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Mendeleev Commun., 2014, **24**, 15–16

Mendeleev Communications

Synthesis and crystal structure of $[B_{12}]_2[CBC][C_2]Mg_{1.42}$, a new modification of $B_{25}C_4Mg_{1.42}$

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DOI: 10.1016/j.mencom.2013.12.004

A new title modification of $B_{25}C_4Mg_{1.42}$ was prepared by self-propagating high-temperature synthesis and characterized by single crystal XRD analysis.

Previously,[1–3] we reported the structure of boron carbide produced by self-propagating high-temperature synthesis (SHS). By varying carbon concentrations from 5 to 30%, we attempted to establish a correlation between lattice parameters and composition. In this work, we determined the composition and structure of $B_{25}C_4Mg_{1.42}$ by single crystal XRD analysis.

The test compound was produced from the commercial powders of Mg (MPF-2 brand; ⩾ 99% purity; particle size, ⩽ 250 μm), boron oxide (98.5%, ⩽ 250 μm), carbon black (P804-T; specific surface area, 12 m^2 g^{-1}), and magnesium perchlorate by magnesiothermic SHS in the presence of carbon.[2]

The synthesized products contained black fine (5–20 μm) crystallites of B_4C and acid-resistant single crystals (up to 1 mm) with a habitus close to isometric one (Figure 1). Their colour varied from amber to black. Composition of the large single crystals could not be identified by XRD (no data in PDF-2 data bank).

Using single crystal XRD analysis, we studied a dark brown crystal (0.25 × 0.25 × 0.3 mm) and established the structure and composition of $B_{25}C_4Mg_{1.42}$, which corresponded to structural formula $[B_{12}]_2[CBC][C_2]Mg_{1.42}$. The main characteristics of the experiment are summarized in Table 1.[†]

We also varied the occupation (q) for four positions of magnesium atoms, every position is located 0.3–0.4 Å from each other. For Mg(1), Mg(2), Mg(3), and Mg(4), the corresponding values of q were obtained: 0.79(1), 0.47(1), 0.08(1), and 0.08(1), respectively.

Table 1 Crystallographic data.

Parameter	This work	Published data[4]
a	9.626(1) Å	8.938(1) Å
b	11.329(1) Å	5.651(1) Å
c	8.966(1) Å	9.602(1) Å
β	105.80(3)°	105.86(1)°
Cell volume (V)	940.8(2) Å^3	466.58(8) Å^3
Space group	$P2_1/c$	$C2/m$
X-ray crystal density	2.505 g cm^{-3}	2.525 g cm^{-3}
Experimental absorption coefficient	0.195 mm^{-1}	0.2 mm^{-1}
Radiation wavelength	0.71069 Å	0.71073 Å
Monochromator	graphite	graphite
θ (min)	2.97°	3.5°
θ (max)	35.84°	35.0°
Reflex number total	4090	3589
Reflex number $I > 2\sigma(I)$	3326	964
Refine number parameters	279	87
R factor all	0.042	0.0336
R factor $[I > 2\sigma(I)]$	0.032	0.0290

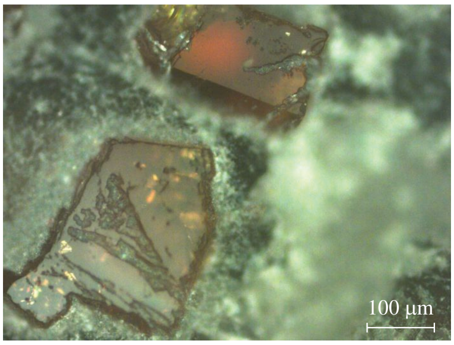

Figure 1 Single crystals of $B_{25}C_4Mg_{1.42}$ in the Wood alloy.

