

Synthesis and crystal structure of $\text{MgB}_{12}\text{Si}_2$ —The first ternary compound in the system B/Mg/Si

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Received 15 November 2005; received in revised form 6 February 2006; accepted 12 February 2006

Available online 6 March 2006

Abstract

We report on the synthesis of $\text{MgB}_{12}\text{Si}_2$ the first ternary compound in the system B/Mg/Si. Yellow transparent single crystals were yielded from the elements at 1600 °C in h-BN crucibles welded in Ta ampoules. $\text{MgB}_{12}\text{Si}_2$ crystallizes orthorhombic in the space group *Pnma* with $a = 10.9797(11)$ Å, $b = 6.1098(7)$ Å, $c = 8.3646(12)$ Å and $Z = 4$. The crystal structure is characterized by layers of B_{12} icosahedra, connected by isolated Si atoms to a three-dimensional framework. Mg atoms are placed in voids of the framework. Each icosahedron forms 8 B–Si bonds and 4 exohedral B–B bonds. The Si atoms are tetrahedrally coordinated by B atoms of the B_{12} icosahedra.

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Keywords: Synthesis; Single crystals; Structure analysis; Boron-rich boride; Boride silicide; Magnesium

1. Introduction

Boron-rich borides are in a class of compounds for their own because they contain a great variety of boron polyhedra and show a unique structure chemistry [1]. Furthermore, they are of growing interest for a number of applications in material sciences. Examples are high-temperature materials [2], abrasives [3], composites [4], HT-semiconductors [5] and HT-thermoelectrics [6]. The remarkable tendency of polyhedra formation is frequently connected to the incorporation of small amounts of foreign elements to stabilize the polyhedra by the additional electrons. Therefore, many boron-rich borides show partial and/or mixed occupations that demands special attention in synthesis, structure determination and analytical characterization (i.e. Na_2B_{29} [7a]/ NaB_{15} [7b]; KB_5C [8a]/ KB_6 [8b]; $\text{RE}_{3-x}\text{B}_{36}\text{Si}_8\text{C}_2$ [9]/ $\text{RE}_{1-x}\text{B}_{12}\text{Si}_{3.3-\delta}$ [10]/ $\text{Mg}_3\text{B}_{36}\text{Si}_9\text{C}$ [11]). But in addition hardness and high thermal stabilities

make the synthesis of boron-rich borides more difficult. Because of the slow-diffusion at low temperatures equilibrium conditions are not easy to reach. By use of molten metals as solvent and reactant we were able to synthesize and characterize single crystals of new borides [12–15].

Motivated by the recent discovery of superconductivity in MgB_2 [16], the excellent thermal stability of Si/B-based ceramics [17] and the growing importance of Mg-containing alloys [18] we have investigated the ternary system B/Mg/Si. Because magnesium shows high reactivity, a low melting point and a high vapour pressure, crucibles of boron nitride were used, welded in tantalum ampoules. In this way, we yielded yellow transparent single crystals of $\text{MgB}_{12}\text{Si}_2$ as the first stoichiometric ternary compound in the system B/Mg/Si.

2. Synthesis and characterization

2.1. Synthesis

B, Mg and Si were mixed in molar ratios 1:2:4 and pressed into a pellet (total mass: 500 mg). The pellet was put into a BN-crucible and sealed in a Ta-ampoule. In an

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atmosphere of argon it was heated up to 1600 °C, held for 40 h, cooled down to 1400 °C with a ratio of 10 K/h and then cooled to room temperature with 600 K/h. The excess of the melt was removed with a mixture of HF/HNO₃. The residue consists of yellow platelets and yellow-greenish crystals which were identified as MgB₁₂Si₂. As a byproduct we observed black crystals of Mg_{1.1}B₁₂Si₂ [11] and in some cases Mg₃B₃₆Si₉C [11] we will report later on [19].

