Crystal Structure of the Terbium Borocarbide $Tb_2B_2C_3$

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Z. Naturforsch. **2008**, *63b,* 929 – 933; received May 8, 2008

The title compound was prepared from the elements by arc-melting followed by annealing in silica tubes at 1270 K for one week. The crystal structure was investigated by means of single-crystal X-ray diffraction: space group *Cmmm*, $a = 3.412(1)$, $b = 13.699(8)$, $c = 3.669(1)$ Å, $V = 171.5(1)$ Å^3, $Z = 2$, $R1 = 0.032$; $wR2 = 0.087$ for 123 unique reflections with $I_o \geq 2\sigma(I_o)$ and 11 refined parameters.

Key words: Terbium Boride Carbide, Crystal Structure

Introduction

The structural chemistry of ternary rare-earth metal boride carbides $M_xB_yC_z$ (M = rare earth or actinoid metal) is particularly rich and varied. The compounds can be classified into three categories, depending upon the arrangement of the non-metal atoms: (a) boron and carbon atoms form infinite, planar 2-D networks, (b) boron and carbon atoms are bonded in 1-D zig-zag chains of boron with carbon atoms being attached, and (c) boron and carbon atoms are assembled in finite chains of different length.

Four different structural types corresponding to the composition MBC (M = rare earth or actinoid metal) have been reported so far, namely UBC [1], ThBC [2], YBC [3], and LaBC [4]. In the structures of UBC and ThBC the non-metal atoms form infinite one-dimensional planar or nearly planar ribbons of category (b). The crystal structure of LaBC consists of a three-dimensional framework of La atoms resulting from the stacking of slightly corrugated 2-D square nets, leading to voids filled with finite B_5C_5 chains [category (c)].

Previous work [5, 6] dealt with the formation and crystal structures of the new compounds $Gd_2B_3C_2$ and $Y_2B_3C_2$, replacing the earlier claimed GdBC with the so-called YBC-type structure [3]. According to these investigations the compounds $M_2B_3C_2$ (M = Y, Gd) belong to category (a) [5, 6]. The building units of the planar layers of the non-metal atoms are boron zig-zag chains connected by C–B–C units with B–B distances of 1.92 Å, and B–C distances of either 1.41 or 1.60 Å. The metal atoms are arranged in 4^23^3 nets forming trigonal prisms and cubes between them.

In the course of systematic phase analytical studies of the Tb-B-C system we have obtained several new phases. A closer inspection of the possible existence of the compounds $Tb_2B_3C_2$ and/or TbBC became the subject of the present work.

Experimental Section

Synthesis

Samples of different compositions, TbBC, $Tb_2B_3C_2$ and $Tb_2B_2C_3$, were prepared from the commercially available pure elements: sublimed bulk pieces of terbium metal with a claimed purity of 99.99 at.-% (Alfa Aesar, Johnson Matthey); crystalline boron powder, purity 99.99 at.-% (H. C. Starck, Germany); graphite powder, purity 99.98 at.-% (Aldrich). Before use, the graphite and boron powders were degassed over night at T = 1220 K and $p < 10^{-5}$ mbar. Mixtures of powders were compacted in stainless steel dies. The pellets were arc-melted under purified argon atmosphere [7] on a water-cooled copper hearth. The alloy buttons (1 g) were turned over and remelted three times to improve homogeneity. Weight losses were shown to be within 1 % of the original mass. Subsequently, the samples were wrapped in molybdenum foil and annealed in silica tubes under an argon atmosphere for one week at 1270 K. Shiny black plate-like single crystals were isolated from the crushed samples. All handling was carried out under an argon atmosphere in a glove box or with conventional Schlenk tube techniques.

Microprobe analysis

For metallographic inspection and electron probe microanalysis (EPMA), the alloys were embedded in Woods metal (melting point 75°C, Fluka Chemie, Switzerland). The embedded samples were polished on a nylon cloth using chromium oxide (Bühler Isomet) with grain sizes 1 –

