

# Structure refinement of quaternary RE-B-C-Si compounds: $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$ ( $x \approx 0.96$ ) and $\text{Dy}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$ ( $x \approx 0.90$ )

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**Abstract.** We refined the crystal structure of quaternary RE-B-C-Si (RE = Y or Dy) compounds  $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  ( $x \approx 0.96$ ) and  $\text{Dy}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  ( $x \approx 0.90$ ). Both compounds have a trigonal crystal structure with space group  $R\bar{3}m$  (No. 166). They have previously been assigned as ternary RE-B-Si compounds, but we incorporated carbon to the new structure refinements. The refinement for  $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  achieved a final  $R1=0.0288$  for 1178 independent reflections with  $F_0 > 4\sigma(F_0)$  and 0.0431 for all 1484 reflections, and the refinement for  $\text{Dy}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  achieved a final  $R1=0.0382$  for 2009 independent reflections with  $F_0 > 4\sigma(F_0)$  and 0.0385 for all 2022 reflections. The new structure refinements suggest the presence of  $(\text{B}_{12})_3\text{-Si-C-(B}_{12})_3$  units, which, together with two other units,  $\text{B}_{12}$  icosahedron cluster and  $\text{Si}_8$  ethane-like cluster, stabilize the  $\text{RE}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  crystal structure.

## 1. Introduction

Rare-earth boron-rich borides have unique crystal structures in which boron framework structure consists mainly of boron icosahedra ( $\text{B}_{12}$ ). Because the  $\text{B}_{12}$  cluster has 5-fold symmetry, simple arrangement of the  $\text{B}_{12}$  clusters cannot achieve periodical long-range order. Thus, the boron framework is rather complicated and the unit cell is large. This framework contains many voids that accommodate the rare earth atoms. Recently cluster-compounds have attracted much attention from both scientific and practical points of view because of their unique crystal structures, chemical and physical properties and potential thermoelectric and superconducting applications [1, 2, 3, 4]. Knowing their crystal structure is crucial for understanding their properties.

We have reported the synthesis and structure analysis of a ternary Y-B-Si compound  $\text{YB}_{17.6}\text{Si}_{4.6}$  [5], which has a trigonal structure with space group  $R\bar{3}m$  (No.166) and lattice constants  $a = 1.00841(4)$  and  $c = 1.64714(5)$  nm. We described the crystal structure of  $\text{YB}_{17.6}\text{Si}_{4.6}$  based on three units of a  $\text{B}_{12}$  icosahedron, a  $\text{Si}_8$  ethane-like cluster and a bonding configuration  $(\text{B}_{12})_3\text{-Si-Si-(B}_{12})_3$ . In the latter, we have first assigned the Si site as a split position, i.e., Si3a and Si3b sites, but then re-assigned the Si3b site to the B site in the structure refinement of  $\text{Dy}_{0.7}\text{B}_{12.33}\text{Si}_3$  [6] that is isotypic to  $\text{YB}_{17.6}\text{Si}_{4.6}$ . Lattice constants of  $\text{Dy}_{0.7}\text{B}_{12.33}\text{Si}_3$  are  $a = b = 1.00782(3)$  and  $c = 1.64651(4)$  nm.

Meanwhile Salvador *et al* [7] reported the crystal structure of  $\text{Tb}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$  as a quaternary boron-rich phase containing  $\text{B}_{12}$  icosahedra. Both structures appear isotypic.

Salvador *et al* reported that  $\text{Tb}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$  could only be synthesized if carbon is introduced into the growth. In the crystal structure of  $\text{Tb}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$  they found a bonding scheme of  $(\text{B}_{12})_3\text{-C-C-(B}_{12})_3$  in addition to  $\text{B}_{12}$  icosahedra and  $\text{Si}_8$  ethane-like clusters. On the contrary, we did not incorporate carbon in the crystal structure because we have used carbon-free raw materials and crucibles in our growth of single crystals by high temperature solution method using Si flux. Further, we have synthesized powder samples of  $\text{REB}_{17.6}\text{Si}_{4.6}$  (RE= Y, Gd-Lu) by solid-state reaction [8]. We undertook Rietveld structure analysis of Tb system compound using powder X-ray diffraction (XRD) data and have assigned only Si to the Si3 site with a partial occupancy of 71%, because the electron density of the site was obviously too high for a C site and we did not detect carbon with either chemical analysis or electron probe microanalysis. However, we have used graphite for a heating element and heat insulation in both synthesis experiments, which might contaminate the samples. Thus, we conducted synthesis experiments of  $\text{YB}_{17.6}\text{Si}_{4.6}$  using a carbon-free furnace to confirm whether or not  $\text{YB}_{17.6}\text{Si}_{4.6}$  can be synthesized without carbon. The result suggested that in absence of carbon, formation of  $\text{YB}_{17.6}\text{Si}_{4.6}$  is difficult, as reported by Salvador *et al*. This finding motivated us to reinvestigate the crystal structure of both Y and Dy compounds.