Table 1
Crystallographic data and refinement for MgB₁₂Si₂

Compound	MgB ₁₂ Si ₂
Temperature	293(2) K
Crystal size	Yellow platelet 0.4 × 0.4 × 0.05 mm ³
Crystal system	Orthorhombic
Space group	<i>Pnma</i> (No. 62)
Unit cell	$a = 10.9797(11) \text{ \AA}$ $b = 6.1098(7) \text{ \AA}$ $c = 8.3646(12) \text{ \AA}$ $V = 561.13(12) \text{ \AA}^3$ $Z = 4$
$d_{\text{calc.}}$	2.488 g/cm ³
Data collection	STOE IPDS II, MoK α ; $\lambda = 0.71073 \text{ \AA}$ (graphite monochromated) $0^\circ \leq \omega \leq 180^\circ$, $\psi = 0^\circ$; $0^\circ \leq \theta \leq 90^\circ$, $\psi = 90^\circ$ $\Delta\omega = 2^\circ$; 120 s exposure time $3^\circ < 2\theta < 65^\circ$ $-17 < h < 17$; $9 < k < 9$; $13 < l < 13$
μ	0.62 mm ⁻¹
Absorption correction	None
$R_{\text{int.}}/R_{\text{sigma}}$	0.0481/0.0054
Refinement	SHELXL [20]; Full-matrix least-squares refinement on F^2
$N(hkl)$ meas.; unique	9387; 1083
$N'(hkl)$ ($I > 2\sigma(I)$)	1013
Parameters refined	80
R -values	$R_1 = 0.019$, $wR_2 = 0.052$
All data	$R_1 = 0.021$, $wR_2 = 0.052$
Weighting scheme	0.0419/0.0 (SHELXL [20])
Extinction correction	0.1805(8) (SHELXL [20])
Goodness of fit	1.074
Residual electron density (max, min, sigma)	+0.39/−0.35/0.08 e ⁻ /Å ³

2.2. Structure analysis

One of the yellow crystals was selected for the structure analysis. Measurements were done using a diffractometer equipped with an image plate detector (IPDS II, Fa. STOE, Darmstadt, Germany). The reflections were indexed with a primitive orthorhombic cell. After refinement values of $a = 10.9797(11) \text{ \AA}$, $b = 6.1098(7) \text{ \AA}$ and $c = 8.3646(12) \text{ \AA}$ were yielded. Up to a limit of $2\theta = 65^\circ$ 9387 intensities were measured and merged to a data set of 1083 unique reflections. According to the reflection conditions space groups *Pnma* and *Pna2*₁, respectively, were suggested. The structure analysis was started in *Pnma*. Direct Methods (SHELXL program [20]) yielded a model for the crystal structure that was refined with 80 variables to R -values of $R_1(F) = 0.019$ (1013 reflections with $I > 2\sigma(I)$) and $wR_2(I) = 0.051$. All atoms were refined with anisotropic thermal displacement parameters. Because partial and mixed occupations are very frequent in boron-rich borides all site occupation factors were checked at the end of the refinement. All positions show only very small deviations from full occupation. The largest deviation was observed for the Mg atom (98.8(3)%). Therefore a stoichiometric composition MgB₁₂Si₂ is assumed. Details of the refinement are listed in Table 1. Coordinates and thermal displacement parameters are given in Tables 2 and 3. Selected distances are shown in Table 4. Further details on the structure refinement (complete list of distances and angles, F_o/F_c -list) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Zusammenarbeit, D-76344 Eggenstein-Leopoldshafen (Germany) (fax: +49 724 808 666; e-mail: crysdta@fiz-karlsruhe.de) on quoting the registry number CSD-412325, the name of the authors and this journal.

