УДК 546:548.736.4

Volodymyr BABIZHETSKYY, Bogdan KOTUR,
Volodymyr LEVYTSKYY

PHASE EQUILIBRIA AND CRYSTAL STRUCTURE OF THE TERNARY COMPOUNDS IN Dy–B–C SYSTEM AT 1270 K

Ivan Franko National University of Lviv,
Kyryla and Mefodiya Str. 6, UA-79005 Lviv, Ukraine
e-mail: v.babizhetskyy@googlemail.com

The phase equilibria at 1270 K in the Dy–B–C system were studied using X-ray diffraction, scanning electron microscopy and electron probe microanalysis. Eleven ternary compounds were detected. The existence of DyB_2C_2, Dy_2B_4C, DyB_2C, $Dy_5B_2C_5$, $Dy_5B_2C_6$, $Dy_2B_2C_3$, $Dy_4B_3C_4$, $Dy_{10}B_7C_{10}$, $Dy_{15}B_4C_{14}$ was confirmed. Two new ternary compounds $\sim Dy_2BC_3$ and $\sim Dy_4B_5C_{18}$ with unknown crystal structure were isolated. The tetragonal structure of DyB_2C_2 was solved from the X-ray single crystal data: space group P4/mbm, Z = 2, a = 5.345(1), c = 3.5600(5) Å, R1 = 0.046 (wR_2 = 0.049) for 585 reflections with $I_o > 2\sigma$ (I_o)). The composition of earlier known ternary compound "DyBC" was refined to be $Dy_2B_2C_3$ by electron probe microanalysis. Additionally, the phase of $Dy_5B_2C_6$ was analyzed showing a broad homogeneity range described by the formula $Dy_5(BC)_x$ where (7.5 $\leq x \leq$ 9.0).

Keywords: phase equilibria, single crystal, crystal structure.

1. Introduction

Up to now the phase relations in the general *RE*–B–C systems were not studied in sufficient detail so far. Majority of the discovered ternary rare-earth metal (*RE*) boron carbides $RE_xB_yC_z$ revealed from partial or complete investigations of ternary *RE*–B–C phase diagrams for *RE* = Sc, Y, La, Ce, Pr, Eu, Gd, Tb, Ho, Er [1–11]. The crystal chemistry of the ternary rare-earth metal (*RE*) boride carbides $RE_xB_yC_z$ comprises different structural arrangements with B_yC_z entities ranging from zero-dimensional (0-D) units isolated from each other in a matrix formed from the rare earth metal atoms to one-, two-, and three-dimensional networks alternating or surrounded by metal sublattices, which are closely related to the *valence electron count* (VEC) per light atoms. Indeed, some new different structural types have been reported so far solely for the most electron-rich compounds, i.e., those containing finite quasi-molecular entities and having a large VEC [1]. These finite B_yC_z chains embedded in voids of the metal atom matrix may have various lengths ranging from 2 to 13 non-metal atoms up to now, and chains of different sizes as well as isolated C atoms can coexist. Novel representatives were discovered during our recent investigation of the La–B–C [4], Ce–B–C [5], Pr–B–C [6] and Tb–B–C systems [9]. Our latest studies of the isothermal section of the ternary Dy–B–C phase diagram at 1270 K, crystallographic data for all its ternary compounds

and the structure refinement of DyB_2C_2 as well as homogeneity range of the solid solution based on $Dy_5B_2C_6$ phase are the subject of present work.

2. Experimental details

2.1. Synthesis of alloys

Polycrystalline samples were prepared from commercially available pure elements: dysprosium with a claimed purity of 99.99 at%, Alfa – Aesar, Johnson Matthey Company, sublimed bulk pieces; 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 degased overnight at 1220 K and $p < 10^{-5}$ mbar. Dysprosium ingots were filed to coarse powders with beryllium bronze files (Dönges GmbH, Germany). Stoichiometric mixtures of the constituents were compacted in stainless steel dies. The pellets were arc-melted under purified argon atmosphere on a water-cooled copper hearth. The alloy buttons of 1g were turned over and remelted two times to improve their homogeneity. The samples were then wrapped in molybdenum foil and annealed in silica tubes under argon for one month at 1270 K. Subsequent heating for some samples just above the melting point was carried out in a high-frequency furnace (TIG-10/300, Hüttinger, FRG) under argon atmosphere for several hours at different temperatures. Finally, the samples were also annealed at 1270 K in evacuated silica tubes for one month by procedure described above and subsequently quenched in cold water. Sample handling was carried out under argon atmosphere in a glove box ($P_{H2O} <$ 0.1 ppm) or through the Schlenk technique.