In this study, we report the structure refinement of both compounds incorporating carbon, which resulted in a new structure description of  $\text{RE}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  (RE=Y and Dy,  $x \approx 0.96$  for Y and 0.90 for Dy) and a new bonding scheme of  $(\text{B}_{12})_3\text{-Si-C-(B}_{12})_3$ .

## 2. Phase formation

The powder synthesis of ternary Y-B-Si compounds was carried out using an RF-induction-heating furnace. To exclude carbon, a composite consisting of BN and  $\text{TiB}_2$  (BN-composite-EC, DENKA, Japan) was used as a heating element. The heating element was centered in a BN container, which was filled with BN granules for heat-insulation. Raw materials were  $\text{YB}_4$  powder (3N, carbon content 0.1 wt%, Shin-Nihon Kinzoku, Japan), amorphous B powder (3N, carbon content 0.1 wt%, SB-Boron, USA) and Si powder (5N, Koujundokagaku, Japan). The synthesis was carried out at approximately 1750 °C under vacuum, for 10 h. The expected reaction equation was  $\text{YB}_4 + 14\text{B} + 5\text{Si} = \text{YB}_{18}\text{Si}_5$  with minor losses of B and Si. The obtained sample was analyzed by powder XRD. The XRD pattern showed contributions of yttrium higher boride ( $\text{YB}_{12}$ ) and boron silicide, which indicated that the phase formation of  $\text{YB}_{17.6}\text{Si}_{4.6}$  without carbon is difficult. Whereas if small amount of carbon was added into the system, the XRD pattern of the phase previously assigned as  $\text{YB}_{17.6}\text{Si}_{4.6}$  appeared. Thus, we concluded that carbon is important for the phase formation, which stimulated us to refine the structure incorporating carbon into it.

## 3. Structure refinement

### 3.1. Structure refinement of $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$

The structure refinement of  $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  was carried out using previously collected single-crystal XRD data and SHELXL97 program [9]. The result was visualized using the crystallographic program CrystalMaker [10]. The previous atomic coordinates were used as an initial solution [5]. Eight atomic sites have previously been assigned to one yttrium atom Y, four boron atoms B1-B4 and three silicon atoms Si1-Si3, in which Si3 site was assigned to the split sites Si3a and Si3b with partial occupancies of 0.50(7) and 0.16(8), respectively, as mentioned above. All remaining sites except yttrium site are fully occupied. Considering the electron density of the sites, carbon incorporation is only possible to the Si3b site; thus, in turn, the Si3b site was re-assigned to the C3 site. The final refinement of 38 parameters for 1178 independent reflections with  $F_0 > 4\sigma(F_0)$  resulted in an  $R1$  value of 2.88% and 4.31% for all 1484 independent reflections. The  $R1$  values are slightly better than those 2.96% and 4.41% obtained previously

[5]. The final atomic coordinates, occupancy factors and temperature factors are listed in table 1.

**Table 1.** Atomic coordinates, site occupancy and isotropic displacement parameters of  $Y_{3-x}(B_{12})_3(CSi)Si_8$

Atom	Site	$x/a$	$y/b$	$z/c$	Occ.	$U_{eq}(\text{\AA}^2 \times 10^3)$
Y	9e	1/6	1/3	1/3	0.68(1)	6.1(1)
B1	36i	0.4916(1)	0.1556(1)	0.1353(1)	1.0	4.5(1)
B2	36i	0.3671(1)	0.0400(1)	0.2181(1)	1.0	4.6(1)
B3	18h	0.4838(2)	0.2419(1)	0.2307(1)	1.0	7.4(2)
B4	18h	0.2900(2)	0.1450(1)	0.2697(1)	1.0	5.1(2)
C3	6c	2/3	1/3	0.2666(12)	0.58(5)*	2.9(5)
Si1	6c	1/3	2/3	0.2379(1)	1.0	2.7(1)
Si2	18h	0.4648(1)	0.5352(1)	0.2730(1)	1.0	4.1(1)
Si3	6c	2/3	1/3	0.2917(3)	0.42(2)*	1.1(2)

\*The sum of those values was fixed at 1.0.

