THE PREPARATION AND SOME PROPERTIES OF NEW LANTHANIDE DIBORIDEDICARBIDES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
NORMAN ALLEN FISHEL
1968

ce
ha
ha
la
the

met
of
to
The
str
co

ABSTRACT

THE PREPARATION AND SOME PROPERTIES OF NEW LANTHANIDE DIBORIDEDICARBIDES

by Norman Allen Fishel

The previously unreported diboridedicarbides of cerium, samarium and thulium have been prepared. These have been studied by X-ray diffraction techniques and have been shown to be members of the isostructural lanthanide diboridedicarbide series. Indications for the existence of an EuB_2C_2 phase are reported.

An examination of LnB_2C_2 stability with varying metal oxidation number has been conducted. A discussion of the diboridedicarbide structure and bonding is related to anomalous lattice parameters observed for YbB_2C_2. The failure to observe diboridedicarbides for calcium, strontium, barium, thorium and metal mixtures is considered.

THE PREPARATION AND SOME PROPERTIES OF NEW LANTHANIDE DIBORIDEDICARBIDES

By

Norman Allen Fishel

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1968

ACKNOWLEDGMENTS

The author is especially indebted to Professor Harry A. Eick for his guidance and personal interest throughout the course of this research.

Particular thanks are due to my colleagues in the High Temperature Group. Their interest and suggestions and the rapport of the laboratory were very helpful in producing these results.

This work would not have been possible without the encouragement, support and patience of my wife Grace. The author is particularly grateful for her understanding.

Financial support of this research by the United States Atomic Energy Commission under contract number AT (11-1)-716 has been very welcome.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

I. INTRODUCTION

A. Preface

The recent rapid advances in nuclear and space technologies have necessitated the development of materials for high temperature applications. Binary compounds of the lanthanides are of particular interest for their unusual electrical and thermal properties which are exhibited along with high temperature thermodynamic stability.

In particular, the lanthanide borides and carbides have been studied frequently, but for many of the phases the physical and thermochemical properties have been only partially characterized. Only the most basic information is available about ternary lanthanide-boron-carbon systems.

B. Incentives for this research

The search for an explanation of the two following observations provided the incentives for this research. First, while trying to study the equilibrium pressure of carbon monoxide for the reaction

$$Sm_2O_3(s) + 3B_4C(s) = 2SmB_6(s) + 3CO(g) \qquad [1]$$

Butherus[1] observed a new pseudo-cubic phase which he thought was a borocarbide. Second, P. K. Smith and Gilles[2] in a study of the lanthanide diboridedicarbides, LnB_2C_2, were unable to prepare this phase for samarium.

The possibility that these two observations were related set the initial course of this research.

C. Historical

Metal borides and carbides frequently are prepared by the carbo-thermal reduction of the metal oxides[3]. Because of the great reactivity of borides at high temperatures, carbon impurities are often present in the form of occlusions of binary or ternary compounds.

The first report of a ternary compound in a lanthanide-boron-carbon system was the observation by Brewer and Haraldsen[4] that CeB_4(s) was not stable in the presence of graphite. Post et al.[5] in attempting to prepare lanthanide borides by reaction of the sesquioxides with boron in a graphite crucible, observed tetragonal phases of composition MB_x (x was reported as either three or four; M was La, Pr, Gd or Yb). In preparations of samarium borides they reported some indications of this MB_x phase, but definite identification was not made. They believed that the phases may have been stabilized by small amounts of carbon.

Johnson and Daane[6] although unsuccessful in their attempts to prepare the MB_x phase reported by Post et al. observed that "a eutectic reaction" of carbon with lanthanum-boron alloys yielded a ternary compound of the estimated formula LaBC. Binder[7,8] obtained an yttrium phase similar to the MB_x one and described it as having

a
v
(
t

M
i
H
b
b
b
o
c
ca

Dy
ch
gr
de
hav
Gd_0
eit
fai
LuB_2
mixt
anal
with

an approximate composition of YB_2C. Eick[9] reacted ErB_4 with graphite in high vacuum at elevated temperatures (> 2200°) and obtained a hard brittle substance similar to the other MB_x borides.

In the reaction of B_2O_3 with either La_2O_3 or CeO_2, Markovskii et al.[10,11] noted that borocarbides similar in properties to alkaline-earth borocarbides were formed. Hoyt and Chorne'[12] hot pressed lanthanide oxides with boron in graphite dies and determined that the resulting borides were boron deficient due to reaction between the borides and graphite. They also reported that the heating of lanthanide tetraborides and hexaborides in graphite crucibles yielded only boron carbide and lanthanide carbides.

P. K. Smith and Gilles[2,13] prepared the Nd, Gd, Tb, Dy, Ho, Er and Yb diboridedicarbides by arc-melting stoichiometric mixtures of the respective tetraborides and graphite. Four other phases in the Gd-B-C system were deduced from the ternary phase diagram and reported as having compositions of $Gd_{0.40}B_{0.35}C_{0.25}$, $Gd_{0.35}B_{0.19}C_{0.46}$, $Gd_{0.35}B_{0.45}C_{0.20}$ and $Gd_{0.30}B_{0.40}C_{0.30}$. The reaction of either lanthanum or samarium hexaboride with graphite failed to yield the diboridedicarbide. The analagous LuB_2C_2 was prepared by Nordine et al.[14] by arc-melting mixtures of the elements. X-ray powder diffraction analyses indicated that these LnB_2C_2 phases were identical with the previously recorded MB_x phases.

c
s
c
C
S
t
w

c
th
an

th
be
pr
ca
gra
dib

sama
star
and
meta
teri

The crystal structure for the homologous lanthanide diboridedicarbide series was determined by P. K. Smith et al.[15] from X-ray diffraction data for a single crystal of TbB_2C_2 and intensity data from powdered HoB_2C_2. G. S. Smith et al.[16] reported the crystal structure of ScB_2C_2 to be of orthorhombic symmetry and therefore to not be isostructural with the lanthanide diboridedicarbides which possess tetragonal symmetry.

A summary of investigations in the actinide-boron-carbon systems is given by Rudy[17]. In the uranium and thorium systems there is no evidence for the existence of any actinide diboridedicarbide phases.

Curtis[18] studied the precipitation of graphite from the lanthanide hexaborides for reaction mixtures which had been heated to temperatures in excess of 2000°. The products from mixtures of NdB_6, PrB_6, CeB_6 and LaB_6 and carbon were the respective hexaboride and recrystallized graphite. Both YbB_6 and YB_6 formed with carbon the diboridedicarbides and the hexaborides.

D. Thesis organization

This work involves primarily a) the preparation of samarium diboridedicarbide from a number of varied starting mixtures and a wide range of reaction conditions, and b) an examination of LnB_2C_2 stability with varying metal oxidation number. The SmB_2C_2 samples were characterized by several methods and the results are presented.

i

T

L

The study included the attempted preparation of other isostructural MB_2C_2 phases in which M was La, Ce, Eu, Gd, Tm, Yb, Lu, Y, Ca, Sr, Ba and Th and mixtures of the following: Sm-Ca, Sm-Th and Ca-Th.

a

a

r

X

l

th

in

an

* C
ec

II. EXPERIMENTAL METHODS

A. Introduction

Materials which were used as reactants, crucibles and bombs are listed in Appendix I along with their sources and purity levels. Appendix II lists by record number and research notebook reference those phases identified by X-ray diffraction analysis.