2.3. Elementar analysis

The composition of several single crystals was confirmed by micro-probe analysis (WDX) using a Cameca SX100. Atomic ratios we found were 80.5% B, 6.6% Mg and 12.8% Si in excellent agreement with the calculated values

Table 2
Atomic coordinates, isotropic displacement parameters (in Å²) and site occupation factors for MgB₁₂Si₂, e.s.d.'s in parentheses

Atom	x	y	z	sof	$U_{\text{eq.}}$
Si1	0.41531(2)	0.25	0.60075(3)	1.018(3)	0.0039(1)
Si2	0.41824(2)	0.75	0.86813(3)	0.996(3)	0.0043(1)
Mg	0.56976(3)	0.25	0.84106(4)	0.988(3)	0.0105(1)
B1	0.59996(8)	0.25	0.55437(10)	1.002(10)	0.0045(1)
B2	0.35264(8)	0.25	0.84455(9)	0.999(10)	0.0045(1)
B3	0.34717(8)	0.75	0.64955(9)	1.004(10)	0.0047(1)
B4	0.59650(7)	0.75	0.94259(10)	0.988(10)	0.0046(1)
B5	0.32762(5)	0.98360(10)	0.53052(6)	1.000(6)	0.0046(1)
B6	0.33100(5)	0.01425(10)	0.96647(6)	1.001(6)	0.0046(1)
B7	0.70816(5)	0.90791(9)	0.83326(7)	1.004(6)	0.0047(1)
B8	0.71264(5)	0.09054(9)	0.66678(7)	1.003(6)	0.0047(1)

Table 3
Anisotropic displacement parameters (in \AA^2) for $\text{MgB}_{12}\text{Si}_2$, e.s.d.'s in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	0.0038(1)	0.0037(1)	0.0043(1)	0	−0.0002(1)	0
Si2	0.0044(1)	0.0045(1)	0.0038(1)	0	−0.0005(1)	0
Mg	0.0070(2)	0.0200(2)	0.0046(2)	0	0.0004(1)	0
B1	0.0044(3)	0.0049(3)	0.0043(3)	0	0.0003(2)	0
B2	0.0047(3)	0.0044(3)	0.0044(3)	0	0.0003(2)	0
B3	0.0054(3)	0.0044(3)	0.0044(3)	0	−0.0001(2)	0
B4	0.0045(3)	0.0052(3)	0.0045(3)	0	−0.0002(2)	0
B5	0.0046(2)	0.0047(2)	0.0045(2)	−0.0002(2)	0.0000(2)	−0.0003(2)
B6	0.0046(2)	0.0047(2)	0.0045(2)	0.0002(2)	−0.0001(2)	−0.0001(2)
B7	0.0049(2)	0.0050(2)	0.0041(2)	−0.0002(2)	−0.0002(2)	0.0002(2)
B8	0.0051(2)	0.0051(2)	0.0038(2)	0.0004(2)	0.0003(2)	0.0001(2)

Table 4
Selected distances and angles in $\text{MgB}_{12}\text{Si}_2$, e.s.d.'s are 0.001 \AA or less

B1–B5 1.781 2x	B2–B6 1.781 2x
B1–B3 1.802	B2–B8 1.822 2x
B1–B8 1.834 2x	B2–B4 1.866
B3–B5 1.753 2x	B4–B7 1.808 2x
B3–B1 1.802	B4–B6 1.813 2x
B3–B7 1.811 2x	B4–B2 1.866
B5–B3 1.753	B6–B8 1.774
B5–B8 1.768	B6–B2 1.781
B5–B1 1.782	B6–B7 1.794
B5–B7 1.798	B6–B4 1.813
B5–B6 1.822	B6–B5 1.822
B7–B8 1.785 (exo)	B8–B5 1.768
B7–B6 1.794	B8–B6 1.774
B7–B5 1.798	B8–B7 1.785 (exo)
B7–B4 1.808	B8–B2 1.822
B7–B3 1.811	B8–B1 1.834
B7–B7 1.930	B8–B8 1.946
Mg–B8 2.355 2x	Si1–B5 1.981 2x
Mg–B2 2.388	Si1–B1 2.067 (next layer)
Mg–B1 2.424	Si1–B2 2.153
Mg–B6 2.527 2x	B–Si1–B 97.17(3)–119.54(6)
Mg–B4 2.570	Si2–B3 1.987
Mg–B7 2.586 2x	Si2–B6 2.050 2x
Mg–Si2 2.433	Si2–B4 2.056 (next layer)
Mg–Si1 2.633	B–Si2–B 100.65(4)–130.67(6)

for the composition $\text{MgB}_{12}\text{Si}_2$: 80.0% B, 6.7% Mg and 13.3% Si. No traces of other elements could be detected, for instance N from the crucible, C as contamination in boron, O from the surrounding or contaminations in Mg.

