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

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Abstract. A novel ternary Y-B-C compound $Y_{10x}B_7C_{10-x}$ is established. $Y_{10x}B_7C_{10-x}$ has a monoclinic crystal structure with 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 $\beta = 98.15(2)^\circ$. $Y_{10x}B_7C_{10-x}$ 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 $R_I = 0.044$ 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 $Y_{10x}B_7C_{10-x}$ (x=0.1), and the unit cell contains 8 formula units. $Y_{10x}B_7C_{10-x}$ 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 $Y_{10x}B_7C_{10-x}$ 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$_2$B$_{11}$C$_{12}$ that has a hexagonal layer structure, and resembles to graphite-intercalation-compounds [5,6]. In its crystal structure, a Sc$_2$C layer is sandwiched along the c-axis by graphite-like BC$_2$ layers, in which the unit lattice of the Sc$_2$C layer and the unit lattice of the BC$_2$ layer commensurately order with a ratio of 7:9. Sc$_2$B$_{11}$C$_{12}$ shows graphite intercalation compound like behavior [7]. It must be interesting whether or not other rare-earth elements can form an isotypic compound with Sc$_2$B$_{11}$C$_{12}$ by replacing Sc.

Bauer and Nowotny have reported the Y-B-C ternary phase diagram [6], where they have established three ternary phases of YBC, YB$_2$C$_2$ and YB$_3$C. In addition, they have reported the existence of Y$_2$BC$_2$ that melts congruently; however, they did not determine the crystal structure. Because of similarity of compositions between Sc$_2$B$_{11}$C$_{12}$ and Y$_2$BC$_2$ we may expect that Y$_2$BC$_2$ is
isotypic with Sc₂B₁₃C₃₂. Meanwhile Rogl has suggested that Y₂BC₃ might rather be Y₂B₃C₆₆ or Y₂BC₁ and exhibit isotypism with the homologous holmium-containing phases [1].

Here we describe the discovery of Y₁₀₄B₇C₁₀₄ (x=0.1), which was initially recognized as Y₂BC₃ by Bauer and Nowotony [8]. Y₁₀₄B₇C₁₀₄ has a new layer structure that is isotypic with neither Sc₂B₁₃C₃₂ nor Y₃B₂C₆₆ or Y₂BC₁; 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 Y₂BC₁ 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 arc-melting 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 MoKα 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.

| Crystallographic and data collection parameters |
|-----------------------------------------------|
| Crystal system                               | Monoclinic                        |
| Space group                                  | C2/c (No.15)                     |
| Lattice constants                            | a = 1.1273(14), b = 1.1159(14), c = 2.3566(30) nm |
|                                              | α = 90°, β = 98.15(2)°, γ = 90°   |
| Unit cell volume                             | 2.9346 nm³                       |
| Unit chemical formula                        | Y₁₀₄B₇C₁₀₄ (x=0.1)               |
| Z                                             | 8                               |
| D₀ (g/cm³)                                   | 4.946                           |
| μ for MoKα (cm⁻¹)                            | 389.0                           |
| Crystal dimensions (mm)                      | 0.3 × 0.15 × 0.1                 |
| 2θ_max (deg)                                 | 53.80                           |
| Reflection measured                          | -12 ≤ h ≤ 13, -14 ≤ k ≤ 13, -29 ≤ l ≤ 26 |
| Structure refinement program                 | SHELXL97                        |
| R1                                            | 0.044 for 1660 (Fᵣ > 4σ(Fᵣ)), 0.089 for 2601 (all Fᵣ) |
| wR2                                          | 0.117(F²)                       |
| Number of variables                          | 166                             |

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 \(a = 1.1273(14) \text{ nm}, b = 1.1159(14) \text{ nm}, c = 2.3566(30) \text{ nm}, \alpha = 90^\circ, \beta = 98.15(2)^\circ \text{ and } \gamma = 90^\circ.\) 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 CY mixed occupancy site. The final refinement of 166 parameters for 1660 independent reflections \((F_o>4\sigma(F_o))\) resulted in an \(R_I\) value of 4.4% and 8.9% for

| Atom | Site | \(x/a\) | \(y/b\) | \(z/c\) | Occup. | \(U_{eq}(\text{Å}^2)\times10^4\) |
|------|------|--------|--------|--------|--------|-------------------------------|
| 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) |
| 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) |
| CY   | 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) |
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 $Y_{10x}B_2C_{10x}$ ($x\approx0.1$). 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, $Y_{10x}B_2C_{10x}$ 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 $Y_3C$ compound [13]. On the other hand, the Y-C distances perpendicular to the Y-C layers vary largely.