B. Sample preparation

1. Starting mixtures

A variety of starting mixtures was used to prepare the diboridedicarbides. Equations [2] through [9] are intended to represent approximate starting stoichiometries and not necessarily simple reactions.

$$LnB_6(s) + 3C(s)^{*} = LnB_2C_2(s) + B_4C(s) \qquad [2]$$

$$2LnB_4(s) + 5C(s) = 2LnB_2C_2(s) + B_4C(s) \qquad [3]$$

$$Ln_2O_3(s) + B_4C(s) + 6C(s) = 2LnB_2C_2(s) + 3CO(g) \qquad [4]$$

$$Ln_2O_3(s) + 4B(s) + 7C(s) = 2LnB_2C_2(s) + 3CO(g) \qquad [5]$$

$$Ln_2O_3(s) + 2B_2O_3(s) + 13C(s) = 2LnB_2C_2(s) + 9CO(g) \qquad [6]$$

$$2Ln(s) + B_4C(s) + 3C(s) = 2LnB_2C_2(s) \qquad [7]$$

$$Ln(s) + 2B(s) + 2C(s) = 2LnB_2C_2(s) \qquad [8]$$

$$LnB_6(s) + 2Ln(s) + 6C(s) = 3LnB_2C_2(s) \qquad [9]$$

The synthetic starting mixtures were usually chosen

---

* C(s) represents the graphitic form of carbon in these equations.

to
cas

2.

met
Sam
met
bee
oxi
con
All
glo

of t
arc-
mond
mort
cess
to a
were
at 8

ough
or b
Bug
If t
Powd

to approach one of the ratios listed above. In selected cases a large excess of one of the components was used.

2. Reactant preparation

All of the reactants except samarium and europium metals, SmB_4 and SmB_6 were available in the form of powders. Samarium metal powder obtained by filing an ingot of the metal was sometimes used after iron contamination had been removed magnetically. Although Sm metal can be oxidized by air, the reaction is slow enough so that oxide contamination was minimal since exposure to air was brief. All handling of Eu metal was performed in a helium filled glove box.

Metal borides were prepared either by direct reaction of the elements or by reduction of metal oxides[19] in the arc-melter. The reacted pellets were crushed in a diamond steel mortar and then ground finely with an agate mortar and pestle. The boride samples were washed successively with 50% HCl and distilled water and allowed to air dry at room temperature. Alkaline-earth oxides were prepared by calcining the metal carbonate or hydroxide at 850° for two days.

The weighed starting compositions were mixed thoroughly either by grinding with an agate mortar and pestle or by shaking in a plastic container mounted on a Wig-L-Bug amalgamator (Crescent Dental Co., Chicago, Illinois). If the sample was to be heated by arc-melting, the mixed powder was compacted into a one-quarter inch diameter

(
S
3

m
w
t

u
e
a
c
i
c
s

th
th
Th
or
wh
sa
on

pellet using a hardened steel die under a hydraulic press (Carver Laboratory Press, Fred S. Carver, Inc., Summit, New Jersey) employing a press pressure of about 3000 psi. Solid metal chips when used were placed together with the powdered reactants in the reaction vessel.

3. Arc-melter

The majority of the samples were fused in an arc-melter equipped with both a water-cooled electrode and a water-cooled copper hearth. A detailed description of this equipment has been given by Butherus[20].

A one-quarter inch diameter tungsten electrode was used for all preparations except one in which a graphite electrode was used. Arc currents varied from 20 to 200 amperes direct current with 75 to 100 amperes being most common. If currents lower than 75 amperes were used, incomplete melting of the sample was often observed, while currents of greater than 100 amperes frequently caused sputtering.

An electric arc was struck by momentarily touching the electrode to the hearth. The arc was then played upon the sample pellet which heated rapidly and then melted. The temperature could be controlled coarsely by raising or lowering the electrode or by operating a foot treadle which controlled the welding generator output. After the sample was fused, heating was continued for approximately one minute after which the sample solidified almost immediately. It was then turned over and remelted to promote homogenity. There was some evidence of pitting of the copper hearth but copper contamination was assumed to be minimal.

The arc-melter was filled with helium which was purged of active gases by arcing a zirconium button before the melting of each pellet. A few reactions were conducted with a carbon monoxide atmosphere.

4. Tantalum bombs

An alternative to arc-melting for sample preparation was to confine the reactants in a tantalum tube which was sealed by welding prior to heating. Before its use as a bomb the tubing was outgassed by inductively heating it at temperatures up to 2100° in high vacuum for periods of up to eight hours. One end of the tube was sealed by heliarc welding, the reactants were placed in the tube which was then placed in a welding chamber. The chamber was alternately evacuated and then flushed with helium several times and finally the open end of the bomb was welded. The bomb was heated by induction. Temperatures were measured using a disappearing filament optical pyrometer (Leeds and Northrup Co., Philadelphia, Pennsylvania) by sighting onto the outer wall of the bomb. No correction was made for window or prism transmittance or for the emissivity of the tantalum surface.

5. Crucibles

In one preparation the reactants were placed in a tungsten crucible which was heated inductively. Although a product composition based upon starting stoichiometry was not obtained because of the interaction of tungsten with boron and boride samples at high temperatures[21], the diboridedicarbide was the major product. Several attempts to prepare samarium diboridedicarbide in a graphite crucible were unsuccessful - samarium dicarbide was the major product.

6. Quartz ampoules

Quartz was found unsatisfactory for SmB_2C_2 preparation because of its degradation by the boron. Attempts to use a platinum foil liner to shield the quartz were equally unsatisfactory because of formation of a platinum-samarium alloy[22].

C. Sample characterization

1. X-ray analysis

All reaction products were subjected to X-ray diffraction analysis. This technique normally detects phases present to the extent of ten per cent or more in a mixture of phases. In the majority of preparations more than one phase was present and it was not always possible to identify all the phases. Quantitative elemental analyses were not performed because of the inability to prepare a pure diboridedicarbide phase.

w
o
c
t
F
r
a
f
w
th

fo
(I
em
of
ac
si
ad
tr

Wi
to
Yor
40x
ent
(En

Debye-Scherrer powder X-ray diffraction analysis with copper K radiation ($\lambda\bar{\alpha}$ = 1.5418Å) was used for most of the samples. The mass absorption coefficient for copper K radiation reaches a maximum near samarium[23] so that long exposure times were required for the X-ray films. Film backgrounds were greatly darkened by the fluorescence radiation from samarium. This condition was partially alleviated by masking the film with a layer of aluminum foil which acted as a screen. Alternately, exposures were made with iron K radiation ($\lambda\bar{\alpha}$ = 1.9373Å) for which the mass absorption coefficient for samarium is low.

Some preparations were examined using a Guinier foward focusing[24] X-ray powder diffraction camera (Ingeniörsfirman Instrumenttjänst, Sundbyberg 1, Sweden) employing copper K$\bar{\alpha}$ radiation. Focusing and separation of the K$\bar{\alpha}$ radiation of the unfiltered primary beam are achieved by isolating the (10$\bar{1}$1) reflection from a curved single crystal quartz plate. The sample was mounted by adhering a thin layer of the powdered sample on Scotch transparent tape covering the hole in the sample disc.

Intensity data using copper K radiation were taken with a Siemens Kristalloflex IV X-ray generator, diffractometer and scaling equipment (Siemens America Inc., New York, New York). Powdered samples were mounted on 40x40x1 mm glass slides using Canada Balsam (Fisher Scientific Co., Pittsburgh, Pennsylvania). Platinum powder (Englehard Industries Inc., Newark, New Jersey) was mixed with the samples to provide an internal standard. The Siemens equipment was also used in the fluorescence mode of operation with a LiF analyzing crystal and tungsten white radiation to determine if tantalum was present as a contaminant in those samples prepared by the bomb technique.

Precise lattice parameters were obtained by a Nelson-Riley extrapolation for Debye-Scherrer data and by a ($\cos \theta \cot \phi$) extrapolation for diffractometer data[25]. A CDC 3600 computer was used for these computations.