2.4. X-ray powder diffraction

Some of the yellow crystals were crushed and used for an X-ray powder diffractogram (STOE STADI-P, $\text{MoK}\alpha 1$ -radiation, Ge-monochromator). All reflections observed were indexed with the orthorhombic unit cell. The measured intensities showed excellent agreement to the

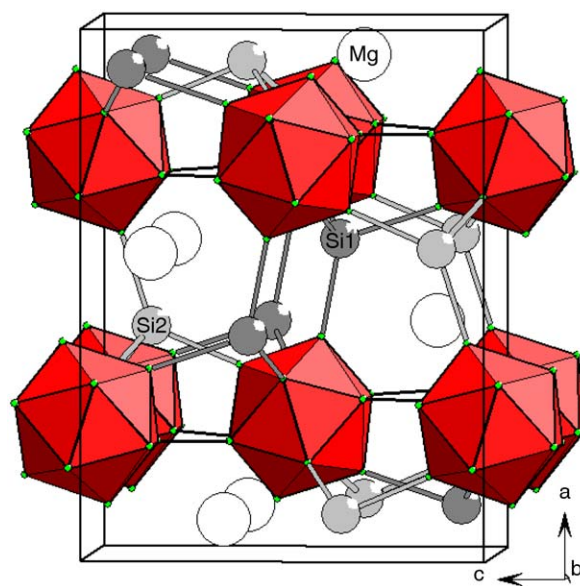


Fig. 1. Crystal structure of $\text{MgB}_{12}\text{Si}_2$.

calculated values on the basis of the refined crystal structure.

3. Structure description and discussion

$\text{MgB}_{12}\text{Si}_2$ is the first ternary compound in the system B/Mg/Si and represents one of the few boron-rich borides with stoichiometric composition. The crystal structure is characterized by B_{12} icosahedra forming nearly hexagonal layers that are connected by Si atoms. Magnesium is in voids of this 3D network of B_{12} icosahedra and Si atoms (Fig. 1).

Fig. 2 shows the nearly regular B_{12} icosahedra built up by 8 symmetry-independent boron atoms. The endohedral B–B distances vary between 1.757(1) and 1.948(1) \AA with an averaged value of 1.808 \AA . B7 and B8 are the only B atoms without B–Si bonds that may explain the unusually long B–B distances of 1.932(1) \AA (B7–B7) and 1.948(1) \AA (B8–B8). The B_{12} icosahedra are connected to layers (Fig. 3) by four exohedral B–B bonds (B7–B8: 1.785(1) \AA) destroying the

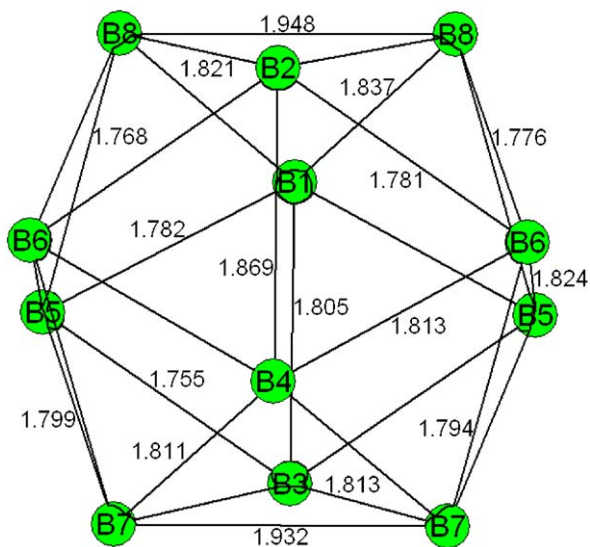


Fig. 2. B_{12} icosahedron in $MgB_{12}Si_2$, distances in [Å], e.s.d.'s are 0.001 Å.