2.2. X-ray diffraction and structure refinement

X-ray powder diffraction patterns were obtained on a powder diffractometer STOE STADI P with $MoK\alpha_1$ radiation, using Lindemann glass capillaries sealed under dried argon to avoid hydrolysis. Refinement of the unit cell parameters for the investigated ternary compounds $Dy_xB_yC_z$, as well as the phase analysis was performed with WinCSD [12] and WinXPOW [13] program packages. The results are given in Table 1. Small irregularly-shaped single crystals of DyB_2C_2 were selected from the mechanically crushed sample of $Dy_{20}B_{40}C_{40}$ nominal composition and sealed under argon atmosphere in glass capillaries. The single crystal X-ray diffraction data of DyB_2C_2 were collected at room temperature on a STOE IPDS II image plate diffractometer with monochromatized $MoK\alpha$ radiation. All relevant crystallographic data are listed in Table 2. The starting atomic parameters were derived via direct methods using the program SIR97 [14]. They were subsequently refined with the program SHELX-97 [15] within the WinGX program package [16] (full matrix least-squares on F^2) with anisotropic atomic displacement parameters for dysprosium atoms. No additional reflections with regard to the DyB_2C_2 type unit cell were detected. The atomic coordinates and displacement parameters are listed in Table 3.

2.3. Microprobe analysis

For metallographic investigation and electron probe microanalysis (EPMA) some alloys were embedded in Woods metal (Fluka Chemie, Switzerland) with a melting point of ca. 350 K. The samples were polished on a nylon cloth using chromium(III) oxide (Bühler Isomet) suspended in dry petroleum with grain sizes 1–5 μm. Qualitative and quantitative composition analyses of the 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. DyB_2C_2 standard was used to deduce the compositions of the new compounds. The boron and dysprosium contents were investigated in the alloys. For the chemical microprobe, the polishing procedure had to be performed or repeated just before the measurements and the surface of the samples was protected by dry petroleum. Metallographic and EPMA analyses of the Dy-B-C samples reveal the ternary boron carbide DyB_2C_2 [17] to be in phase equilibria with new compound $\sim Dy_2BC_3$ and $Dy_2B_2C_3$. $Dy_5B_{2.6}C_{6.4}$ ($La_5B_2C_6$ structure type) [18] is in phase equilibrium with $Dy_5B_2C_5$ [19] and $Dy_4B_3C_4$ [20]. The results of the EPMA for dysprosium boron carbide $Dy_5(B,C)_x$ ($7.5 \leq x \leq 9.0$) samples are listed in Table 4.

3. Results and discussion

3.1. Phase equilibria at 1270 K in the Dy–B–C ternary system

The isothermal section of the Dy–B–C phase diagram at 1270 K is shown in Fig. 1. According to the phase diagram the boundary Dy–B system there occur five binary dysprosium borides. Four of them DyB_2, DyB_6, DyB_{12} and DyB_{66} are formed by peritectic reactions at $\sim$2370 K, 2470 K, 2370 K and 2300 K, respectively. DyB_4 melts congruently at 2770 K. DyB_6 exhibits a narrow homogeneity range [21]. The data on the binary Dy–C phase diagram was recently assessed [22].
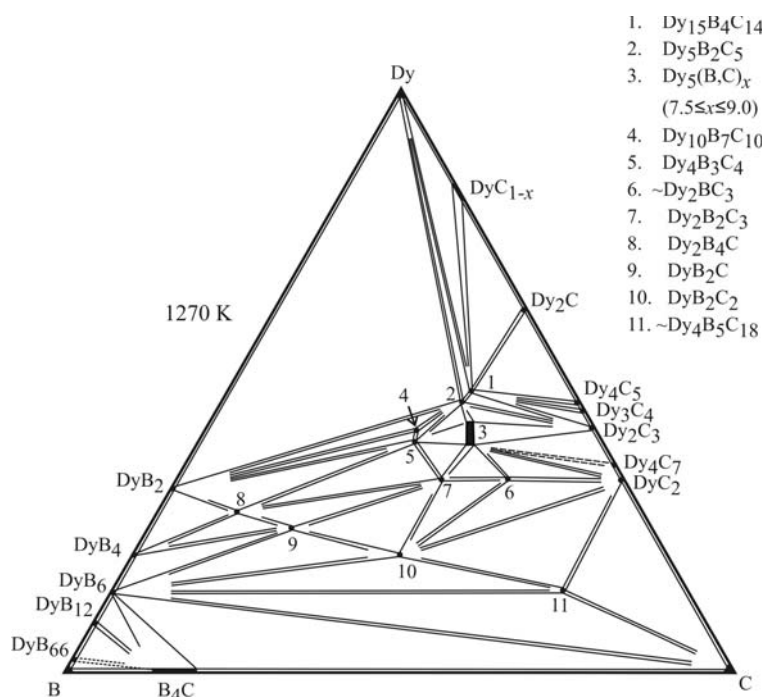

1. $Dy_{15}B_4C_{14}$
2. $Dy_5B_2C_5$
3. $Dy_5(B,C)_x$
   $(7.5 \leq x \leq 9.0)$
4. $Dy_{10}B_7C_{10}$
5. $Dy_4B_3C_4$
6. $\sim Dy_2BC_3$
7. $Dy_2B_2C_3$
8. Dy_2B_4C
9. DyB_2C
10. DyB_2C_2
11. $\sim Dy_4B_5C_{18}$

Fig. 1. Isothermal section of the Dy–B–C phase diagram at 1270 K.

