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A new "old" boron-rich compound: $Be_{8(1-x)}(B_{48})B_2$—single crystal growth and structure analysis

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Abstract

Single crystals with formula of $Be_{8(1-x)}(B_{48})B_2$ ($x\sim0.6$) were grown from high temperature Cu solution. Single crystal XRD measurements indicate that it is in tetragonal symmetry (space group of $P4_2/nnm$ (No. 134)) and lattice constant of $a = b = 8.8557$ Å and $c = 5.1157$ Å, which is very similar with the compound BeB_{12} reported in 1960s'. However, we found the Be position in the crystal is quite different from the "old" compound BeB_{12}. The structure was also confirmed with high resolution transmission electron microscopy (HRTEM) observations and its composition was obtained from electron energy loss spectrum (EELS) measurements.

Keywords: Boron-rich compounds; Single crystal; XRD

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1. Introduction

The beryllium borides are potential useful ceramic materials. Various investigators have suggested the existence of at least seven stable phases in Be–B system [1–5]: Be_4B, Be_2B, BeB_2, BeB_4, BeB_6, BeB_9 and BeB_{12}. However, the phase diagram of Be–B system has not been well established up to now, especially in the boron-rich region. Most of the Be–B compounds are thermodynamically stable and can be fabricated by solid-state reaction or chemical vapor deposition method.

It is difficult to obtain single crystals directly from the melt for most boron-rich solids. High temperature solution growth is thus an important method used in obtaining of single crystals for these compounds. Single crystals of many newly found boron-rich solids have been successfully grown with high temperature solution method using metal flux [6–10]. We have obtained thin plate-like crystals in Be–B system by using Cu flux. The XRD measurements indicate that it is in tetragonal symmetry and the lattice constants are very close to that of BeB_{12} reported before [11,12]. The BeB_{12} is believed to be isostructural with MB_{25} (M = Ti, Ni, etc.). Our structural analysis revealed that the boron icosahedral framework in the crystal is just the same as that in MB_{25} or $MB_{24}C$ [13–16] (M = Ti, Ni, V, etc.), but the Be position is completely different from M in the "old" compounds.

2. Experiments

The starting materials used in our experiments are pure Be (Alfa Chem. 99.5%), amorphous B (3N, SB-Boron Inc. USA) and copper (>99.7%). Well mixed powders (5–10 g) with composition of Be:B:Cu = 1:10:50 was pressed into pellet and placed into a BN crucible (Be is very toxic and care should be taken during the whole handling process). The reaction was performed at flowing argon atmosphere in a RF furnace with graphite susceptor. After heated to 1650°C and keeping at the temperature for 8 h, the melt was cooled down slowly (40°C/h) to less than 1000°C till the Cu flux solidified. Then switch off the power and let the ingot cooled naturally down to room temperature. In order to isolate

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the BeB single crystals, the obtained ingot was put into nitric acid to remove the copper. The remains Be–B single crystals are very thin (<0.05 μm) silver plates with regular or irregular shapes and they were washed with deionized water and methonal and finally dried at room temperature. XRD measurements found that the yields are nearly single phase with little amount of impurities. The quality of the crystal was examined with Weisenberg camera first and XRD data of high quality BeB crystal were collected with a Brucker single crystal X-ray diffraction facility (smart CCD). The crystal was also analyzed with a HRTEM instrument (JEL-300). The observed images were simulated with MacTempas software package [17] based on the structure model derived from single XRD data. The composition of crystal was analyzed with electron energy loss spectrum (EELS) measurements.

3. Structure analysis and discussions

The single crystals obtained above are very thin plate-like sheets. They are metallic silver like color, not transparent with thickness of 10–50 μm. Fig. 1 is the optical microscope image of such a crystal and it seems to have a hexagonal habit in shape. However, the index of XRD data gave a tetragonal symmetry (space group $P4_2/nnm$, No. 134) and lattice constants of $a = b = 8.8557$ Å and $c = 5.1157$ Å for the crystal. The cell parameters are very close to those of BeB_9 crystal found by Higashi in Al–Be–B systems [12]. The author did not give any structural details there and just believe that it is the same compound of BeB_{12} reported before. The "old" compound BeB_{12} is regarded as isostructural with TiB_{25}, where Ti is replaced with Be. However, structural analysis results show that the Be position in our crystals is completely different from Ti in TiB_{25} or $TiB_{24}C$ [14,15] and our crystals thus have a different structure from the "old" compound BeB_{12} (or BeB_9).

