Novel ternary Y-B-C compound: $Y_{10+x}B_7C_{10-x}$ (x \approx 0.1)

Takaho Tanaka, Akira Sato, Katsuaki Watanabe, Masahiro Nagao, Yoshio Matsui, Tetsuya Kawashima and Takashi Aizawa

National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: TANAKA.Takaho@nims.go.jp

Abstract. A novel ternary Y-B-C compound $Y_{10+x}B_7C_{10-x}$ is established. $Y_{10+x}B_7C_{10-x}$ has a monoclinic crystal structure with space group $C_{2/c}$ (No.15) and lattice constants a = 1.1273(14) nm, b = 1.1159(14) nm, c = 2.3566(30)nm and $\beta = 98.15(2)^{\circ}$. $Y_{10+x}B_7C_{10-x}$ crystal rods were grown by floating zone technique and consisted of a predominant crystal phase and impurity phases. A small crystal having sufficient quality for single crystal XRD analysis could be selected. Structure refinement achieved a final R1 = 0.044 for 1660 independent reflections with $F_o > 4\sigma(F_o)$. 10 Y sites, 8 B sites, 9 C sites and one C/Y mixed occupancy site with about 0.9/0.1 occupation ratio were assigned. The unit chemical formula is $Y_{10+x}B_7C_{10-x}$ (x ≈ 0.1), and the unit cell contains 8 formula units. $Y_{10+x}B_7C_{10-x}$ has a layer structure: Y-C double layers, in which Y and C bond alternatively like in the NaCl structure, spread parallel to the (001) plane and stack along the c-axis. The Y-C double layer is connected to the neighboring Y-C double layers via C-B-C chains or C-B-B-C chains. This structure was confirmed by electron diffraction and high-resolution electron microscopy. Magnetic susceptibility measurement indicated that the $Y_{10+x}B_7C_{10-x}$ phase has no superconductivity above 2 K. A minor superconducting phase with $T_c=7.5$ K was observed, but ascribed to an unidentified impurity phase.

1. Introduction

Ternary rare-earth-boron-carbon compounds have attracted continuous scientific interests because of a variety of structures and chemical and physical properties [1]. Discovery of a new intermetallic compound may relate to useful functional properties such as superconductivity and high-efficiency thermoelectric energy conversion. For example, Y_2C_3 exhibits superconductivity bellow a relatively high T_c of 18 K [2, 3]. The recent discovery of superconductivity in the Fe-based layered pnictide oxide has explosively raised interest to intermetallic compounds among the superconductivity researchers [4].

We have reported a ternary Sc-B-C compound $Sc_2B_{1,1}C_{3,2}$ that has a hexagonal layer structure, and resembles to graphite-intercalation-compounds [5, 6]. In its crystal

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structure, a Sc₂C layer is sandwiched along the *c*-axis by graphite-like BC₂ layers, in which the unit lattice of the Sc₂C layer and the unit lattice of the BC₂ layer commensurately order with a ratio of 7:9. Sc₂B_{1.1}C_{3.2} shows graphite intercalation compound like behavior [7]. It must be interesting whether or not other rare-earth elements can form an isotypic compound with Sc₂B_{1.1}C_{3.2} by replacing Sc.

Bauer and Nowotony have reported the Y-B-C ternary phase diagram [8], where they have established three ternary phases of YBC, YB₂C₂ and YB₂C. In addition, they have reported the existence of Y₂BC₂ that melts congruently; however, they did not determine the crystal structure. Because of similarity of compositions between $Sc_2B_{1,1}C_{3,2}$ and Y₂BC₂ we may expect that Y₂BC₂ is isotypic with $Sc_2B_{1,1}C_{3,2}$. Meanwhile Rogl has suggested that Y₂BC₂ might rather be Y₅B₂C_{6+x} or Y₂BC₃ and exhibit isotypism with the homologous holmium-containing phases [1].

Here we describe the discovery of $Y_{10+x}B_7C_{10-x}$ (x ≈ 0.1), which was initially recognized as Y_2BC_2 by Bauer and Nowotony [8]. $Y_{10+x}B_7C_{10-x}$ has a new layer structure that is isotypic with neither $Sc_2B_{1.1}C_{3.2}$ nor $Y_5B_2C_{6+x}$ or Y_2BC_3 ; however, a structural similarity to the latter could be seen.