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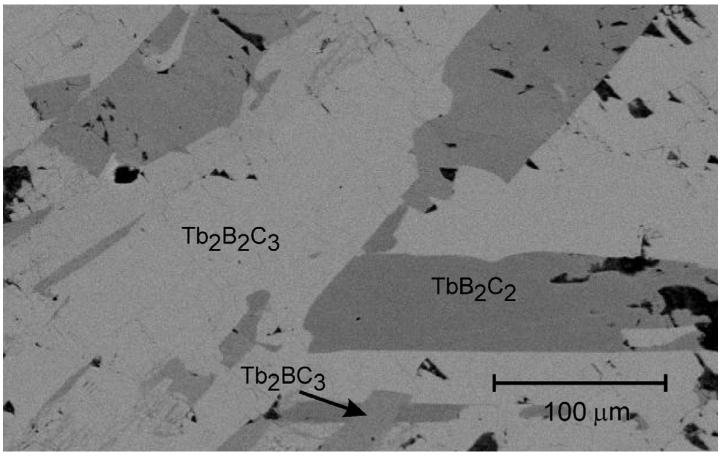

Fig. 1. Backscattered electron image of the annealed bulk sample with nominal atomic composition Tb/B/C = 27/26/43.

5 μm. Quantitative and qualitative composition analyses of the polished samples were performed by energy-dispersive X-ray spectroscopy (EDX) and wavelength-dispersive X-ray spectroscopy (WDX) on a scanning electron microscope TESCAN 5130 MM with an Oxford Si-detector and with an Oxford INCA WAVE 700 detector. TbB_2C_2 was used as standard. From the WDX analysis the composition $Tb_{2.0(1)}B_{2.0(3)}C_{3.0(4)}$ was deduced. For the chemical microprobe, the polishing procedure had to be performed or repeated just before the measurements. The surface of the phase $Tb_2B_2C_3$ appears to be quite stable in air. Metallographic investigation, X-ray powder diffraction and EPMA analyses revealed the new compound $Tb_2B_2C_3$ to be in phase equilibria with TbB_2C_2 [8], TbB_2C [9], $Tb_{10}B_7C_{10}$, and Tb_2BC_3 (Fig. 1) [10] at 1270 K. No indication for the existence of $Tb_2B_3C_2$ and/or TbBC was found.

Small and irregularly platelet-shaped single crystals were selected from crushed samples for X-ray investigation and sealed under argon atmosphere into glass capillaries. These crystals were first examined by Buerger precession methods in order to establish their suitability for intensity collection.

X-Ray diffraction and structure refinement

X-Ray powder diffraction patterns were obtained on a powder diffractometer Stoe STADI P with MoK_α radiation, using capillaries sealed under dried argon to avoid hydrolysis. The unit-cell parameters were refined with the help of the CSD program package [11]. The indexing of the X-ray powder patterns was ensured through intensity calculations taking the atomic positions determined from the single-crystal investigation. The unit-cell parameters refined from X-ray powder data are a = 3.410(1), b = 13.699(2), c = 3.662(1) Å. The small differences between the lattice parameters determined from single-crystal and powder diffraction, respectively, are quite normal.

Table 1. Crystallographic data for $Tb_2B_2C_3$.

Empirical formula	$Tb_2B_2C_3$
Crystal size, mm^3	$0.12 \times 0.07 \times 0.05$
Crystal system	orthorhombic
Space group	*Cmmm* (no. 65)
Pearson symbol	oC14
a, Å	3.412(1)
b, Å	13.699(8)
c, Å	3.669(1)
Unit cell volume V, Å^3	171.5(1)
Calculated density, g cm^{-3}	7.04
Absorption coefficient, cm^{-1}	40.6
Radiation and wavelength, Å	MoK_α, 0.71069
Diffractometer	Stoe IPDS II
Refined parameters	11
Refinement	F^2
$2\theta_{max}$; $(\sin\theta/\lambda)_{max}$	63.54; 0.673
hkl range	$-5 < h < +2$, $-7 < k < +19$, $-3 < l < +5$
Collected reflections	152
Independent reflections	123 (R_{int} = 0.029)
Reflections with $I_o \geq 2\sigma(I_o)$	118
R_σ	0.013
Final R_1 (R_1 all data)[a]	0.032 (0.033)
Weighted wR_2 (wR_2 all data)[b]	0.087 (0.088)
Extinction coefficient	0.013(4)
Goodness-of-fit on F^2	1.1
Largest diff. peak/hole, e Å^{-3}	4.2/−2.9

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w[(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (0.071P)^2 + 3.938P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

