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Crystal Structure of $YB_{41}Si_{1.2}$

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The crystal structure of a new compound, $YB_{41}Si_{1.2}$, has been determined by single-crystal X-ray diffractometry. The crystal was grown by the floating-zone method. The intensity data were collected on a four-circle diffractometer using CuK_α radiation. The structure was solved by direct methods and refined with the aid of a full-matrix least-squares program to the $R(R_w)$ value of 0.034 (0.040); 2686 independent reflections were used for 232 variable parameters. The structure of $YB_{41}Si_{1.2}$ belongs to the orthorhombic system (space group *Pbam*), with lattice constants $a = 16.674(1)$ Å, $b = 17.667(1)$ Å, and $c = 9.5110(7)$ Å, and is composed of B_{12} icosahedra and a new $B_{12}Si_3$ polyhedral unit. Three Si sites of the $B_{12}Si_3$ unit are assumed to be fully occupied by both Si and B atoms, and the actual chemical composition of this unit is estimated to be $B_{12}Si_{1.5}B_{1.5}$. The boron framework is thus proved to be of a new structure type which is made up of five crystallographically different five B_{12} icosahedra and the $B_{12}Si_3$ unit. The Y atom occupies a large hole outside the icosahedra and the $B_{12}Si_3$ unit. Interstitial sites, one Si and seven B sites, are also found outside the polyhedral units, with various occupancies from 100% to 9%.

INTRODUCTION

Recently, a single crystal of a boron-rich compound of the Y–B–Si system has been grown by Tanaka *et al.* (1). From the results of chemical analysis and preliminary X-ray diffraction work, it was thought to be a new compound of a new structure type. Therefore, we undertook structure determination by single-crystal diffractometry. From the similarity of the lattice constants, the structure of this compound seemed to exhibit some relation to that of γ-AlB_{12} (2, 3) (space group, $P2_12_12_1$; $a = 16.573(4)$, $b = 17.510(3)$, $c = 10.144(1)$ Å) (3). After examining the final structural data, however, we have realized that the structure is quite different from those of the boron-rich solids published so far (4). In this paper we report a new type of icosahedral B_{12} arrangement in which a new structural polyhedron $B_{12}Si_3$ is involved.

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EXPERIMENTAL

The crystal was grown by an indirect heating floating-zone method (1). The crystal obtained was examined by precession photography and found to be of single phase. The specimen for the intensity measurements was selected from the fragments obtained by cracking the grown crystal.

The reflections were measured with an Enrauf-Nonius CAD-4 four-circle diffractometer using Cu$K\alpha$ radiation monochromated by a graphite monochromator. Crystal data and intensity measurements data are given in Table 1. The intensities were corrected for Lorentz and polarization effects. The absorption effects were corrected by the semiemperical method of North *et al.* (5) Extinction effects were checked in the final stage of the structure refinement and found to be negligible. Independent reflections with structure factors larger than 3.0 times the standard deviations were collected by averaging the F_o's for equivalent reflections.

The structure was solved by direct methods with MULTAN78 (6) and refined with a full-matrix least-squares program (UNICS-III) (7) to the R (R_w) value of 0.034 (0.040). The function minimized was $\sum w(|F_o|-|F_c|)^2$, where the weights w were $1/\sigma^2(F_o)$. A final difference synthesis showed no significant residual peaks. The X-ray scattering factors and the anomalous dispersion correction factors were taken from the International Tables for X-ray Crystallography (1974) (8).