Data collection conditions and index results for the BeB crystal are listed in Table 1. From the collected XRD data, space group of $P4_2/nnm$ (No. 134) was selected according to the extinction rules. The crystal structure was solved by direct method with program SIR2002 [18]. Six atomic positions were derived from the XRD data. One was assigned as Be and other five positions were assigned as B. The structure was further refined by least-square method with program SHELXL97 [19]. Two boron atoms (B1 and B4) in the site of $8m$ and another two in the $16n$ site (B2, B3) build the interconnected icosahedral framework. The boron icosahedron is slightly distorted with B–B–B bonding angles ranging from 57.5° to 65.0° (average: 60.3°). The tetragonal boron icosahedral framework is as same as that found in other tetragonal borides MB_{25} (M = Ti, Ni, Zn) [13,14]. The 5th boron atom (B5), which occupies the $2b$ position, was also found in MB_{25} compounds. The 5th boron atom in TiB_{25} was later reinterpreted as carbon [14,15]. The compound BeB_{12} reported before was assumed as isostructural with TiB_{25} or $TiB_{24}C$ [11,13], and the Ti position ($2a$) is replaced with Be. The assumption is just based on powder XRD data [11]. As is well known, both Be and B are light

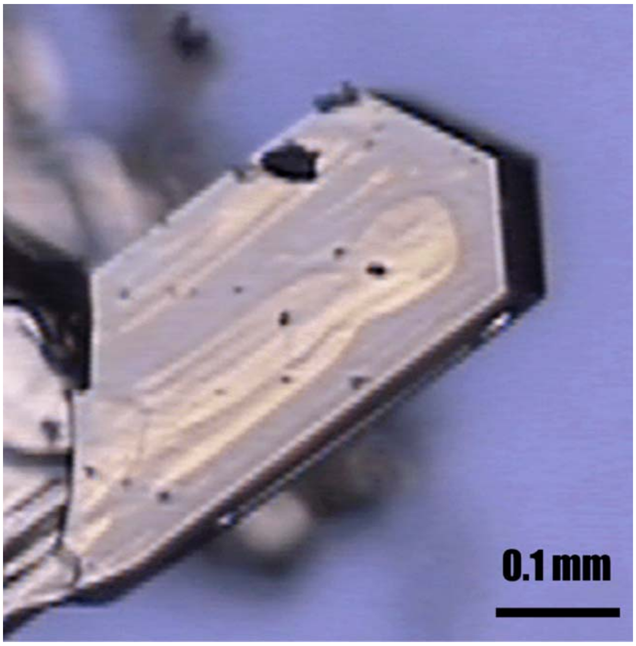

Fig. 1. Optical image of the grown $Be_{8(1-x)}(B_{48})B_2$ crystals.

Table 1
Crystal data and structure refinement for $Be_{8(1-x)}(B_{48})B_2$

Identified code	$Be_{8(1-x)}(B_{48})B_2$
Empirical formula	$B_{3.125}Be_{0.20}$
Formula weight	35.61
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Tetragonal, $P4_2/nnm$ (No. 134)
Unit cell dimensions	$a = 8.8557(5)$ Å, $b = 8.8557(5)$ Å, $c = 5.1157(4)$ Å
Volume	401.19(4) $Å^3$
Z, Calculated density	16, 2.358 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
$F(000)$	263
Crystal size	$0.25 \times 0.25 \times 0.10\,mm^3$
Theta range for data collection	3.25–30.06°
Limiting indices	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-7 \leqslant l \leqslant 7$
Reflections collected/unique	5234/322
Completeness to theta	30.06 100.0%
Absorption correction	Emperical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	322/0/40
Goodness-of-fit on F^2	1.082
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0667$, $wR_2 = 0.1740$
R indices (all data)	$R_1 = 0.0951$, $wR_2 = 0.1854$
Largest diff. peak and hole	0.745 and $-0.403\,e\,Å^3$