A small range of homogeneity of DyC_{1-x} at the composition DyC_x ($0.33 < x < 0.45$) was detected. At low temperatures (proper temperature is unknown) and at 2:1 stoichiometry ($x=0.5$) the compound undergoes an ordering of carbon atoms in the structure, leading to the trigonal anti- $CdCl_2$-type structure. According to the XRD powder data, Dy_4C_5 belongs to the αY_4C_5 structure type. The sesquicarbide, Dy_2C_3 crystallizes in the Pu_2C_3-type structure and the binary compound Dy_4C_7 is isomorphic with αHo_4C_7-type structure. No extension into the ternary domain has been detected for the known binary compound $''B_4C''$ [23].

Table 1

Crystallographic data for ternary compounds detected in the Dy–B–C system

№	Compound	Space group	Structure type	Unit cell parameters (Å)		
				a	b	c
1.	$Dy_{15}B_4C_{14}$	$P4/mnc$	$Tb_{15}B_4C_{14}$	8.0882(1)		15.8846(3)
2.	$Dy_5B_2C_5$	$P4/ncc$	$Gd_5B_2C_5$	8.0987(1)		10.795(1)
3.	$Dy_5(BC)_x$ ($7.5 \le x \le 9.0$)	$P4/ncc$	$La_5B_2C_6$	8.012(1) 8.0220(7)		11.499(2) 12.193(2)
4.	$Dy_{10}B_7C_{10}$	$C2/c$	$Tb_{10}B_7C_{10}$	11.387(3)	11.147(3) $\beta = 98.06(2)$	23.715(4)
5.	$Dy_4B_3C_4$	$P\text{-}1$	$Gd_4B_3C_4$	3.5545(6) $\alpha = 93.23(1)$	3.5999(6) $\beta = 96.74(1)$	11.739(1) $\gamma = 90.16(1)$
6.	~Dy_2BC_3	–	–	–	–	–
7.	$Dy_2B_2C_3$	$Cmmm$	$Tb_2B_2C_3$	3.396(1)	13.694(8)	3.627(1)
8.	Dy_2B_4C	$Immm$	Dy_2B_4C	3.2772(9)	6.567(1)	7.542(2)
9.	DyB_2C	$Pbam$	LuB_2C	6.7893(3)	6.7776(3)	3.7254(1)
10.	DyB_2C_2*	$P4/mbm$	DyB_2C_2	5.3433(6)	–	3.5567(4)
11.	~$Dy_4B_5C_{18}$	–	–	–	–	–

* - X-ray powder data.

Eleven ternary compounds have been detected. They are of constant composition, except for (3) $Dy_5(B,C)_x$ ($7.5 \le x \le 9.0$). Nine ternary compounds, which were reported earlier, have been confirmed. Two ternaries (6) ~Dy_2BC_3 and (11) ~$Dy_4B_5C_{18}$ have been synthesized for the first time. Their crystal structure remains unknown. Metallographic investigation, X-ray powder diffraction and EPMA analyses revealed the new compound ~Dy_2BC_3 to be in equilibria with $Dy_2B_2C_3$ and DyB_2C_2 (Fig. 2 a) as well ~$Dy_4B_5C_{18}$ to be in equilibria with DyB_2C_2 and DyB_6.

The composition of "DyBC" [24] was defined as $Dy_2B_2C_3$ via EPMA analyses and the crystal structure of $Dy_2B_2C_3$ belongs to the $Tb_2B_2C_3$ structure type [25].

Fig. 2b shows the two-phase region of the Dy–B–C ternary system between $Dy_5B_{2.0}C_{5.5}$ and $Dy_5B_2C_5$ confirmed by refinement of the X-ray powder diffraction data and EPMA. Supplementary, the chemical analysis of alloy $Dy_{15}B_4C_{14}$ was performed in the Mikroanalytisches Labor Pascher in Remagen-Bandorf, Germany. The obtained data of Dy 44.9 at. %, B 11.0 at. % and C 44.1 at. % are in good agreement with the crystal structure model [26].

The crystallographic parameters of ternary phases in the Dy–B–C system are listed in Table 1. Two new ternary compounds ~Dy_2BC_3, ~$Dy_4B_5C_{18}$ have been discovered and characterized by EPMA in the samples being homogenizeted at 1270 K. Their crystal

structure needs additional study. The crystal structure of Dy_2B_4C was solved from X-ray single crystal data [27] and $Dy_{14}B_4C_{14}$ from X-ray powder diffraction data [26]. For the reported earlier tetragonal structure of DyB_2C [24], the crystal system was corrected in [28] to orthorhombic and crystallize in LuB_2C structure type. It is worth noting that contrary to the known data on RE–B–C systems no new phases in the Dy–B–C system were found in the arc melted alloys.