2. Micrographic analysis

Some of the arc-melted pellets were examined micrographically with magnifications up to 800x with a Bausch and Lomb model DMZ-D3 Dyna-Zoom Metallograph (Bausch and Lomb,Inc., Rochester, New York). The samples were prepared for examination by encapsulating them using Meta-Test Cold Mount (Precision Scientific Co., Chicago, Illinois) and then polishing with silicon carbide papers of successively finer grits. Samples were observed under a variety of viewing conditions (dark field, polarized light, green field) and after having been treated with a variety of etchant solutions (HCl, HNO_3, HNO_2). Distinguishable domains were never seen even with a sample which was later shown by X-ray analysis to contain more than one phase.

III. RESULTS

A. Synthesis experiments

1. Lanthanum diboridedicarbide

Two samples which were prepared by arc-melting nearly stoichiometric mixtures of the sesquioxide, boron and graphite in accordance with equation [5] , contained LaB_2C_2 as the major product with LaB_6 and other unidentified phases as minor constituents. The calculated lattice parameters are $a_o = 3.816 \pm 0.002^*$ and $c_o = 3.975 \pm 0.003$Å.

2. Cerium diboridedicarbide

The preparation of CeB_2C_2 was conducted in a manner similar to that used for the LaB_2C_2 preparation. X-ray powder diffraction data for a typical preparation, a cerium(IV) oxide-boron-graphite reaction product, are given in Table I. The extrapolated lattice parameters are $a_o = 3.817 \pm 0.001$ and $c_o = 3.852 \pm 0.001$Å.

3. Samarium diboridedicarbide

The first two syntheses were conducted with a carbon monoxide atmosphere in the arc-melter in the belief that the reaction was represented by equation [1] . Subsequent arc-melter syntheses were conducted with a helium atmosphere. The phase which was identified later as SmB_2C_2

---

* Errors reported are standard deviations.

Table I. X-ray diffraction data for a cerium(IV) oxide-boron-graphite reaction product
Copper Kα radiation

No.	CeB_2C_2 d (Å)# calc.	CeB_2C_2 (hkl)	CeB_6 d (Å)* calc.	CeB_6 (hkl)	$\sin^2\theta_{obs.}$	d (Å)$_{obs.}$
1			4.103	100	0.0353	4.103
2	3.832	001			0.0405	3.832
3	3.781	100			0.0416	3.781
4	graphite	(002)			0.0536	3.331
5					0.0617	3.102
6			2.901	110	0.0702	2.909
7	2.712	101			0.0818	2.697
8			2.369	111	0.1051	2.378
9					0.1228	2.200
10	1.928	002			0.1605	1.924
11	1.908	200			0.1641	1.903
12			1.835	200	0.1742	1.847
13	1.720	102			0.2011	1.719
14	1.710 1.716	201 210			0.2052	1.712
15			1.625	211	0.2248	1.626
16	1.568	112			0.2427	1.567
17	1.560	211			0.2448	1.558
18			1.368	300	0.3134	1.377
19	1.356	202			0.3242	1.354
20	1.349	220			0.3255	1.351
21			1.297	310	0.3482	1.306
22	1.278	212			0.3650	1.276
23	1.273 1.270	221 300			0.3671	1.272
24			1.237	311	0.3840	1.242
25			1.237	311	0.3867	1.240
26	1.218	103			0.3998	1.219
27	1.207 1.206	301 310			0.4082	1.207
28	1.160	113			0.4417	1.160
29	1.151	311			0.4509	1.148
30					0.4705	1.123

a_o = 3.781Å, c_o = 3.832Å

* a_o = 4.103Å

was found to be a reaction product whenever graphite or a carbon containing compound was present as a reactant.

The purest samples of SmB_2C_2 were obtained when either the sesquioxide or metal was arc-melted with boron and graphite. SmB_2C_2 was a product when any of the mixtures represented by equations [4] through [9] was arc-melted. Samarium tetraboride was never prepared free of the hexaboride, so the stoichiometry given in equation [3] could not be tested. Attempts to prepare SmB_2C_2 from the hexaboride and graphite [2] were unsuccessful.

SmB_2C_2 was the major product in bomb preparations from metal, boron and graphite. Contamination by tantalum borides was often evident. Differences in product composition were not noted for preparations at temperatures from 1100° to 1640°.

X-ray diffraction data for SmB_2C_2 are presented in Table II. The extrapolated lattice parameters are $a_o = 3.796 \pm 0.001$ and $c_o = 3.696 \pm 0.001$Å. A comparison among the diffraction patterns for GdB_2C_2 and SmB_2C_2 and other diboridedicarbides is presented in Figure I.

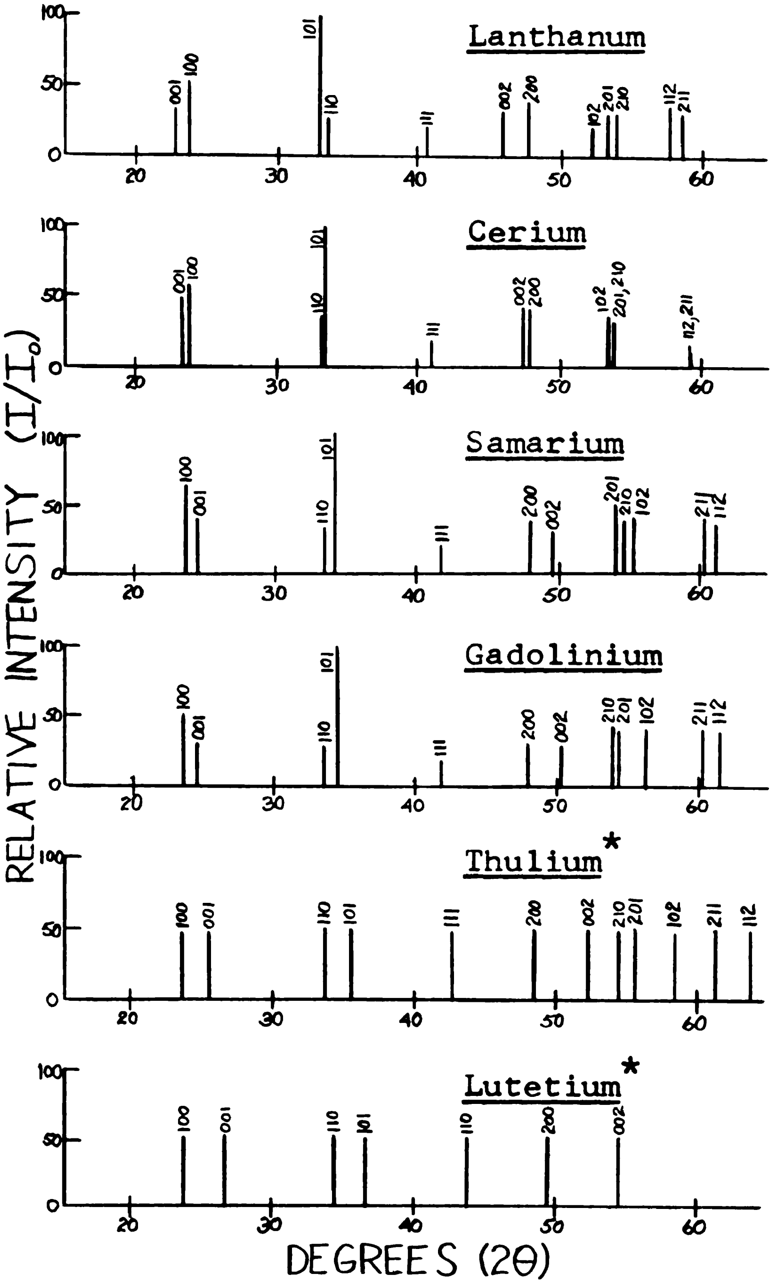
Although additional phases were frequently present in the SmB_2C_2 preparations it was not possible to index the diffraction data on cubic or tetragonal symmetries. None of these phases was identified as being similar to the four other borocarbides reported by P. K. Smith in the Gd-B-C ternary system.

