

# A New Boron-Rich Compound in the Y–B–Si Ternary System

F. X. Zhang, A. Sato, and T. Tanaka<sup>1</sup>*National Institute for Materials Science, Advanced Materials Laboratory, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

Received September 28, 2001; in revised form December 28, 2001; accepted January 11, 2001

A new rare earth boron-rich compound was found in the Y–B–Si ternary system. The powders were synthesized by solid state reaction method and single crystals were grown by the high temperature solution method with silicon flux. The structure was solved from single crystal x-ray diffraction data with space group  $R\bar{3}m$  (No.166) and lattice constants of  $a=b=10.0841$  Å and  $c=16.4714$  Å. Thirty-six parameters refined with 1484 unique reflections gave a residual  $R_F=0.0296$ . The calculated chemical composition of the new compound is  $YB_{17.6}Si_{4.6}$ .

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**Key Words:** Y–B–Si ternary system; rare earth boron-rich compound; single crystal; XRD, structure.

## 1. INTRODUCTION

Rare earth borides have been the subject of continuous scientific interest with regard to a variety of structures and chemical and physical properties (1–3). As to boron-rich systems, their unique bonding enables them to form compounds with very complicated crystal structures and some fascinating properties (4). Carbon is very active in phase formation in rare earth boron carbon systems and phase relations in the ternary systems have been illustrated in Ref. 5. Many new borocarbides, however, have been found recently in the Sc–B–C systems containing the smallest rare earth element (6, 7). As to the Y–B–C system, only a new series of homologous phases (3, 8) and two kinds of superstructures (9) have been found in the boron-rich regime. The boron atoms in all these boron-rich compounds form stable clusters and interconnected clusters, which build up a rigid framework of the crystal structure. However, most of these boron-rich compounds decompose before melting and large single crystals cannot be grown by the melt growth method. Previous experiments suggested that addition of silicon is a powerful method in the crystal growth of these compounds. For instance, large single crystals of  $YB_{44}Si_{1.0}$  (10), which is

isostructural with  $YB_{50}$  (11), were successfully grown by the melt method. In this paper, we describe the synthesis, crystal growth and structural analyses of a new boron-rich Y–B–Si compound, in which the boron icosahedra stack in a different way.

## 2. EXPERIMENTAL

Powder samples were synthesized by the solid state reaction method from starting materials of  $YB_4$  (99%, Japan New Metals Co., Ltd),  $SiB_6$  (98%, CERAC, USA), and Si (99.96%, CERAC, USA). Starting materials with various compositions were first well mixed and pressed into pellets with a hydrostatic pressure of about 250 MPa, then reacted in a BN crucible. The reaction process was performed in a RF furnace and soaked at about 1600°C for 10 to 15 h with a graphite susceptor and a vacuum of  $10^{-4}$  Pa. It was not easy to obtain pure single phase just by adjusting the composition of the starting materials, because some other phases such as  $YB_4$ ,  $YB_6$ , and the boron-rich compound  $YB_{44}Si_{1.0}$  always appeared during reaction. In fact, the last one, which is isostructural with  $YB_{50}$ , is built up of boron clusters and very stable once it is formed. The starting composition of our samples was  $YB_xSi_y$  ( $10 \leq x \leq 20$ ,  $3 \leq y \leq 10$ ), and such a composition range could suppress the formation of  $YB_{44}Si_{1.0}$ . After reaction, the  $YB_4$  and  $YB_6$  were easily removed by nitric acid. In addition, unreacted Si could be removed with a mixture of HF and  $HNO_3$ , if this impurity existed in the final product.

The phase purity of the processed powders was monitored with a powder x-ray diffractometer (Rigaku-2000 and Philips PW1710). The chemical composition of the final pure single phase was determined by inductively coupled plasma atomic emission spectroscopy after the sample was dissolved into a concentrated  $HNO_3$  + concentrated HCl (1:1) solution by keeping it in an air-tight vessel at 110°C for about 12 h.

