

Interaction of Lanthanum with Boron and Carbon: Phase Diagram and Structural Chemistry

Volodymyr Babizhetskyy, Arndt Simon, Josef Bauer

▶ To cite this version:

Volodymyr Babizhetskyy, Arndt Simon, Josef Bauer. Interaction of Lanthanum with Boron and Carbon: Phase Diagram and Structural Chemistry. Chemical Monthly = Monatshefte für Chemie, 2014, 145 (6), pp.869-876. 10.1007/s00706-014-1172-2. hal-01024172

HAL Id: hal-01024172 https://hal.science/hal-01024172

Submitted on 15 Jul2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Interaction of Lanthanum with Boron and Carbon: Phase Diagram and

- 2 Structural Chemistry
- 4 Volodymyr Babizhetskyy Arndt Simon Josef Bauer
- 5

3

6 Received:/Accepted ... 7

8 Abstract

9 The isothermal section of the La–B–C phase diagram at 1270 K has been investigated by 10 means of X-ray, neutron powder diffraction, microstructure and EPMA analyses. Eight ternary 11 compounds were found, and for six of them the crystal structures have been established. The 12 phase with the structure type of La₅B₂C₆ has a broad homogeneity range described by the 13 formula $La_5(BC)_x$ (5.6 $\leq x \leq 8.8$). The lanthanum sesquicarbide La_2C_3 exhibits an extended solid 14 solution in the ternary domain $La_2C_{3-x}B_x$ (x=0.4). The boron substitution of carbon leads to the 15 decrease of the superconducting temperature from 13.4 K for La₂C₃ to 10.0 K for La₂C_{2.8}B_{0.2} and 16 from 5.6K for $La_2C_{2,7}$ to 4.1K for $La_2C_{2,6}B_{0,4}$. The compositions of two new compounds, 17 ~La₄B₃C₁₂ and ~La₄B₅C₁₈ were found via WDX analysis.

18

19 Keywords: Carbides • Solid state • Crystal structure • Phase diagrams

20

21 V. Babizhetskyy (🖂)

- 22 Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla &
- 23 Mefodiya Str. 6, UA-79005 Lviv, Ukraine
- 24 E-mail address: v.babizhetskyy@googlemail.com
- 25 V. Babizhetskyy, A. Simon
- 26 Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 800665,
- 27 D-70569 Stuttgart, Germany
- 28 J. Bauer
- 29 Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Université de
- 30 Rennes 1-ENSCR, Institut de Chimie, Campus de Beaulieu, Avenue du Général Leclerc,
- 31 F-35042 Rennes Cedex, France

1 Introduction

3 The search for new ternary boride carbides predicted from several structural models 4 recently led to a systematic study of ternary phase diagrams, especially of carbides, borides and 5 boride carbides. The structures of the ternary rare earth (RE) boride carbides display a variety of 6 different arrangements with boron carbon substructures. They extend from zero-dimensional 7 units to chains and two-dimensional nets embedded in the metal atom sublattices as well as 8 interconnected boron icosahedra [1, 2]. The substructures can be divided into three groups. In the 9 first group the finite (0-D) quasi-molecular entities fill voids of the metal atom matrix and can 10 have different lengths ranging from 2 to 13 non-metal atoms. Stretched units of different sizes as 11 well as isolated C atoms can coexist. In the second category, the non-metal atoms form infinite one-dimensional planar or nearly planar ribbons $(BC)_{\infty}$ of zigzag chains of boron atoms to which 12 13 carbon atoms are attached. In the third family, the boron and carbon atoms form infinite planar 14 (2-D) nets which alternate with sheets of metal atoms.

15 The phase relations in the general *Ln*-B-C systems were not studied in sufficient detail so far. The solid-state phase equilibria in the ternary phase diagrams with Ln = Y, Eu, Gd, Ho were 16 17 reported [3 - 6]. The crystal structures of the known La-containing compounds were determined 18 from X-ray single crystal data. Two essential structural features of the model for LaB₂C₂ solved in space group $P\overline{4}2c$ presented in [7] remain uncertain. They adress the questions, firstly, 19 20 whether B and C atoms within the eight-membered rings are alternating or arranged in pairs and, 21 secondly, whether B and C atoms are stacked identically or alternatingly along c. The 22 reexamination of the LaB_2C_2 structure using neutron powder diffraction has been performed [8]. 23 The underlying coloring problem in extended networks and the correlation between symmetry 24 and electronic stability has been thoroughly treated by Burdett et al. [9], and on the basis of 25 Extended Hückel calculations they reached the conclusion that a coloring scheme with only 26 heteroatomic B-C bonds in contrast to [7] should represent the stable pattern in the LaB_2C_2 27 structure family. Refinements in P4/mbm are in agreement with the predicted structure

characterized by only heteroatomic B-C bonds, however, in distorted 2-D squares and octagons, 1 2 in contrast to the structural model proposed in [8].

