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Structure Refinement of YB_{62} and YB_{56} of the YB_{66}-Type Structure

Iwami Higashi[1] and Kimiko Kobayashi

The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

and

Takaho Tanaka and Yoshio Ishizawa

National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

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The crystal structure of YB_{62} and YB_{56} of the YB_{66}-type structure (cubic; space group, $Fm3c$) has been studied by single-crystal X-ray diffractometry. The crystals were grown by the indirect heating floating-zone method; YB_{62} ($a = 23.4364(6)$ Å) was obtained by growth at a congruent composition and YB_{56} ($a = 23.4600(9)$ Å) by growth at an incongruent composition. The structure was refined with the aid of a full-matrix least-squares program to the R (R_w) values of 0.069 (0.062) for YB_{62} and 0.075 (0.069) for YB_{56}. The boron framework of the present crystals is almost identical to that of YB_{66} (S. M. Richards and J. S. Kasper, 1969, *Acta Crystallogr.* 25, 237). However, as expected from the chemical compositions of YB_{62} and YB_{56}, obtained by chemical analysis, there is a significant increase in the yttrium site occupancy; 0.532(4) for YB_{62} and 0.575(5) for YB_{56}. A marked anisotropy of thermal parameters was observed for the Y site, suggesting that disordered accommodation of the Y atom in the "Y-hole" has occurred. © 1997 Academic Press

INTRODUCTION

The compound YB_{66}[2] was discovered by Seybolt (1) in 1960 and its structure determined by Richards and Kasper in 1969 (2). The crystal system is cubic with $a = 23.440(6)$ Å, and the space group is $Fm3c$. The boron framework of YB_{66} is basically made up of a 13-icosahedron unit $(B_{12})_{13}$. There are approximately 1584 boron atoms and 24 yttrium atoms in the unit cell. The majority of the boron atoms (1248) belong to eight 13-icosahedron units, and the rest (336) form nonicosahedral cages; the latter are accommodated in a large hole resulting from the arrangement of the giant $(B_{12})_{13}$ units. The yttrium atoms are statistically distributed over 48 sites per unit cell with 0.5 occupancy.

Recently, single crystaline YB_{66} was proved to possess various desirable properties as a soft X-ray monochromator for synchrotron radiation, and high quality YB_{66} single crystals were prepared by Tanaka *et al.* (3, 4). In the present work, therefore, the structure of this compound was reinvestigated by single-crystal X-ray diffractometry using two different crystals, both of which possess significantly different chemical compositions from that (YB_{66}) reported in the literature (2).

EXPERIMENTAL

The crystals were grown by an indirect heating floating-zone method (3, 4). In this method the molten zone is heated by radiation from an inductively heated tungsten ring. The tungsten ring is placed between the work coil and the molten zone. High-quality single crystals were successfully grown by self-flux under an incongruent melting condition, where the chemical composition of the feed rod and the molten zone were controlled to be $[B]/[Y] = 56$ and 40, respectively. This condition lowered the growth temperature compared with that in growing crystals at a congruent composition of $[B]/[Y] = 62$.

Two kinds of specimens for the intensity measurements were selected from the fragments obtained by cracking two crystals, YB_{62} and YB_{56}; the former was grown at the congruent composition and the latter at the incongruent composition. The chemical compositions were determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy).

The reflections were measured with an Enraf–Nonius CAD-4 four-circle diffractometer with Cu$K\alpha$ radiation, monochromated by the use of a graphite monochromator. Crystal data and intensity measurements data are given in

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[1] To whom correspondence should be addressed. Present address: Department of Chemistry, Chiba Institute of Technology, Shibazono, Narashino, Chiba 275, Japan.

[2] As presented in the results of the present work, this type of compound seems to crystallize in a significantly wide range of chemical compositions. In this text, however, the chemical composition YB_{66} is conveniently utilized as the name of this type of crystal phase.

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TABLE 1
Crystal and Intensity Measurement Data

Crystal	YB_{62}[a]	YB_{56}[a]
Crystal system	Cubic	Cubic
Space group	*Fm*3*c*	*Fm*3*c*
a (Å)	23.4364(6)	23.4600(9)
B/Y[b]	62	57
Structural formula[c]	$Y_{3.2}\cdot(B_{12})_{13}\cdot B_{42}$	$Y_{3.5}\cdot(B_{12})_{13}\cdot B_{42}$
D_x (g/cm^2)	2.49(2)	2.53(2)
Z	8	8
μ for Cu$K\alpha$ (cm^{-1})	44.5	48.3
Crystal dimensions (mm)	0.31 × 0.34 × 0.25	0.22 × 0.27 × 0.23
Reflections measured	$0 \le h \le 28$	$0 \le h \le 28$
	$0 \le k \le 28$	$0 \le k \le 28$
	$0 \le l \le 28$	$0 \le l \le 28$
$2\theta_{\max}{}^\circ$	136	136
NR[d]	551	534
NV[e]	106	106

[a] Obtained by chemical analysis.
[b] Obtained by structure analysis.
[c] 24 times the asymmetric unit.
[d] Number of independent reflections.
[e] Number of variable parameters.