Single crystals were grown by the high-temperature solution method with Si flux and a starting composition Y:B:Si of about 1:20:100. The reaction was performed at 1600°C for 8 to 10 h in a flowing argon atmosphere. The

<sup>1</sup>To whom correspondence be addressed. E-mail: TANAKA.Takaho@nims.go.jp.

cooling rate was about 30°C/h until the sample reached the temperature of 1300°C. Then the power was switched off and the sample was allowed to cool freely down to room temperature. After Si was removed by a mixture of nitric acid and hydrofluoric acid, single crystals with various dimensions were taken out. The composition of single crystals with good shapes was examined with EPMA analysis. The quality of the single crystals was first checked with a Weissenberg camera and reflections data were collected with an Enraf-Nonius CAD-4 four-circle diffractometer using MoK $\alpha$  radiation monochromated by a graphite monochromator. The intensities were corrected for Lorentz and polarization effects. The absorption effects were corrected by a semiempirical method.

The structure was solved by the direct method with the program SIR97(12) and refined with a full-matrix least-squares method SHELX97(13).

### 3. RESULTS AND DISCUSSION

The XRD pattern of the purified powder sample is shown in Fig.1a. Indexing results reveal that it is a new pure single phase. All the reflections can be well indexed with a hexagonal unit cell of  $a=b=10.0794(5)\text{\AA}$  and  $c=16.4294(4)\text{\AA}$  by the program TREOR90(14) (the first 20 reflections gave fitting results of  $M20=98$  and  $F20=141$ ). The observed  $d$  values and intensities, as well as the calculated  $d$  values for various indices, are listed in Table 1. The chemical analysis showed a composition of  $\text{YB}_{18.5}\text{Si}_{3.8}$  for the powders.

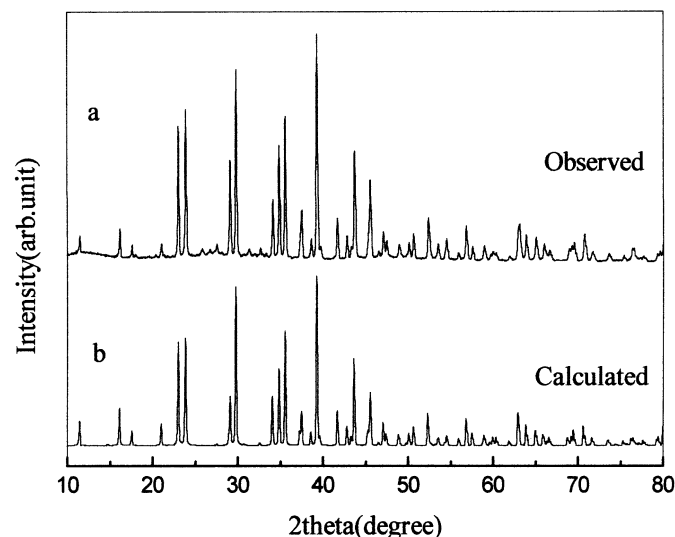


FIG. 1. Powder XRD patterns for the new compound in Y-B-Si system. (a) Observed XRD patterns for the synthesized powder sample  $\text{YB}_{18.5}\text{Si}_{3.8}$ . (b) calculated powder XRD pattern according to the structure model.

TABLE 1  
Results of Indexing  $\text{YB}_{17.6}\text{Si}_{4.6}$  with a Trigonal Unit Cell ( $a=b=10.0798\text{\AA}$ ,  $c=16.4298\text{\AA}$ ), and I Corresponds to Observed Intensities