3 From the first category with 0-D quasi-molecular entities, the phase $La_5B_2C_6$ containing 4 CB₃ units and isolated carbon atoms has recently been described in detail [10, 11]. The atom 5 displacements in the structure are indeed due to real structure effects and are not a consequence 6 of experimental artefacts (e. g. absorption) or inappropriate structure models (e. g. wrong choice 7 of space group, superstructures, or twinning). Tetragonal rare earth boride carbides with structure 8 types derived from $\sim La_5B_2C_6$ and Sc_3C_4 , respectively, can intergrow coherently. Slabs of both 9 types with various thicknesses from one unit cell up to macroscopic domains may occur, sharing 10 a common square net of metal atoms [12]. In the crystal structures additional $La_x B_y C_7$ 11 compounds were found with B/C chains of different lengths. So, the structure of LaBC contains 12 non-linear B_5C_5 chains [13]. The structure of $La_{10}B_9C_{12}$ contains slightly corrugated two-13 dimensional metal atom square nets forming two types of chains with 26 and 18 La atoms, 14 respectively, wherein B₄C₄ and B₅C₈ units are located [14]. The structure of La₅B₄C_{5-x} (x = 0.15) 15 is composed of slightly corrugated two-dimensional metal atom square nets hosting the finite 16 boron-carbon units B₄C₄, B₃C₃, BC₂ and isolated carbon atoms. The positions of the carbon 17 atoms in the unit BC_2 are not fully occupied [15]. Longer oligometric anions are observed when 18 the boron-carbon ratio increases. Eleven-membered chains of different B/C ratio, B_4C_7 and B_5C_6 , 19 exist in $La_{15}B_{14}C_{19}$ [16].

20

In order to pursue our systematic research on the $La_x B_y C_7$ phases, we focused on the 21 solid-state phase equilibria in the ternary La-B-C phase diagram. Hence, the presentation of the 22 isothermal section of the ternary La-B-C phase diagram at 1270 K, crystallographic data of the 23 ternary compounds and the structure and determination of the homogeneity range of $\sim La_5B_2C_6$ 24 are subjects of this work.

25

1 2

Results and discussion

3 4

Phase equilibria in the the La-B-C ternary system

5 The isothermal section of the La-B-C phase diagram at 1270K is presented in Fig. 1. In 6 agreement with Schlesinger et al. [17], two binary compounds, LaB₄ and LaB₆ have been found 7 in the La–B binary system at 1270K. The existence of two binary compounds, La_2C_3 and LaC_2 , 8 have been confirmed according to the data of Gschneidner et al. [18]. The superconducting 9 properties of the rare earth sesquicarbide and homogeneity region of La₂C_{3-δ} (T_c=13.4 K for 10 La_2C_3 and 5.6K for $La_2C_{2.7}$) were recently studied [19, 20]. The standardized cell parameters at 11 293K (Germanium 99.9999%, a_{Ge} =5.657905 Å, served as internal standard) for La₂C_{3- δ} changes from a=8.8149(5) for La₂C₃ to 8.8079(5)Å for La₂C_{2.7}. The results of EPMA analysis show that 12 this phase is extended in a ternary domain. The influence of the boron addition at the La₂C_{3- δ} was 13 14 also observed by magnetic measurements of crushed alloys buttons. So, the boron substitution in La₂C₃ leads to the composition La₂C_{2.8(1)}B_{0.2(1)} (a=8.8136(4) Å) and decreasing T_c from 13.4 K to 15 16 10.0 K. For La₂C_{2.7} a limit of the homogeneity was observed at La₂C_{2.6}B_{0.4(1)} (a=8.8218(6) Å), the phase becoming superconducting at 4.1 K in contrast to $T_c = 5.6$ of La₂C_{2.7} [19]. The results 17 will be published separately. A very small range of homogeneity of LaC₂ was detected by 18 19 neutron and physical properties experiments [21]. No extension of a ternary domain has been 20 detected for the binary compound " B_4C " [22, 23]. The phase boundary of the La-rich liquid was 21 not defined within the ternary system. The micrograph analysis was unsuccessful because of 22 high sensitivity of samples against moisture. The form of the solid phases arrangements below 23 1190 K is sketched in Fig. 1 by dashed lines corresponding to the literature data of binary 24 systems presented in [17, 18].