Table II. X-ray diffraction data for SmB_2C_2
Copper $K\alpha$ radiation

No.	I/I_o obs.	d (Å) calc.#	d (Å) obs.	$\sin^2 \theta_{calc.}$#	(hkl)
1	64	3.796	3.761	0.04123	100
2	36	3.696	3.657	0.04351	001
3	48	3.684	3.667	0.08247	110
4	100	2.648	2.630	0.08474	101
5	25	2.172	2.160	0.12598	111
6	32	1.898	1.889	0.16494	200
7	28	1.848	1.840	0.17403	002
8	40	1.698	1.692	0.20617	210
9	36	1.688	1.683	0.20844	201
10	36	1.662	1.655	0.21526	102
11	38	1.543	1.537	0.24968	211
12	32	1.522	1.517	0.25650	112
13	16	1.342	1.339	0.32987	220
14	20	1.324	1.321	0.33896	202
15	5	1.265	1.264	0.37110	300
16	8	1.262	1.259	0.37338	221
17	25	1.250	1.248	0.38020	212
18		1.232		0.39156	003
19	16	1.200	1.196	0.41234	310
20		1.197		0.41461	301
21	5	1.172	1.170	0.43279	103
22	5	1.142	1.140	0.45585	311
23	5	1.120	1.118	0.47403	113
24	1	1.086	1.086	0.50390	222
25	1	1.053	1.050	0.53604	320
26	5	1.044	1.043	0.54513	302
27	1	1.033	1.032	0.55650	203
28	1	1.013	1.012	0.57957	321
29	5	1.007	1.006	0.58637	312
30	1	1.000	0.997	0.59770	213
31		0.949		0.65974	400
32		0.924		0.69611	004
33		0.920		0.70098	410
34		0.919		0.70325	401
35	5	0.915	0.915	0.71007	322

a_o = 3.696Å, c_o = 3.796Å

Figure I. X-ray powder diffraction data for LnB_2C_2
Copper Kᾱ radiation



* Relative intensities were not determined.

4. Europium-boron-carbon

Tantalum bomb preparations from the metal, boron and graphite yielded europium hexaboride, europium dicarbide and graphite. When Eu_2O_3-B-C mixtures were arc-melted, the products were EuB_6, graphite and an unknown phase or phases. Table III lists the Guinier X-ray powder diffraction record for the products from the arc-melter. A partial indexing of the unknown lines was achieved on tetragonal symmetry with lattice parameters of $a_o = 3.771$ and $c_o = 4.028$Å. The diffraction pattern of the unknown phase was always of poor quality so that relative intensities of the lines could not be compared with the relative intensities of the diboridedicarbide lines.

5. Thulium diboridedicarbide

The products of arc-melted mixtures of Tm_2O_3-B-C were TmB_2C_2 and a mixture of thulium borides. Table IV lists the diffraction lines for a typical arc-melted sample. The extrapolated lattice parameters for TmB_2C_2 are $a_o = 3.776 \pm 0.011$ and $c_o = 3.477 \pm 0.008$Å.

6. Other diboridedicarbides

The diboridedicarbides for gadolinium, ytterbium, lutetium and yttrium were prepared by arc-melting mixtures of the respective sesquioxides, boron and graphite. Calculated lattice parameters for all the diboridedicarbides are compared with the values previously reported in Table V. Figure II is a graphical display of the varia-

Table III. X-ray diffraction data for an Eu_2O_3-B-C reaction product
Copper $K\alpha_1$ radiation

			EuB_6		Unknown phase	
No.	d (Å) obs.	$\sin^2 \theta$ obs.	d (Å) calc.#	(hkl)	d (Å) calc.*	(hkl)
1	4.276	0.0325				
2	4.178	0.0340	4.178	100		
3	4.075	0.0358				
4	4.028	0.0369			4.028	001
5	3.939	0.0383				
6	3.771	0.0417			3.771	100
7	3.676	0.0440				
8	3.570	0.0466				
9	3.457	0.0497				
10	3.336	0.0532	graphite	(002)		
11	3.046	0.0604				
12	2.926	0.0692	2.955	110		
13	2.795	0.0760				
14	2.783	0.0767			2.753	101
15	2.664	0.0837			2.667	110
16	2.608	0.0873				
17	2.402	0.1028	2.410	111		
18	2.316	0.1108				
19	2.221	0.1216			2.223	111
20	2.073	0.1382	2.087	200		
21					2.014	002
22	1.915	0.1620				
23					1.886	200
24	1.854	0.1727	1.867	210		
25	1.789	0.1857				
26	1.761	0.1916			1.776	102
27	1.675	0.2118				

a_o = 4.178Å

* a_o = 3.771Å, c_o = 4.028Å

Table IV. X-ray diffraction data for a Tm_2O_3-B-C reaction product

No.	TmB_2C_2		TmB_4		TmB_2		
	d (Å)# calc.	(hkl)	d (Å)* calc.	(hkl)	d (Å)## calc.	(hkl)	d (Å) obs.
1							6.622
2							5.448
3							4.368⌿(111)
4			3.976	001			3.995
5	3.775	100			3.731	001	3.771⌿(200)
6			3.519	200			3.497
7							3.458
8							3.363
9							3.229
10			3.147	210			3.146
11							3.026
12							2.946
13							2.833
14							2.736
15	2.669	110					2.666
16			2.635	201			2.628
17							2.602⌿(220)
18	2.557	101					2.555
19			2.468	211			2.470
20							2.374
21					2.249	101	2.249⌿(311)
22			2.226	310			2.227
23	2.117	111					2.115
24			1.988	002			1.992
25			1.942	311			1.942
26	1.888	200			1.886	002	1.884
27			1.846	112			1.849
28							1.812
29			1.731	321			1.737
30							1.719⌿(331)
31			1.707	410			1.706
32	1.688	210	1.681	212			1.684
33	1.660	201	1.659	330			1.656
34					1.565	102	1.578
35	1.518	211					1.516
36			1.483	312			1.456
37	1.335	220					1.333
38			1.304	511	1.318	201	1.306
39			1.295	412			1.297
40	1.278	202	1.274	332			1.277
41	1.258	300					1.257
42	1.246	221	1.240	203			1.244
43							1.231
44			1.222	213	1.226	112	1.226

Table IV. Continued

No.	TmB2C2		TmB4		TmB2		d (Å) obs.
	d (Å) calc.#	(hkl)	d (Å) calc.*	(hkl)	d (Å) calc.##	(hkl)	
45	1.211	212					1.210
46	1.194	310					1.192
47	1.183	301					1.182
48			1.156	531			1.157
49	1.129	311					1.129
50							1.108
51	1.058	222					1.062
52	1.047	320					1.045
53	1.019	302					1.018
54	1.002	321					1.002
55							0.983
56							0.955
57	0.944	400					0.942
58	0.916	410					0.915
59	0.897	322					0.896
60	0.890 0.885	330 411					0.889
61							0.875
62	0.862	331					0.861
63	0.852	303					0.852
64	0.844	420					0.847
65							0.832
66	0.829	402					0.829
67	0.820	421					0.820
68	0.810	412					0.810
69	0.792	332					0.792
70							0.789

a_o = 3.775Å, c_o = 3.476Å

* a_o = 7.071Å, c_o = 3.997Å

a_o = 3.250Å, c_o = 3.731Å

† These lines can be assigned to TmB_{12} a_o = 7.476Å

tion of the diboridedicarbide lattice parameters with ionic radii. Both a_o and c_o are plotted on the same scale to emphasize the difference.

7. Other preparations

Attempts to prepare isostructural tetragonal diboridedicarbides for calcium, strontium, barium, thorium and mixtures of samarium with calcium or thorium and calcium with thorium were all unsuccessful. The method of preparation was arc-melting a mixture of the respective oxides, boron and graphite.

