

Different Structural Models of YB_2C_2 and GdB_2C_2 on the Basis of Single-Crystal X-Ray Data

Olaf Reckeweg and Francis J. DiSalvo

Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA

Reprint requests to Dr. Olaf Reckeweg. Fax: ++1-607-255-4137. E-mail: olaf.reykjavik@gmx.de

Z. Naturforsch. **2014**, *69b*, 289–293 / DOI: 10.5560/ZNB.2014-3333

Received December 16, 2013

Samples of YB_2C_2 and GdB_2C_2 were synthesized by arc-melting and subsequent annealing of the products. Single crystals of the title compounds were examined with single-crystal X-ray methods. Five different tetragonal unit cell settings from the literature (obtained on the basis of symmetry considerations) were used for the refinement of the crystal structure of YB_2C_2 , but a converging refinement was only achieved for the structural model in the space group $P4/mbm$ (no. 127, $Z = 2$) with $a = 533.27(3)$ and $c = 354.58(3)$ pm, without obvious inconsistencies. Nevertheless, the results for the five different unit cell settings are compared and discussed. A refinement of the crystal structure of the isotypic compound GdB_2C_2 was also performed with the lattice parameters $a = 537.46(6)$ and $c = 364.98(11)$ pm. Neither EuB_2C_2 nor YbB_2C_2 were obtained by melting cold-pressed pellets with the nominal composition $\text{RE}_{1.5}\text{B}_2\text{C}_2$ in an arc-furnace or an induction furnace, or by just heating the pellets in sealed Ta ampoules.

Key words: Yttrium, Gadolinium, Boride, Carbide, Structure Elucidation

Introduction

The structures and properties of rare-earth metal boride carbides with the composition REB_2C_2 ($\text{RE} = \text{Sc}$ [1, 2], Y, La, Ce–Lu except for Pm [3–19]) have been investigated intensively, and their structure has been discussed for quite a while. Planar 4.8^2 B–C nets are held together by metal atoms – this is and has never been in question. Due to the small differences in their X-ray scattering power, the distribution of B and C atoms with respect to each other – the so-called ‘coloring problem’ [20, 21] – is hard to settle conclusively with X-ray methods only. Recently, this problem was tackled and settled employing powder neutron diffraction [12–18] and DFT calculations relying on NMR measurements [22]. Still, different metal cations might cause different coloring patterns due to varying RE–B and RE–C distances and interactions. This question was raised for the crystal structure of YB_2C_2 [23, 24] (which has not been reported in detail as yet), which differs from the now accepted “standard model” for all REB_2C_2 -type compounds (except for ScB_2C_2 [1, 2]). Because different crystallographic models using group-subgroup relationships were recently predicted

as possible candidates for REB_2C_2 compounds [19], some of which were already proposed in the past, we explored YB_2C_2 experimentally with a regular single-crystal X-ray diffractometer using Mo radiation to see if there is some indication for the validity of these doubts.

We also tried to tackle some more gaps in the REB_2C_2 field: physical data [18] and the lattice parameters [4, 5, 18] are well established for GdB_2C_2 , but to our knowledge no refinement of the structural parameters has been reported as yet. And last, but not least, the existence of YbB_2C_2 and EuB_2C_2 seems to be questionable, since lattice parameters have been reported ‘tentatively’ [5], and more recent synthesis attempts failed [10, 16]. Therefore, we wanted to try our luck and skill on these two compounds as well. The results of our attempts to fill these gaps are also reported here.

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless otherwise stated. The starting materi-

als consisted of Y, Eu, Gd and Yb, respectively (metals filed freshly from a metal ingot, Alfa Aesar, 99.9%), B (Strem, crystalline, 99.5%), and C (Strem, powder, 99.999%) of which the latter two were degassed at 670 K under dynamic vacuum for 2 h prior to use. The starting materials were ground together in an agate mortar and cold-pressed without additional binder into pellets of an approximate mass of 0.5 g, but for Eu and Yb an excess of 50% was used to make up for losses due to the high vapor pressure of the materials at elevated temperatures. The pellets were arc-melted on a water-cooled copper hearth in an argon atmosphere. The samples were turned over and remelted several times to ensure homogeneity. The resulting buttons were sealed in a clean Ta container by arc-welding and subsequently sealed in an evacuated silica tube. The samples were annealed at 900 °C for three days. The annealed samples were crushed with an iron mortar into small pieces. All title compounds are moderately sensitive to normal atmosphere and decompose slowly.