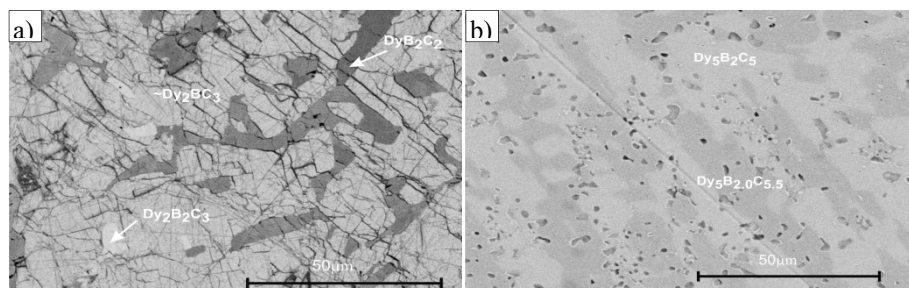**Fig. 2.** Backscattered electron image of the annealed bulk samples: a) $Dy_{30}B_{25}C_{45}$; b) $Dy_{40}B_{16}C_{44}$. Phase composition is in accordance with the XRD and EPMA data.

3.2. Crystal structure of DyB₂C₂

A recent reinvestigation of the structures of $RE B_2C_2$ (RE = La–Nd, Tb–Tm, Lu) has been performed using powder X-ray diffraction data [29]. Refinements in $P4/mbm$ are in agreement with the earlier predicted crystal structure characterized by only heteroatomic B–C bonds, however, in distorted squares and octagons, in contrast to the structural model proposed in [30, 31]. Here we report on the single crystal X-ray investigations of DyB_2C_2, the phase with the interesting magnetic properties [32, 33]. The metrics of the unit cell alone leads to the structural model proposed and refined on the basis of the powder XRD data by Yamauchi et al. [17] and by van Duijn et al. [34], space group $P4/mbm$ with alternating B and C atoms. The cell parameters, atomic coordinates and displacement parameters are given in Table 2 and 3, respectively.

Two types of B–C bonds are present: long bonds of 1.60(4)Å, with B-C-B angle of 135.1(3)° in the four- and eight-member rings and short bonds of 1.518(9) Å, with B-C-B angle of 84.5(7)°, unique to the eight-member rings (Fig. 3). Dy atoms located above the centers of the eight-member rings have slightly shorter contacts to C (2.673(8) Å) than to B (2.733(9) Å). Dy atoms are packed in a slightly distorted simple cubic array. Dy–Dy distances are of 3.560(1) Å parallel to [001] and of 3.780(1)Å in (001) plane. They are comparable with other RE-RE distances observed in the neutron diffraction and X-ray single crystal studies taking into account the lanthanoid contraction [29, 35].

3.3 Solid solution Dy₅(BC)ₓ (7.5 ≤ x ≤ 9.0)

The crystal structure, twinning and intergrowth of the samples with different compositions on the $\sim La_5B_2C_6$ compound were investigated in [36, 37]. These samples exhibit a pronounced tendency to form besides crystal twins and coherently intergrowth domains of different phases. For $Dy_5B_2C_6$ only the unit cell parameters and structure type was assigned.
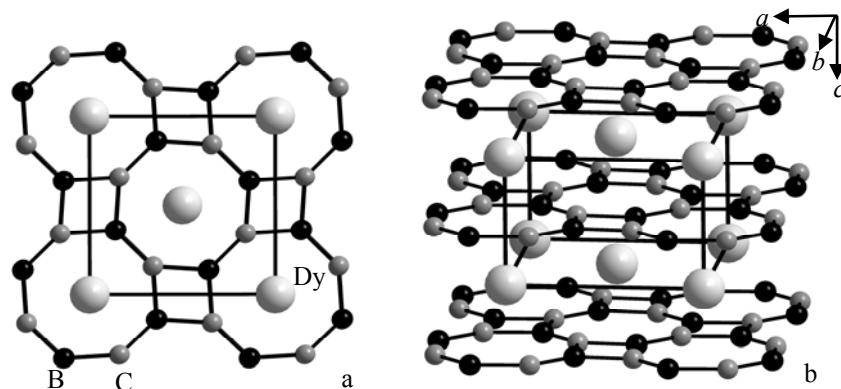
Fig. 3. Projection on the (001) plane (a) and side view (b) of the DyB$_2$C$_2$ crystal structure. Boron-carbon rings are emphasized.

Table 2

Crystal structure data and structure refinement parameters for DyB$_2$C$_2$

Empirical formula	DyB$_2$C$_2$
Crystal system	Tetragonal
Space group	*P4/mbm (*No. 127*)*
Pearson symbol	*tP*10
Formula per unit cell (Z)	2
Lattice parameters	
a / Å	5.345(1)
c / Å	3.5600(5)
Unit cell volume / Å^3	101.73(4)
Calculated density / (g/cm^3)	6.174
Absorption coefficient / (1/cm)	27.694
Crystal size / mm^3	0.030 x 0.022 x 0.019
Radiation and wavelength / Å	Mo *Kα*, 0.71069
Diffractometer	STOE IPDS II
Refined parameters	8
Refinement	*F^2*
2θ_{max} and (sinθ/λ)$_{max}$	70.4, 0.807
h, k, l	-8< *h* <8, -7< *k* <7
	-5< *l* <5
Collected reflections	1134
Independent reflections	190 (R_{int} = 0.094)
Reflections with I_o>2σ(I_o)	90 (R_σ = 0.033)
Final $R_1{}^a$ indices ($R_1{}^a$ all data)	0.046 (0.049)
Weighted w$R_2{}^b$ factor (w$R_2{}^b$ all data)	0.046 (0.096)
Goodness-of-fit on *F^2*:	1.2
Extinction coefficient	0.0028(6)
Largest diff.peak and hole / (*e*/Å^{-3})	-2.47/1.32