- 25
- 26
- .

< Fig. 1 >

1	Metallographic investigation, X-ray powder diffraction and EPMA analyses revealed the
2	new compound $\sim La_7B_9C_{34}$ to be in equilibrium with LaB_6 (Fig.2 a, b). Fig. 2 c, d shows the
3	three-phase region of the La-B-C ternary system between LaB ₄ , LaBC and La confirmed by X-
4	ray powder diffraction and EPMA analyses.
5	The crystallographic characteristics of the ternaries in the La-B-C system are listed in
6	Table 1. It is worth noting that after annealing at 1270 K the phase $La_{15}B_{14}C_{19}$ [16] was not
7	found. It exists only in arc-cast samples. The compositions of two new compounds \sim La ₄ B ₃ C ₁₂
8	
9	
10	< Fig. 2 >
11	
12	and $\sim La_4B_5C_{18}$ were found using WDX analysis. They show up in the phase diagram according
13	to Fig. 1.
14	
15	Solid solution $La_5(BC)_x$ (5.6 $\leq x \leq 8.8$)
16 17	$RE_5B_2C_6$ was first discovered and labeled as "Gd ₂ BC ₂ " [5a]. The phase exhibits a large
18	homogeneity region. The X-ray powder diagrams of " RE_2BC_2 " show a similarity with
19	
20	< Table 1 >
21	
22	corresponding rare earth dicarbides (CaC ₂ type structure) with an observed a parameter slightly
23	smaller than in REC_2 and doubled c parameter. Firstly, the crystal structure of $\sim La_5B_2C_6$ has
24	been determined in space group P4 from single crystal x-ray data [24] and the correct formula
25	and superconducting transition at 6.9 K was deduced. Later, the structure of $\sim La_5B_2C_6$ [10] was
26	reinvestigated in space group P4/ncc ($a = 8.590$, $c = 12.398$ Å). Crystal structure and real
27	structure investigations on the intermittent superconductivity of $\sim La_5B_2C_6$ indicated in [11]

1	clearly show that superconductivity is not an intrinsic property of the phase, but must be ascribed
2	to precipitations of a B containing La_2C_{3-x} phase in the C rich region and β -La in the metal-rich
3	region. Obviously, the complete coverage of borocarbide crystallites by La can result in a total
4	magnetic shielding of the samples
5	
6	< Fig. 3 >
7	
8	The structural arrangement of $\sim La_5B_2C_6$ compounds consists of a three-dimensional
9	framework of rare-earth atoms resulting from the stacking of slightly corrugated two-
10	dimensional squares, which lead to the formation of octahedral voids and distorted bicapped
11	square antiprismatic cavities (Fig. 3 a-c). They are filled with isolated carbon atoms and twofold
12	disordered CBCC units, respectively. The C1, C2/B2 atoms in ~La ₅ B ₂ C ₆ form bent CBCC units
13	with C/B-C distances of 1.32 Å indicative of double bond character and C/B - C/B distances of
14	1.65 Å. The C– C/B – C/B angle is 158.1°.
15	Unambiguous locations of C/B in Wyckoff position 16g in disordered CBCC units as
16	well as occupation of light atoms are not always obvious from the X-ray measurements.
17	Therefore supplementary powder neutron and synchrotron single crystal experiments were
18	performed. The
19	
20	< Table 2 >
21	
22	
23	< Table 3 >
24	
25	results of the structure refinement are in good agreement with WDX analyses. Tables 2 and 3
26	present the results of Rietveld refinements of x-ray, neutron and synchrotron single crystal