Since this straightforward method was only successful for YB₂C₂ and GdB₂C₂, but not for EuB₂C₂ and YbB₂C₂, we tried to achieve the synthesis of the latter compounds by melting pellets of the composition RE_{1.5}B₂C₂ in an induction furnace under argon, or by just heating pellets in sealed tantalum ampoules. As indicated by their respective powder

X-ray patterns, the products were mostly amorphous or binary borides.

Crystallographic studies

Samples of the annealed and crushed product buttons were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90%) for single-crystal selection. Suitable single crystals of both compounds were selected under a microscope, mounted in a drop of polybutene oil sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen ($T = 173(2)$ K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK α radiation ($\lambda = 71.073$ pm). All further data processing was performed with the Bruker Smart software [25].

The data for YB₂C₂ indicated a small tetragonal unit cell with $a = 377.12(1)$ and $c = 354.65(3)$ pm if only strong reflections with the criterion $I > 10 \sigma(I)$ were used for the unit cell determination routine. When all reflections were used which were found by the routine implemented in the Bruker software, a primitive tetragonal unit cell with the

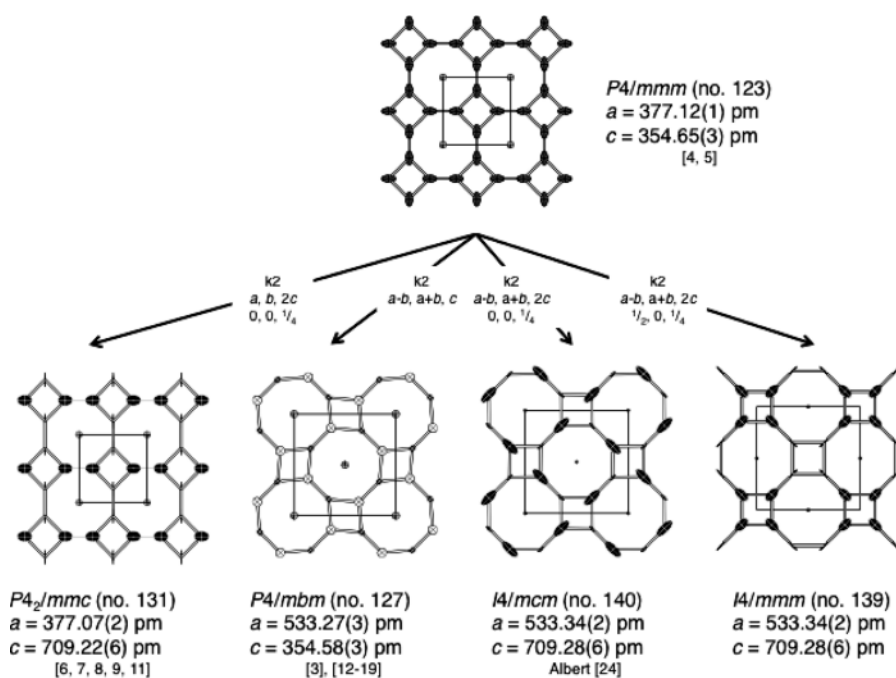


Fig. 1. View perpendicular to the planar B–C net parallel to the crystallographic c axis. RE, B and C are displayed as hatched light grey, crossed black or white circles, respectively. Displacement ellipsoids are drawn at the 99% probability level.

lattice parameters $a = 533.27(3)$ and $c = 354.58(3)$ pm always resulted. If the reflections for the unit cell determination were selected by chance from the pool found by the search routines and not restricted, either the primitive tetragonal unit cell mentioned before was found, or another primitive tetragonal unit cell was detected fitting the lattice parameters $a = 377.07(2)$ and $c = 709.22(6)$ pm (occurrence about 9 : 1). No tetragonal body-centered unit cell could be found without giving restrictions regarding the unit cell parameters to the program search routines. For YB₂C₂, the in-

tensity data for five different settings, which have been found by group-subgroup relations [19], were integrated and corrected for Lorentz and polarization effects as well as for absorption with the program SADABS [26]. Following previous work [19], the coordinates for the respective settings were used as a starting model. These were refined by full-matrix least-squares calculations on F^2 in SHELXL-97 [27, 28]. Most refinements converged except for the body-centered unit cell refined in the space groups $I4/mmm$ (no. 139) and $I4/mcm$ (no. 141). The refinement in the space group