RESULTS AND DISCUSSIONS

The structure of $YB_{41}Si_{1.2}$ belongs to the orthorhombic system (space group *Pbam*), with lattice constants $a = 16.674(1)$ Å, $b = 17.667(1)$ Å, and $c = 9.5110(7)$ Å (Table 1), and is composed of B_{12} icosahedra and a new $B_{12}Si_3$ polyhedral unit. The boron framework is thus proved to be of the new structure type which is made up of five crystallographically different B_{12} icosahedra (B_{12}-1, B_{12}-2,

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TABLE 1
Crystal and Structure Analysis Data for $YB_{41}Si_{1.2}$

Crystal system	orthorhombic
Space group	*Pbam*
a (Å)	16.674(1)
b (Å)	17.667(1)
c (Å)	9.5110(7)
Chemical composition[a]	$YB_{41}Si_{1.2}$
D_x (g/cm^3)	2.668(2)
Z	8
μ for Cu$K\alpha$ (cm^{-1})	65.7
Crystal dimensions (mm)	$0.22 \times 0.20 \times 0.18$
Reflections measured	$-20 \le h \le 20$
	$-21 \le h \le 21$
	$0 \le l \le 11$
$2\theta_{max}$ (degree)	136
NR[b]	2681
NV[c]	232

[a] Obtained by structure analysis.
[b] Number of independent reflections.
[c] Number of variable parameters.

B_{12}-3, B_{12}-4, and B_{12}-5) and the $B_{12}Si_3$ unit (Fig. 1, 2). The structural data are given in Table 2, where the number n in the atom designation Bn.n' refers to the $B_{12}-n$ icosahedron to which the Bn.n' belongs. Si6.n' and B6.n' belong to the $B_{12}Si_3$ unit.

The structure of the $B_{12}Si_3$ unit is presented in Figs. 3, 4, and 5, where the figures are projected along the c, a, and b axes, respectively. As indicated in the figures, the Si sites are on the mirror plane. They are coordinated to six B sites in a hexagonal arrangement (Figs. 4 and 5).

On the other hand, boron sites are coordinated with five sites (3B + 2Si or 4B + 1Si sits) in a pentagonal arrangement (Figs. 3, 4, and 5). The three Si sites (Si6.7, Si6.8, Si6.9 in Table 2) are assumed to be occupied by both Si and B atoms. That is because, between two equivalent $B_{12}Si_3$ units in the crystals (Fig. 2), there appears on unusually short Si6.9–Si6.9′ distance ($\approx$ 1.65 Å) the simultaneous occupation of which by Si atoms is impossible for. In addition, when occupational refinement was made on the assumption that these sites are occupied solely by Si atoms, the relative Si content [Si]/[Y] obtained was 1.35, which is significantly greater than that ([Si]/[Y] = 1.04) determined by chemical analyses (ICP-AES for Si and B, and chelatometry for Y). By imposing the constraint P(Si) + P(B) = 1, where P(Si) and P(B) are occupancies of Si and B atoms, respectively, the occupancies of the Si sites were refined to give the following results: P(Si6.7) + P(B6.7) = 0.575(6) + 0.425(6); P(Si6.8) + P(B6.8) = 0.478(6) + 0.522(6); P(Si6.9) + P(B6.9) = 0.440(6) + 0.560(6). As a result, the relative Si content decreased to [Si]/[Y] = 1.15(1), in approximate agreement with that obtained by the chemical analysis. In this refinement, the positional parameters of each boron atom are adjusted