1	investigations of $\sim La_5B_2C_6$. The unit cell parameter c for $\sim La_5B_2C_6$ varies significantly and
2	ranges from 12.315(2) to 12.843(4) Å. However, the occupation of the large voids by only
3	disordered CBCC units is improbable. The observation of large displacement parameters for the
4	central C/B atoms of the CBCC units is in line with the disorder of occupation by either CBC or
5	CBCC units for the large voids and single carbon atoms in octahedral voids. That is the reason
6	for the large homogeneity region of this compound. The structure refinement clearly shows that
7	for the unit cells with $c/a < 1.474$ the BC ₃ unit does not fully occupy the La ₁₀ voids (Fig. 3c). The
8	boron content in $[C=B-C=C]^{7-}$ varies from 15(1) to 21(1) at % which leads to a decrease in
9	charge as well as disorder [5]. The overall charge of the anionic part seems to be compensated by
10	introduction of single carbon atoms (C3) in La octahedra. The octahedron volume increases from
11	30.524\AA^3 for empty octahedra to 32.146\AA^3 for fully occupied ones by C3 atoms (Fig. 3b). So,
12	the homogeneity region of $\sim La_5B_2C_6$ is defined as $La_5(BC)_x$ (5.6 $\leq x\leq 8.8$) and presented in Fig. 1.

13

14 Conclusion

The isothermal section of the La-B-C phase diagram at 1270 K has been investigated by 15 16 means of X-ray, neutron powder diffraction, microstructure and EPMA analyses. In the system 17 eight ternary compounds were found. For six of them, namely ~La₅B₂C₆, La₅B₄C₅, LaBC, 18 $La_{10}B_9C_{12}$, $La_{15}B_4C_{14}$, LaB_2C_2 , the crystal structures have been established. The phase $La_5B_2C_6$ 19 has a wide homogeneity range described by the formula $La_5(BC)_x$ (5.6 $\leq x \leq 8.8$). For the boundary 20 compounds of the La-B system no extension in the ternary domain was found. In contrast to 21 binary borides the lanthanum sesquicarbide La_2C_3 exists as solid solution $La_2C_{3-x}B_x$ (x=0.4). The 22 carbon substitution by boron leads to a decrease in T_c from 13.4 K for La₂C₃ to 10.0 K for 23 $La_2C_{2.8}B_{0.2}$ and from 5.6K for $La_2C_{2.7}$ to 4.1K for $La_2C_{2.6}B_{0.4}$. The new compounds $\sim La_4B_3C_{12}$ 24 and ~La₄B₅C₁₈ show broad diffraction peaks. In contrast to the rare earths with small atomic 25 radius lanthanum boride carbides form no compounds with infinite one-dimensional planar or 26 nearly planar ribbons $(BC)_{\infty}$. The investigated structures contain finite (0-D) quasi-molecular 27 B/C entities which fill voids of the lanthanum matrix and can have different lengths ranging from

2 to 13 non-metal atoms. Linear or bent units of different sizes as well as isolated C atoms can
 coexist.

3 **Experimental**

4 Synthesis and analysis

5 Polycrystalline samples were prepared from commercially available pure elements: lanthanum with a claimed purity of 99.99 at%, Alfa – Aesar, Johnson Matthey Company, 6 7 sublimed bulk pieces; crystalline boron powder, purity 99.99 at%, H. C. Starck, Germany; 8 graphite powder, purity 99.98 at%, Aldrich. Before use, the graphite and boron powders were outgased overnight at 1220 K, $p < 10^{-5}$ mbar. Lanthanum ingots were filed to coarse powders 9 10 with beryllium bronze files (Dönges GmbH, Germany). Stoichiometric mixtures of the 11 constituents were compacted in stainless steel dies. The pellets were arc-melted under purified 12 argon atmosphere [25] on a water-cooled copper hearth. The alloy buttons of 1g were turned 13 over and remelted three times to improve homogeneity. The samples were then wrapped in 14 molybdenum foil and annealed in silica tubes under argon for 1 month at 1270 K. Subsequent 15 heating for some samples just above the melting point was carried out in a high-frequency 16 furnace (TIG-10/300, Hüttinger, FRG) under argon atmosphere for several hours at different 17 temperatures. Finally, the samples were wrapped in molybdenum foils, annealed in evacuated 18 silica tubes for one month at 1270 K and subsequently guenched in cold water. Sample handling 19 was carried out under argon atmosphere in a glove box ($P_{H2O} < 0.1$ ppm) or through the Schlenk 20 technique.