2. Experimental

We tried to grow single crystal by floating zone technique using a double halogen-lamp image furnace (Ascal Co., Ltd.). The feed rod for the floating zone crystal growth was prepared by arc-melting method using elemental sources of Y (Furuuchi-Kagaku Inc., flake, nominal purity 99.9%), B (Yamanaka Chem., Inc., granular, nominal purity 98%) and C (Nippon Carbon Co., granular graphite, nominal purity 99.9%). A raw material with composition of Y_2BC_2 was firstly synthesized by the arc-melting method turning the arc-melted button several times to obtain uniform composition. It was then cracked into several pieces, which were put in a groove of a water-cooled Cu plate of the arcmelting furnace. Successive arc-zone-melting through the groove produced a feed rod, 6 mm in diameter and 60 mm long, for the floating zone crystal growth. The crystal growth was carried out under a flowing Ar gas atmosphere using a growth rate of 7 mm/h and a counter-rotation of the growing crystal and the feed rod at ±20 rpm. Similar to rare-earth carbides, the obtained compound was unstable under ambient atmosphere. Therefore, the samples were stored in an airtight sample storage or in kerosene.

A single-crystal specimen for single-crystal X-ray diffraction (XRD) data collection could be obtained by cracking a part of the grown crystallite. The specimen was covered by a nail varnish to shield from atmosphere before the data collection. The single-crystal XRD data were collected by an Enraf-Nonius CAD4 automatic 4-circle diffractometer with graphite-monochromated MoK? radiation. The crystal data and XRD measurement parameters are given in table 1. The intensity data were corrected for Lorentz and polarization effects. The absorption correction applied to the collected data was empirical, based on Ψ -scans.

Crystal system	Monoclinic
Space group	C2/c (No.15)
Lattice constants	a = 1.1273(14), b = 1.1159(14), c = 2.3566(30) nm
	$\alpha = 90^{\circ}, \beta = 98.15(2)^{\circ}, \gamma = 90^{\circ}$
Unit cell volume	2.9346 nm^3
Unit chemical formula	$Y_{10+x}B_7C_{10-x} \ (x\approx 0.1)$
Z	8
$Dx (g/cm^3)$	4.946
μ for MoK α (cm ⁻¹)	389.0
Crystal dimensions (mm)	$0.3 \times 0.15 \times 0.1$
$2\theta_{max}$ (deg)	53.80
Reflection measured	$-12 \le h \le 13, -14 \le k \le 13, -29 \le l \le 26$
Structure refinement program	SHELXL97
R1	0.044 for 1660 $(F_o > 4\sigma(F_o))$, 0.089 for 2601 (all F_o)
wR2	$0.117(F^2)$
Number of variables	166

 Table 1. Crystallographic and data collection parameters.

The initial structure was solved by applying the direct method SIR92 to the data set assuming Y, B and C atoms in the unit cell [9]. The structure was refined using SHELXL97 program [10] and visualized using the crystallographic program CrystalMaker [11].

The high-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) observations were carried out on a Hitachi H-1500 instrument operated at 800 kV. HRTEM image simulation by multislice method was performed using WinHREM simulation package (HREM Research Inc.) [12].

The magnetic susceptibility measurements were performed using a SQUID magnetometer (Quantum Design, MPMS) at a magnetic field of 10 Oe in the temperature range from 2 to 20 K by zero field cooling (ZFC) and field cooling (FC) processes.

3. Results and discussion

Inspection under optical microscope for the cracked surface of the rod grown by the floating zone method indicated that the rod consisted of mm-size thin crystallites and much smaller inclusions. The thin crystallites had large flat cleavages as compared with its thickness, which suggested a layer characteristic of the crystallites. The inclusions were not identified.

3.1. Structure analysis

An initial solution was obtained according to a monoclinic crystal structure with the space group C2/c (No.15) and lattice constants a = 1.1273(14) nm, b = 1.1159(14) nm, c = 2.3566(30) nm, $\alpha = 90^{\circ}$, $\beta = 98.15(2)^{\circ}$ and $\gamma = 90^{\circ}$. The solution gave 28 atomic positions in which eleven Y sites, eight B sites and nine C sites were assigned. Visualization of the crystal structure suggested that one Y site with partial occupancy should be assigned as a carbon site; however, the electron density was too high for a carbon site, and thus the site was assigned as a C/Y mixed occupancy site. The final refinement of 166 parameters for 1660 independent reflections ($F_o > 4\sigma(F_o)$) resulted in an R1 value of 4.4% and 8.9% for all 2601 independent reflections. The final atomic coordinates, occupancy factors and temperature factors are listed in table 2. All sites, except for the B6 and B8 sites that have the 4e site symmetry, are general positions (8f); thus, the number of atoms that accommodate at the B6 and B8 sites is half of others and unit chemical formula can be described as $Y_{10+x}B_7C_{10-x}$ ($x\approx0.1$). There are eight formula units per unit cell. The occupancy ratio of C:Y at the C/Y mixed occupancy site is approximately 0.91:0.09.