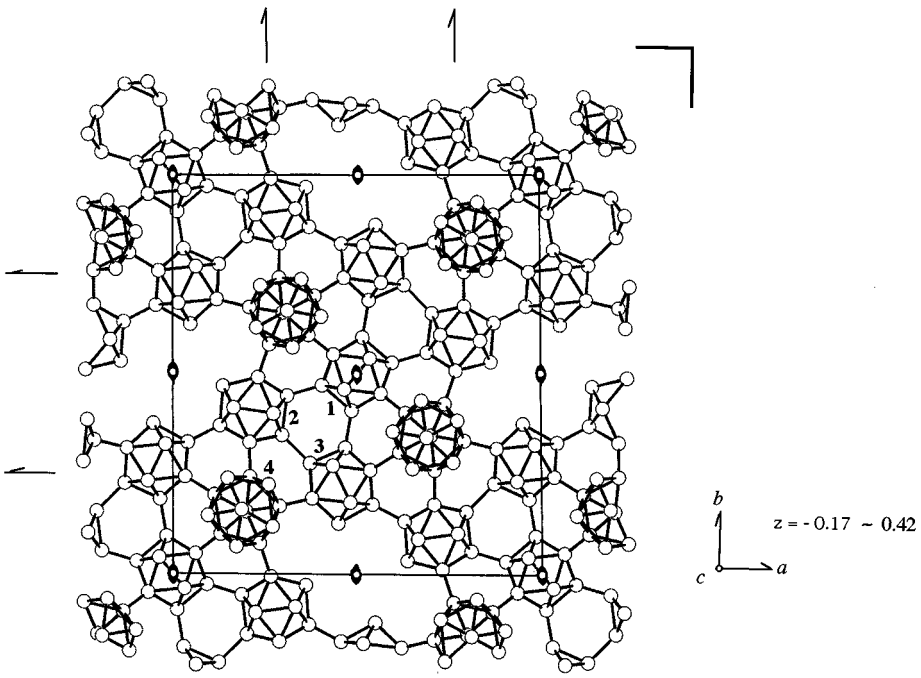

FIG. 1. Icosahedral B_{12} arrangement as seen along the c axis. In this figure, B_{12}-1, B_{12}-2, B_{12}-3, and B_{12}-4, within the range $z = -0.17$–0.42 are drawn.

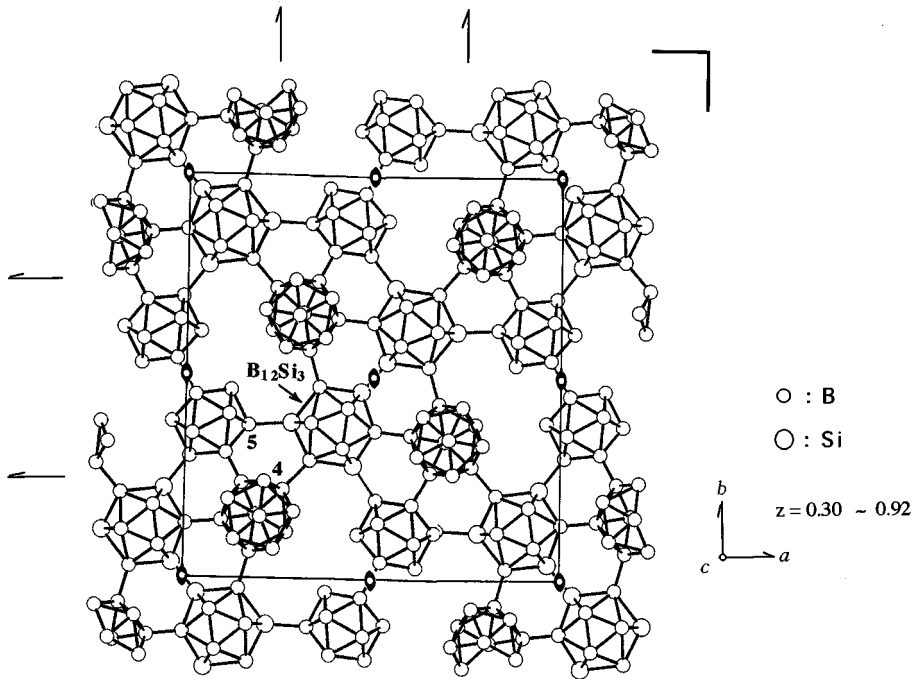

FIG. 2. Arrangement of B_{12}-4 and B_{12}-5 icosahedra and $B_{12}Si_3$ units as seen along the *c* axis. In this figure the polyhedral units within the range $z = 0.30$–0.92 are drawn.

independently by fixing the thermal parameter at the same value as for the Si atom in the same interstice. It can be seen from Table 2 that there are noticeable differences in the atomic coordinates of the Si and B atoms in the same interstices.