For the mixed metal preparations, the samarium content was varied from 90 to 10 atom per cent. There was no variation of the lattice parameters when SmB_2C_2 was observed as one of the products. In the samarium-thorium preparations containing about 50 atom per cent or more of thorium, the diffraction pattern of the products was complex. It was not possible to determine if any of the actinide borocarbides reported by Rudy[17] was present since he gave no diffraction data.

B. Diboridedicarbide characterization

1. Appearance

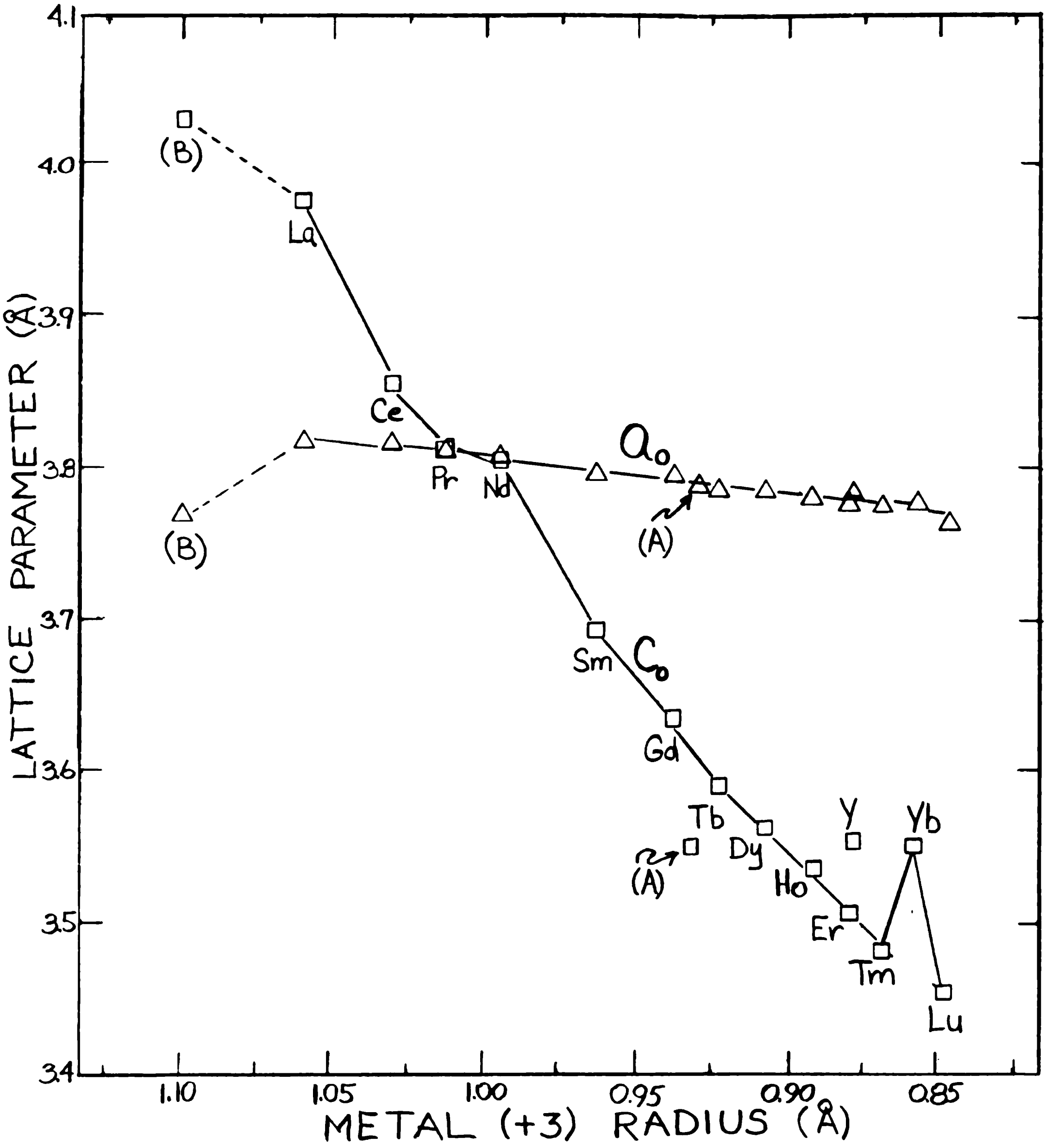
All samples containing LnB_2C_2 were hard, brittle substances colored black or dark grey. The samples had no characteristic appearance even when viewed with low power magnification.

Table V. Lattice parameters for tetragonal LnB_2C_2

Ln	This work		Other work		
	a_o (Å)	c_o (Å)	a_o (Å)	c_o (Å)	
La	3.816	3.975	3.82	3.96	(a)
Ce	3.817	3.852			
Pr			3.81	3.81	(a)
Nd			3.803	3.794	(b)
Sm	3.796	3.696			
Eu	(3.771)	(4.028)			
Gd	3.793	3.635	3.792	3.640	(b)
Tb			3.784	3.591	(b)
Dy			3.782	3.560	(b)
Ho			3.780	3.537	(b)
Er			3.778	3.508	(b)
Tm	3.776	3.477			
Yb	3.775	3.552	3.775	3.560	(b)
Lu	3.762	3.453	3.763	3.447	(c)
Y	3.788	3.551	3.78	3.55	(d)

(a) Reference 5
(b) Reference 13
(c) Reference 14
(d) Reference 7

Figure II. LnB_2C_2 lattice parameter variation



Lanthanide ionic radii: (Å)

La(+3)---1.061-(a)
Ce(+3)---1.03--(a)
Pr(+3)---1.013-(a)
Nd(+3)---0.995-(a)
Sm(+3)---0.964-(a)
Sm(+2)---1.11--(b)

Eu(+3)---0.95--(a)
Eu(+2)---1.10--(b)
Gd(+3)---0.938-(a)
Tb(+3)---0.923-(a)
Dy(+3)---0.908-(a)
Ho(+3)---0.894-(a)

Er(+3)---0.881-(a)
Tm(+3)---0.869-(a)
Yb(+3)---0.858-(a)
Yb(+2)---0.93--(b)
Lu(+3)---0.848-(a)
Y (+3)---0.88--(c)

(a) Reference 29
(b) Reference 31
(c) Reference 30

2. Hydrolysis

Most of the samples were unstable in air at room temperature. Partial decomposition took place in periods ranging from a few hours to a few days. Powdered samples vigorously reacted with 50% HCl solution evolving acetylene and frequently another gas with an obnoxious odor. No further characterization of these gases was undertaken.

P. K. Smith[13] reported that the lanthanide diboride-dicarbides were stable in air and stable to hydrochloric acid. The explanation for this apparent difference is that the observed hydrolysis is not a reaction of the diboridedicarbide but rather a reaction of a carbon rich impurity. LnB_2C_2 was observed in the X-ray diffraction patterns of samples which had been exposed to air for several months. The source of the obnoxious odor is not readily explained.

3. Vaporization

The high temperature vaporization behavior of one sample of SmB_2C_2 was observed in the Bendix time-of-flight mass spectrometer model 12-107. The sample was confined in a tungsten crucible which was heated by electron bombardment. As the temperature was increased above 1500°, Sm(g) was identified in the mass spectrum. This was the only species observed up to 1700° at which temperature the experiment was terminated.

The X-ray powder diffraction pattern of the residue contained only three diffuse lines, one of which had a _d_ value of approximately 13.1Å.

4. Annealing

Samples of SmB_2C_2 were annealed by heating in a graphite container. The diffraction lines were sharper for those samples which had been heated for about an hour at 1000° under an atmosphere of helium. No change in lattice parameters was observed for annealed _vs_. non-annealed samples.

The density of SmB_2C_2 based upon one formula unit per unit cell and lattice parameters of $a_o = 3.796$ and $c_o = 3.696$Å is 6.11 g cm^{-3}. This value is in agreement with the pycnometric density of GdB_2C_2 in nitrobenzene of 6.1 g cm^{-3} as determined by Smith[13].