[a] R_1(F) = [Σ(|F$_o$|-|F$_c$|)]/Σ|F$_o$|;
[b] wR_2(F^2) = [Σ[w(F$_o{}^2$-F$_c{}^2$)^2/Σ[w(F$_o{}^2$)^2]]$^{1/2}$, [w^{-1} = σ^2(F$_o$)^2+(0.0766P)^2+ 0P], where P = (F$_o{}^2$+2F$_c{}^2$)/3.

Table 3

Positional and anisotropic displacement parameters for DyB$_2$C$_2$

Atom	Site	x	y	z	U_{eq}/U_{iso}, Å^2
Dy*	2a	0	0	0	0.0069(8)
B	4h	0.355(1)	0.144(1)	0.5	0.008(2)
C	4h	0.159(3)	0.340(3)	0.5	0.010(8)

*$U_{11} = U_{22} = 0.00694(9)$; $U_{33} = 0.0054(9)$; $U_{13} = U_{23} = U_{12} = 0$.

We observed a large variation of cell parameters of this phase [38]. This was also evidenced for other rare earths. The structural arrangement of ~Dy$_5$B$_2$C$_6$ (La$_5$B$_2$C$_6$ structure type) consists of a 3 D-framework of rare-earth atoms resulting from the stacking of slightly corrugated two-dimensional squares, which lead to the formation of octahedral voids and distorted bicapped square antiprismatic cavities. They are filled with isolated carbon atoms and two-fold disordered [CBCC] units, respectively. Our systematical studies of the crystal structure and the similar solid solution La$_5$B$_{2-x}$C$_{6+y}$ led to the formula La$_5$(BC)$_x$ ($5.6 \leq x \leq 8.8$) [4]. The studied samples with different compositions nearby to ~Dy$_5$B$_2$C$_6$ exhibited different cell parameters (see Table 4). These data evidenced on the homogeneity range of this ternary compound. Variation of the values of the lattice parameters are pronounced depending upon Dy and non-metal atoms stoichiometry (see Table 4). This is the reason for the large homogeneity region of this compound. The WDX analysis of the investigated samples shows that the boron content in the anionic chains [C1=B–C2=C1]$^{7-}$ in the crystal structure (assuming the formal charge for the B/C atoms obey the octet rule) of ~Dy$_5$B$_2$C$_6$ varies from 16(1) to 19(1) at.% B (Table 4). This leads to a decrease in the charge of [C1=B–C2=C1]$^{7-}$ as well as to disorder of light elements B and C2. The overall charge of the anionic part seems to be compensated by the introduction of single carbon atoms (C3) into Dy octahedra. The crystallographic analysis of La$_5$B$_2$C$_6$ structure type and the solid solution was described in detail in [4, 36]. So, the homogeneity region of ~Dy$_5$B$_2$C$_6$ was defined as Dy$_5$(BC)$_x$ ($7.5 \leq x \leq 9.0$) and is shown in Fig. 1. The electron balance of ~Dy$_5$B$_2$C$_6$ can be written as (Dy^{3+})$_5$(C^{4-})$_{0.25}$(CBCC^{7-})$_2$. The isostructural lanthanum compound ~La$_5$B$_2$C$_6$ exhibits a more pronounced homogeneity region than ~Dy$_5$B$_2$C$_6$ due to the fact that contrary to the La–B–C system in the Dy–B–C another ternary compound Dy$_5$B$_2$C$_5$ with close composition also exists.

Table 4

Results of EPMA investigation for alloys* Dy$_5$(B,C)$_x$, $7.5 \leq x \leq 9.0$

Composition	Lattice parameters (a, c in Å)	c/a	V (Å^3)	B, at. %
Dy$_5$B$_{2.0}$C$_{5.5}$^{a}	8.012(1) 11.499(2)	1.435	738.2(5)	16(1)
Dy$_5$B$_{2.6}$C$_{6.4}$^{b}	8.0220(7) 12.193(2)	1.519	784.6(4)	19(1)

* Phase equilibria in alloys were also confirmed by X-ray powder diffraction:
^{a} Dy$_5$B$_{2.0}$C$_{5.5}$ + Dy$_5$B$_2$C$_5$, ^{b} Dy$_5$B$_{2.6}$C$_{6.4}$ + Dy$_4$B$_3$C$_4$