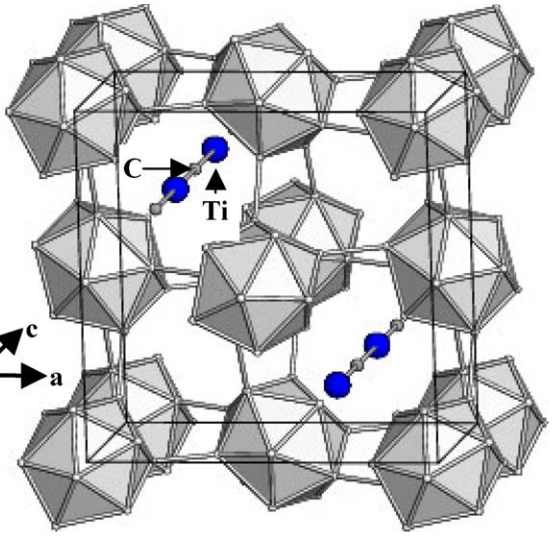

Fig. 2. Schematic diagram of the crystal structure for TiB_{25} or $TiB_{24}C$ ($Ti_{2(1-x)}(B_{48})C_2$). The polyhedra are B12 icosahedra. The big black spots are Ti and smaller ones are B or C.

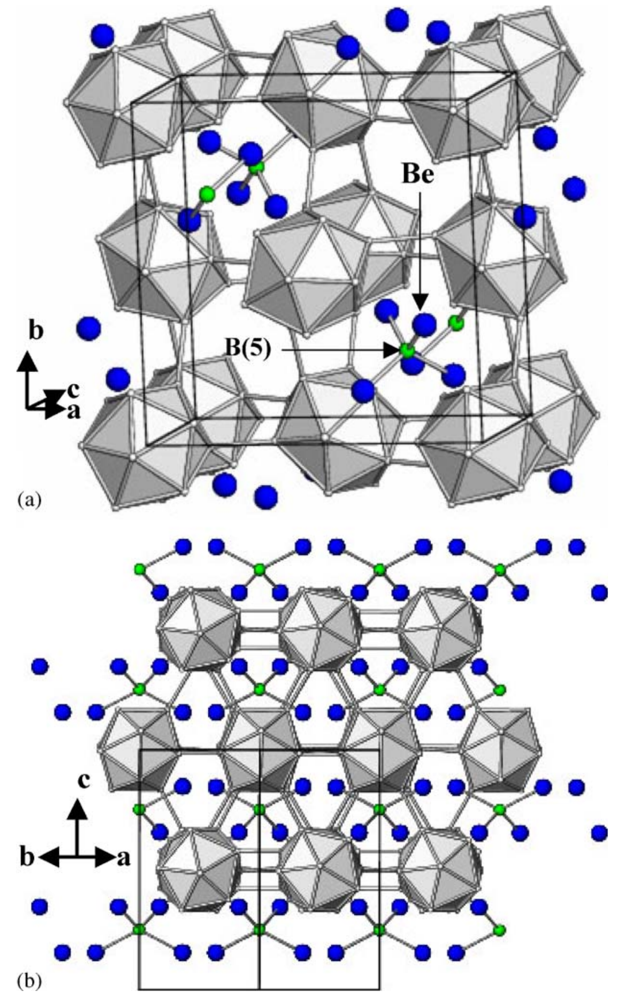

Fig. 3. Schematic diagram of the crystal structure for (a) $Be_{8(1-x)}(B_{48})B_2$; (b) projecting along the [101] direction and the boron icosahedra show a pseudohexagonal symmetry four Be atoms (big black spots) coordinated with B(5) in the voids of B12 icosahedral framework.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Be_{8(1-x)}(B_{48})B_2$

Atom	Wyckoff	*x*	*y*	*z*	Occu.	*U*(eq)
B(1)	8*m*	6239(3)	3761(3)	1170(8)	1.0	6(1)
B(2)	16*n*	4843(3)	6665(3)	1617(5)	1.0	6(1)
B(3)	16*n*	6652(3)	5774(3)	1517(6)	1.0	7(1)
B(4)	8*m*	5062(3)	4938(3)	3299(8)	1.0	6(1)
B(5)	2*b*	7500	2500	2500	1.0	4(2)
Be	8*m*	6546(9)	3454(9)	5160(20)	0.407(1)	8(3)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