The interatomic distances are summarized in table 3. The Y-C bond distances range from 0.224 to 0.274 nm. As will be discussed later, $Y_{10+x}B_7C_{10-x}$ has a layer structure in which layers are composed of Y and C, span parallel to the a - b plane and stack along the *c*-axis. The Y-C bond distances within the layers are approximately 0.25 nm, which is comparable to that (0.248 nm) in the binary Y₂C compound [13]. On the other hand, the Y-C distances perpendicular to the Y-C layers vary largely from 0.224 to 0.274 nm due to the irregular thickness of the Y-C layers. $Y_{10+x}B_7C_{10-x}$ has two chain structures of C-B-C and C-B-B-C. The C-B bond distances within both the C-B-B-C and C-B-C chains range from 0.1444 to 0.1482 nm and are normal to a C-B bond distance. The B-B distances range from 0.1925 to 0.2127 nm, which is rather large compared with typical B-B bond distances of 0.17-0.19 nm.

3.2. Structure description

The obtained crystal structure viewed close to the [110] direction is shown in figure 1(a). As expected, $Y_{10+x}B_7C_{10-x}$ has a layered structure. Y-C double layers, in which Y and C alternatively bond like the NaCl structure, are dominant. The Y-C double layers spread parallel to the (001) plane and stack along the *c*-axis. A Y-C double layer is shown in figure 1(b).; it is connected to neighbor Y-C double layers via C-B-C chains or C-B-B-C chains.

A Y-C double layer connected by the C-B-C chains to another Y-C double layer mutually rotates 45° along the *c*-axis. Distance between the Y-C double layers is approximately 0.293 nm. C atoms in the Y-C double layer face to C atoms in the counter Y-C layer; thus, they can form a C-B-C chain. The C/Y mixed occupancy site should be originally a C site to maintain the alternative bonding scheme between Y and C atoms, as shown in figure 1(a) by a blue arrow. However, the counter part of the C/Y

mixed occupancy site is not a C site but a Y site, which does not allow forming a C-B-C chain and changes it from the C site to the C/Y mixed occupancy site. On the contrary, the Y-C double layers connected by the C-B-B-C chains are parallel each other along C and Y atoms alignment, thus, the C-B-B-C chains regularly line up forming an infinite zigzag B chain, as can be seen in figure 1(a). Distance between the double layers connected by the C-B-B-C chains is much longer than that connected by the C-B-C chains and is approximately 0.36 nm.