TABLE 2
Structure Refinements Using Form Factors for Various Ionization States of the Y Atom

	YB_{62}[a]			YB_{56}[a]		
I. S.[b]	R_w (R)	Occupancy[c]	[B]/[Y]	R_w (R)	Occupancy[c]	[B]/[Y]
Y^{+3}	0.0617 (0.069)	0.532(4)	62	0.0688 (0.075)	0.575(5)	57
$Y^{+2.5}$	0.0620	0.530(4)	62	0.0690	0.572(5)	58
Y^{+2}	0.0623	0.527(4)	63	0.0694	0.569(5)	58
Y^{+1}	0.0631	0.523(4)	63	0.0701	0.563(5)	59
Y^{+0}	0.0641	0.516(4)	64	0.0711	0.558(5)	59

[a] Determined by chemical analysis.
[b] Ionization state.
[c] Occupancy of the Y site.

Table 1. The intensities were corrected for Lorentz and polarization effects. The absorption effects were corrected by the semi-empirical method of North *et al.* (5). Extinction effects were checked in the final stage of structure refinement and found to be negligible. Independent reflections with structure factors larger than 4.0 times the standard deviations were collected by averaging the F_o values for equivalent reflections.

RESULTS AND DISCUSSION

Starting from the published data (2), the structure was refined with the aid of a full-matrix least-squares program (UNICS-III) (6). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weights w were $1/\sigma^2(F_o)$. The R values, $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2\}^{1/2}$, obtained are given in Table 2. 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" (7).

To see whether the Y atoms in the crystals are in an ionized state or not, five kinds of form factors, $f(Y^{3+})$, $f(Y^{+2.5})$, $f(Y^{+2})$, $f(Y^{+})$, and $f(Y)$ were tested in the structure refinement. As $f(Y^{3+})$ and $f(Y)$ were available from the literature (7), $f(Y^{2.5+})$, $f(Y^{2.0+})$, and $f(Y^{+})$ were calculated assuming the relation $f(Y^{n+}) = f(Y) - (n/3)\{f(Y) - f(Y^{3+})\}$. To keep neutrality in the crystals, the charges removed from the neutral Y atom are equally allotted to all the boron atoms, and newly estimated form factors for $B^{\delta-}$ ($\delta < 0.05$) were applied for the B atoms. Since $f(B)$ and $f(B$, He Core) were available in the literature, the form factors for $B^{\delta-}$ were calculated again assuming the relation $f(B^{\delta-}) = f(B) + (\delta/3)\{f(B) - f(B, \text{He Core})\}$.

Table 2 shows the variation of the R_w value, occupancy of the Y site, and the atomic ratio [B]/[Y] with the use of