Compound	YB ₂ C ₂	GdB ₂ C ₂
M_r	134.55	202.89
Crystal color	metallic black	metallic black
Crystal shape	rectangular plate	rectangular plate
Crystal size, mm ³	0.10 × 0.15 × 0.20	0.02 × 0.04 × 0.07
Space group (no.); Z	$P4/mbm$ (127); 2	$P4/mbm$, (127); 2
Lattice parameters a ; c , pm	533.27(3); 354.58(3)	537.46(6); 364.98(11)
V , Å ³	100.83(1)	105.43(4)
$D_{\text{calcd.}}$, g cm ⁻³	4.43	6.39
$F(000)$, e ⁻	122	172
μ , mm ⁻¹	28.4	31.0
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD	
Radiation; λ , pm	MoK α ; 71.073; graphite monochromator	
Scan mode; T , K	ϕ - and ω -scans; 173(2)	
Ranges, $2\theta_{\text{max}}$; h , k , l	77.0; ± 7 , ± 9 , $-6 \rightarrow 4$	73.9; ± 8 , $-7 \rightarrow 8$, $-6 \rightarrow 5$
Data correction	Lp, SADABS [26]	Lp, SADABS [26]
Transmission: min./max.	0.3180/0.7471	0.4389/0.7473
Reflections: measured/unique	1192/176	893/165
Unique reflections with $F_0 > 4 \sigma(F_0)$	131	114
$R_{\text{int}}/R_{\sigma}$	0.0367/0.0265	0.0216/0.0175
Refined parameters	11	11
$R1^a/wR2^b/\text{GooF}^c$ (all refls.)	0.0283/0.0414/1.140	0.0184/0.0276/1.161
Weight factors x/y^b	0.0166/0.035	0.0106/0
Max. shift/esd, last refinement cycle	< 0.00005	< 0.00005
$\Delta\rho_{\text{fin}}$ (max), e ⁻ Å ⁻³	0.80 (58 pm to Y)	1.23 (142 pm to Gd)
$\Delta\rho_{\text{fin}}$ (min), e ⁻ Å ⁻³	-0.76 (62 pm to Y)	-1.12 (65 pm to Gd)
CSD number	427 155	427 156

Table 1. Details of the final results of the X-ray single-crystal structure refinement on YB₂C₂ and GdB₂C₂.

^a $R1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2]/3$; ^c GooF: $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, with n being the number of reflections and p being the number of parameters.

Table 2. Atomic coordinates, anisotropic displacement parameters U_{ij}^a and equivalent isotropic displacement parameters U_{eq}^b (all in pm²) for YB₂C₂ and GdB₂C₂. $U_{23} = U_{13} = 0$ due to the symmetry of the crystallographic site.

Atom	Wyckoff Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Y	2a	0	0	0	31(1)	U_{11}	18(2)	0	27(1)
B	4h	0.3638(5)	1/2 + x	1/2	49(10)	U_{11}	31(22)	-3(11)	43(8)
C	4h	0.1619(5)	1/2 + x	1/2	30(8)	U_{11}	51(20)	5(9)	37(7)
Gd	2a	0	0	0	45(1)	U_{11}	54(1)	0	48(1)
B	4h	0.3601(8)	1/2 + x	1/2	45(14)	U_{11}	48(37)	-3(18)	46(13)
C	4h	0.1612(8)	1/2 + x	1/2	76(15)	U_{11}	108(40)	3(17)	87(14)

^a The anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c}U_{23} + 2hla^{*c}U_{13} + 2hka^{*b}U_{12})]$; ^b U_{eq} is defined as one third of the orthogonalized U_{ij} tensors.

Table 3. Bond lengths (pm) with multiplicities and angles (deg) for YB₂C₂ and GdB₂C₂.

Atoms	Bond length	Atoms	Angle
Y–B (8×)	267.20(9)	C–B–C (2×)	130.1(1)
Y–C (8×)	272.66(12)	C–B–C (1×)	99.8(2)
B–C (2×)	159.5(4)	B–C–B (2×)	139.92(11)
B–C (1×)	152.3(6)	B–C–B (1×)	80.2(2)
Gd–B (8×)	276.4(2)	C–B–C (2×)	131.0(2)
Gd–C (8×)	272.0(2)	C–B–C (1×)	98.1(4)
B–C (2×)	162.2(6)	B–C–B (2×)	139.0(2)
B–C (1×)	151.2(9)	B–C–B (1×)	81.9(4)

P4/mbm (no. 127) resulted in a stable model without any obvious faults such as high numbers for the R_{int} or ill-defined or unreasonably low or high anisotropic displacement parameters (Fig. 1).