All the 15 apical atoms of this polyhedral unit are linked to the surrounding fourteen B_{12} icosahedra and one $B_{12}Si_3$, and the linkages are effected along one of the quasi-fivefold axes of each icosahedron and along similar directions of the $B_{12}Si_3$ units. Therefore, one of the significant features of the structure of $YB_{41}Si_{1.2}$ is that the pair $B_{12}Si_3$–$B_{12}Si_3$ is present in a large hole of the icosahedral B_{12} arrangement. The linkage between two $B_{12}Si_3$ units is effected between Si sites. However, the actual linkage between the two sites may be either the Si–B or the B–B bond; the interatomic distance was calculated to be about 2.0 Å, which is acceptable for the Si–B or the B–B bond.

Besides the atomic sites belonging to the five crystallographically independent icosahedra and the new structural unit $B_{12}Si_3$, there are interstitial Y, Si(1) and seven boron (B(1–7)) sites. The Y site is fully occupied and the Si(1) site is occupied up to 0.798((6). The occupancies of the B(1–7)

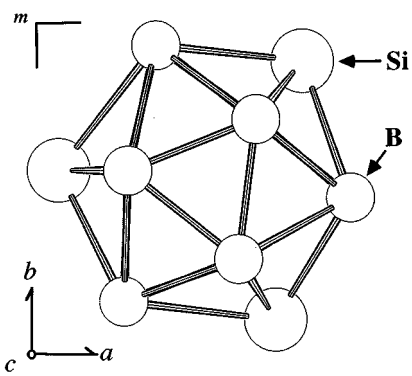

FIG. 3. $B_{12}Si_3$ unit as seen along the *c* axis. The larger circles represent Si sites and the smaller ones B sites.

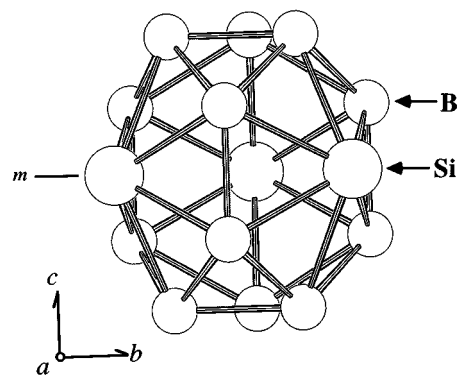

FIG. 4. $B_{12}Si_3$ unit as seen along the *a* axis. The larger circles represent Si sites and the smaller ones B sites.

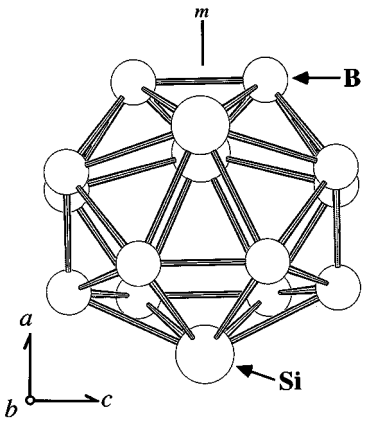

FIG. 5. $B_{12}Si_3$ unit as seen along the *b* axis. The larger circles represent Si sites and the smaller ones B sites.

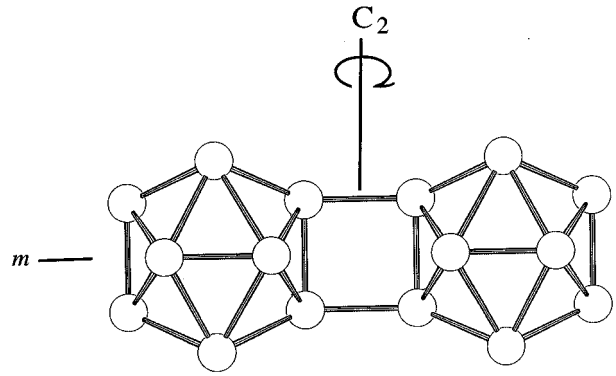

FIG. 7. Unusual linkage between B_{12}-5 icosahedra effected through two apical atoms of each icosahedron, forming an approximately square plane. This figure is projected along some direction lying on the mirror plane at $z = 1/2$ (see also Fig. 2)

sites are in the range from 0.08(1) to 1.0. The chemical composition obtained by the structure analysis is $YB_{40.83(1)}Si_{1.15(1)}$, in approximate agreement with the composition $YB_{44.4}Si_{1.04}$ by the chemical analysis.