Figure 2 shows the projection of the $B_{25}C_4Mg_{1.42}$ structure onto the 0ac plane. In the independent part of a unit cell, there

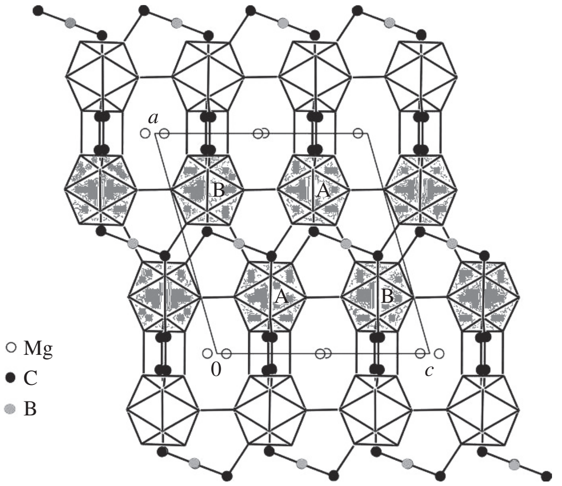

Figure 2 Projection of the $B_{25}C_4Mg_{1.42}$ structure onto the 0ac plane (the block of icosahedra of boron carbide structure is marked by shading).

[†] The structure was determined by a direct method followed by the successive Fourier synthesis and full-matrix least-square refinement using the SHELXL-86 and SHELXL-97 programs. All atoms were refined anisotropically to $R = 0.03$.

CCDC 974255 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2014.

are two B_{12} icosahedra (A and B) and C_{sp^3}–B–C_{sp^3} and C_{sp^2}=C_{sp^2} linear groups joined into a 3D net of covalent bonds containing disordered Mg atoms in its channels.

The crystal structures of Mg–B–C systems have been studied widely.[4–7] Namely, $Mg_3B_{50}C_8$ ($2Mg_{1.5}B_{25}C_4$) is the best studied compound.[4] At a glance, this structure corresponds to the test $B_{25}C_4Mg_{1.42}$ (composition, structure, crystal colour, hardness). But difference in space groups and cell parameters is the principal distinction (Table 1). Thus having similar a and c (for transition to another cell parameters a and c should be replaced with one another), the parameter b is two times smaller in another space group. It allows us to consider both structures as the polytypic modifications of a compound. The possibility of modification production depends on synthesis conditions.

The diffraction experiment [b = 11.329 Å; the presence of reflections $h + l = 2n + 1$ excepting group $C2/m$; number of the measured reflections with $I > 2\sigma(I)$] shows doubled period b and $P2_1/c$ space group. This phenomenon and detailed analysis of distinctions require a detached publication, but the $B_{25}C_4Mg_{1.42}$ structure is more promising for materials science than $Mg_3B_{50}C_8$.

Adasch *et al.*[4] produced $Mg_3B_{50}C_8$ at 1300 °C and a cooling time of 76 h; they supposed that $Mg_3B_{50}C_8$ crystals have a modulated structure. Weak satellite reflections and diffuseness of main reflections for $Mg_3B_{50}C_8$ crystals denote it. In our experiment, such satellite reflections were not revealed during single crystal XRD analysis, probably, because of different synthesis conditions. In our synthetic procedure (SHS), the $B_{25}C_4Mg_{1.42}$ structure was formed at 2400 °C; then, the product was cooled to room temperature for 1 h.

The nearest analogue for $B_{25}C_4Mg_{1.42}$ is B_4C, which has a 3D net of covalent bonds and can be produced by various methods[1,3,8,9] including the use of a low-voltage nonstationary electrical arc.[8] In $B_{25}C_4Mg_{1.42}$, four types of bonds between icosahedra were identified: B–C_{sp^3} [1.616–1.622 Å (I)]; B–C_{sp^2} [1.595–1.606 Å (II)]; B–B [1.735–1.778 Å (III)]; and B–B [1.848 and 1.885 Å (IV)]. In the $Mg_3B_{50}C_8$ structure,[4] the bond length range is 1.614–1.616 Å for type I; 1.594 Å for type II; 1.737–1.755 Å and 1.865 Å for types III and IV, respectively. In B_4C, only bonds I and III with the length of 1.597–1.627 Å and 1.695–1.743 Å, respectively, are known.[1,3,9–13] In other boron-rich compounds containing Mg, Li, Na, P, Se and O atoms, only bonds I and III or II and IV exist.[4–7, 9,14]

The structure of $B_{25}C_4Mg_{1.42}$ can be considered as two boron carbide fragments connected by C=C bonds (Figure 2).