For GdB₂C₂, a tetragonal unit cell with the lattice parameters $a = 537.46(6)$ and $c = 364.98(11)$ pm ($Z = 2$) was found with a primitive tetragonal symmetry and extinction conditions indicating the space group *P4/mbm* (no. 127). Using the crystallographic parameters of the ‘standard model’, refinement with full-matrix least-squares techniques with the use of SHELXL-97 [27, 28] resulted without problems in a stable model, also without any obvious faults such as high numbers for the R_{int} or ill-defined or unreasonable low or high anisotropic displacement parameters.

Additional crystallographic details are given in Table 1. Atomic coordinates and anisotropic and equivalent isotropic displacement coefficients are shown in Table 2; Table 3 displays selected bond lengths and angles.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdta@fiz-karlsruhe.de), on quoting the depository number CSD-427155 for YB₂C₂ and CSD-427156 for GdB₂C₂.

Results and Discussion

Syntheses

The syntheses of YB₂C₂ and GdB₂C₂ were straightforward, but all our attempts to synthesize YbB₂C₂ and EuB₂C₂ failed as yet – as happened before [10, 16]. This can indicate either that our experimental approach was not suitable, or that these compounds do not exist – which might be plausible if one remembers the close similarity of divalent Yb and Eu to the alkaline earth metals Ca and Sr, respectively. In any case, negative proof is impossible, but positive indications are lacking here.

Crystal structure

Except for ScB₂C₂ [1, 2], all REB₂C₂ compounds have a tetragonal symmetry with B and C atoms forming two-dimensional 4.8² nets of condensed four- and eight-membered rings with the respective cation occupying a position between the two-dimensional B–C sheets close to the middle of two eight-membered rings of two neighboring layers.

The small unit cell with pseudo-cubic symmetry *P4/mmm* (no. 123) contains regular octagons and squares [4, 5]. Here, boron and carbon occupy the same position. For the ‘standard model’ refined with *P4/mbm* (no. 127) symmetry, only heteroatomic B–C bonds are present, both the squares and the octagons are distorted, and the atoms of the same sort are stacked above each other (Fig. 2). The model refined in the space group *P4₂/mmc* (no. 131) is derived from the structure originally reported by Bauer *et al.* [9] exhibiting regular polygons with some homoatomic contacts. The remaining body-centered unit cells are very similar to the aforementioned structure descriptions – they are just differing in their long-range order of the stacking along the crystallographic *c* axis. The crystal structure refined in the space group *I4/mmm* (no. 141) is adopted by CaB₂C₂ [24], but there is no report of a refinement of an REB₂C₂ compound in the space group *I4/mmm* (no. 139). Unfortunately, the crystal struc-

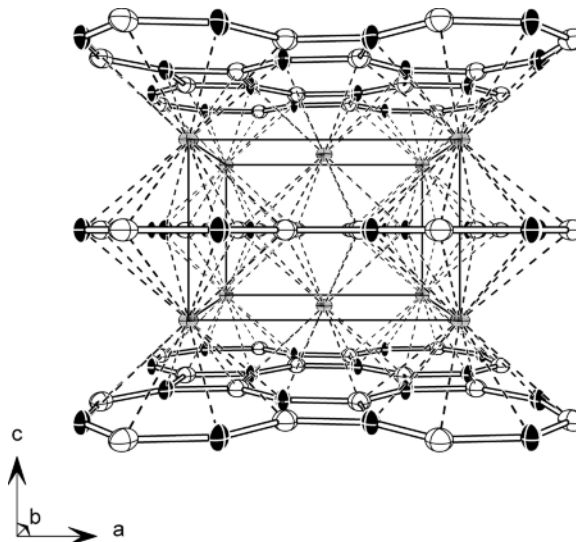


Fig. 2. Perspective view of YB₂C₂. The same parameters as in Fig. 1 are used for the display. Dotted lines indicate metal-nonmetal bonds.

tures described in body-centered unit cells suffered not only from a high merging factor R_{int} for the symmetry-equivalent models, but they both also did not converge and showed unusually high and low anisotropic displacement parameters in the refinement. All models with the tetragonal primitive space groups could be refined and converged, but for all models except for the “standard model” irregular anisotropic displacement parameters were observed. This is visualized in Fig. 1. The displacement ellipsoids are displayed with 99% probability. It is noteworthy that next to all the other quality factors of a refinement ($R1$, $wR2$, GooF, residual electron density *etc.*) remain in an acceptable range.

A perspective view of the crystal structures of YB₂C₂ and GdB₂C₂ is shown in Fig. 2, selected bond lengths and angles are displayed in Table 3.

Conclusion

YbB₂C₂ and EuB₂C₂ could not be prepared using various synthetic strategies.