In this structure, four icosahedra (B_{12}-1, B_{12}-2, B_{12}-3, B_{12}-5) are located on the mirror plane (perpendicular to the *c* axis as defined by the space group *Pbam*) with one of their twofold axes parallel to the *c* axis (Figs. 1, 2). On the other hand, the remaining icosahedron (B_{12}-4) is located on a general position, and links along one of its quasi-fivefold axes with the equivalent icosahedron reflected by the mirror plane, thus giving an infinite icosahedral B_{12} chain running

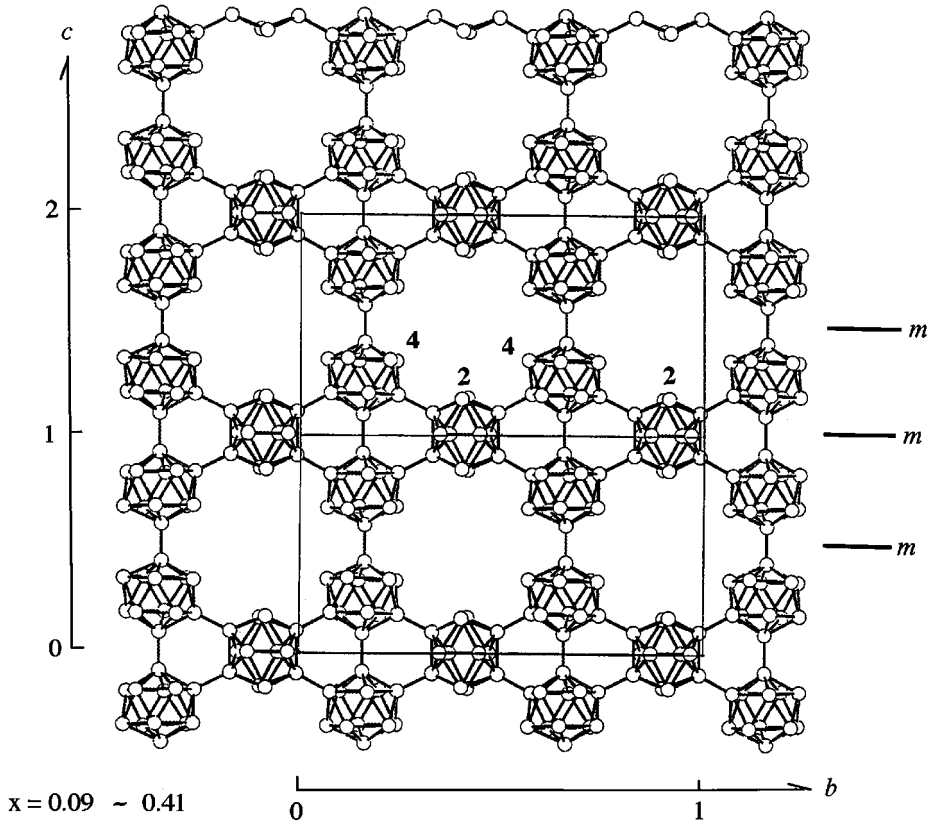

FIG. 6. Arrangement of B_{12}-2 and B_{12}-4 icosahedra as seen along the *a* axis. The icosahedral network within $x = 0.09$–0.41 is drawn.

