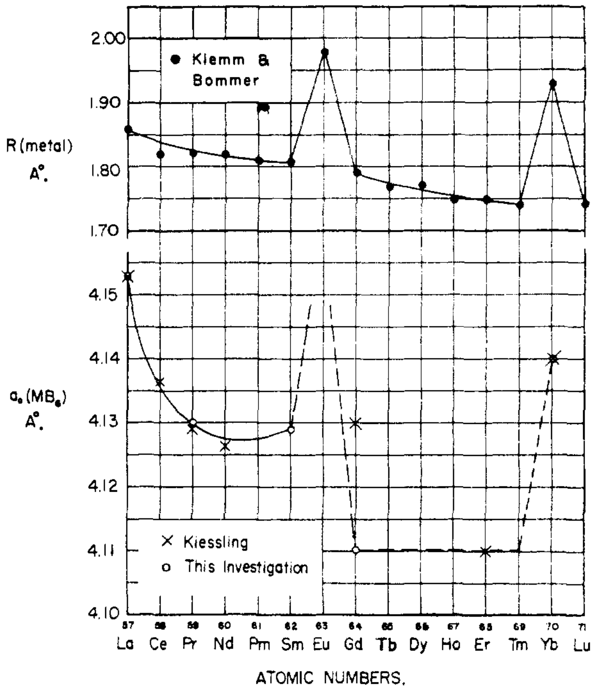

Fig. 1.—Atomic radii of rare earth metals and lattice parameters of rare earth hexaborides *versus* atomic number.

V. Discussion

A careful X-ray study of the effective atomic sizes of the rare earth elements was carried out by Klemm and Bommer.[12] They found that, with the exception of Eu and Yb, these elements showed a regular decrease in atomic size as we proceed from La to Lu. The atomic radii of the two exceptions, Eu and Yb, are about 10% above the "normal" curve that may be drawn for the other rare earth elements (Fig. 1). These anomalies are associated with the abnormal valencies of these metal atoms; while most of the rare earth metals are essentially trivalent, Eu and Yb show a large amount of divalent character. The withdrawal of one electron from the outermost orbit to fill a gap in an inner one results in the observed increased sizes of these atoms.

The dimensions of the cubic MB_6 unit cells (Table I) show a similar, though less pronounced, anomaly in the case of YbB_6, as shown in Fig. 1 (EuB_6 has not yet been prepared).

It appears, therefore, that the effective valence state of the rare earth metals in the MB_6 compounds is very much like that of the uncombined metals.

The ionic sizes of the rare earth metals (M^{+++}) show no anomalies comparable to the above. The ionic radii of the trivalent rare earth ions decrease regularly from La^{+++} (1.061 Å.) to Lu^{+++} (0.848 Å.).[13] The lattice dimensions of the various MB_4 and MB_x compounds listed in Tables II and III, respectively, also show a regular diminution with increasing atomic number of the metal.

A distinction may, therefore, be drawn between the relatively "metallic" character of the metal atoms in the MB_6 compounds and their relatively "ionic" character in the MB_4 and MB_x compounds.

Measurements of electrical conductivity, Hall constant, etc., should furnish critical tests of the above hypotheses.

Yonkers, N. Y.

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[12] W. Klemm and H. Bommer, *Z. anorg. Chem.*, **231**, 138 (1937).

[13] D. H. Templeton and C. H. Dauben, This Journal, **76**, 5327 (1954).