21 X-ray powder diffraction patterns were obtained on a powder diffractometer STOE 22 STADI P with $MoK_{\alpha 1}$ radiation, using capillaries sealed under dried argon to avoid hydrolysis. 23 The unit cell parameters for the investigated compounds $La_xB_yC_z$, as well as the Rietveld 24 refinements for some samples containing the $La_5B_2C_6$ phase were refined with the help of the 25 CSD program package or FULLPROF programs packages [26, 27]. The results are given in 26 Tables 1, 2. < Fig. 4 >For neutron powder experiments the ¹¹B containing sample ~La₅B₂C₆ of 10 g was sealed

5 into a vanadium can under 1 bar of He and measured at 300 K using the GEM diffractometer at 6 the ISIS laboratory. The structural parameters as well as the composition were gained from 7 Rietveld refinements using the FULLPROF program. Figure 4 shows the neutron powder diffraction patterns of composition $La_5B_2C_{6-x}$. The refined parameters of the $La_5B_2C_{6-x}$ (x = 1.4) 8 9 phase include the lattice constants, the fractional coordinates of the La, B/C and C atoms, 10 isotropic displacement parameters, (anisotropic in case of La). After refinements with the 11 aforementioned parameters, in a last step, the C occupancy was refined and the convergence by 12 varying the occupancy was checked in those cases where the other refined parameters are fixed 13 or free. For both cases, a C deficiency in 4c and 16g sites is derived consistently. The results of 14 the refinements at T=300 K are listed in Table 1. The single crystal diffraction data of La₅B_{2-x}C₆₋ 15 _v were collected at room temperature on a synchrotron facility with $\lambda = 0.41328$ Å. The starting 16 atomic parameters taken from [10] were refined with the program SHELX-97 [28] within the WinGX program package [29] (full matrix least-squares on F^2) with anisotropic atomic 17 18 displacements for La atoms. The atomic coordinates and atoms displacement parameters are 19 listed in Tables 3 and 4.

20

1

2

3

4

21 Microprobe analysis.

For metallographic inspection and electron probe microanalysis (EPMA) some alloys were embedded in Woods metal (Fluka Chemie, Switzerland) with a melting point of ca. 75°C. The samples were polished on a nylon cloth using chromium oxide (Bühler Isomet) with grain sizes 1-5 μm. Quantitative and qualitative composition analyses of the samples were performed by energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy

1	(WDX) on a scanning electron microscope TESCAN 5130 MM with an Oxford Si-detector and
2	with an Oxford INCA WAVE 700 detector. LaB_4 and LaB_2C_2 standards were used to deduce the
3	compositions of compounds. For the chemical microprobe, the polishing procedure had to be
4	performed or repeated just before the measurements. Metallographic and EPMA analyses of the
5	La-B-C ternary system reveal the compound LaBC [13] to be in phase equilibrium with $La_5B_4C_5$
6	[15], $La_{10}B_9C_{12}$ [14] and $La_5(BC)_x$ (5.6 $\leq x \leq 8.8$) ($La_5B_2C_6$ structure type) [11] and LaB_4 at
7	1270K. Metallographic and EPMA analyses are in good agreement with results from x-ray
8	powder diffraction (e. g. see Fig. 2). Chemical analysis of the sample La ₅ B _{2.4} C _{5.3} (La ₅ B ₂ C ₆
9	structure) was performed in the Mikroanalytisches Labor Pascher in Remagen-Bandorf,
10	Germany. The results of the EPMA and chemical analyses are listed in Tabl. 2.
11	
12	Magnetical properties.
13	The magnetic properties were studied in the temperature interval 1.8 - 330 K by use of a MPMS
14	XL-7 SQUID magnetometer (Quantum Design, Inc.) in external fields up to 7 T. The crushed
15	alloys buttons of irregular shapes were used for the measurements.
16	
17	Acknowledgements
18	
19	The authors gratefully thank M. Babizhetska for the sample preparation, Dr. C. Hoch for X-
20	ray intensity data collection, E. Brücher for the magnetization measurements, V. Duppel for
21	EPMA analysis.
22	
23	