Single-crystal X-ray data of $Tb_2B_2C_3$ were collected at r. t. on a Stoe IPDS II image plate diffractometer with monochromatized MoK_α radiation in oscillation mode. The lattice parameters were determined from 1905 reflections in the region $5.9 \leq \theta \leq 64.1°$. For the structure determination the intensity data set was corrected using an analytical absorption program based on the shape of the single crystal

Atom	Site	x	y	z	U_{eq}/U_{iso}	U_{11}	U_{22}	U_{33}
Tb	4*i*	0	0.13492(6)	0	0.0052(5)	0.0029(6)	0.0086(6)	0.0042(6)
B	4*j*	0	0.717(2)	1/2	0.009(3)			
C1	4*j*	0	0.605(1)	1/2	0.005(3)			
C2	2*c*	0	1/2	1/2	0.009(5)			

Table 2. Atomic coordinates and displacement parameters (in Å^2) for $Tb_2B_2C_3$[a].

[a] $U_{23} = U_{13} = U_{12} = 0$.

Table 3. Bond lengths (d, Å) and angles (deg) with multiplicities for $Tb_2B_2C_3$.

	Multiplicity	d	Bond	Multiplicity	Angle
Tb–Tb	2	3.711(1)	B–Tb	2	2.74(2)
Tb–Tb	1	3.696(1)	B–B	2	1.93(2)
Tb–Tb	2	3.669(1)	B–C1	1	1.53(3)
Tb–Tb	2	3.412(1)	C2–C1	2	1.44(2)
Tb–B	4	2.74(1)	C2–C1–C2	1	180
Tb–B	2	2.74(2)	B–B–B	2	123.7(1)
Tb–C1	4	2.538(3)	C1–B–B	2	118.1(1)
B–Tb	4	2.74(1)			

($T_{max/min}$ = 0.282/0.178) [12] within the WinGX program package [13]. All relevant details concerning the data collection are listed in Table 1.

The starting atomic parameters derived *via* Direct Methods using the program Sir 97 [14] were subsequently refined with anisotropic displacement parameters for the terbium atoms using the program Shelxl-97 [15] (full-matrix least-squares on F^2). The refinement converged well, and the light atoms could be easily established from difference Fourier maps. The arrangement of the atom subsets of Tb, B, C1 in Table 1 is identical with that in the earlier derived structure type of $Gd_2B_3C_2$ [5]. Taking bond lengths and WDXS measurements into account, position 2*c* was refined with occupation by carbon atoms instead of boron atoms in $Gd_2B_3C_2$. The final difference Fourier synthesis was flat, and the composition obtained from the structure refinement is in very good agreement with the EPMA results.

The atomic coordinates and displacement parameters are given in Table 2. Selected interatomic distances and bond angles are reported in Table 3. The programm Diamond was used for the drawing of the crystal structure [16].

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-419476.

Discussion

The crystal structure of $Tb_2B_2C_3$ is shown in perspective representation in Fig. 2. A planar 2-D network of non-metal atoms is sandwiched between planar 4^23^3 metal atom layers. $Tb_2B_2C_3$ adopts a structure very similar to that of $Gd_2B_3C_2$ with the same arrangement of the metal atoms, but different distributions of the boron and carbon atoms. The boron atoms are connected to zig-zag chains with the distance d_{B-B} = 1.93(2) Å and the bond angle φ_{B-B-B} = 123.7(4)°. These chains are oriented parallel to the a axis. Neighboring chains are connected *via* C_3 groups, C1–C2–C1 being oriented parallel to the b axis with d_{B-C1} = 1.53(3) and d_{C1-C2} = 1.44(2) Å, $\varphi_{C1-C2-C1}$ = 180.0(1)°. The central B atom in the C–B–C bridge of $Gd_2B_3C_2$ is replaced by the carbon atom C2 in $Tb_2B_3C_2$. It is difficult to distinguish between B and C atoms by X-ray diffraction, but EPMA as well as bond-length analyses support the assignment. The distance d = 1.41 Å in the bridging group would be abnormally short for C–B–C. The B atoms are in triangular prismatic metal coordination, as is usual for most metal borides, and the C1–C2–C1 fragment lies within a slightly distorted cube of metal atoms.