Atom	Site	x/a	y/b	z/c	Occ.	$U_{eq}(\text{\AA}^2 \times 10^3)$
Y1	8f	0.4030(1)	0.2766(1)	0.4247(1)	1	0.0078(3)
Y2	8f	0.4665(1)	0.0715(1)	0.3194(1)	1	0.0069(3)
Y3	8f	0.3033(1)	-0.0252(1)	0.4281(1)	1	0.0078(3)
Y4	8f	0.3667(1)	-0.2206(1)	0.3194(1)	1	0.0063(3)
Y5	8f	0.4989(1)	0.4243(1)	0.5752(1)	1	0.0078(3)
Y6	8f	0.1750(1)	0.1707(1)	0.3198(1)	1	0.0067(3)
Y7	8f	0.7018(1)	0.1736(1)	0.4245(1)	1	0.0082(3)
$\mathbf{Y8}$	8f	0.1037(1)	0.3749(1)	0.4245(1)	1	0.0076(3)
Y9	8f	0.5751(1)	0.3787(1)	0.3197(1)	1	0.0068(3)
Y10	8f	0.2682(1)	0.4752(1)	0.3100(1)	1	0.0088(3)
C/Y	8f	0.2703(6)	-0.0245(7)	0.3155(3)	0.911/0.089(5)	0.0260(27)
C1	8f	0.6010(9)	0.2251(9)	0.5840(4)	1	0.0057(21)
C2	8f	0.1988(9)	0.1750(9)	0.4159(4)	1	0.0078(23)
C3	8f	0.6651(9)	0.1756(9)	0.3084(5)	1	0.0091(23)
C4	8f	0.5668(9)	-0.1271(7)	0.3069(5)	1	0.0082(23)
C5	8f	0.4992(9)	0.0756(7)	0.4165(4)	1	0.0081(22)
C6	8f	0.3700(9)	0.2740(10)	0.3074(5)	1	0.0126(25)
C7	8f	0.5984(9)	0.3745(9)	0.4165(5)	1	0.0100(23)
C8	8f	0.2998(9)	0.4746(10)	0.4110(4)	1	0.0100(21)
C9	8f	0.4686(9)	-0.4234(9)	0.3075(5)	1	0.0096(23)
B1	8f	0.3154(12)	0.4753(13)	0.4742(6)	1	0.0206(29)
B2	8f	0.2806(13)	0.3198(13)	0.5212(7)	1	0.0269(35)
B3	8f	0.5185(13)	0.0750(12)	0.4788(6)	1	0.0244(33)
B4	8f	0.5820(13)	0.2307(13)	0.5214(6)	1	0.0240(33)
B5	8f	0.6149(13)	0.3736(13)	0.4800(7)	1	0.0256(34)
B6	4e	0.5	-0.1216(14)	0.25	1	0.0072(34)
B7	8f	0.6537(11)	0.2268(11)	0.2513(6)	1	0.0122(26)
B8	4e	0.5	-0.4290(16)	0.25	1	0.0170(41)

Table 2. Atomic coordinates, site occupancy and isotropic displacement parameters.

Y10-C/Y

2.926(8)

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Y1-C7	2.491(11)	Y2-C5	2.265(11)	¥3-C1	2.512(10)	
-C8	2.497(11)	-C/Y	2.447(7)	-C2	2.522(10)	
-C5	2.510(10)	-C6	2.507(11)	-C5	2.527(10)	
-C2	2.547(10)	-C4	2.524(10)	-C7	2.547(11)	
-C6	2.736(12)	-C3	2.568(10)	-C/Y	2.628(7)	
Y4-C1	2.255(11)	Y5-C1	2.498(10)	Y6-C2	2.244(11)	
-C/Y	2.439(8)	-C8	2.514(11)	-C/Y	2.437(8)	
-C3	2.532(10)	-C7	2.518(10)	-C9	2.532(11)	
-C4	2.540(10)	-C2	2.525(10)	-C6	2.535(11)	
-C9	2.571(10)	-C9	2.737(11)	-C4	2.563(10)	
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Y7-C5	2.515(10)	Y8-C2	2.495(10)	Y9-C7	2.258(11)	
-C8	2.520(11)	-C5	2.526(10)	-C/Y	2.466(7)	
-C7	2.522(11)	-C8	2.534(11)	-C9	2.511(10)	
-C1	2.527(10)	-C1	2.545(10)	-C3	2.513(10)	
-C3	2.708(11)	-C4	2.743(11)	-C6	2.571(11)	
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Y10-C8	2.357(10)					
-C3	2.518(10)					
-C6	2.527(11)					
-C4	2.532(11)					
-C9	2.536(11)					
	X /					
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Table 3. Interatomic distances (described in $\times 10^{-1}$ nm=Å unit).

Bonds in C-B-B-C chain					
C1-B4	1.461(17)	B1-B2	2.127(21)	B4-B5	1.933(20)
C2-B2	1.467(18)	B1-B5	2.095(20)		
C5-B3	1.454(18)	B2-B2	1.925(29)		
C7-B5	1.482(18)	B3-B3	2.022(28)		
C8-B1	1.474(16)	B3-B4	2.083(20)		
Bonds in C-B-C chain					
C3-B7	1.451(16)	C4-B6	1.444(11)	C6-B7	1.468(16)
C9-B8	1.450(11)				

C/Y mixed occupancy sites or vacancy sites in (rare earth)-boron-carbon compounds often exhibit ordering. We examined the possibility of the ordering of the



Figure 1. (a) Crystal structure of $Y_{10+x}B_7C_{10-x}$ viewed close to the [110] direction. Red, green and black spheres correspond to Y, B and C atoms, respectively. Blue arrow indicates one of the C/Y mixed occupancy sites. (b) Y-C double layer viewed close to the [111] direction.

present C/Y mixed occupancy site, which may appear by solving the crystal structure using a lower symmetry space group than C2c (No.15). Extinction rule allowed us to use an alternative space group of Cc (No. 9). The structure refinement did not show any evidences of the ordering, thus we concluded that C and Y atoms are randomly distributed over the C/Y mixed occupancy sites.