1 References

- 2 [1] Bauer J, Halet J-F, Saillard J-Y (1998) Coord Chem Rev 178–180:723
- 3 [2] Mori T, (2008) Higher borides. In: Gschneidner K A Jr, Bunzli J-C, Pecharsky V (eds)
- 4 Handbook on the Physics and Chemistry of Rare Earths. North-Holland, Amsterdam, p. 105
- 5 [3] Bauer J, Nowotny H (1971) Monatsh Chem 102: 1129
- 6 [4] Schwetz K A, Hoerle M, Bauer J (1979) Ceramurgia Intl 5 (3):105
- 7 [5] a) Smith P K, Gilles P W (1967) J Inorg Nucl Chem 29:375
- 8 b) Ruiz D, Garland M. T, Saillard J-Y, Halet J.-F, Bohn M, Bauer J (2002) Solid State
- 9 Sciences 4:1173
- 10 [6] Bauer J, Vernnegues P, Vergneau J. L (1985) J Less Comm Met 110:295
- 11 [7] Bauer J, Bars O (1980) Acta Crystallogr Sec B 36:1540
- [8] Onoyama K, Kaneko K, Indoh K, Yamauchi H, Tobo A, Onodera H, Yamaguchi Y (2001) J
 Phys Soc Japan 70:3291
- 14 [9] Burdett J K, Canadell E, Hughbanks T (1986) J Am Chem Soc 108:3971
- 15 [10] Oeckler O, Bauer J, Mattausch Hj, Simon A (2001) Z Anorg Allg Chem 627:779
- 16 [11] Simon A, Babizhetskyy V, Oeckler O, Mattausch Hj, Bauer J, Kremer R K (2005) Z Anorg
- 17 Allg Chem 631:316
- 18 [12] Oeckler O, Duppel V, Bauer J, Mattausch Hj, Simon A (2002) Z Anorg Allg Chem628:1607
- 20 [13] Babizhetskyy V, Mattausch Hj, Gautier R, Bauer J, Halet J-F, Simon A (2005) Z Anorg
- 21 Allg Chem 631:1041
- 22 [14] Babizhetskyy V, Mattausch Hj, Simon A (2004) Z Kristallogr NCS 219:11
- 23 [15] Babizhetskyy V, Mattausch Hj, Simon A (2003) Z. Kristallogr NCS 218:417
- 24 [16] Gougeon P, Halet J-F, Ansel D, Bauer J Z. Kristallogr (1996) NCS 211:822
- 25 [17] Schlesinger M E, Liao P K, Spear K E (1999) Journal of Phase Equilibria 20:73
- 26 [18] Gschneidner K A Jr, Calderwood F W (1986) Bull All Phase Diagr 7:446
- 27 [19] Simon A, Gulden Th (2004) Z Anorg Allg Chem 630:2191
- 28 [20] Kim J S, Xie W-H, Kremer R K, Babizhetskyy V, Jepsen O, Simon A, Ahn K S, Raquet B,
- 29 Rakoto H, Broto J M, Ouladdiaf B (2007) Phys Rev B 76(1):014516/1
- 30 [21] Babizhetskyy V, Jepsen O, Kremer R K, Simon A, Ouladiaff B, Stolovits A (2014) J Phys
- 31 Condens Matter 26:025701
- 32 [22] Morosin B, Kwei G H, Lawson A C, Aselage T L, Emin D (1995) J Alloys Compd 226:121

- 1 [23] Sologub O, Michiue Y, Mori T (2012) Acta Cryst E68:i67 and references therein
- 2 [24] Bauer J, Bars O (1983) J Less-Common Met 95:267
- 3 [25] Horvath B, Strutz J, Geyer-Lippmann J, Horvath G (1981) Z Anorg Allg Chem 483:205
- 4 [26] Akselrud L G, Grin Yu N, Zavalii P Yu, Pecharskii V K (1993) WinCSD Universal
- 5 Program Package for Single Crystal and/or Powder Structure Data Treatment, Materials Science
- 6 Forum 335:133
- 7 [27] Rodriguez-Carvajal J (1993) Phys B 192:55
- 8 [28] Sheldrick G M (1997) SHELXL-97, Program for the Refinement of Crystal Structures,
- 9 University of Göttingen (Germany)
- 10 [29] Farrugia L J (1999) WinGX (Version 1.64.05), J Appl Crystallogr 32:837
- 11