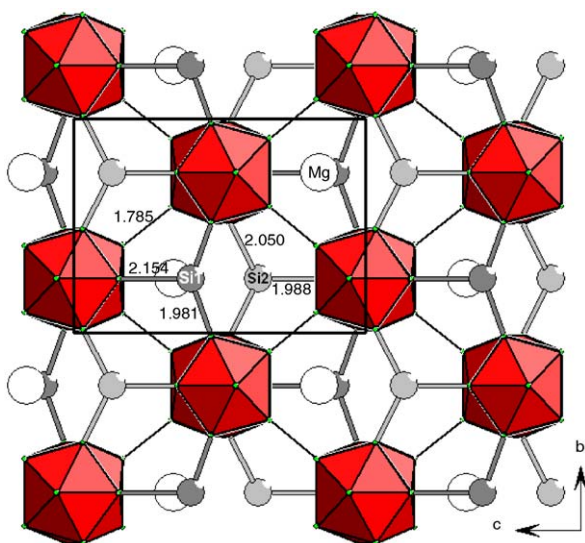


Fig. 3. Layer of icosahedra in $MgB_{12}Si_2$ with Si (grey) and Mg (white) above and below the layer (see text).

pseudohexagonal metric ($c/b \approx 1.37$). The layers are stacked in direction (100) by turns in way that the centres of the icosahedra are shifted by $b/2$. This motif of B_{12} icosahedra connected by four exohedral B–B bonds to layers is frequently found in boron-rich borides, i.e. $Li_2B_{12}C_2$ [21], $LiB_{13}C_2$ [21], $Mg_3B_{50}C_8$ [14], $MgB_{12}C_2$ [13,14], MgB_7 [22]. The two independent Si atoms are placed between the layers with a distorted tetrahedral coordination (B–Si–B angles between 97.1° and 137.7°) of four B atoms of four different icosahedra. The Si–B distances vary between 1.981(1) and 2.153(1) Å with very similar averaged values of 2.045 Å (Si1) and 2.038 Å (Si2), respectively (Fig. 3). The Si atoms connect the layers of B_{12} icosahedra to a 3D framework in which three of the four coordinating boron atoms are in the same layer and the fourth B atom is in the neighbouring layer

(bonds Si1–B1 and Si2–B4). The optimization of Si–B bonds can be seen as a reason for the 16° rotation of the icosahedra around the twofold axis in b -direction.

A comparison to other Si–B distances is not easy because the number of stoichiometric compounds with Si–B bonds is limited. In SiB_3 the Si–B distances are between 1.973 and 2.026 Å [23] in $Mg_3B_{36}Si_9C$ 2.034–2.040 Å [11,19] and in $Mg_{1.1}B_{12}Si_2$ 2.034 Å [11,19]. Magnesium is placed in voids of the framework of B_{12} icosahedra and Si atoms. It is coordinated by 9 B atoms in distances of 2.355(1) to 2.568(1) Å and two Si atoms (2.433(1) and 2.633(1) Å). The projection of the structure on the b – c plane (Fig. 4) shows, that with respect to the B_{12} centres Mg occupies nearly the same positions as the Si atoms, but the rotation of the icosahedra leads to significant differences of the Si–B and Mg–B distances. The Mg–B and Mg–Si distances are comparable to the values in other Mg borides [14,15] and boridesilicides [11,19].

The U_{eq} value of Mg is significantly higher than values for the Si and B atoms. This can be understood as a consequence from the different bonding situations. Si and B are part of a framework with strong covalent bonds while Mg shows mainly an ionic interaction to the framework carrying a negative charge: $Mg^{2+}/[(B_{12}Si_2)]^{2-}$. The shape of the thermal displacement ellipsoid is a result of the anisotropic surrounding (Fig. 5). The elongation of the ellipsoid is observed in the direction where the Mg atom can avoid the vicinity of boron and silicon.

