



## Full length article

Crystal structure of  $\text{Th}_2\text{B}_2\text{C}_3$  with unique mixed B-C structural units<sup>☆</sup>P.F. Rogl<sup>a,\*</sup>, R. Podloucky<sup>b</sup>, H. Noël<sup>c</sup>, G. Giester<sup>d</sup><sup>a</sup> Institute of Materials Chemistry and Research, University of Vienna, A-1090 Wien, Währingerstrasse 42, Austria<sup>b</sup> Institute of Physical Chemistry, University of Vienna, A-1090 Wien, Währingerstrasse 42, Austria<sup>c</sup> Laboratoire de Chimie du Solide et Matériaux, UMR-CNRS 6226, Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes, Cedex, France<sup>d</sup> Institute of Mineralogy and Crystallography, University of Vienna, Althanstr.14, A-1090 Wien, Austria

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## ABSTRACT

X-ray single crystal data for “ $\text{ThBC}_2$ ” defined the crystal structure as orthorhombic (space group  $Pnmm$ ;  $a = 1.30655(3)$  nm,  $b = 0.39757(1)$  nm,  $c = 0.36507(1)$  nm;  $R_{F2} = 0.0130$ ) with the correct formula  $\text{Th}_2\text{B}_2\text{C}_3$ . According to the new findings phase relations for the Th-B-C system at 1400 °C have been revised confirming the hitherto known thorium-boron-carbon compounds: ThBC,  $\text{ThB}_2\text{C}$  and  $\text{Th}_3\text{B}_2\text{C}_3$ . The crystal structure of  $\text{Th}_2\text{B}_2\text{C}_3$  as a unique structure type is characterized by a C2-branched infinite chain ... B-C1-B-B-C1-B ... whereby each boron atom is additionally linked to a C2-atom. Boron atoms are in a typical triangular prismatic metal coordination, C1-atoms center a bi-pyramid,  $\text{Th}_4\text{B}_2$ , and C2-atoms are surrounded by 5 pyramidal Th-atoms and one B-atom. Density functional theory calculations were made within the pseudopotential approach of VASP utilizing the general gradient approximation for the exchange correlation functional. Structural parameters were optimized resulting in the orthorhombic lattice parameters of  $a = 1.3144$  nm,  $b = 0.3989$  nm, and  $c = 0.3656$  nm. Relativistic calculations by including spin-orbit coupling were performed for the electronic structure. Atomic volumes and charges were computed by the concept of Bader yielding the ionic charges  $\Delta q(\text{Th}) = +0.99$ ;  $\Delta q(\text{B}) = +0.61$ ;  $\Delta q(\text{C1}) = -1.20$ ;  $\Delta q(\text{C2}) = -1.10$ . The analysis of the electronic structure shows features of chains and corresponding structural subunits with  $\sigma$ -like bonding. The compound appears weakly metallic with a Sommerfeld constant of  $\gamma = 3.12$  mJ/(molK<sup>2</sup>) per formula unit.

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## 1. Introduction

Although the high temperature reactor with actinoid-metal carbide fuel was pursued already within the Dragon Project in the fifties of the last century [1], recent generation IV fission plants reconsidered dense carbide and carbide/oxide fuels [2,3]. Substantial reserves of thorium-bearing minerals have even turned the attention to application of thorium fuels in the not-too-distant future [4]. Within these activities also a detailed understanding is essential of the physical and chemical behaviour of the nuclear fuel during fabrication processes, during normal operation and in accident situations. In this context also the ternary system thorium - boron - carbon has drawn interest, particularly the combination of Th-carbide with  $\text{B}_{4+\delta}\text{C}$  fission control material.