<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{obs.}}$	$d_{\text{cal.}}$	$I/I_0$	<i>h</i>	<i>k</i>	<i>l</i>	$d_{\text{obs.}}$	$d_{\text{cal.}}$	$I/I_0$
1	0	1	7.7084	7.7085	13	2	1	8	1.7434	1.7435	21
0	0	3	5.4758	5.4763	16	3	2	5	1.7096	1.7100	9
1	1	0	5.0400	5.0396	9	3	3	0	1.6800	1.6799	11
2	0	1	4.2184	4.2181	10	4	2	1	1.6413	1.6414	6
2	0	2	3.8542	3.8542	61	4	2	2	1.6174	1.6173	17
1	0	4	3.7164	3.7165	67	3	2	6		1.6164	
1	1	3		3.7084		4	0	7	1.5984	1.5982	8
2	1	1	3.2348	3.2347	9	2	1	9		1.5973	
2	1	2	3.0620	3.0615	46	4	1	6	1.5643	1.5637	9
2	0	4	2.9917	2.9911	85	3	0	9	1.5462	1.5463	5
3	0	2		2.7427		5	1	2	1.5396	1.5399	6
0	0	6	2.7379	2.7382	8	4	2	4	1.5309	1.5308	6
2	0	5	2.6256	2.6250	29	3	3	5		1.4957	
2	1	4		2.5721		4	0	8	1.4956	1.4956	4
3	0	3	2.5701	2.5695	52	1	1	10	1.4705	1.4707	18
2	2	0	2.5198	2.5198	65	6	0	0	1.4548	1.4548	13
2	2	2		2.4090		6	0	2		1.4325	
1	1	6	2.4062	2.4060	13	1	1	11		1.4320	
3	1	1	2.3951	2.3951	24	3	3	6	1.4317	1.4319	12
2	1	5	2.3282	2.3281	11	4	3	2		1.4136	
2	2	3	2.2895	2.2892	100	2	0	11	1.4132	1.4131	10
1	0	7	2.2663	2.2665	8	4	2	6		1.4130	
4	0	1	2.1632	2.1632	21	5	0	7	1.4011	1.4008	7
4	0	2	2.1092	2.1091	13	4	0	9		1.4002	
2	1	6		2.1071		2	1	11		1.3606	
3	1	4	2.0851	2.0856	8	5	1	6	1.3603	1.3605	7
2	0	7	2.0670	2.0671	50	3	1	10		1.3594	
3	2	1	1.9877	1.9878	38	4	3	4		1.3547	
3	1	5	1.9490	1.9491	6	5	2	3	1.3544	1.3543	9
4	0	4	1.9271	1.9271	15	4	2	7	1.3500	1.3496	10
2	1	7	1.9126	1.9125	11	6	0	5		1.3303	
2	0	8	1.8582	1.8582	9	5	0	8	1.300	1.3301	14
4	0	5	1.8186	1.8179	10	4	3	5	1.3149	1.3051	6
3	2	4	1.7998	1.8000	14	6	2	8	1.2853	1.2861	5
4	1	3		1.7991		6	0	6		1.2848	

The size of single crystals grown from the Si flux ranges from 0.05 to 5 mm and the composition determined by EPMA analysis is  $\text{YB}_{21.2}\text{Si}_{4.8}$ . Figure 2 shows the SEM picture of such a crystal. A crystal with good quality, which was checked by a Weissenberg camera, was used for reflection data collection. The extinction rule determined by the four circle diffractometer suggested that the crystal belonged to rhombohedral system with a possible space group of  $R\bar{3}m$  (No.166),  $R3m$  (No.160),  $R32$  (No.155),  $R\bar{3}$  (No.148), or  $R3$  (No.146). A reasonable structure model was finally built on the highest symmetry space group of  $R\bar{3}m$ .

The crystal data measurement and refinement results are listed in Table 2. The direct method gave the positions of one Y atom, two silicon atoms, four boron atoms and two additional positions. The two unknown positions are very close (0.4374 $\text{\AA}$ ) and, in fact, they are only one crystal site

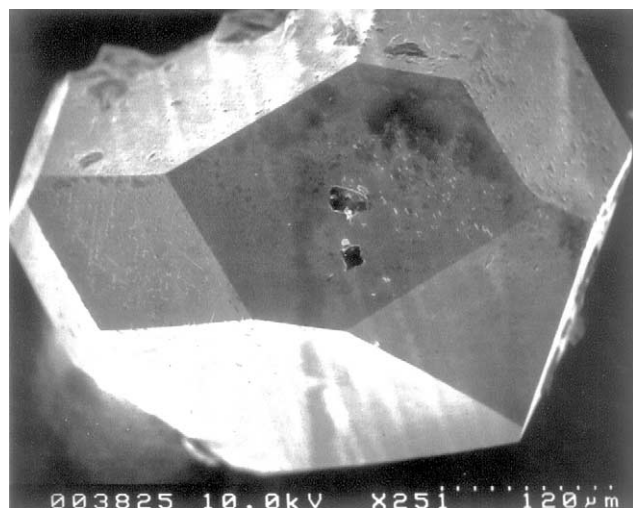


FIG. 2. Sem picture of a single crystal of  $\text{YB}_{17.6}\text{Si}_{4.6}$  grown from silicon flux.

being split into two along the  $c$  axis. Final least-square refinement revealed that they were partially occupied (0.50 and 0.16) by silicon atoms. The refined atomic coordinates and their occupancies are listed in Table 3 together with the isotropic displacement parameters.