TABLE 2
Structure Data for $YB_{41}Si_{1.2}$[a]

Atom	Site	x	y	z	Occupancy	B(Å^2)
B1.1	8*i*	0.4362(2)	0.5491(2)	0.0938(3)	1.0	0.12(5)
B1.2	8*i*	0.4660(2)	0.4610(2)	0.1572(3)	1.0	0.15(5)
B1.3	4*g*	0.4063(3)	0.4711(3)	0	1.0	0.19(7)
B1.4	4*g*	0.4852(3)	0.4078(3)	0	1.0	0.14(6)
B2.1	8*i*	0.2326(2)	0.4909(2)	0.0981(3)	1.0	0.14(5)
B2.2	8*i*	0.2101(2)	0.3281(2)	0.0956(3)	1.0	0.13(5)
B2.3	8*i*	0.1664(2)	0.4147(2)	0.1632(3)	1.0	0.19(5)
B2.4	8*i*	0.2740(2)	0.4005(2)	0.1586(3)	1.0	0.13(4)
B2.5	4*g*	0.1293(3)	0.3702(3)	0	1.0	0.11(6)
B2.6	4*g*	0.1379(3)	0.4694(3)	0	1.0	0.11(6)
B2.7	4*g*	0.3106(3)	0.4451(3)	0	1.0	0.15(7)
B2.8	4*g*	0.2972(3)	0.3466(3)	0	1.0	0.20(7)
B3.1	8*i*	0.3793(2)	0.1879(2)	0.0975(3)	1.0	0.19(5)
B3.2	8*i*	0.5354(2)	0.2580(2)	0.0946(3)	1.0	0.13(5)
B3.3	8*i*	0.4823(2)	0.1772(2)	0.1640(3)	1.0	0.11(4)
B3.4	8*i*	0.4350(2)	0.2693(2)	0.1584(3)	1.0	0.12(5)
B3.5	4*g*	0.4501(3)	0.1247(3)	0	1.0	0.19(6)
B3.6	4*g*	0.3728(3)	0.2753(3)	0	1.0	0.28(7)
B3.7	4*g*	0.4682(3)	0.3146(3)	0	1.0	0.12(6)
B3.8	4*g*	0.5424(3)	0.1724(3)	0	1.0	0.14(6)
B4.1	8*i*	0.2006(2)	0.1543(2)	0.0880(3)	1.0	0.16(5)
B4.2	8*i*	0.1315(2)	0.0978(2)	0.1785(3)	1.0	0.09(4)
B4.3	8*i*	0.1156(2)	0.1965(2)	0.1737(3)	1.0	0.18(5)
B4.4	8*i*	0.2107(2)	0.2414(2)	0.1753(3)	1.0	0.15(4)
B4.5	8*i*	0.2905(2)	0.1676(2)	0.1833(3)	1.0	0.10(4)
B4.6	8*i*	0.2377(2)	0.0745(2)	0.1817(3)	1.0	0.15(4)
B4.7	8*i*	0.1741(2)	0.0671(2)	0.3370(3)	1.0	0.23(5)
B4.8	8*i*	0.0972(2)	0.1445(2)	0.3316(3)	1.0	0.15(5)
B4.9	8*i*	0.1508(2)	0.2379(2)	0.3301(3)	1.0	0.11(4)
B4.10	8*i*	0.2612(2)	0.2215(2)	0.3352(3)	1.0	0.15(4)
B4.11	8*i*	0.2720(2)	0.1169(2)	0.3434(3)	1.0	0.20(5)
B4.12	8*i*	0.1884(2)	0.1594(2)	0.4149(3)	1.0	0.28(5)
B5.1	8*i*	0.1150(2)	0.4078(2)	0.3354(3)	1.0	0.19(5)
B5.2	8*i*	0.1066(2)	0.3127(2)	0.4060(3)	1.0	0.18(5)
B5.3	8*i*	0.0255(2)	0.4553(2)	0.4053(3)	1.0	0.20(5)
B5.4	8*i*	0.0175(2)	0.3589(2)	0.3358(3)	1.0	0.18(4)
B5.5	4*h*	0.4628(3)	0.1121(3)	1/2	1.0	0.27(7)
B5.6	4*h*	0.1675(3)	0.3812(3)	1/2	1.0	0.39(7)
B5.7	4*h*	0.1202(3)	0.4681(3)	1/2	1.0	0.31(7)
B5.8	4*h*	0.0108(3)	0.3023(3)	1/2	1.0	0.28(7)
B6.1	8*i*	0.3311(2)	0.3858(2)	0.3061(3)	1.0	0.19(4)
B6.2	8*i*	0.3530(2)	0.4752(2)	0.4064(3)	1.0	0.35(5)
B6.3	8*i*	0.4294(2)	0.4214(2)	0.3063(3)	1.0	0.14(4)
B6.4	8*i*	0.4150(2)	0.3223(2)	0.3052(3)	1.0	0.18(4)
B6.5	8*i*	0.5013(2)	0.3652(2)	0.4046(3)	1.0	0.20(5)
B6.6	8*i*	0.3268(2)	0.2925(2)	0.4058(3)	1.0	0.43(5)
Si6.7[b]	4*h*	0.2784(3)	0.3866(3)	1/2	0.575(6)	0.22(6)
B6.7[b]	4*h*	0.2785(13)	0.3961(11)	1/2	0.425(6)	0.22(6)
Si6.8[c]	4*h*	0.4429(3)	0.2787(3)	1/2	0.478(6)	0.17(7)
B6.8[c]	4*h*	0.4492(11)	0.2818(12)	1/2	0.522(6)	0.17(7)
Si6.9[d]	4*h*	0.4655(3)	0.4626(3)	1/2	0.440(6)	0.17(8)
B6.9[d]	4*h*	0.4589(9)	0.4537(7)	1/2	0.560(6)	0.17(8)
B7.1	8*i*	0.3911(4)	0.3747(4)	0.1181(8)	1.0	0.30[e]
B7.2	8*i*	0.3182(17)	0.2183(16)	0.502(31)	0.46(1)	0.30[e]
B7.3	4*g*	0.4569(3)	0.0212(2)	0	0.23(1)	0.30[e]
B7.4	4*g*	0.0766(4)	0.1555(6)	0	0.29(1)	0.30[e]
B7.5	4*g*	0.1438(11)	0.2507(11)	0	0.18(1)	0.30[e]
B7.6	4*g*	0.2552(10)	0.2629(9)	0	0.43(1)	0.30[e]
B7.7	4*h*	0.2054(15)	0.0230(14)	1/2	0.08(1)	0.30[e]
Y	8*i*	0.29628(1)	0.05199(1)	0.22964(3)	1.0	0.22[f]
Si	4*h*	0.34402(8)	0.07974(8)	1/2	0.798(6)	0.29[f]