### Table 3. Interatomic distances (described in $\times10^{-1}$ nm=Å unit)

| Bonds between $Y$ and $C$ | 2.491(11) | 2.655(11) | 2.512(10) |
|---------------------------|-----------|-----------|-----------|
| Y1-C7                     | Y2-C5     | Y3-C1     |
| -C8                       | 2.497(11) | 2.447(7)  | -C2       |
| -C5                       | 2.510(10) | 2.507(11) | -C5       |
| -C2                       | 2.547(10) | 2.524(10) | -C7       |
| -C6                       | 2.736(12) | 2.568(10) | -C/Y      |
|                           |           |           |           |
| Y4-C1                     | 2.255(11) | 2.498(10) | 2.244(11) |
| -C/Y                      | 2.439(8)  | 2.514(11) | -C/Y      |
| -C3                       | 2.532(10) | 2.518(10) | -C9       |
| -C4                       | 2.540(10) | 2.525(10) | -C6       |
| -C9                       | 2.571(10) | 2.737(11) | -C4       |
|                           |           |           |           |
| Y7-C5                     | 2.515(10) | 2.495(10) | 2.258(11) |
| -C8                       | 2.520(11) | 2.526(10) | -C/Y      |
| -C7                       | 2.522(11) | 2.534(11) | -C9       |
| -C1                       | 2.527(10) | 2.545(10) | -C3       |
| -C3                       | 2.708(11) | 2.743(11) | -C6       |
|                           |           |           |           |
| Y10-C8                    | 2.357(10) |           |           |
| -C3                       | 2.518(10) |           |           |
| -C6                       | 2.527(11) |           |           |
| -C4                       | 2.532(11) |           |           |
| -C9                       | 2.536(11) |           |           |

**Direct bond between $Y$-$C$ double layers**

| Y10-C/Y2.926(8) |

**Bonds in C-B-B-C chain**

| Bond  | Distance (Å) |
|-------|--------------|
| C1-B4 | 1.461(17)    |
| C2-B2 | 1.467(18)    |
| C5-B3 | 1.454(18)    |
| B1-B2 | 2.127(21)    |
| B1-B5 | 2.095(20)    |
| B2-B2 | 1.925(29)    |
| B4-B5 | 1.933(20)    |
from 0.224 to 0.274 nm due to the irregular thickness of the Y-C layers. Y_{10x}B_xC_{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_{10x}B_xC_{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.

![Figure 1](image-url)

Figure 1. (a) Crystal structure of Y_{10x}B_xC_{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.
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.

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 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.

![Figure 2](image_url)

Figure 2. HRTEM image of Y10x6B10-C10x4 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.

Structural similarity can be seen in Ho2B5C3 [14] and Th2B3C3 [15]. Ho2B5C3 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. Th2B3C3 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 \( HoB_7C_{6+x} \) and \( ThB_7C_3 \) 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 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.

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.

![Figure 3. Temperature dependence of magnetic susceptibility of \( Y_{10+x}B_7C_{10-x} \).](image-url)
4. Conclusions

We established a new yttrium borocarbide $Y_{10x}$B$_x$C$_{10-x}$ (x=0.1) that has previously [8] been reported as $Y_2$BC$_2$. Crystal structure of $Y_{10x}$B$_x$C$_{10-x}$ 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 Ho$_2$B$_4$C$_6$ and Th$_2$B$_4$C$_6$. $Y_{10x}$B$_x$C$_{10-x}$ does not exhibit superconductivity above 2 K.

This result does not completely deny our expectation that a ternary Y-B-C compound isotopic to Sc$_2$B$_1$C$_{12}$ may exist. During the course of this investigation we noticed an unidentified compound whose composition is close to $Y_{10x}$B$_x$C$_{10-x}$. 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.

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