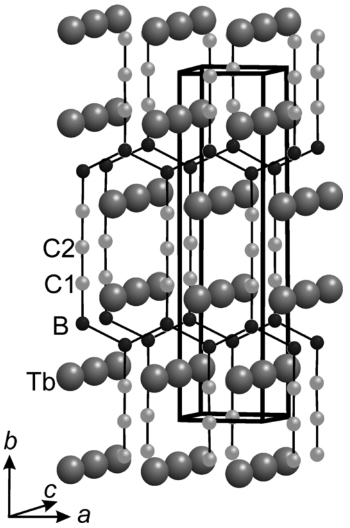

Fig. 2. Perspective view of the crystal structure of $Tb_2B_2C_3$.

The structural motif of C_3 units has been observed in a few examples. They are isolated and are not part of anionic two-dimensional nets as in the structure of $Tb_2B_3C_2$. In $Sc_5Re_2C_7$ and Mg_2C_3 the C_3 unit is exactly linear imposed by crystallographic symmetry, and C–C distances are between 1.35 and 1.33 Å, respectively [17, 18]. The C–C distances in the C_3 units in two modifications of Ho_4C_7 are similar with values of 1.32 or 1.38 Å and only 1.31 Å [19, 20], respec-

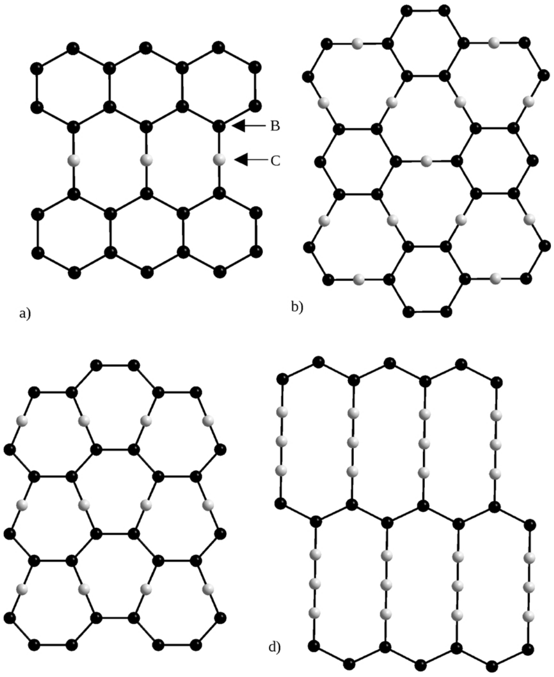

Fig. 3. Layers of boron and carbon atoms in the structures of Dy_2B_4C (a), ThB_2C (b), α-UB_2C (c), and $Tb_2B_2C_3$ (d).

tively. The corresponding values for Lu_4C_7 are 1.35 and 1.32 Å [20], and 1.34 Å for Sc_3C_4 [21]. These distances all differ slightly from the typical C–C double bond distances of 1.34 Å in olefins.

The crystal structure of $Tb_2B_2C_3$ is closely related to the structures of other ternary rare-earth metal boride carbides containing planar 2-D networks of boron and carbon atoms which alternate with sheets of metal atoms such as in structures with compositions M_2B_4C [22], MB_2C [23, 24]. The characteristic non-metal atom layers in the structure of $Tb_2B_2C_3$ show similarities with motifs in related boride carbides, as illustrated in Fig. 3. All of them contain B/C rings condensed in different ways. The connection of B_6 hexagons *via* opposite edges and *via* B–C–B bridges involving opposite corners in the structure of Dy_2B_4C [22] leads to a layer of condensed B_6 and B_6C_2 rings with two-fold symmetry and distances d_{B-C} = 1.51 Å and distances d_{B-B} ranging from 1.77 to 1.82 Å (Fig. 3a). The interconnection of the B_6 hexagons *via* B–C–B bridges involving all six corners results in a layer of condensed B_6 and B_6C_3 rings. The hexagonal symmetry is preserved in the crystal structure of ThB_2C [23] with distances d_{B-C} = 1.50 and d_{B-B} = 1.80 Å (Fig. 3b). The non-metal atom layer in α-UB_2C is formed only from condensed B_6C_2 rings [24] with B–B and B–C distances of 1.80 and 1.50 Å, respectively. The characteristic non-metal atom layers in the structure of $Tb_2B_2C_3$ are formed only from condensed B_6C_6 rings with similar B–B and B–C distances as in M_2B_4C and MB_2C.

Acknowledgements

The authors thank M. Babizhetska for the sample preparation and Dr. C. Hoch for X-ray intensity data collection.

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