4. Conclusions

The isothermal section of the Dy–B–C phase diagram at 1270 K was investigated by means of X-ray diffraction, microstructure and EPMA analyses. Eleven ternary compounds were found to occur. For nine of them, namely DyB_2C_2, Dy_2B_4C, DyB_2C, $Dy_5B_2C_5$, $Dy_5B_2C_6$, $Dy_2B_2C_3$, $Dy_4B_3C_4$, $Dy_{10}B_7C_{10}$, $Dy_{15}B_4C_{14}$ the crystal structures were reported earlier. Elemental composition for $Dy_2B_2C_3$ was determined by electron probe microanalysis. For the first time we observed that the ~$Dy_5B_2C_6$ compound has a broad homogeneity range described by the formula $Dy_5(BC)_x$, $7.5 \leq x \leq 9.0$. Two new ternary compounds were localized, namely ~Dy_2BC_3 and ~$Dy_4B_5C_{18}$. Binary compounds of the boundary Dy–B and Dy–C systems practically do not dissolve the third element C and B, respectively. In contrast to other rare earth metals with larger atomic radii (La-Sm), dysprosium boride carbides form structures with infinite one-dimensional planar or nearly planar $(BC)_\infty$ ribbons. Single crystal X-ray diffraction study confirms that the four- and eight-member slightly puckered rings in the DyB_2C_2 structure consist of alternating B and C atoms.

Acknowledgements

LITERATURE

1. *Babizhetskyy V., Bauer J., Gautier R., Hiebl K., Simon A., Halet J.-F.* Chapter 302: Structural, electronic and physical properties of solid-state rare-earth boride carbides, in: Handbook on the Physics and Chemistry of the Rare Earths: including Actinides. Volume 53 (Eds. Bünzli J.-C. G., Pecharsky V. K.). North-Holland, Amsterdam, 2018. -pp. 145–269. doi: 10.1016/bs.hpcre.2018.05.001
2. *Shi Y., Leithe-Jasper A., Tanaka T.* New ternary compounds $Sc_3B_{0.75}C_3$, $Sc_2B_{1.1}C_{3.2}$, $ScB_{15}C_{1.60}$ and subsolidus phase relations in the Sc–B–C system at 1700°C // J. Solid State Chem. 1999. Vol. 148. P. 250–259. doi: 10.1006/jssc.1999.8446
3. *Bauer J., Nowotny H.* Der Dreistoff Yttrium–Bor–Kohlenstoff // Monatsh. Chem. 1971. Vol. 102. P. 1129–1145. doi: 10.1007/BF00909940
4. *Babizhetskyy V., Simon A., Bauer J.* Interaction of lanthanum with boron and carbon: phase diagram and structural chemistry // Monatsh. Chem. 2014. Vol. 145. P. 869–876. doi: 10.1007/s00706-014-1172-2
5. *Babizhetskyy V., Hembara M., Levytskyy V.* Phase equilibria in Ce–B–C system at 1270 K and 970 K // Proc. Shevchenko Sci. Soc. Chem. Sci. 2016. Vol. XLIV. P. 21–29 (in Ukrainian).
6. *Babizhetskyy V., Simon A., Halet J.-F.* Investigations in the ternary praseodymium-boron-carbon system: solid-state phase diagram and structural chemistry // Solid State Sci. 2015. Vol. 47. P. 73–77. doi: 10.1016/j.solidstatesciences.2014.12.008
7. *Schwetz K. A., Hoerle M., Bauer J.* Contribution to the system Europium–Boron–Carbon // Ceramurgia Intl. 1979. Vol. 5. P. 105–109. doi: 10.1016/0390-5519(79)90014-0
8. *Ruiz D., Garland M. T., Saillard J.-Y., Halet J.-F., Bohn M., Bauer J.* Electron probe microanalysis in the ternary Gd–B–C system // Solid State Sci. 2002. Vol. 4. P. 1173–1178. doi: 10.1016/S1293-2558(02)01382-1

9. *Babizhetskyy V., Levytskyy V.* Phase equilibria and crystal structure of compounds of the Tb–B–C system at 1270 K // Visnyk Lviv Univ. Ser. Khim. 2019. Is. 60. Pt. 1. P. 12–20 (in Ukrainian). doi: 10.30970/vch.6001.012

10. *Bauer J., Venneguès P., Vergneau J. L.* The ternary system Holmium–Boron–Carbon; isothermal section at 1500 °C // J. Less-Common Met. 1985. Vol. 110. P. 295–298. doi:10.1016/0022-5088(85)90335-2

11. *Babizhetskyy V.* Phase equilibria in Er–B–C system at 1270 K // Visnyk Lviv Univ. Ser. Khim. 2017. Is. 58. Pt. 1. P. 3–12 (in Ukrainian).

12. *Akselrud L., Grin Y.* WinCSD: software package for crystallographic calculations (Version 4) // J. Appl. Crystallogr. 2014. Vol. 47. P. 803–805. doi:10.1107/S1600576714001058

13. Stoe WinXPOW (Version 2.1). Stoe & Cie GmbH, Darmstadt, Germany, 2004.

14. *Altomare A., Burla M. C., Camalli M. et al.* SIR97: a new program for solving and refining crystal structures // J. Appl. Crystallogr. 1999. Vol. 32. P. 115–119.

15. *Sheldrick G. M.* A short history of SHELX // Acta Crystallogr. 2008. Vol. A64. P. 112–122. doi:10.1107/S0108767307043930

16. *Farrugia L. J.* WinGX and ORTEP for Windows: an update // J. Appl. Crystallogr. 2012. Vol. 45. P. 849–854. doi:10.1107/S0021889812029111

17. *Yamauchi H., Onodera H., Ohoyama K., et al.* Antiferroquadropular ordering and magnetic properties of the tetragonal DyB_2C_2 compound // J. Phys. Soc. Japan. 1999. Vol. 68. N 6. P. 2057–2066.