From an early study of the thermodynamic stability of a variety

of refractory metal borides against carbon, Brewer and Haraldsen [5] indicated a preliminary phase triangulation for the system Th-B-C defining key equilibria such as  $\text{ThB}_6 + \text{ThC}_2 + \text{C}$ ,  $\text{ThB}_6 + \text{B}_{4+\delta}\text{C} + \text{C}$  and  $\text{ThB}_4 + \text{ThC}$  at unspecified high temperature. A first detailed study of phase relations in the system Th-B-C on hot-pressed alloys is due to Toth et al. [6], who observed four ternary compounds  $\text{ThBC}_2$ ,  $\text{ThB}_2\text{C}$ , ThBC and  $\text{Th}_2\text{BC}_2$ . Samples in the compound-free region Th-ThC- $\text{ThB}_4$  were annealed at ~1000 °C (Ar, 5 h), whereas samples in the remaining part of the diagram were annealed at about 1400 °C (Ar, 15 h). The crystal structures remained unknown except for  $\text{ThB}_2\text{C}$ , to which a subcell close to the  $\text{AlB}_2$ -type was assigned. A reinvestigation [7] of the system at 1400 °C essentially confirmed the phase triangulation given by Toth et al. [6], and provided X-ray single crystal data (from four circle diffractometer) for  $\text{ThB}_2\text{C}$  [8] (also employing neutron powder diffraction data),  $\text{Th}_3\text{B}_2\text{C}_3$  [9] (earlier  $\text{Th}_2\text{BC}_2$  [6]) and ThBC [10,11]. So far the crystal structure of  $\text{ThBC}_2$  remained unsolved. At this stage reviews on the Th-B-C system have been provided by Kleykamp [12] and Rogl [13]; electronic bonding in ThBC and  $\text{ThB}_2\text{C}$  has been discussed by the group of Saillard et al. [14–16].

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The present investigations provide (i) a structure determination of Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub> (earlier ThBC<sub>2</sub>) complemented (ii) by detailed DFT calculations on the electronic structure and bonding, triggering (iii) a revision (reinvestigation) of the phase relations in the isothermal section at 1400 °C. Because of its carbon-rich constitution, the crystal structure of Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub> consists of unique mixed boron-carbon chains and corresponding structural subunits, which hitherto are unknown.

## 2. Experimental

### 2.1. Sample preparation and characterisation techniques

Samples (each of a mass of about 1 g) were prepared by argon arc melting starting either from powders of 99.9 mass% pure thorium (Cerac Inc., USA), reactor grade graphite (impurities < 200 ppm; Carbone Lorraine, France) and amorphous boron (99.7%; Strem Chemicals Inc., USA), or from Th-ingot (Merck AG, Germany, 99%), graphite foil (99.8%, Alpha Aesar, Germany) and crystalline B-chunks (99.75%, H.C. Starck, Germany). Whereas for the first method the carefully mixed powder blends were cold compacted in steel dies without lubricants, the second method fused elemental pieces directly in the arc furnace. All specimens were melted at least three times to ensure homogeneity. Weight losses generally were less than 1 mass%. The samples were annealed at 1400 °C for 48 h each in a crucible of pyrolytic graphite (Carbone Lorraine) in a high vacuum furnace of  $3 \times 10^{-4}$  Pa with a W-sheet metal heater. Contamination from the crucible material (carbon pick-up) was found to be negligible. Alloys from the binary system Th-B were obtained by sintering and/or melting together Th/B powder compacts on a water cooled Cu-boat in a Ti/Zr-gettered Ar atmosphere using a 25 kW-500 kHz high frequency furnace. Slow cooling from the melt ensured primary crystallization of the various phases.

The microstructure of the alloys were inspected by a Reichert optical microscopy (under reflected or polarized light) on surfaces prepared by SiC-grinding and polishing the resin-mounted alloys with diamond pastes down to 1/4 μm grain size. Due to the sensitivity for moisture, especially of the carbon-rich grades, all metallographic preparations were performed under water-free protective mineral oil. A CAMEBAX SX50 wavelength dispersive X-ray microanalyser (XMA) was used for proper identification of the phases and precipitates. Quantitative analyses were performed comparing the Th-Mα<sub>1</sub>, B-Kα<sub>1</sub> and C-Kα<sub>1</sub> emissions of the three elements in the alloys with those from elemental C, Th or ThB<sub>4</sub> as reference materials applying the PAP correction procedure [17]. The experimental parameters employed were: 15 kV acceleration voltage, 100 nA sample current and spectrometer crystals such as PET for the Th-Mα<sub>1</sub> and PC3 for B-Kα<sub>1</sub> and PC1 for C-Kα<sub>1</sub> radiation.

X-ray powder diffraction (XPD) data were collected using a Huber Guinier camera with monochromatic Cu Kα<sub>1</sub> radiation (λ = 0.154056 nm) and an image plate recording system (model G670). Pure Si (a<sub>Si</sub> = 0.5431065 nm) was used as internal standard to determine precise lattice parameters via least-squares fitting to the indexed 2θ values employing the program STRUKTUR [18]. For quantitative Rietveld refinements we applied the program FULLPROF [19].