IV. DISCUSSION

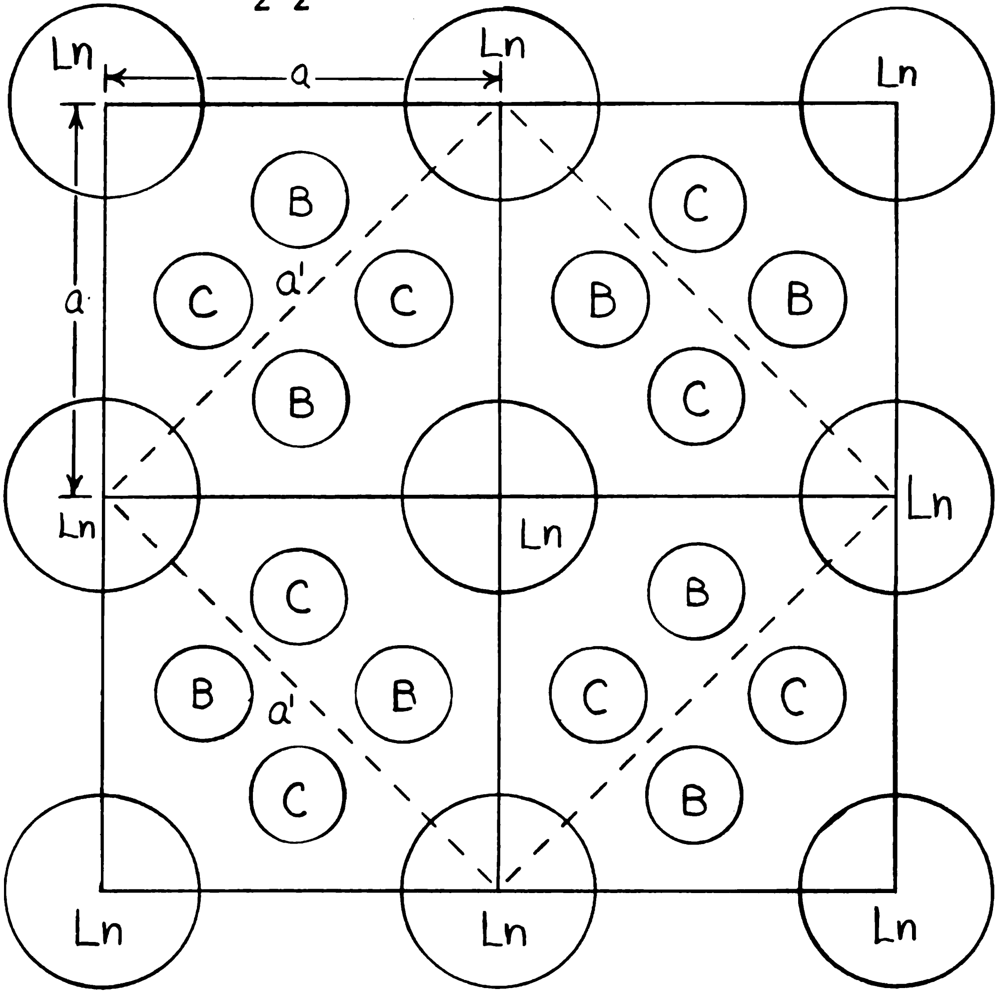
A. Lattice parameter variations

1. Correct unit cell

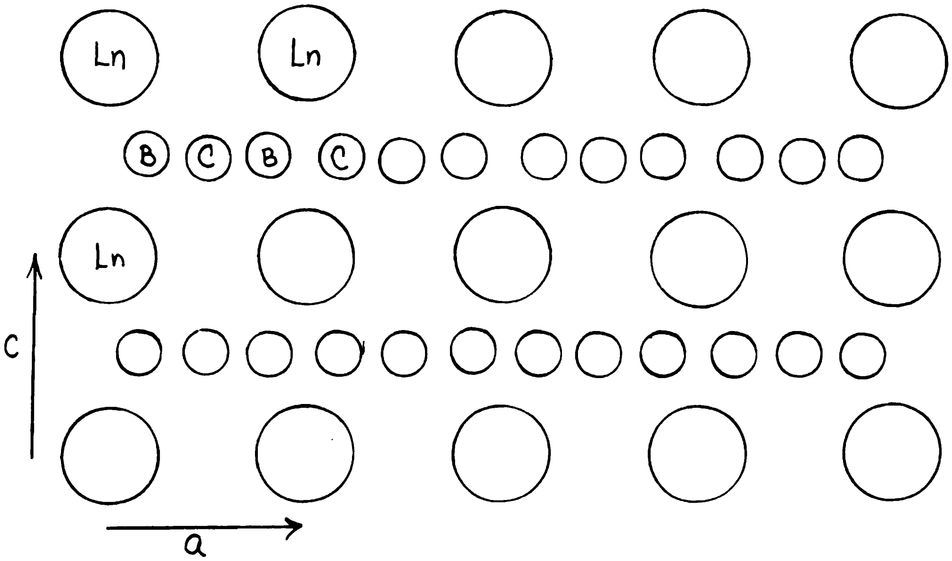
The structure of the lanthanide diboridedicarbides as determined by P. K. Smith[13,15] consists of planar light atom sheets at $z = \frac{1}{2}$, with sheets of metal atoms sandwiched between them at $z = 0$. The non-metal sheets contain fused, regular, equilateral eight- and four-membered light atom rings with each atom bonded to three others in the sheet. The metal atoms are situated above and below the centers of the eight-membered rings. The length of the a-axis of the unit cell is thus dependent upon the dimension of the boron-carbon rings. The size of the metal atoms determines the interlayer spacing which is equal to the length of the c-axis.

Since the X-ray data did not permit a distinction between the boron and carbon atoms in the structure, the resulting space group is $\underline{P}4/\underline{mmm}$ (No. 123)[26] with one LnB_2C_2 unit per cell. P. K. Smith assumed that the most probable light atom ordering scheme consisted of alternating boron and carbon atoms distributed according to space group $\underline{P}4/\underline{mbm}$ (No. 127) and a cell twice as large, $a' = 1.414a$. This structure maintains the four-fold axis required for tetragonal symmetry. The two possible unit cells are indicated in Figure III.

Figure III. LnB_2C_2 structure



a) Projection of four unit cells along the z-axis. The metal atoms are at z = 0 and the light atoms are at z = ½. The dashed lines show the outline of the larger unit cell.



b) Projection showing alternating metal and light atom layers. Some light atoms are omitted for clarity.

A neutron diffraction investigation would allow the boron positions to be distinguished and the ordering scheme established firmly.

2. Chemical bonding

The bonding scheme invoked by P. K. Smith[13] requires the lanthanides to be trivalent. If both lanthanide atoms in the larger unit cell each contribute three valence electrons to each eight-membered ring of light atoms, a total of 34 electrons are available for light atom bonding. This scheme permits each atom in the ring to satisfy the octet rule and the overall ring to have aromatic resonance stabilization ($4n + 2$ electrons where n is an integer).

The nearly linear relationship between the ionic radius and the interlayer spacing-c is shown in Figure II. Ytterbium shows the greatest deviation from this relationship and perhaps is more properly situated at point A (Figure II) which represents the Yb^{+2} radius. An ytterbium valence between two and three provides the best fit.

The exact valence of the metal is questionable for several lanthanide compounds. Westrum[27] has studied the metal valence in the lanthanide hexaborides. Low temperature heat capacity measurements indicate a Schottkey anomaly that cannot be explained on the basis of excitation of the metal in the +3 state. Investigations of the fine structure of the main L absorption edges of the hexaborides and oxides show a shift indicative of the divalent state for Sm, Eu and Yb. Magnetic susceptibility measurements for CeB_6 are consistent with the behavior expected for Ce^{+2}. For most of the metals the proportion of Ln^{+2} increases as the temperature is decreased. In view of this information, it is necessary to consider the possibility that the metals are not +3 in the diboridedicarbides.