[a] The number n in the atom designation B$n.n'$ refers to the B_{12}-n icosahedron to which the B$n.n'$ belongs. Si6.n' and B6.n' belong to the $B_{12}Si_3$ unit.

[b,c,d] The Si and B sites are in the same interstice, which is assumed to be fully occupied by both Si and B atoms with occupancies of P(Si) and P(B) respectively, where $P(\mathrm{Si}) + P(\mathrm{B}) = 1$. The positional parameter of the boron atom was adjusted independently by fixing the thermal parameters at the same value as for the Si atom in the same interstice.

[e] The temperature factor is fixed at this value.

[f] Equivalent isotropic temperature factor. It was calculated from the relation $B_{\mathrm{eq.}} = 4/3 \cdot (a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33})$

along the c axis (Fig. 6). It is of interest to point out that the unusually short distance (4.7555(4) Å) between the neighboring two icosahedra within the chain is manifested in the c axis length of this compound (9.5110(7) Å), which is significantly shorter than an axis length (≥ 10 Å) defined by a similar icosahedral B_{12} chain in numerous other icosahedral B_{12} crystals.

It is well known that the intericosahedral bond in boron-rich solids always occurs along one of the quasi-fivefold axes of the icosahedron. Therefore, it is noteworthy that the bonding of the B_{12}-5 icosahedral pair (Fig. 2) is unusual, since the linkage is accomplished through two apical atoms of each icosahedron, forming an approximately square plane (Fig. 7). No such bonding has previously been reported.

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