1 Figure Captions

2	Fig. 1 Isothermal section of the La–B–C phase diagram at 1270 K. Dashed tie-lines correspond
3	to equilibria in the solid state below 1190 K and $La_{15}B_{14}C_{19}$ observed in arc-cast samples.
4	
5	Fig. 2 Secondary electron image (a) and x-ray powder pattern (b) of the annealed bulk sample
6	with nominal atomic composition La/B/C = $14/32/54$. Indicated (*) reflections are from LaB ₆
7	and other of \sim La ₇ B ₉ C ₃₄ . Backscattered electron image (c) and x-ray powder pattern (d) of the
8	annealed bulk sample with nominal atomic composition $La/B/C = 40/45/15$. Indicated (*)
9	reflections are from LaB_4 , (•) LaBC and (+) La.
10	
11	Fig. 3 Crystal structure of $\sim La_5B_2C_6$ (a). The chains of edge-sharing La_6C octahedra are
12	emphasized. The rare earth metal atoms environments of discrete carbon atoms (b) and
13	C-B/C-B/C-C (c) units are shown. Lanthanum atoms in (b) and (c) are represented by their
14	anisotropic displacement ellipsoids at the 99.9% probability level.
15	

16 Fig. 4 Comparison of observed and calculated neutron powder profiles for $La_5B_2C_{4.6}$

Table 1 Crystallographic data of ternary compounds in the La–B–C system

Compound	Space	Structure	Unit cell parameters (Å)		References	
	group	type	а	b	С	
$La_5(BC)_x$	P4/ncc	$La_5B_2C_6$	8.584(1)-		12.315(2) -	[10], ^{a)}
$(5.6 \le x \le 8.8)$			8.598(1)		12.730(1)	
$La_5B_4C_{5-x}(x=0.15)$	$Pna2_1$	$Ce_5B_4C_5$	24.682(3)	8.612(1)	8.647(1 b)	[15], ^{a)}
LaBC	$P2_{1}2_{1}2_{1}$	LaBC	8.666(1)	8.707(1)	12.485(2)	[13], ^{a)}
$La_{10}B_9C_{12}$	$P4_{1}2_{1}2$	$Ce_{10}B_9C_{12}$	8.6678(5)		25.689(3)	[14], ^{a)}
$La_{15}B_{14}C_{19}^{b)}$	$P2_{1}/c$	$La_{15}B_{14}C_{19}$	8.640(3)	8.636(4)	19.823(6)	[16], ^{a)}
				β=94.28(3)°		
LaB_2C_2	P4/mbm	LaB_2C_2	5.4050(2)		3.9623(2)	[8], ^{a)}
$\sim La_4B_3C_{12}$						
\sim La ₄ B ₅ C ₁₈						

^{a)} Powder data of the present work, ^{b)} observed in arc-cast samples.

Table 2 Crystallographic and chemical composition data for alloys $La_5(BC)_x$ (5.6 $\leq x \leq 8.8$)

Composition	Lattice parameters	c/a	$V(\text{\AA}^3)$	В,	(C1-C2/B2)	C3
	(<i>a</i> , <i>c</i> in Å)			at % ¹⁾	occupation	occupation
$La_5B_{2.8}C_6$	8.622(1)	1.489	955.0(4)	21(1)	1.00	1.00
	12.843(4)					
La ₅ B _{2.8} C _{5.7}	8.5837(1)	1.487	940.39(4)	20(1)	1.00	0.75(4)
	12.7632(2)					
La ₅ B _{2.4} C _{5.3} ²⁾	8.5807(1)	1.474	931.70(4)	19(1)	0.8(1)	0.50(4)
	12.6539(3)					
$La_5B_2C_{4.6}^{3)}$	8.5810(1)	1.458	921.44(4)	17(1)	0.8(1)	0.20(3)
	12.5140(2)					
La ₅ B _{1.8} C _{3.9}	8.5746(4)	1.450	914.4(2)	16(1)	0.7(2)	0.10(5)
	12.437(1)					
$La_5B_{1.75}C_{3.8}^{4)}$	8.578(1)	1.438	908.3(3)	16(1)	0.7(2)	0.0
	12.342(2)					
La ₅ B _{1.5} C _{4.1}	8.584(1)	1.434	907.5(4)	15(1)	0.7(2)	0.0
	12.315(2)					