The free refinement of the Mg occupation factor reveals a deficit of about 1.2%. The deviation from full occupation is only four e.s.d.'s. Single crystals from samples with a shorter holding time at $1600^\circ C$ (5 h) and a higher cooling rate to $1400^\circ C$ (20 K/h) showed a somewhat larger Mg deficit of 3–4%. Similar observations were made for B/C/Mg compounds [14] and MgB_7 [14,22]. In the case of MgB_7 it could be shown that there exist besides crystals with Mg deficit (4%) also single crystals with stoichiometric composition depending on reaction time and cooling rate. For $MgB_{12}Si_2$ the situation is not yet clear. Probably, the band structure calculations that are a part of our further investigations will give an answer to this question.

Despite of the small deviation from full occupation we regard $MgB_{12}Si_2$ as a stoichiometric compound because of the transparency and the yellow colour of the crystals that indicate a compound with large band gap and filled bands. Preliminary investigations on the UV–Vis spectra (Varian, Cary 3) showed no absorption between 220 and 800 nm.

$MgB_{12}Si_2$ is another example for the importance of electron counting rules for the structure of boron-rich borides. According to the rules of Wade closo-cluster like icosahedra need two additional electrons [24] provided that each cluster atom has an exohedral $2e2c$ bond. The Wade rules were transferred to solid compounds by Longuet-Higgins and Roberts [25]. Applied to $MgB_{12}Si_2$ it is easy to see that a stoichiometric composition fits perfectly the rules of Wade and Longuet-Higgins. Each boron atom of the B_{12} icosahedron performs a $2e2c$ bond (8 Si–B

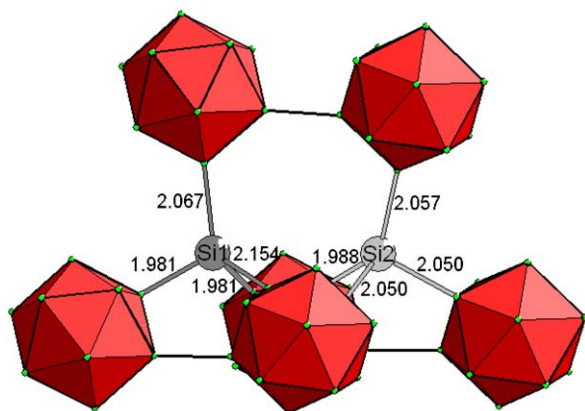


Fig. 4. Coordination of Si in $\text{MgB}_{12}\text{Si}_2$, distances in [Å], e.s.d.'s are 0.001 Å.

bonds, 4 exohedral B–B bonds). Two electrons of the Mg atom can be transferred to the icosahedron. Silicon has four covalent Si–B bonds in a tetrahedral coordination according the expected sp^3 -hybridization. Therefore, $\text{MgB}_{12}\text{Si}_2$ can be formulated as $\text{Mg}^{2+}(\text{B}_{12})^{2-}(\text{Si})_2$ or $\text{Mg}^{2+}[(\text{B}_{12})(\text{Si})_2]^{2-}$ if the anionic 3D-framework of B_{12} icosahedra and Si atoms is emphasized.