TABLE 3
Structure Data[a] for YB_{62} and YB_{56}

Atom	Site	*x*	*y*	*z*	Occupancy	$B_{eq.}$(Å^2)[b]
B1[a]	96*j*	0.0	0.0375(3)	0.0600(3)	1.0	0.9(3)
B1[a]	96*i*	0.0	0.0376(4)	0.0599(3)	1.0	0.8(3)
B2	96*i*	0.0	0.0762(3)	0.1172(3)	1.0	1.0(3)
B2	96*i*	0.0	0.0763(4)	0.1169(4)	1.0	0.9(3)
B3	96*i*	0.0	0.0386(3)	0.1815(3)	1.0	0.8(3)
B3	96*i*	0.0	0.0387(3)	0.1815(3)	1.0	0.7(3)
B4	96*i*	0.0	0.1482(3)	0.2421(3)	1.0	0.7(3)
B4	96*i*	0.0	0.1482(3)	0.2419(3)	1.0	0.7(2)
B5	96*i*	0.0	0.1857(3)	0.1718(3)	1.0	0.7(3)
B5	96*i*	0.0	0.1856(3)	0.1716(4)	1.0	0.8(3)
B6	192*j*	0.0391(2)	0.1400(2)	0.1219((2)	1.0	1.0(2)
B6	192*j*	0.0389(2)	0.1400(2)	0.1217((2)	1.0	1.0(2)
B7	192*j*	0.0396(2)	0.0813(2)	0.2296(2)	1.0	0.8(2)
B7	192*j*	0.0397(2)	0.0812(2)	0.2296(2)	1.0	0.7(2)
B8	192*j*	0.0633(2)	0.0773(2)	0.1591(2)	1.0	0.9(2)
B8	192*j*	0.0631(2)	0.0773(2)	0.1590(2)	1.0	0.8(2)
B9	192*j*	0.0637(2)	0.1458(2)	0.1950(2)	1.0	0.9(2)
B9	192*j*	0.0635(3)	0.1457(2)	0.1947(3)	1.0	0.9(2)
B10	192*j*	0.1319(4)	0.1745(4)	0.1964(5)	0.72(2)	2.6(5)
B10	192*j*	0.1318(5)	0.1745(4)	0.1960(6)	0.71(3)	2.7(6)
B11	192*j*	0.2341(7)	0.1582(6)	0.3000(7)	0.66(2)	6.1(9)
B11	192*j*	0.2329(8)	0.1586(6)	0.3004(8)	0.64(2)	5.8(1.0)
B12	192*j*	0.1726(8)	0.1282(7)	0.2590(10)	0.30(3)	1.9(1.1)
B12	192*j*	0.1734(11)	0.1279(7)	0.2588(14)	0.33(3)	3.3(1.4)
B13	64*g*	0.2363(9)	*x*	*x*	0.23(2)	1.4(5)
B13	64*g*	0.2362(12)	*x*	*x*	0.22(2)	1.7(6)
Y	48*f*	0.05629(7)	1/4	1/4	0.532(4)	1.52(6)
		($\beta_{11} = 0.00095(4)$	$\beta_{22} = \beta_{33} = 0.00056(2)$[c]			
Y	48*f*	0.05789(9)	1/4	1/4	0.575(5)	2.09(7)
		($\beta_{11} = 0.00157(5)$	$\beta_{22} = \beta_{33} = 0.00064(3)$)[c]			

[a] The first data are for YB_{62} and the second for YB_{56}.
[b] Equivalent isotropic temperature factors are calculated from the relation $B_{eq.} = 4/3 \cdot a^2(\beta_{11} + \beta_{22} + \beta_{33})$.
[c] The anisotropic temperature factor has the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

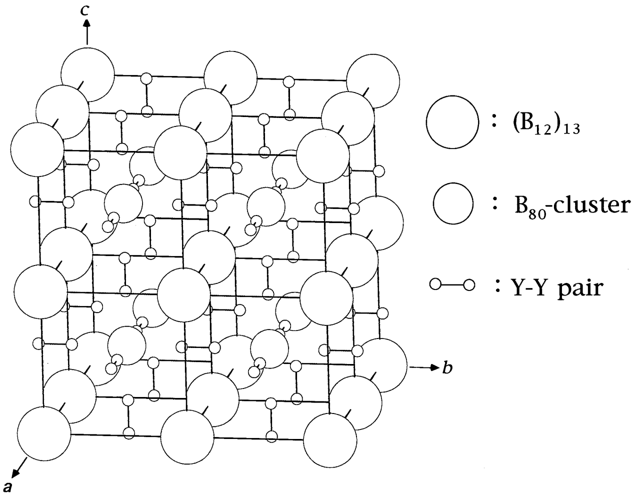

FIG. 1. Arrangement of $(B_{12})_{13}$ units, B_{80} clusters, and Y–Y pairs.

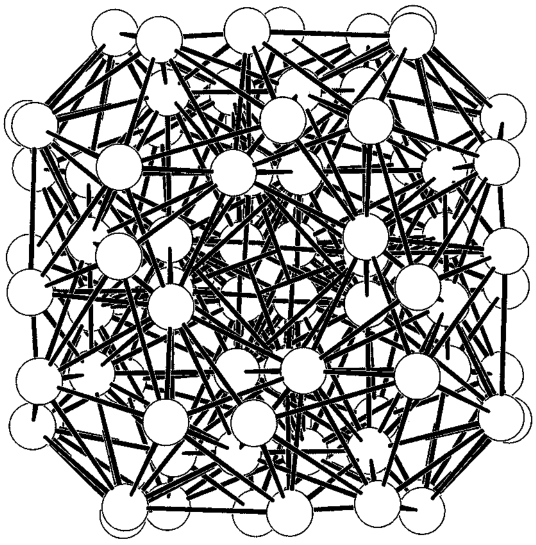

FIG. 3. B_{80} cluster as seen along the fourfold axis. This cluster consists of 80 boron sites belonging to four crystallographic positions (B10–B13 in Table 3). In this cluster, all the sites are partially occupied, and thus actual number of boron atoms within the cluster is about 42.

various form factors for the Y atom. The R_w values have converged to within 0.1%. The results of the structure refinement suggest that the Y atom is in an ionized state (possibly in the Y^{3+} state); with an increase in charge number, R_w decreases and the atomic ratio approaches YB_{62} or YB_{56} determined by chemical analysis.