If the two metal atoms in the larger unit cell of LnB_2C_2 are divalent, the total number of electrons available for light atom bonding would be 32 (two from each of two metals, three from each of four borons and four from each of four carbons). On this basis, 24 electrons would participate in sigma bonding in the eight-membered ring and only eight in pi bonding. Eight electrons are not sufficient to provide aromatic stabilization for the ring. However, if the rings are not aromatic, their planarity is not easily explained.

An alternative to the planar structure would be a puckered light atom ring. A regular octagon has interior angles of 135^o. This bond angle would produce large angular strain in the light atom structure for either sp^2 or sp^3 hybridization. The carbon analog of the eight-membered B-C rings with alternating single and double bonds is cyclooctatetraene which has been shown to be in a "tub" conformation[28]. Resonance energy gained in the planar structure is not sufficient to overcome the unfavorable angular strain. The energy of interconversion between conformers is estimated to be 10 kcal mole^{-1} at room temperature. The aromatic anion of cyclooctatetraene $(C_8H_8)^{-2}$ has 10 pi electrons and appears to exist in a planar configuration.

Another factor which casts doubt on P. K. Smith's structure is the large metal-carbon distance. In HoB_2C_2 the Ho-C distance is 2.70Å which is about 0.2Å larger than the Ho-C distance in Ho_3C, Ho_2C_3 or HoC_2. The metal-boron and boron-carbon bond lengths in HoB_2C_2 are similar to those observed in other compounds.

For a puckered ring structure the metal atoms need not be centered between the light atom layers. This situation would permit Ln-C and Ln-B distances to be in better agreement with the bond lengths observed in related compounds. There are many possible orientations of the light atoms (e.g. AAAA, ABAB, etc.) with respect to superposition along the c-axis. Until the light atom positions can be determined better one cannot distinguish between the orientations.

If the rings are planar, and thereby most probably aromatic, the substitution of two carbon atoms for two boron atoms per larger unit cell would permit a +2 metal valence. For those compounds with +3 metal ions, the samples would be expected to show metallic conduction with about one conduction electron per metal atom. The formula for this system is then $Ln_2B_xC_{8-x}$. It should be

noted that P. K. Smith's elemental analysis for GdB_2C_2 was $Gd_{1.00\pm0.20}B_{2.03\pm0.01}C_{2.66}$. The above discussion indicates there may be a composition range for various boron-carbon ratios for which the structure is stable. The loss of the four-fold symmetry by the substitution of a boron for a carbon must be so small that it would be unobservable by X-ray diffraction.

B. The problem of europium diboridedicarbide

The preparation of borides (other than EuB_6) and carbides of europium has continued to be a problem. Similarly, it appears that the conditions necessary to prepare EuB_2C_2 are elusive.

The agreement between the ionic sizes of the heavier lanthanides and the length of the c-axis of LnB_2C_2 is excellent with the exception of ytterbium as noted. For the lighter lanthanides, the c parameter exceeds the ionic size and the rate of increase is greater with increasing size.

The tetragonal phase observed in the europium system (Table III) may be the analogous diboridedicarbide but the X-ray data are not conclusive. Point B (Figure II) correlates the observed parameters with the Eu^{+2} radius. It is possible that the Eu^{+2} ion is at the upper size limit for the diboridedicarbide structure. It has already been shown that there is a small size limit since ScB_2C_2 is not a member of the isostructural series.

C. Suggestions for future research

Perhaps more than anything else, conductivity measurements would establish the valency of the metals. Magnetic susceptibility measurements would be difficult for the samarium and europium compounds since the excited states are so low-lying that they are populated at room temperature.

If the ytterbium anomaly does indicate that less than three electrons per metal are necessary to stabilize the structure, the failure to observe the analogous alkaline-earth diboridedicarbides may be due to a problem of structure. The non-existence of the calcium compound may be explained by the lack of d and f type orbitals and therefore may not possess the proper electron radial distribution to bond to the eight-membered rings. The need for f type orbitals may be discounted by the existence of the yttrium compound. The failure to observe the diboridedicarbide for strontium and barium may indicate that more than two electrons per metal are necessary. The large size of strontium and barium may also be a restricting factor.

It should be possible to prepare a diboridedicarbide from an alkaline-earth-thorium mixture. By varying the ratio of the metals, the number of electrons necessary to stabilize the structure may be determined. Further, diboridedicarbides may exist for some of the metals of group VIII.

Definite composition limits as well as possible solid solution ranges need to be established for the diboride-dicarbide. A preparative technique other than arc-melting will have to be developed; the arc-melter cannot possibly produce equilibrium conditions.

BIBLIOGRAPHY

1. A. D. Butherus, Michigan State University, personal communication, 1966.
2. P. K. Smith and P. W. Gilles, J. Inorg. Nucl. Chem., 29, 375 (1967).
3. P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals," The Macmillan Co., New York, N. Y., 1953.
4. L. Brewer and H. Haraldsen, J. Electrochem. Soc., 102, 399 (1955).
5. B. Post, D. Moskowitz and F. W. Glaser, J. Am. Chem. Soc., 78, 1800 (1956).
6. R. W. Johnson and A. H. Daane, J. Phys. Chem., 65, 909 (1961).
7. I. Binder, Powder Met. Bull., 7, 74 (1956).
8. I. Binder, J. Am. Ceram. Soc., 43, 287 (1960).
9. H. A. Eick in "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, Part 5, pp. 297-305.
10. L. Ya. Markovskii, N. V. Vekshina and G. F. Pron', Zh. Prikl. Khim., 35, 2090 (1962); J. Appl. Chem. USSR, 35, 2004 (1962).
11. L. Ya. Markovskii, N. V. Vekshina and G. F. Pron', Zh. Prikl. Khim., 38, 245 (1965); J. Appl. Chem. USSR, 38, 248 (1965).
12. E. W. Hoyt and J. Chorne', "Preparation of Self Bonded Borides," GEAP-3332, Vallecitos Atomic Laboratory, General Electric Co., Pleasanton, California, (1960).
13. P. K. Smith, Ph. D. Thesis, University of Kansas, Lawrence, Kansas, 1964.
14. P. C. Nordine, G. S. Smith and Q. Johnson, UCRL-12205, Lawrence Radiation Laboratory, Livermore, California (1964).
15. P. K. Smith, S. Westman and P. W. Gilles, "Crystal Structure of Rare Earth Diboride Dicarbides," personal communication, 1967.

16. G. S. Smith, Q. Johnson and P. C. Nordine, Acta. Cryst., 19, 668 (1965).

17. E. Rudy in "Thermodynamics of Nuclear Materials, Proceedings," May 1962, International Atomic Energy Agency, Vienna, 1962, Ch. 4, pp. 243-269.

18. B. J. Curtis, Carbon (Oxford), 4, 483 (1966).

19. N. E. Topp, "Chemistry of the Rare-Earth Elements," Elsevier Publishing Co., New York, N. Y., 1961.

20. A. D. Butherus, Ph. D. Thesis, Michigan State University, East Lansing, Michigan, 1967.

21. G. L. Galloway, Ph. D. Thesis, Michigan State University, East Lansing, Michigan, 1967.

22. K. A. Gschneider, Jr., "Rare Earth Alloys," D. Van Nostrand Co., Princeton, N. J. 1961.

23. H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954.

24. P. M. de Wolff, Acta. Cryst., 1, 207 (1948).

25. L. V. Azaroff and M. J. Buerger, "The Powder Method," McGraw Hill Book Co., New York, N. Y., 1958.

26. "International Tables for X-ray Crystallography," International Union of Crystallography, Kynoch Press, Birmingham, England, 1952.

27. E. F. Westrum, Jr. and W. G. Lyon, "Thermodynamics of Semi-metallic Compounds," presented at the Symposium on Thermodynamics of Nuclear Materials with Emphasis on Solution Systems, Vienna, 1967.