For YB₂C₂ (exhibiting a 4.8² B-C net, typical for most compounds of that stoichiometry), five different tetragonal unit cell settings, previously discussed in the literature, were used for the integration and refinement of the intensity data. The only refinement without obvious inconsistencies was obtained in the “standard model” with the space group $P4/mbm$ (no. 127), but it is clear that “biased” absorption corrections may lead to a different space group not obvious from the results since most other quality factors of the refinement are still in an acceptable range. To the best of our knowledge the crystal structure of the isotopic compound GdB₂C₂ has been determined for the first time.

- [1] G. S. Smith, Q. Johnson, P. X. Nordine, *Acta Crystallogr.* **1965**, *19*, 668–673.
- [2] O. Reckeweg, F. DiSalvo, W. Scherer, R. Pöttgen, in preparation.
- [3] P. K. Smith, Ph.D. Thesis, University of Kansas, Lawrence **1964**.
- [4] P. K. Smith, P. W. Gilles, *J. Inorg. Nucl. Chem.* **1967**, *29*, 375–382.
- [5] N. A. Fishel, H. A. Eick, *J. Inorg. Nucl. Chem.* **1969**, *31*, 891–893.
- [6] J. Bauer, H. Nowotny, *Monatsh. Chem.* **1971**, *102*, 1129–1145.
- [7] T. Bréant, D. Pensec, J. Bauer, J. Debuigne, *C. R. Seances Acad. Sci., Ser. C* **1978**, *287*, 261–264.
- [8] K. A. Schwetz, M. Hoerle, J. Bauer, *Ceramurgia Int.* **1979**, *5*, 105–109.
- [9] J. Bauer, O. Bars, *Acta Crystallogr.* **1980**, *B36*, 1540–1544.
- [10] T. Sakai, G. Adachi, J. Shiokawa, *Solid State Comm.* **1981**, *40*, 445–449.
- [11] K. Cenzual, L. Gelato, M. Penzo, E. Parthé, *Acta Crystallogr.* **1991**, *B47*, 433–439.
- [12] T. Onimaru, H. Onodera, K. Ohoyama, H. Yamauchi, Y. Yamaguchi, *J. Phys. Soc. Jpn.* **1999**, *68*, 2287–2291.
- [13] T. Onimaru, H. Onodera, K. Ohoyama, H. Yamauchi, M. Ohashi, Y. Yamaguchi, *J. Phys. Chem. Solids* **1999**, *60*, 1435–1438.
- [14] J. van Duijn, K. Suzuki, J. P. Attfield, *Angew. Chem. Int. Ed.* **2000**, *39*, 365–366.
- [15] K. Kaneko, K. Ohoyama, H. Onodera, Y. Yamaguchi, *J. Phys. Soc. Jpn.* **2000**, *69*, 3762–3763.
- [16] K. Ohoyama, K. Kaneko, K. Indoh, H. Yamauchi, A. Tobo, H. Onodera, Y. Yamaguchi, *J. Phys. Soc. Jpn.* **2001**, *70*, 3291–3295.
- [17] K. Ohoyama, K. Kaneko, K. Indoh, A. Tobo, H. Onodera, Y. Yamaguchi, *Appl. Phys.* **2002**, *A74 (Suppl.)*, S661–S663.
- [18] Y. Yamaguchi, K. Ohoyama, K. Ohoyama, H. Yamauchi, K. Indoh, H. Onodera, *Appl. Phys.* **2002**, *A74 (Suppl.)*, S877–S879.
- [19] V. Babizhetskyy, C. Hoch, H. J. Mattausch, A. Simon, *Z. Naturforsch.* **2006**, *61b*, 727–732.
- [20] J. K. Burdett, S. Lee, T. J. McLarnan, *J. Am. Chem. Soc.* **1985**, *107*, 3083–3089.
- [21] J. K. Burdett, E. Canadell, T. Hughbanks, *J. Am. Chem. Soc.* **1986**, *108*, 3971–3976.
- [22] X. Roquefelte, S. E. Boulfefel, M. B. Yahia, J. Bauer, J.-Y. Saillard, J.-F. Halet, *Angew. Chem. Int. Ed.* **2005**, *44*, 7542–7545.
- [23] R. Pöttgen, **1996**, unpublished results.
- [24] B. Albert, K. Schmitt, *Inorg. Chem.* **1999**, *38*, 6159–6163.
- [25] APEX2 (version 1.22), SAINT PLUS, XPREP (version 6.14), Software for CCD Systems, Bruker Analytical X-ray Instruments Inc., Madison, WI (USA) **2004**.
- [26] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.
- [27] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [28] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.