8

 WDX microprobe analyses
 Chemical analysis in at % :La-38.1, B-19.0, C-42.9
 Neutron powder diffraction data

⁴⁾ Synchrotron single crystal diffraction data

- Table 3 Comparison of refinement results by synchrotron single crystal and neutron powder diffraction data of ${\sim}La_5B_2C_6^{~a)}$

Methode	Neutron	Synchrothron	
	powder data ^b)	single-crystal data ^{c)}	
Composition	$La_5B_2C_{4.6}$	$La_5B_{1.75}C_{3.8}$	
La1 x	0.6502(3)	0.64998(3)	
У	0.0508(3)	0.05149(2)	
Z.	0.1083(3)	0.10687(2)	
$B_{ m eq}$	0.38(2)	0.86(1)	
La2 z	0.1363(6)	0.13729(4)	
$B_{ m eq}$	0.76(3)	1.10(1)	
C1 <i>x</i>	0.6545(5)	0.6550(6)	
У	0.0457(6)	0.0448(6)	
Z.	-0.09351(4)	-0.0890(4)	
$B_{ m iso}$	0.98(3)	1.03(1)	
C2/B2 x	0.6269(5)	0.6292(6)	
У	0.0632(6)	0.0609(6)	
Z.	-0.2010(3)	-0.2000(4)	
$B_{ m iso}$	1.16(3)	1.46(1)	
C3 z	0.357(1)		
$B_{ m iso}$	1.51(3)		
Occupancy:			
C1	0.80(1)	0.7(2)	
C2/B2	0.30(1)/0.50(1)	0.3(2)/0.4(2)	
C3	0.20(3)	-	

6 7

^{a)} La2 and C3 in 4c (1/4, 1/4, z) ^{b)} $R_{\rm I}$ =0.067, $R_{\rm F}$ =0.056, $R_{\rm p}$ =0.10, $R_{\rm exp}$ =0.14, χ^2 =1.7 ^{c)} $R_{\rm I}$ =0.035, $wR_{\rm I}$ =0.087 for 2997 reflections with $I < 2\sigma(I_{\rm o})$.

Table 4

Anisotropic displacement parameters for lanthanum atoms in ~La₅B₂C₆

Atom	B_{11}	B ₂₂	<i>B</i> ₃₃	B_{23}	<i>B</i> ₁₃	<i>B</i> ₁₂
La1 ^{a)}	0.32(2)	0.40(3)	1.25(6)	0.002(6)	-0.0022(9)	-0.010(7)
La2 ^{a)}	0.30(2)	B_{22}	1.88(1)	0.000	0.000	0.000
La1 ^{b)}	0.501(6)	0.656(7)	1.68(1)	0.004(4)	-0.0059(6)	-0.021(5)
La2 ^{b)}	0.466(9)	<i>B</i> ₂₂	2.28(1)	0.000	0.000	0.000

^{a)} neutron powder diffraction data ^{b)} synchrotron single crystal data

Fig. 1 Isothermal section of the La–B–C phase diagram at 1270 K. Dashed tie-lines correspond to equilibria in the solid state below 1190 K and $La_{15}B_{14}C_{19}$ observed in arc-cast samples.



Fig. 2 Secondary electron image (a) and x-ray powder pattern (b) of the annealed bulk sample with nominal atomic composition La/B/C = 14/32/54. Indicated (*) reflections are from LaB₆ and other reflections are of \sim La₇B₉C₃₄. Backscattered electron image (c) and x-ray powder pattern (d) of the annealed bulk sample with nominal atomic composition La/B/C = 40/45/15. Indicated (*) reflections are from LaB₄, (•) LaBC and (+) La.



Fig. 3 Crystal structure of $\sim La_5B_2C_6$ (a). The chains of edge-sharing La₆C octahedra are emphasized. The rare earth metal atoms environments of discrete carbon atoms (b) and C-B/C-B/C-C (c) units are shown. Lanthanum atoms in (b) and (c) are represented by their anisotropic displacement ellipsoids at the 99.9% probability level.





Fig. 4. Comparison of observed and calculated neutron powder profiles for La₅B₂C_{4.6}

Graphics for use in the Table of Contents