The final structural data of YB_{62} and YB_{56}, obtained by using the form factors of Y^{3+} and the corresponding ones of $B^{+\delta}$, are compared in Table 3. The boron framework of the present crystals is almost identical to that reported in the literature (2). Although the YB_{66} structure has been described in detail by Richards and Kasper (2), a brief description will be given here to facilitate the discussion. As shown in Fig. 1, the boron framework is composed of the 13-icosahedron unit $(B_{12})_{13}$ (Fig. 2) and the B_{80} cluster (Fig. 3). The $(B_{12})_{13}$ units are located in one orientation at the face-centered cubic lattice points. It also occurs at the centers of the cell and the cell edges rotated by 90° (Fig. 4). As a consequence, there are eight $(B_{12})_{13}$ units (1248 boron

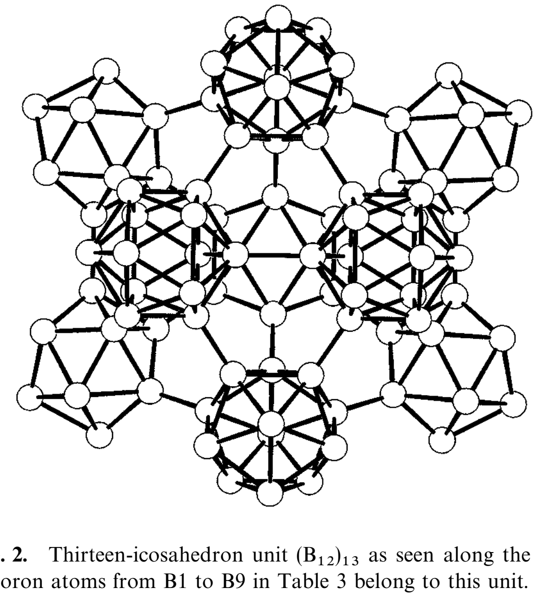

FIG. 2. Thirteen-icosahedron unit $(B_{12})_{13}$ as seen along the twofold axis. Boron atoms from B1 to B9 in Table 3 belong to this unit.

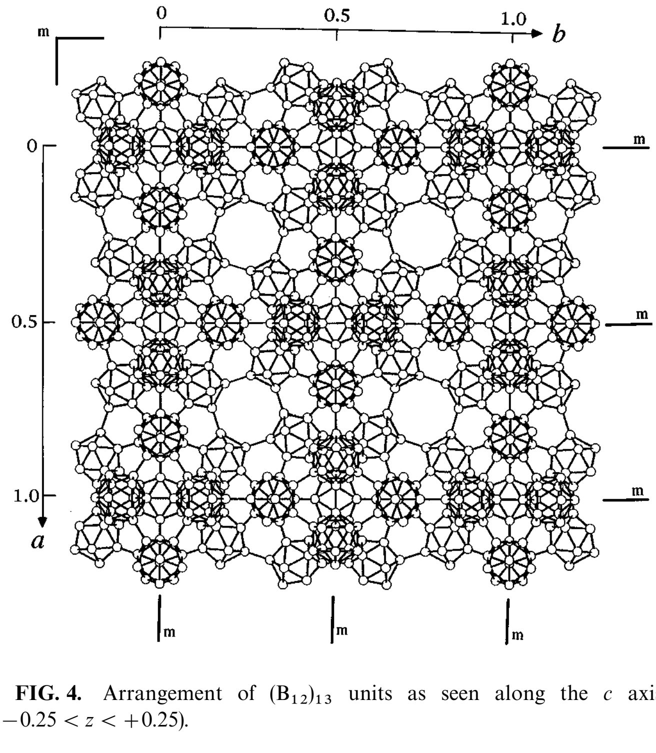

FIG. 4. Arrangement of $(B_{12})_{13}$ units as seen along the c axis $(-0.25 < z < +0.25)$.