Single crystals of Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub> were mechanically isolated from the crushed as cast alloy with nominal composition ThBC<sub>2</sub>. X-ray single crystal diffraction data (XSCD) were collected on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated MoKα radiation (λ = 0.071073 nm). Orientation matrix and unit cell parameters for a cubic system were derived using the program DENZO [20]. Besides the general treatment of absorption effects using the multi-

scan technique (SADABS; redundancy of integrated reflections > 8), no individual absorption correction was necessary because of the rather regular crystal shape and small dimensions of the investigated specimens. (35 × 27 × 40 μm). The structures were refined with the aid of the SHELXL-97 program [21].

### 2.2. DFT calculations

The density functional theory (DFT) calculations for Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub> were performed by means of the Vienna ab initio simulation package (VASP) [22,23] with its pseudopotential construction according to the projector-augmented-wave method [24]. For the construction of the Th pseudopotential the 12 valence states 6s<sup>2</sup>, 6p<sup>6</sup>, 6d<sup>2</sup>, 7s<sup>2</sup> were considered, whereas for C the 4 valence states 2s<sup>2</sup>, 2p<sup>2</sup> and for B the 3 valence states 2s<sup>2</sup>, 2p<sup>1</sup> were taken into account. For the exchange-correlation functional the generalized gradient approximation according to Perdew et al. (PBE) [25] was chosen. The VASP calculations were done with high precision according to the energy cutoff of 600 eV.

For *k* space integration the Gaussian smearing method with a value for σ of 0.1 eV was taken. A very fine *k* space grid of 5 × 16 × 18 points was constructed according to the parameter KSPACING = 0.1 in the INCAR file of VASP. Assuming the experimental structure as starting point, the atomic positions as well as the unit cell parameters were fully relaxed. The thus obtained lattice parameters of the fully relaxed calculation are a = 1.3144 nm, b = 0.3989 nm, and c = 0.3656 nm. Relativistic calculations by including spin-orbit coupling were performed for the electronic

**Table 1**

X-ray single crystal structure data (MoKα) for Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub> (Th<sub>2</sub>B<sub>2</sub>C<sub>3</sub>-type); space group *Pnmm*; No. 58; structure standardized with program *Structure Tidy* [34]. (For easy comparison DFT values of lattice and atom parameters have been inserted in italics within square brackets).

Parameter/compound	Crystal data
Phase composition (WDX, at.%)	Th <sub>31</sub> B <sub>27</sub> C <sub>42</sub>
Refinement composition (at.%)	Th <sub>28.6</sub> B <sub>28.6</sub> C <sub>42.8</sub> ≡ Th <sub>2</sub> B <sub>2</sub> C <sub>3</sub>
Structure type	Th <sub>2</sub> B <sub>2</sub> C <sub>3</sub> -type
θ range (deg)	2 ≤ 2θ ≤ 72.8
Crystal size	35 × 27 × 40 μm <sup>3</sup>
Linear absorption coeff. [mm <sup>-1</sup> ]	78.1
<i>a</i> [nm] [DFT]	1.30655(3) [1.314425]
<i>b</i> [nm] [DFT]	0.397566(7) [0.398934]
<i>c</i> [nm] [DFT]	0.365074(7) [0.365655]
Reflections in refinement	504 ≥ 4σ(F <sub>o</sub> ) of 518
Number of variables	15
Mosaicity	<0.46
R <sub>F2</sub> = Σ F <sub>o</sub> <sup>2</sup> - F <sub>c</sub> <sup>2</sup>  /ΣF <sub>o</sub> <sup>2</sup>	0.0130
wR2	0.0283
R <sub>int</sub>	0.056
GOF	1.087
Extinction (Zachariasen)	0.0033(3)
Th in 4 g (x, y, 0); occ.	0.35636(1); 0.35667(3); 1.0 (-) Th
DFT data	[0.356085; 0.358805]
U <sub>11</sub> ; U <sub>22</sub> ; U <sub>33</sub> ;	0.0070(1); 0.0042(1); 0.0034(1);
U <sub>12</sub> ; U <sub>23</sub> = U <sub>13</sub> = 0	-0.0001(0)
B1 in 4 g (x,y,0); occ.	0.0492(4); 0.336(1); 1.00(1) B
DFT data	[0.051397; 0.33294]
U <sub>iso</sub>	0.0096(8)
C1 in 2a (0,0,0); occ.	1.00(1) C
U <sub>iso</sub>	0.0094(9)
C2 in 4 g (x,y,0); occ.	0.8332(3); 0.6156(9); 1.00(1) C
DFT data	[0.833050; 0.608300]
U <sub>iso</sub>	0.0082(6)
Residual electron density; max; min in (electron/nm <sup>3</sup> ) × 10 <sup>3</sup>	2.17 (0.17 nm from Th); -2.94

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