Structural similarity can be seen in Ho₅B₂C_{6+x} [14] and Th₃B₂C₃ [15]. Ho₅B₂C_{6+x} has a tetragonal structure (P4), where Ho and C form a double layer. In that layer, Ho and C bond alternatively forming a tetragonal network and incorporating C₂ dumbbells that can be seen in CaC₂. The Ho-C double layer stacks along the *c*-axis and connects each other by C-B-C chains. Th₃B₂C₃ has a monoclinic structure (P2/m), where Th and C form a NaCl-like triple layer that stacks along the *c*-axis. The Th-C triple layers are connected by the C-B-B-C chains. Thus, $Y_{10+x}B_7C_{10-x}$ structure can be understood as an admixture of Ho₅B₂C_{6+x} and Th₃B₂C₃ structures or, in a broad sense, to be homologous to them. This makes the crystal structure of $Y_{10+x}B_7C_{10-x}$ more complicated, with a much larger unit cell size than those other two structures.

Very recently, Babizhetsky [16] has refined crystal structure of $RE_{10}B_7C_{10}$ (RE = Gd - Er) that appears to be isotypic to $Y_{10+x}B_7C_{10-x}$ because they all have a monoclinic crystal structure with same space group and approximately same lattice constants. This



Figure 2. HRTEM image of $Y_{10+x}B_7C_{10-x}$ taken for the incident beam parallel to the [010] direction. The right-top inset indicates an ED pattern taken along this direction, and a computer simulation image of the proposed structure is shown in the bottom-right inset.

similarity is plausible because Y and Gd - Er have similar chemical nature and atomic radii.

3.3. HRTEM and Ed observations

Figure 2 presents an HRTEM lattice image for the incident electron beam close to the [010] direction. The image clearly reveals the layered structure of the compound.

In the computer-simulated image, the black double layer separated by a thin white line corresponds to the Y-C double layer. The bright, continuous white line corresponds to the C-B-B-C chain layer and the weaker white line with periodical intensity variation corresponds to the C-B-C chain layer. The observed lattice image is reproduced well by the simulation. Bundles with four black double layers are separated by 2.3 nm, which is consistent with the lattice constant c = 2.36 nm obtained by XRD. All these facts confirm the $Y_{10+x}B_7C_{10-x}$ crystal structure proposed by the XRD structure analysis. Note that ED analysis along the [010], [100], [110] and [001] axes indicated no evidence of the ordering of the C/Y mixed occupancy site.



Figure 3. Temperature dependence of magnetic susceptibility of $Y_{10+x}B_7C_{10-x}$

3.4. Magnetization measurement

The measured magnetic susceptibility is shown in figure 3. Superconducting transition can be seen at 7.5 K; however, the observed magnetic susceptibility is of the 10^{-6} emu/g order, which is too small for bulk superconductivity. We attributed this superconductivity to an unidentified impurity phase and concluded that $Y_{10+x}B_7C_{10-x}$ does not exhibit superconductivity above 2 K.

4. Conclusions

We established a new yttrium borocarbide $Y_{10+x}B_7C_{10-x}$ (x ≈ 0.1) that has previously [8] been reported as Y₂BC₂. Crystal structure of Y_{10+x}B₇C_{10-x} is monoclinic (space group C2/c (No.15) and lattice constants a = 1.1273(14) nm, b = 1.1159(14) nm, c = 2.3566(30) nm and $\beta = 98.15(2)^{\circ}$), and it is "homologous" to Ho₅B₂C_{6+x} and Th₃B₂C₃. Y_{10+x}B₇C_{10-x} does not exhibit superconductivity above 2 K.

This result does not completely deny our expectation that a ternary Y-B-C compound isotypic to $Sc_2B_{1,1}C_{3,2}$ may exist. During the course of this investigation we noticed an unidentified compound whose composition is close to $Y_{10+x}B_7C_{10-x}$. Electron diffraction analysis revealed that the compound has a hexagonal structure with a = 0.94 nm. The compound may be responsible for the superconductivity shown in figure 3.

Acknowledgement

T. T. thanks Mr. E. Bannai, NIMS for technical support on the arc-melting and floating zone crystal growth processes.

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