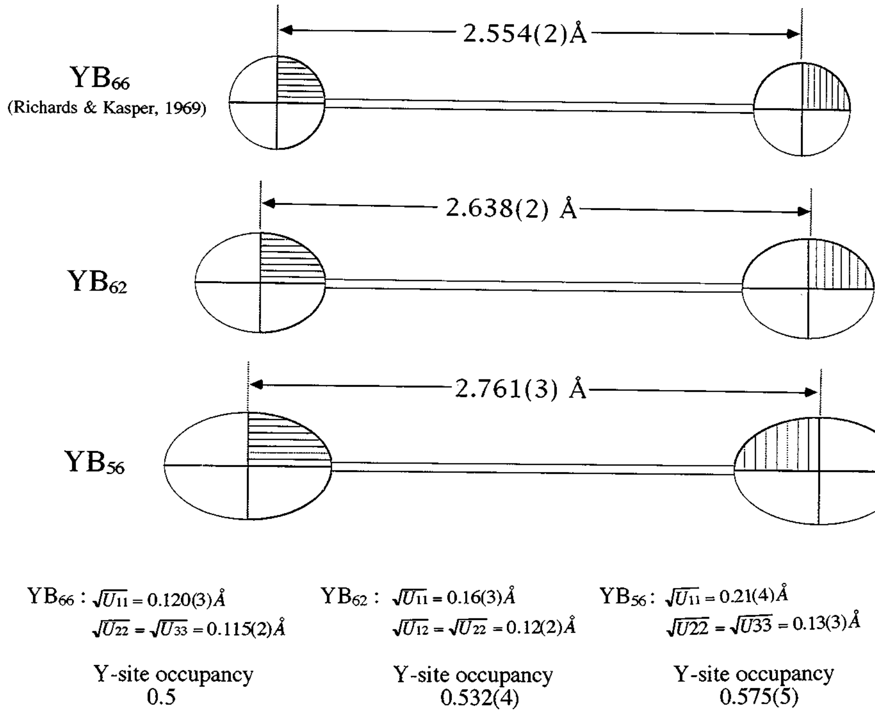

FIG. 5. Comparison of Y–Y distances and thermal displacement along the principal axes of thermal motion of the Y atom in YB_{66}, YB_{62}, and YB_{56}. Thermal ellipsoids are drawn at the 70% probability level.

atoms) in one unit cell. The B_{80} cluster consists of 80 boron sites belonging to four crystallographic positions of the space group *Fm*3*c*: (3 × 192*j*, 64*g*)/8. In this cluster, however, all the positions are partially occupied with occupancies ranging from 28 to 71% (Table 3), and the actual number of boron atoms within the B_{80} cluster is about 42, in agreement with the literature (2). The B_{80} cluster is centered at the 8*a* position (1/4, 1/4, 1/4), and thus there are eight B_{80} clusters (336 B atoms) per unit cell. As a result, the total number of boron atoms per unit cell is the same as that determined in the literature (2). However, as expected from the chemical compositions YB_{62} and YB_{56}, obtained by chemical analysis, there is a significant increase in the yttrium site occupancy; 0.532(4) for YB_{62} and 0.575(5) for YB_{56}. The chemical compositions obtained by the structure refinement are almost the same as those obtained by chemical analysis. The Y sites are enclosing the B_{80} cluster in an octahedral form. Consequently, there are eight octahedral Y arrangements per unit cell. Each of the octahedral arrangements can be connected to neighboring six octahedra through its apical Y sites. Such a connection is indicated in Fig. 1 as a Y–Y pair.

A marked anisotropic feature of thermal parameters was observed for both crystals. In Fig. 5, Y–Y distances and thermal displacement along the principal axes of thermal motion of the Y atom in YB_{66}, YB_{62}, and YB_{56}, are compared. The occupancies of the three sites are 0.5, 0.532(4), and 0.575(5), respectively. Therefore, some simultaneous occupation of neighboring Y–Y sites in the present crystals is inevitable. Since the atomic and ionic radius for Y and Y^{3+} are 1.82 and 0.92 Å, respectively (8), simultaneous occupation of the Y sites is allowed only for ionized Y atoms. This is consistent with the results of the structure refinement (Table 2). When the Y–Y sites are occupied simultaneously by ionized Y atoms, the Y ions may exert a repulsive force on their counterpart and thus the position of the Y ions will shift in the opposite direction to their counterparts, resulting in a longer Y–Y distance. This may cause a disordered accommodation of the Y atom in the "Y-hole" (static disorder), giving apparently significant anisotropic thermal motion with the longest thermal displacement along the Y–Y direction. In the literature (2) approximately isotropic thermal parameters were reported. This is ascribable to the 50% occupation of the Y site which enables the Y–Y site pair to avoid the simultaneous occupation.

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