The example of $\text{MgB}_{12}\text{Si}_2$ shows that X-ray structure determinations on the basis of high-quality single-crystal data allow a detailed discussion of occupation factors and thermal displacement parameters that is usually a problem for light elements like boron. The thermal parameters for the boron atoms are very small and nearly equal describing a spherical shape of the ellipsoid. This indicates a strong and isotropic covalent network where each boron atoms is in a comparable bonding situation. The occupation factors of boron and silicon are very close to the ideal values with remarkably small standard deviations. Together with the analytical investigations (WDX) this are good reasons for the correct assignment and the absence of carbon in the crystal structure of $\text{MgB}_{12}\text{Si}_2$. To our experience single crystals of boron-rich borides yielded from molten metals are always of high quality that enables a clear assignment of the framework atoms showing full occupation. There are no hints for substitution of icosahedral boron atoms by other carbon or silicon as it was observed for B_4C [26] and rhombohedral $\text{SiB}_{2.8}$ [27,28]. With reference to carbon as the most likely and difficult element for a substitution of boron the limit of detectability can be estimated to about 10–20% on the basis of X-ray data. The reliability of the analyses can be decisively improved by WXD measurement on single crystals. A comparison to other boron-rich borides with known carbon content ($\text{Al}_{2.7}\text{B}_{48}\text{C}_2$ [29], $\text{MgB}_{12}\text{C}_2$, $\text{Mg}_2\text{B}_{24}\text{C}$ [14], $\text{Mg}_3\text{B}_{36}\text{Si}_9\text{C}$ [11,19]) gives a lower limit of about 2% for the detection of carbon.

The crystal structure of $\text{MgB}_{12}\text{Si}_2$ shows also some similarities to SiB_3 (resp., $\text{B}_{12}(\text{Si}_2)_2$) [23] where the B_{12} icosahedra form similar layers by formation of four exohedral B–B bonds. These layers were connected by the Si atoms that form zick zack chains of Si_2 units. Similar to

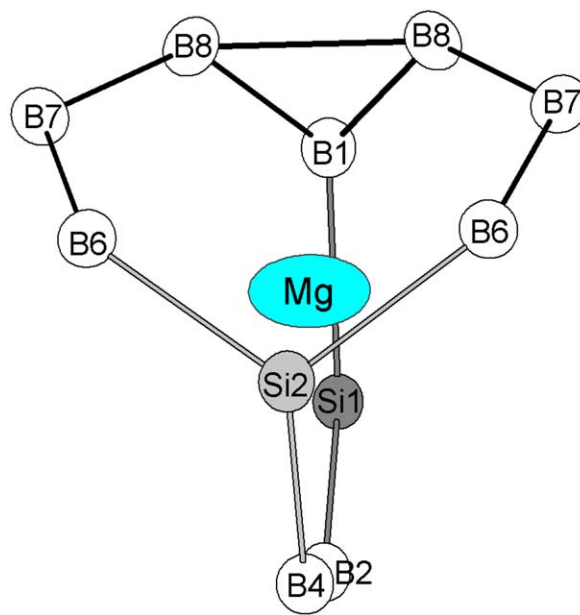


Fig. 5. Coordination of Mg in $\text{MgB}_{12}\text{Si}_2$; ellipsoids represent 99% probability.

$\text{MgB}_{12}\text{Si}_2$ each B_{12} icosahedron has four exohedral B–B bonds and eight B–Si bonds. $\text{MgB}_{12}\text{Si}_2$ continues the row of boron-rich borides with icosahedra as the dominant feature $M_a(\text{B}_{12}) X_b$ (M = electropositive metal; X = C, Si, N). The closest relation occurs to the two forms of $\text{MgB}_{12}\text{C}_2$ that were recently described by our group. Although, the number of valence electrons is the same the connectivity of the icosahedra is different. In the monoclinic form of $\text{MgB}_{12}\text{C}_2$ [13,14] there are isolated carbon atoms and B_{12} icosahedra that form four exohedral bonds to neighbored icosahedra and eight B–C bonds (Fig. 6). The C atoms are tetrahedrally coordinated by boron. But in contrast to $\text{MgB}_{12}\text{Si}_2$ the icosahedra are linked by vertices to linear rods which are very rare in boron-rich borides. The structure of orthorhombic $\text{MgB}_{12}\text{C}_2$ [14] (Fig. 6) is closely related to MgB_7 [14,22]. As in $\text{MgB}_{12}\text{Si}_2$ the icosahedra form a pseudo-hexagonal layer by four exohedral B–B bonds connecting the icosahedra's corners. The layers are connected by the C atoms and additional exohedral B–B bonds. In total each icosahedron has six exohedral B–B bonds and six B–C bonds. The C atom has also tetrahedral coordination with three B atoms and one C atom with a remarkably long distance of 1.727 Å. In both cases, the Mg atoms spend the two additional electrons that are needed by the B_{12} icosahedra confirming the importance of rules given by Wade and Longuet-Higgins.