18. *Bidaud E., Hiebl K., Bauer J.* Structural and magnetic properties of the rare-earth borocarbides. $R_6B_2C_6$ (R=Y, Ce–Tm). // J. Alloys Compd. 2001, Vol. 316, P. 75–81.

19. *Oeckler O., Mattausch Hj., Bauer J., Simon A.* Ordnung und Fehlordnung der Anionen in tetragonalen Boridcarbiden der Seltenerdmetalle // Z. Naturforsch. 2004, Vol. 59b, P. 1551–1562.

20. *Babizhetskyy V., Mattausch Hj., Simon A.* Infinite and finite boron carbon branched chains: the crystal structures of new ternary boride carbides RE10B7C10 and RE4B3C4 // Z. Anorg. Allg. Chem. 2009, Vol. 635, P. 737–742. doi: 10.1002/zaac.200900021

21. *Kuz'ma Yu., Chaban N.* Binary and ternary systems containing boron. Metallurgia. Moscow. 1990.

22. *Babizhetskyy V., Kotur B., Levytskyy V., Michor H.* Chapter 298: Alloy systems and compounds containing rare earth metals and carbon, in: J.-C.G. Bünzli, V.K. Pecharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earths Including Actinides, Amsterdam: North-Holland, 2017. – pp. 1–263. doi:10.1016/bs.hpcre.2017.09.001

23. *Rogl P.F., Vrestal J., Tanaka T., Takenouchi S.* The B-rich side of the B–C phase diagram // CALPHAD. 2014. Vol. 4. P. 3-12. doi: 10.1016/j.calphad.2013.07.016

24. *Bauer J., Debuigne J.* Sur les borocarbures de dysprosium. // J. C. R. Acad. Sci. (Paris), Sbr. C. 1972. Vol. 274. P. 1271–1274.

25. *Babizhetskyy V., Mattausch Hj., Simon A.* Crystal structure of terbium borocarbide $Tb_2B_2C_3$ // Z. Naturforsch. 2008. Vol. 63b. P. 929–933. doi: 10.1515/znb-2008-0802

26. *Babizhetskyy V., Simon A., Mattausch Hj., Hiebl K., Zheng C.* New ternary rare-earth metal boride carbides $R_{15}B_4C_{14}$ (R = Y, Gd–Lu) containing BC_2 units: crystal and electronic structures, magnetic properties // J. Solid State Chem. 2010. Vol. 183. P. 2343–2351. doi: 0.1016/j.jssc.2010.07.046

27. *Babizhetskyy V., Zheng C., Mattausch Hj., Simon A.* Ternary rare earth metal boride carbides containing two-dimensional boron-carbon network: The crystal and electronic structure of R_2B_4C (R – Tb, Dy, Ho, Er) // J. Solid State Chem. 2007. Vol. 180. P. 3515–3520. doi: 10.1016/j.jssc.2007.10.014

28. *Babizhetskyy V., Simon A., Hoch C., et al.* Structural, electronic and magnetic properties of layered REB$_2$C compounds (RE = Dy, Tm, Lu) // J. Solid State Chem. 2012. Vol. 191. P. 121–128. doi: 10.1016/j.jssc.2012.02.062

29. *Onoyama K., Kaneko K., Indoh K., Yamauchi H., Tobo A., Onodera H., Yamaguchi Y.* Systematic study on crystal structures in tetragonal RB$_2$C$_2$ (R=Rare Earth) compounds // J. Phys. Soc. Jpn. 2001. Vol. 70. P. 3291–3295. doi: 10.1143/jpsj.70.3291

30. *Smith P.K., Gilles P.W.* High temterature rare-earth–boron–carbon studies-III. LnB$_2$C$_2$ and the terary phase diagram // J. Inorg. Nucl. Chem. 1967. Vol. 29, 375–382.

31. *Rocquefelte X., Boulfelfel S. E., Ben Yahia M., Bauer J., Saillard J-Y., Halet J.-F.* Structural preference versus metal within the MB$_2$C$_2$ (M=Mg, Sc, Ca, Y, Ln) phases: The coloring problem revisited by DFT calculations // Angew. Chem. Int. Ed. 2005.Vol. 44, P. 7542–7545. doi: 10.1002/anie.200503080

32. *Yamauchi H, Osakabe T.* High-pressure studies of DyB$_2$C$_2$ // J. Korean Phys. Soc. 2013. Vol. 62, P. 2084–2087.

33. *Ohoyama K., Indoh K, Yamaguchi H. Tobo A., Matsuoka E, Sato M, Katano S, Onodera H.* Field-induced magnetic structures in antiferroquadrupolar ordering compound DyB$_2$C$_2$ // J. Phys. Soc. Japan 2008. Vol. 77, 114703. doi: 10.1143/JPSJ.77.114703

34. *van Duijn J., Suzuki K., Attfield J. P.* Boron–Carbon Order in CeB$_2$C$_2$ // Angew. Chem. 2000. Vol. 112. P. 373–374.