### 3.2. Structure refinement of $Dy_{3-x}(B_{12})_3(CSi)Si_8$

The structure refinement of  $Dy_{3-x}(B_{12})_3(CSi)Si_8$  was carried out in a similar fashion, using previously collected single-crystal XRD data and SHELXL97 program [9], and the previous atomic coordinates were used as an initial solution [6]. The B(5) site was re-assigned to the C3 site. The final refinement of 34 parameters for 2009 independent reflections with  $F_0 > 4\sigma(F_0)$  resulted in an  $R1$  value of 3.82% and 3.85% for all 2022 independent reflections. The final atomic coordinates, occupancy factors and temperature factors are listed in table 2.

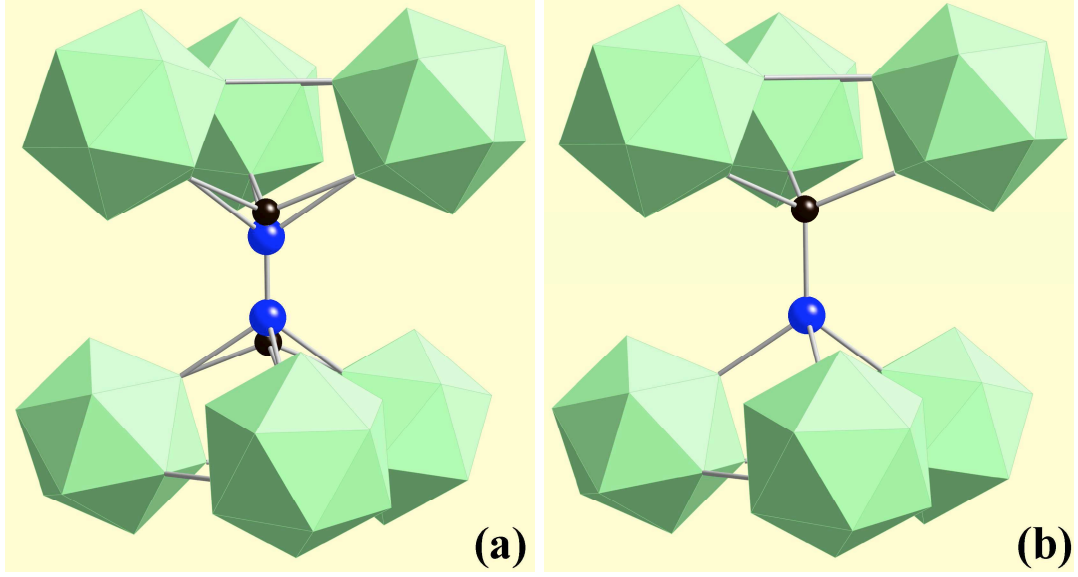
**Table 2.** Atomic coordinates, site occupancy and isotropic displacement parameters of  $Dy_{3-x}(B_{12})_3(CSi)Si_8$

Atom	Site	$x/a$	$y/b$	$z/c$	Occ.	$U_{eq}(\text{\AA}^2 \times 10^3)$
Dy	9e	1/6	1/3	1/3	0.70(0)	10.4(1)
B1	36i	0.4916(1)	0.1556(1)	0.1354(1)	1.0	4.9(2)
B2	36i	0.3669(1)	0.0397(2)	0.2180(1)	1.0	5.1(2)
B3	18h	0.4840(1)	0.2420(1)	0.2306(1)	1.0	8.1(2)
B4	18h	0.2900(1)	0.1450(1)	0.0636(1)	1.0	5.6(3)
C3	6c	2/3	1/3	0.2642(3)	0.50(1)*	2.9(5)
Si1	6c	1/3	2/3	0.2378(1)	1.0	6.2(1)
Si2	18h	0.4647(1)	0.5353(1)	0.2731(1)	1.0	6.0(1)
Si3	6c	2/3	1/3	0.2909(3)	0.50(1)*	3.2(3)

\*The sum of those values was fixed at 1.0.

## 4. Discussion

The distances between the C3 and Si3 sites and the surrounding sites for  $Y_{3-x}(B_{12})_3(CSi)Si_8$  and  $Dy_{3-x}(B_{12})_3(CSi)Si_8$  are summarized in table 3. The shortest distances between C3 and Si3 split positions are only 0.413 and 0.438 Å for  $Y_{3-x}(B_{12})_3(CSi)Si_8$  and  $Dy_{3-x}(B_{12})_3(CSi)Si_8$ , respectively, as shown in figure 1(a). Therefore, locally in such a pair positions, either the C3 or the Si3 position, but not both, is occupied.