In the structure, we found some channels oriented parallel to the b axis where Mg atoms are located in the partly occupied positions. Such disordering and partial occupation of positions by metal atoms in B–C–Me systems can be often observed by single crystal XRD analysis.[4,9,15] According to quantum-chemical calculations,[16] there is practically no interaction between metal atoms located in the tunnels and icosahedra atoms. Thus, metal atoms in the B–C–Me systems can be placed in different positions with unusual coordinations.

Thus, a new modification of $B_{25}C_4Mg_{1.42}$, *viz.* $[B_{12}]_2[CBC][C_2]Mg_{1.42}$, was produced by SHS and its crystal structure was studied. The 3D net of icosahedra B_{12} joined by strong covalent bonds B–C and B–B, determined acid resistance and hardness as well as possibility of structure modification allow one to expect for excellent properties and prospects of obtaining other materials based on boron.

This work was supported by the Presidential Programme on the Support of Leading Scientific Schools (NSh-5093.2012.3).

References

1 S. V. Konovalikhin and V. I. Ponomarev, *Russ. J. Inorg. Chem.*, 2009, **54**, 197 (*Zh. Neorg. Khim.*, 2009, **54**, 229).

2 I. D. Kovalev, V. I. Ponomarev, V. I. Vershinnikov and S. V. Konovalikhin, *Int. J. SHS*, 2012, **21**, 134.

3 V. I. Ponomarev, I. D. Kovalev, S. V. Konovalikhin and V. I. Vershinnikov, *Crystallogr. Reports*, 2013, **58**, 422 (*Krystallografia*, 2013, **58**, 410).

4 V. Adasch, M. Schroeder, D. Kotzott, T. Ludwig, N. Vojteer and H. Hillebrecht, *J. Am. Chem. Soc.*, 2010, **132**, 13723.

5 T. Ludwig and H. Hillebrecht, *J. Solid State Chem.*, 2006, **179**, 1623.

6 N. Vojteer, M. Schroeder and H. Hillebrecht, *Chem. Eur. J.*, 2008, **14**, 7331.

7 A. Guette, M. Barret, R. Naslain, P. Hagenmüller, R.-E. Tergenius and T. Lundström, *J. Less Common Met.*, 1981, **82**, 325.

8 D. V. Demchuk, A. A. Grachev, I. V. Mishin and E. K. Starostin, *Mendeleev Commun.*, 2013, **23**, 329.

9 V. I. Matkovich, *Boron and Refractory Borides*, Springer, New York, 1977, p. 96.

10 H. L. Yakel, *Acta Crystallogr.*, 1975, **B31**, 1797.

11 A. Kirfel, A. Gupta and G. Will, *Acta Crystallogr.*, 1979, **B35**, 1052.

12 G. H. Kwei and B. Morozin, *J. Phys. Chem.*, 1996, **100**, 8031.

13 M. Bouchacourt and F. Thevenot, *J. Less Common Met.*, 1979, **82**, 219.

14 N. B. Bolotina, T. I. Dyuzheva and N. A. Bendeliani, *Crystallogr. Reports*, 2001, **46**, 734 (*Kristallografia*, 2001, **46**, 809).

15 I. Higashi and T. Ito, *J. Less Common Met.*, 1983, **92**, 239.

16 Y. Lee and B. N. Harmon, *J. Alloys Compd.*, 2002, **338**, 242.

Received: 22nd May 2013; Com. 13/4124