35. *Babizhetskyy V., Hoch C., Mattausch Hj., Simon A.* Boron–carbon order and symmetry control: single-crystal X-ray study of SmB$_2$C$_2$. Z. Naturforsch. 2006, Vol. 61b, P. 727–732. doi: 10.1515/znb-2006-0612

36. *Oeckler O., Mattausch Hj., Bauer J., Simon A.* Über die Kristallstruktur der Phase La$_5$B$_2$C$_6$ // Z. Anorg. Allg. Chem. 2001. Vol. 627. P. 779–788. doi: 10.1002/1521-3749(200104)627: 4%3C779::AID-ZAAC779%3E3.0.CO;2-Y

37. *Oeckler O., Duppel V., Bauer J., Mattausch Hj., Simon A.* Twinning and intergrowth of rare earth boride carbides // Acta Cryst. 2002. Vol. B 58. P. 161–167. doi: 10.1107/ S01087 68101019772.

38. *Köhler J., Babizhetskyy V.* New ternary borocarbides in the Dy–B–C system. Proceedings of the 4th International Symposium on Structure - Property Relationships in Solid State Materials, Bordeaux, France, 24-29 June 2012, P. 43.

РЕЗЮМЕ

Володимир БАБІЖЕЦЬКИЙ, Богдан КОТУР, Володимир ЛЕВИЦЬКИЙ

ФАЗОВІ РІВНОВАГИ ТА КРИСТАЛІЧНІ СТРУКТУРИ ТЕРНАРНИХ СПОЛУК У СИСТЕМІ Dy–B–C ПРИ 1270 K

Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія, 6, 79005 Львів, Україна
e-mail: v.babizhetskyy@googlemail.com

Зразки для дослідження синтезовано сплавлянням вихідних компонентів високої чистоти. Порошки графіту та бору перед використанням дегазували прожарюванням за температури 1270 K та тиску *p* < 10^{-5} мбар. Стружку Dy перемішували з порошками бору та графіту, взятими у стехіометричних співвідношеннях, і пресували у сталевій прес-формі. Спресовані таблетки масою 1,000 г сплавляли в електродуговій печі в атмосфері очищеного аргону. Гомогенізуючий відпал сплавів, загорнутих у молібденову фольгу, проводили при 1270 K упродовж 800 год у вакуумованих кварцових ампулах. Відпалені зразки гартували у холодній воді, не розбиваючи ампул. Зразки для дослідження готували в атмосфері очищеного аргону, використовуючи посудини Шленка, шафу з інертною атмосферою та капіляри Ліндемана, заповнені і запаяні під аргоном.

Побудовано ізотермічний переріз діаграми стану системи Dy–B–C при 1270 К. Ідентифіковано одинадцять тернарних сполук постійного складу, за винятком $Dy_5(B,C)_x$ ($7,5 \leq x \leq 9,0$). Для дев'яти з них визначено кристалічну структуру та уточнено періоди елементарної комірки. За допомогою методу рентгенівської спектроскопії за довжиною хвилі та РФА визначено склади двох нових сполук $\sim Dy_2BC_3$ і $\sim Dy_4B_5C_{18}$ з невідомою кристалічною структурою. Сполука $\sim Dy_2BC_3$ утворює рівноважні двофазні області зі сполуками DyB_2C_2, DyC_2 та $Dy_5(B,C)_x$ ($7,5 \leq x \leq 9,0$), а фаза з найбільшим вмістом Карбону $\sim Dy_4B_5C_{18}$ – зі сполуками DyC_2, DyB_2C_2, DyB_6 та Карбоном. Область з високим вмістом Бору поблизу бінарного бориду DyB_{66} не досліджено. Для сполуки $\sim Dy_2B_2C_6$, що кристалізується у структурному типі $La_5B_2C_6$ (просторова група $P4/ncc$) визначено область гомогенності, яку описано формулою $Dy_5(B,C)_x$ ($7,5 \leq x \leq 9,0$). Виявлено значну зміну параметрів елементарної комірки, яка зумовлена особливостями кристалічної структури CT $La_5B_2C_6$. Сполуку DyB_2C_2 (CT LaB_2C_2) використано нами як стандарт під час дослідження сполук системи Dy–B–C методом рентгенівської спектроскопії за довжиною хвилі раніше досліджували лише методом порошкової дифракції. Її кристалічну структуру уточнено рентгенівським дифракційним методом монокристала: ПГ $P4/mbm$, $Z = 2$, $a = 5,345(1)$, $c = 3,5600(5)$ Å, $R1 = 0.046$ ($wR_2 = 0,049$) для 585 рефлексів з $I_o > 2\sigma$ (I_o)). Склад сполуки, раніше описаної в літературі як "DyBC", за допомогою методу рентгенівської спектроскопії за довжиною хвилі уточнено як $Dy_2B_2C_3$ (CT $Tb_2B_2C_3$).

Ключові слова: фазові рівноваги, монокристал, кристалічна структура.