The four boron atoms form an icosahedron and their occupancies are considered to be full. The bridge site of Si1 and Si2 are also fully occupied. Just as in other rare earth boron-rich compounds (3, 15), the occupancy of the Y in the crystal is not full (only 0.68). Table 4 gives the anisotropic displacement parameters for Y atom and the two fully occupied silicon atoms. Refinement of 36 parameters with 1484 unique reflections gave the  $R_F$  value of 0.0296 and goodness of 1.118. The simulated powder x-ray diffraction pattern are shown in Fig. 1b together with the observed pattern and they fit very well.

The boron icosahedra in the new structure is only slightly distorted. The B–B bond distances in the icosahedron vary from 1.7834 Å to 1.8195 Å (average: 1.8053 Å)

TABLE 2  
Crystal Data and Structure Refinement for  $\text{YB}_{17.6}\text{Si}_{4.6}$

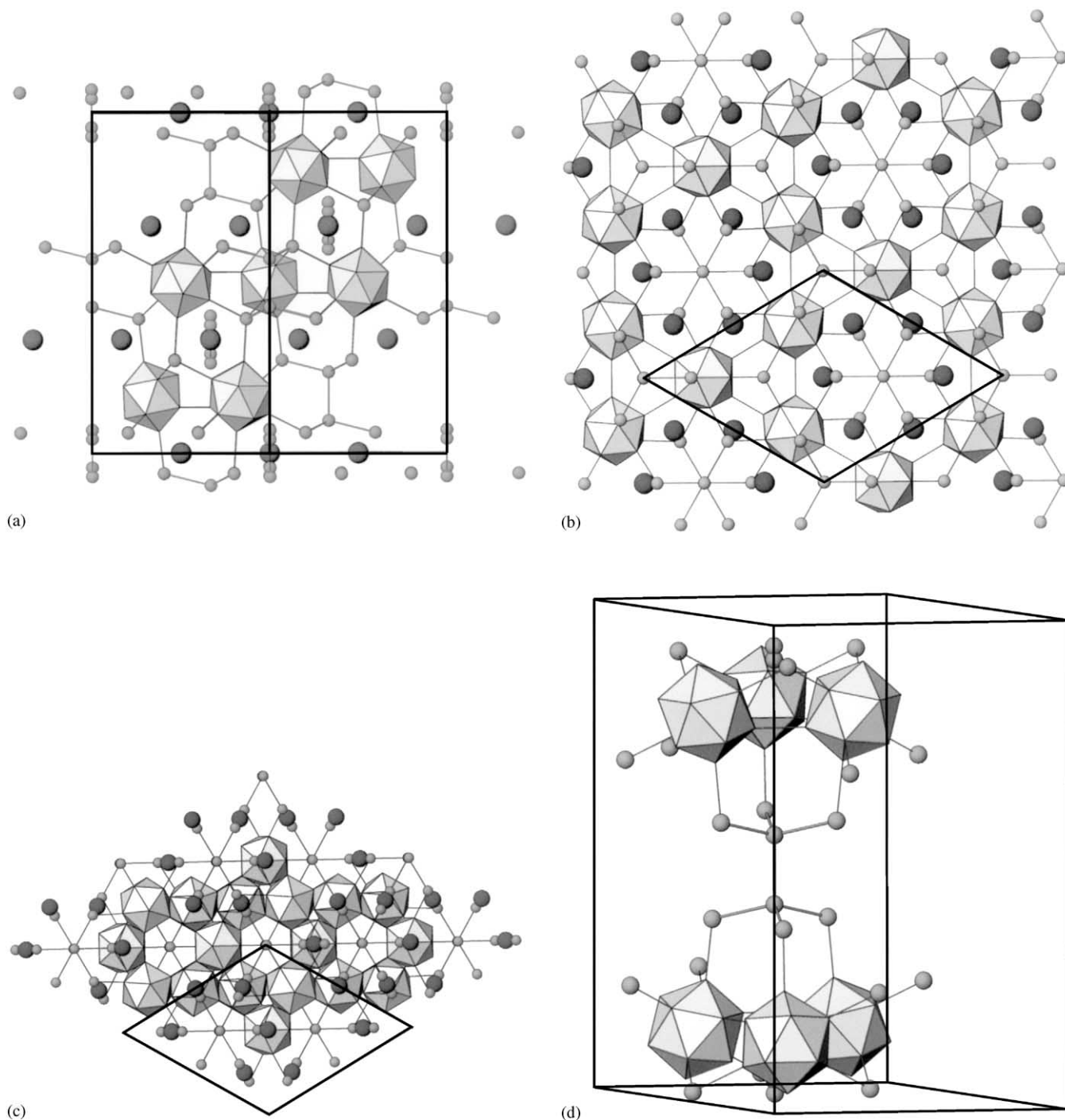
Identification code	YBSi
Empirical formula	$\text{Y}_{0.51}\text{B}_9\text{Si}_{2.34}$
Formula weight	208.37
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system, space group	Rhom., $R\bar{3}m$ (No.166)
Unit cell dimensions	$a = 10.0841(4)$ Å $\alpha = 90^\circ$ $b = 10.0841(4)$ Å $\beta = 90^\circ$ $c = 16.4714(5)$ Å $\gamma = 120^\circ$
Volume	$1450.56(9)$ Å <sup>3</sup>
Z, Calculated density	12, 2.862 Mg/m <sup>3</sup>
Absorption coefficient	6.692 mm <sup>-1</sup>
$F(000)$	1172
Crystal size	0.4 × 0.4 × 0.5 mm
Theta range for data collection	2.64° to 44.93°
Limiting indices	$0 \leq h \leq 17, 0 \leq k \leq 17, -32 \leq l \leq 32$
Reflections collected / unique	3024/1484 [ $R(\text{int}) = 0.0264$ ]
Completeness to $\theta = 44.93$	100.0%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1484/0/36
Goodness-of-fit on $F^2$	1.118
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0296, wR2 = 0.0747$
$R$ indices (all data)	$R1 = 0.0440, wR2 = 0.0808$
Extinction coefficient	0.0010(4)
Largest diff. peak and hole	1.891 and $-1.028 e \text{ \AA}^{-3}$