28. R. A. Raphael in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, ed., Interscience Inc., New York, N. Y., 1959, Ch. 8, pp. 465-476.

29. D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc., 76, 5237 (1954).

30. W. H. Zachariasen in "The Actinide Elements," G.T. Seaborg and J. J. Katz, eds., McGraw Hill Book Co., New York, N. Y. 1954.

31. F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry," 2nd ed., Interscience Inc., New York, N. Y., 1966.

APPENDIX I

Sources and purities of materials employed

Source	Material	Purity
Michigan Chemical Corp. St. Louis, Michigan	Eu	99 %
	Sm_2O_3	99.9
	Gd_2O_3	99.9
	Tm_2O_3	99.9
	Yb_2O_3	99.9
	Lu_2O_3	99
	Y_2O_3	99.9
Lunex Co. Davenport, Iowa	Sm	99.9+
American Potash Corp. West Chicago, Illinois	CeO_2	unknown
	Eu_2O_3	unknown
Matheson Coleman & Bell East Rutherford, N. J.	$CaCO_3$	unknown
	B_2O_3	99
J. T. Baker Chemical Co. Phillipsburg, N. J.	$Sr(OH)_2$	99.49
	$BaCO_3$	99.2
Research Chemicals Phoenix 19, Arizona	La_2O_3	99.9
Norton Chemical Worcester, Mass 01606	B_4C	unknown
	ThO_2	unknown
Fisher Scientific Co. Fairlawn, N. J.	Graphite	Acheson grade #38
Fairmount Chemical Co. Newark 5, N. J.	B	99
United Carbon Products Bay City, Michigan	Graphite rod	Spectroscopic
Fansteel Metallurgical North Chicago, Illinois	Ta tube	unknown

APPENDIX II

Index to X-ray records

Debye-Scherrer

Film number	Notebook reference	Phases identified
A 1940	NAF 203-1	Sm_2O_3
A 1941	NAF 202-2A	SmB_6
A 1943	reactant	B_4C
A 1944	NAF 203-3A	SmB_6
A 1945	NAF 203-4A	SmB_6
A 1946	NAF 204-2A	SmB_6 + ?
A 1946R	NAF 204-2A	SmB_6 + ?
A 1947	NAF 204-1A	?
A 1950	NAF 205-1A	SmB_2C_2, SmB_6
A 1951	NAF 205-6A	SmB_6
A 1952	NAF 205-3A	SmB_6
A 1953	NAF 205-4A	?
A 1965	NAF 207-2A	SmB_2C_2
A 1967	NAF 206-1AB	SmB_2C_2
A 1970	NAF 207-1A	SmB_2C_2,C,?
A 1971	NAF 206-1ABC	SmB_2C_2
A 1972	NAF 206-1D	SmB_2C_2
A 1973	NAF 206-1E	?
A 1973R	NAF 206-1E	?
A 1974	NAF 205-6B	SmB_6
A 1975	camera background	
A 1977	camera background	
A 1978	reactant	Gd_2O_3
A 1983	reactant	B
A 1985	NAF 211-1A	GdB_2C_2, ?
A 1985R	NAF 211-1A	GdB_2C_2,?
A 1986	reactant	Gd_2O_3
A 1991	NAF 213-7	?
A 2010	NAF 213-1A	SmB_2C_2

APPENDIX II - Continued

Film number	Notebook reference	Phases identified
A 2011	NAF 213-6A	SmB_2C_2
A 2072	NAF 217-6	SmC_2, C
A 2086	NAF 222-1	SmB_6, SmB_4
A 2090	NAF 224-1	BaB_6, C
A 2091	camera background	
A 2094	NAF 224-2	SrB_6, C
A 2095	reactants	B, C
A 2096	NAF 224-4	SrB_6
A 2097	NAF 224-4	SrB_6
A 2103	NAF 226-1A	?
A 2138	NAF 227-1	EuC_2, C,+?
A 2139	NAF 227-3	GdB_2C_2,+?
A 2140	NAF 227-4	SmB_2C_2 + ?
A 2142	NAF 228-2	EuB_6, C, +?
A 2143	NAF 228-6	EuB_6, + ?
A 2153	NAF 228-3	?
A 2154	NAF 228-4	EuB_6
A 2157	NAF 228-5	EuB_6, +?
A 2158	NAF 228-5A	?
A 2159	NAF 228-1	?
A 2160	NAF 228-5	EuB_6, +?
A 2167	NAF 231-1	EuB_6, TaB_x
A 2168	NAF 231-1A	EuB_6, TaB_x
A 2169	NAF 231-1	EuB_6, TaB_x
A 2171	NAF 231-2	EuO•OH
A 2174	NAF 236-1	EuO•OH
A 2186	NAF 237-1	EuB_6, +?
A 2186R	NAF 237-1	EuB_6, +?
A 2190	camera background	
A 2191	NAF 239-1	?
A 2192	NAF 240-1	TmB_2C_2, TmB_2, TmB_4, TmB_{12}
A 2195	NAF 242-1	SmB_2C_2
A 2198	NAF 243-1	SmB_2C_2, +?

APPENDIX II - Continued

Film number	Notebook reference	Phases identified
A 2199	NAF 243-1A	SmB_2C_2, +?
A 2202	NAF 243-2	SmB_2C_2
A 2203	NAF 243-4	?
A 2205	NAF 244-1	SmB_6
A 2207	NAF 244-2	CaB_6
A 2208	NAF 244-3	blank
A 2216	NAF 247-1	YB_2C_2, +?
A 2217	NAF 247-4	CeB_2C_2, CeB_6, C
A 2218	NAF 247-5	LuB_2C_2, +?
A 2219	NAF 244-5	CaO,+?
A 2220	NAF 248-1	LaB_2C_2, +?
A 2221	NAF 247-3	YbB_2C_2, +?
A 2222	NAF 248-2	LuB_2C_2, +?
A 2223	NAF 248-3	CeB_2C_2, +?
A 2224	NAF 249-1	SmB_2C_2
A 2225	NAF 249-3	?
A 2226	NAF 248-3	CeB_2C_2, +?
A 2227	NAF 249-1	?
A 2231	NAF 250-1	EuC_2,+?
A 2233	NAF 250-1	EuC_2,+?
A 2234	NAF 250-2	EuC_2?
A 2237	reactant	W
A 2249	reactant	W
A 2250	NAF 250-2	EuC_2, +?
A 2260	NAF 247-3	YbB_2C_2, +?
<u>Guinier</u>		
G 0080	NAF 250-2	EuC_2, +?
G 0109	NAF 228-6	EuB_6, +?
G 0100	NAF 228-6	EuB_6, +?
G 0126	NAF 248-1	LaB_2C_2, +?
G 0134	NAF 247-1	YB_2C_2, +?

APPENDIX II - Continued

Diffractometer

Record number	Notebook reference	Phases identified
D 0001	NAF 217-2	SmB_6
D 0002	standard	Pt
D 0003	NAF 216-4	SmC_2, +?
D 0004	NAF 217-3	SmB_2C_2, SmB_6
D 0005	NAF 217-6	SmC_2, C
D 0006	NAF 216-3	SmB_2C_2
D 0007	NAF 217-4	SmB_2C_2, SmB_6
D 0008	NAF 224-4	SrB_6, C
D 0009	reactant	Sm_2O_3
D 0010	NAF 217-5	SmB_6, SmB_2C_2
D 0011	NAF 216-2	SmB_2C_2, +?
D 0012	standard	Au
D 0013	NAF 248-1	LaB_2C_2, +?
D 0014	NAF 217-1	SmB_2C_2
D 0015	NAF 216-1	SmB_6
D 0016	NAF 248-3	CeB_2C_2, CeB_6, +?
D 0017	NAF 227-4	SmB_2C_2, +?