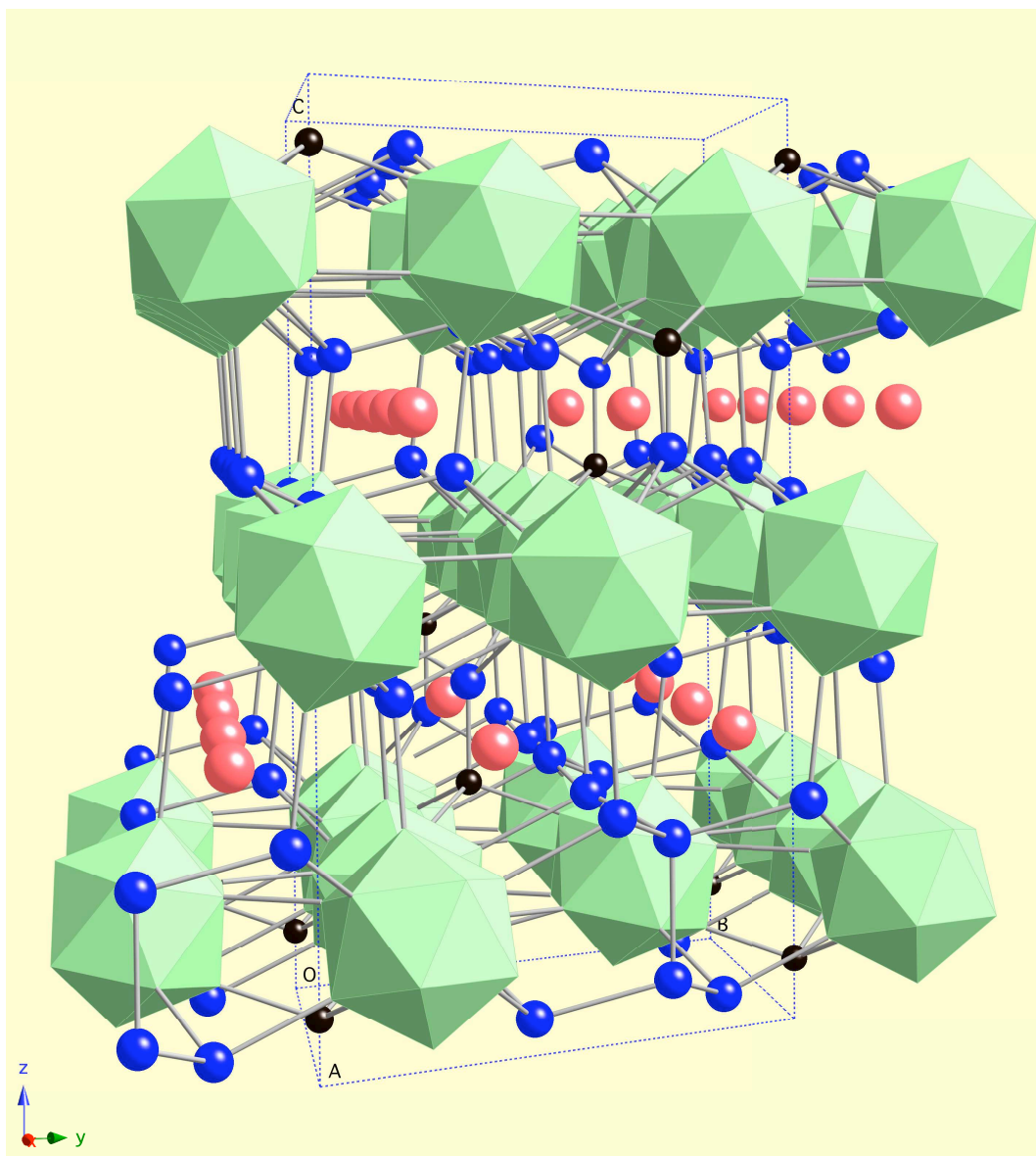
**Figure 1.** (a) C3 and Si3 split positions are simultaneously shown, and (b)  $(B_{12})_3\text{-Si-C-}(B_{12})_3$  bonding scheme (green:  $B_{12}$  icosahedron, black: carbon, blue: silicon).