and angles of B–B–B range between 58.65° and 61.17° with an average of 60.03°. The whole framework of the crystal shows a layer structure (Fig. 3a) and selected atomic distances are listed in Table 5. Figure 3b shows a slice of the icosahedral layer which is parallel to the (001) plane. Each icosahedron connects with four neighbors through B1–B1 bonds. In contrast to other boron-rich compounds, the boron icosahedra in different layers are not connected directly and they are only linked through Si–Si bridges. Every three neighboring icosahedra form a triangle and six icosahedra form a big hexagon. The whole layer is an icosahedral net built up of these triangle and hexagons. Similar to the situation in other boron icosahedron

TABLE 3  
Atomic Coordinates, Occupancy, and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{YB}_{17.6}\text{Si}_{4.6}$

Atom	Site	$x$	$y$	$z$	Occupancy	$U(\text{eq})^a$
Y	9e	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.68(1)	10(1)
Si1	6c	$\frac{1}{3}$	$\frac{1}{3}$	0.2379(1)	1.00	6(1)
Si2	18h	0.4649(1)	0.5352(1)	0.2730(1)	1.00	6(1)
Si3a	6c	$\frac{1}{3}$	$\frac{1}{3}$	0.2913(1)	0.50(7)	3(1)
Si3b	6c	$\frac{1}{3}$	$\frac{1}{3}$	0.2647(4)	0.16(8)	5(1)
B1	36i	0.4916(1)	0.1556(1)	0.1353(1)	1.00	4(1)
B2	36i	0.3671(1)	0.0399(5)	0.2181(1)	1.00	5(1)
B3	18h	0.4839(2)	0.2420(1)	0.2307(1)	1.00	7(1)
B4	18h	0.2899(2)	0.1449(1)	0.2697(1)	1.00	5(1)

<sup>a</sup> $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.



**FIG. 3.** Structure model for  $\text{YB}_{17.6}\text{Si}_{4.6}$  (a) projected along the  $[110]$  direction; (b) slice of icosahedral layer parallel to the  $(001)$  plane; (c) projected along the  $[001]$  direction; (d) three icosahedral layers connected through the Si bridge (the middle icosahedral layer is not shown). Big black spot represents Y atoms, gray smaller one is Si atoms, and polyhedra are boron icosahedra.

compounds, the intericosahedron B1–B1 bonding distance is  $1.7380\text{\AA}$ , less than for special “two electrons, three centers” B–B bonds (average  $1.8053\text{\AA}$ ). Silicon atoms align on the axes which pass through the centers of these

triangles and hexagons and parallel to the  $c$ -axis of the unit cell. Y atoms reside between two neighboring icosahedral layers. Their sites projected on the  $(001)$  plane form hexagons. The Y atoms at both sides of icosahedral layers