4. Conclusions

Our results on $\text{MgB}_{12}\text{Si}_2$ show that the use of molten metals enables the access to new boron-rich borides. $\text{MgB}_{12}\text{Si}_2$ is one of the few examples for a stoichiometric boron-rich boride and for well-defined Si–B bonds in a

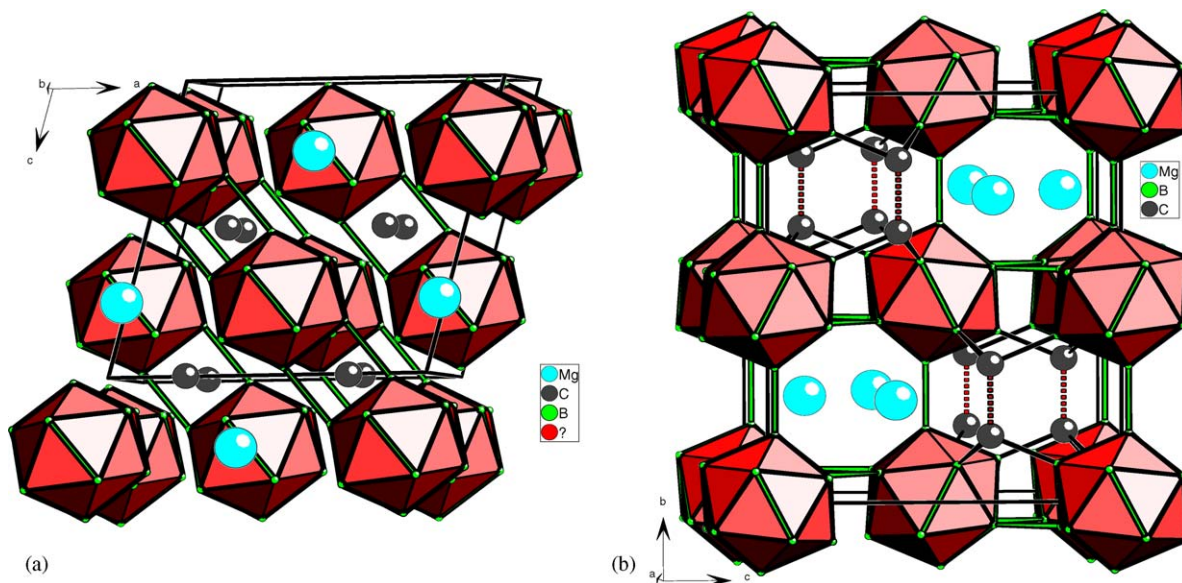


Fig. 6. Crystal structures of monoclinic MgB₁₂C₂ (above) and orthorhombic MgB₁₂C₂ (below).

solid-state compound. The crystal structure is characterized by a framework of B₁₂ icosahedra and isolated Si atoms. Composition and atom labelling are confirmed by high-quality X-ray data and WDX measurements. According to the rules of Wade and Longuet-Higgins a charge transfer Mg²⁺(B₁₂)²⁻(Si)₂ or Mg²⁺ [(B₁₂)(Si)₂]²⁻ can be assumed that explains colour and stability of MgB₁₂Si₂. Remarkable is the high chemical stability of MgB₁₂Si₂. It is stable against conc. HCl and mixtures of HF/HNO₃.

Acknowledgments

We thank Dr. M. Ade (University of Freiburg, Institute for Inorganic Chemistry) and Dr. H. Müller-Sigmund (University of Freiburg, Institute for Mineralogy and Geochemistry) for the WDX measurements.

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