**Table 3.** Interatomic distances between the listed sites. Left and right values correspond to  $Y_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$  and  $Dy_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$ , respectively

Atoms	Distance (Å)	Atoms	Distance (Å)
C3-B3	1.703(7)/1.688(3)	C3-C3	2.198(6)/2.268(4)
Si3-B3	1.887(3)/1.878(2)	Si3-C3	0.413(3)/0.438(2)
C3-Si3	1.786(24)/1.838(6)	Si3-Si3	1.373(10)/1.398(4)

Three combinations of C3 and Si3 sites are possible: Si-C, C-C and Si-Si. The latter two are unlikely because of too large C-C atom separation of 2.198/2.268 Å and too short Si-Si separation of 1.373/1.398 Å. Because the Si-C bond length in SiC is 1.89 Å, the separation of 1.786/1.838 Å more likely originates from Si-C than C-C or Si-Si pairs. Formation of Si-C pair at the C3 and Si3 sites agrees well with the fact that the occupancies of both the C3 and Si3 sites are close to 50% for  $Y_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$  and equal to 50% for  $Dy_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$ . Then, we can expect that a new bonding scheme of  $(B_{12})_3\text{-Si-C-}(B_{12})_3$  is available in the  $\text{RE}_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$  crystal structure and it can effectively stabilize the crystal structure. Thus the carbon incorporation must be important for the phase formation of  $\text{RE}_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$ . The  $(B_{12})_3\text{-Si-C-}(B_{12})_3$  unit and overall crystal structure are shown in figures 1(b) and 2, respectively.

In their analysis of  $\text{Tb}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ , Salvador *et al* [7] found only carbon atoms at the Si3/C3 site, and they did not detect split positions. Thus, their bonding scheme is  $(B_{12})_3\text{-C-C-}(B_{12})_3$ , where the C-C distance is 1.695 Å. This value is much shorter than the C3-Si3 distances of  $Y_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$  and  $Dy_{3-x}(B_{12})_3(\text{CSi})\text{Si}_8$ . Meanwhile, in our Rietveld structure analysis using powder XRD data of the Tb system compound we assigned only Si atoms to the Si3 site with a partial occupancy of 71% [8]. The electron density at this site is obviously too high for carbon. Considering the importance of the Si3 site in bridging the  $B_{12}$  icosahedron framework, it is unlikely that vacancies are available on 29% of the Si3 site. Instead, we think that the introduction of Si/C mixed occupation with 100% occupancy to the site is



**Figure 2.** Crystal structure of  $\text{RE}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  ( $\text{RE}=\text{Y}$  or  $\text{Dy}$ ) viewed along the direction close to  $[100]$ . Red, black and blue spheres indicate the Y or Dy, C and Si atoms, respectively. Vacancies at the Y or Dy site are ignored. Green polyhedra indicate the  $\text{B}_{12}$  icosahedra.

more reasonable, which immediately results in equal occupancy of Si and C to the site. This result is consistent with that obtained for  $\text{Y}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  and  $\text{Dy}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$ . Thus the composition should be  $\text{Tb}_{3-x}(\text{B}_{12})_3(\text{CSi})\text{Si}_8$  ( $x \approx 0.96$ ) and it should include  $(\text{B}_{12})_3\text{-Si-C-(B}_{12})_3$  units. However, we did not detect a splitting of the site. This is probably due to a lower resolution of the Rietveld method compared to that of single-crystal XRD method. The structure refinement by Salvador *et al* indicated the existence of  $(\text{B}_{12})_3\text{-Si-C-(B}_{12})_3$  units, probably because they intentionally added carbon during the growth, and thus their crystals had higher carbon content than ours; carbon incorporation to our sample was accidental.

Existence of both bonding schemes of  $(\text{B}_{12})_3\text{-Si-C-(B}_{12})_3$  and  $(\text{B}_{12})_3\text{-C-C-(B}_{12})_3$  suggests a solid-solubility region of carbon on the site from 50 to 100%. On the other hand,  $(\text{B}_{12})_3\text{-Si-Si-}$

(B<sub>12</sub>)<sub>3</sub> bonding scheme is unlikely because of too short Si-Si distance, which suggests that the minimum carbon occupancy at the site is 50%. Some B atoms may replace C atoms at the C3 site, as previously assigned to the B site [6]. However, the C occupation is more likely because the site is tetrahedrally coordinated, and the B occupation at the site needs extra electron transfer to complete tetrahedral bonding. Thus, carbon is indispensable for the phase formation of this group of compounds.

## 5. Conclusion

Crystal structures of Y<sub>3-x</sub>(B<sub>12</sub>)<sub>3</sub>(CSi)Si<sub>8</sub> ( $x \approx 0.96$ ) and D<sub>3-x</sub>(B<sub>12</sub>)<sub>3</sub>(CSi)Si<sub>8</sub> ( $x \approx 0.90$ ) were refined. The newly found bonding scheme (B<sub>12</sub>)<sub>3</sub>-Si-C-(B<sub>12</sub>)<sub>3</sub>, together with the B<sub>12</sub> icosahedron and the Si<sub>8</sub> ethane-like cluster, plays an important role in phase formation of this type of rare-earth borocarbo-silicide.

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