**TABLE 4**  
Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ )  
for  $\text{YB}_{17.6}\text{Si}_{4.6}$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Y	11(1)	12(1)	7(1)	−3(1)	−1(1)	6(1)
Si1	5(1)	5(1)	6(1)	0	0	3(1)
Si2	6(1)	6(1)	5(1)	0(1)	0(1)	4(1)

Note. The anisotropic displacement factor exponent takes the form

$$-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hk a^* b^* U_{12}]$$

lie just over and beneath the icosahedra of neighboring icosahedral layers. The stacking of all the icosahedral layers projected on the (001) plane is shown in Fig. 3c. It is interesting that all icosahedra distribute with a form of hexagon cylinders and Si1 atoms are in the center of these cylinders.

The Si–Si bond is similar to that in cubic Si. Si1–Si1 pairs aligned along the *c*-axis lie in the icosahedral layers. Every Si1 bonds with four neighbor atoms forming a tetrahedron in which the Si1 atom bonds with three Si2 atoms and another Si1, and the Si2 atom bonds with three boron atoms of icosahedra besides the bond with Si1. The bond lengths of Si1–Si1 and Si1–Si2 are 2.3450(15)Å and 2.3687(5)Å, respectively. The Si–Si bond length in crystal-line Si is 2.3516Å and the Si–Si–Si bonding angle is about 109°. The Si2–Si1–Si2 and Si1–Si1–Si2 bonding angles are 114.24° and 104.13°, respectively. So the Si atom environment in the new structure is very similar with that in cubic silicon.

Three icosahedral layers are interconnected through the bridge of (Si2)<sub>3</sub>Si1–Si1(Si2)<sub>3</sub>. Figure 3d shows such a bridge and its connection with icosahedra. In fact, at the end of the bridge, every Si2 atom connects with the boron atoms of three icosahedra, in which two lies in the middle layer and another icosahedron in the neighboring layer.

**TABLE 5**  
Selected Atomic Distances (Å) for  $\text{YB}_{17.6}\text{Si}_{4.6}$

Atom–Atom	Distance(Å)	Atom–Atom	Distance(Å)
Y–Si1	3.3087(4)	Si3a–B3	1.8820(2)
Y–Si2	2.8378(2)	Si3b–B3	1.6920(3)
Y–B1	2.7515(10)	B1–B1	1.7380(2)
Y–B2	2.7959(10)	intraicosahedron	
Y–B4	2.9345(8)	B(1)–B(1)	1.8195(2)
Si1–Si1	2.3450(15)	B(1)–B(2)	1.8089(14)
Si1–Si2	2.3687(5)	B(1)–B(3)	1.8161(18)
Si2–B2	2.0296(11)	B(1)–B(4)	1.7970(16)
Si2–B4	2.0555(15)	B(2)–B(2)	1.7950(2)
Si3a–Si3a	1.3855(2)	B(2)–B(3)	1.7834(15)
Si3b–Si3b	2.2602(5)	B(2)–B(4)	1.8096(14)
Si3a–Si3b	0.4374(2)	B(3)–B(4)	1.8130(2)

It is special that Si3a and Si3b seem to have equivalent positions with Si1, but they, in fact, do not form Si–Si pairs. They are very close (only 0.4374Å), so they are, in fact, one split position. The minimum distance between the symmetry positions between them is only 1.3855Å much less than the normal Si–Si bond length (2.350Å). Silicon atoms can not occupy these positions simultaneously to form pairs, because their occupancies are only 0.50 and 0.16 respectively. However, they can bond with neighboring boron atoms in the icosahedra.

Other rare earth elements from Gd to Lu can also form the same structure with B and Si. Single crystal growth and cell parameter determination of these new compounds are under way.

#### 4. CONCLUSION

New yttrium borosilicide of  $\text{YB}_{17.6}\text{Si}_{4.6}$  was found by solid state reaction method and the single crystals have been grown by high temperature solution method with Si flux. The crystal structure was solved and refined from single crystal XRD data with a rhombohedral cell: space group  $R\bar{3}m(\text{No.166})$  and lattice constants  $a=b=10.0841(4)\text{\AA}$  and  $c=16.4714(5)\text{\AA}$ .

#### ACKNOWLEDGMENTS

The first author acknowledges the support of an STA fellowship from JST. The authors thank Mr. S. Takenouchi for chemical analysis and Mr. K. Kosuda for EPMA analysis.

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