elements and they both have quite low-X-ray scattering ability, so powder XRD data is impossible to give any structural details. Refined with single crystal XRD data, we found that the Be occupies a different position (8*m*). It is quite different from *M* in the MB_{25} compounds. Figs. 2 and 3 show the schematic structure diagrams for TiB_{25} (or $TiB_{24}C$) and our crystals, respectively. All the five light atoms in the two compounds have the same positions. In TiB_{25} compound, Ti occupies the 2*a* site with symmetry of $\bar{4}2m$ and bonds with the 5th boron (or carbon) atom forming straight chains. The –Ti–C– chains, go through the voids of the boron icosahedral framework and parallel the *c*-axis (Fig. 2). In BeB crystal, Be occupies the 8*m* site with *m* symmetry and four Be atoms surround the 5th boron atom forming a distorted tetrahedron (Fig. 3). Similar with other MB_{25} compounds, the Be position is not fully occupied (only 0.4) in our crystal. The refined atomic positions, anisotropic displacement parameters are listed in Tables 2 and 3, respectively. The cell formula of the compound is $Be_{8(1-x)}B_{48}B_2$ ($x \sim 0.6$). The selected bonding length is listed in Table 4. The three centered type B–B bonding length in icosahedral is a little larger than the normal B–B bonding length. The distance between Be atoms and the boron atoms in the icosahedra is 2.16–2.60 Å, which is comparable with the Be–B distances in other Be–B compounds, such as 2.02 Å in Be_2B [20] and 1.94–2.07 Å in Be_4B [21], etc. However, the 5th boron atom outside the icosahedron has a short bonding distance to Be (1.81 Å). Four Be atoms forming a tetrahedron and B5 resides at the center. The tetrahedron is highly distorted with three Be–B5–Be bonding angle of 124.3° and another one 82.6°. The partial occupation of Be position can be interpreted from the point of electron balance. Boron cluster is electron deficiency and an icosahedron needs two external electrons for all the bonds. As a electron donor atom, every Ti atom contributes four electrons and the Ti–B compound reported before can be written as $Ti^{4+}(B_{12}^{2-})_2C$ based

Table 3
Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Be_{8(1-x)}(B_{48})B_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	5(1)	5(1)	8(2)	0(1)	0(1)	1(1)
B(2)	6(1)	7(1)	7(1)	0(1)	−1(1)	−1(1)
B(3)	7(1)	6(1)	8(1)	0(1)	1(1)	0(1)
B(4)	6(1)	6(1)	6(2)	0(1)	0(1)	0(1)
B(5)	3(2)	3(2)	5(3)	0	0	0
Be	10(4)	10(4)	6(6)	−2(3)	2(3)	4(4)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$.

Table 4
Selceted bond lengths (Å) for $Be_{8(1-x)}(B_{48})B_2$ compound

Intraicosahedron		Intericosahedron	
B(1)–B(2)	1.759(4)	B(2)–B(2)	1.733(6)
B(1)–B(3)	1.828(4)	B(3)–B(3)	1.807(6)
B(1)–B(4)	1.832(6)	B(4)–B(4)	1.747(8)
B(2)–B(2)	1.889(6)	Others	
B(2)–B(3)	1.795(4)	B(1)–B(5)	1.720(4)
B(2)–B(4)	1.766(5)	Be–B(5)	1.809(11)
B(3)–B(3)	1.902(6)	Be–B(1)	2.062–2.093
B(3)–B(4)	1.834(4)	Be–B(2)	2.061–2.140
		Be–B(4)	2.087–2.164
		Be–Be	2.39(2)

on the closed-shell requirement rules of the borane clusters [22]. Different from Ti, Be only has two outside electrons and the calculated formula of our crystal can be written as $Be^{2+}_{8(1-x)}(B^{2-}_{12})_4B_2$. Be atoms occupy the 8*m* site and it is clear that less than half occupancy is reasonable for them according to the electron balance rule. The vacancy of metal atoms is driven by valence precision in other boron-rich solids has also been confirmed by density of state calculations [23].

The structural refinement results show that the Be cannot replace any of the B atoms in the icosahedron. If we replace any of the boron atoms in the icosahedron with Be, the fitting results will become very bad (with $wR > 25\%$). So we believe that there is no Be cooperated in the icosahedra. In addition, EELS analysis also revealed that there is no carbon atom in the crystals.

Our BeB crystal was also analyzed by electron diffraction and high resolution transmission electron microscope observations. The results confirmed our structure model. Figs. 4a and b show the HRTEM images of our crystal projecting along the [101] and [111] directions, respectively. The corresponding selected area electron diffraction patterns are pasted on the upper right corner of the HRTEM images. The simulated HRTEM images which were calculated with MacTempas software package are also inserted in the image and they match the observed images quite well.

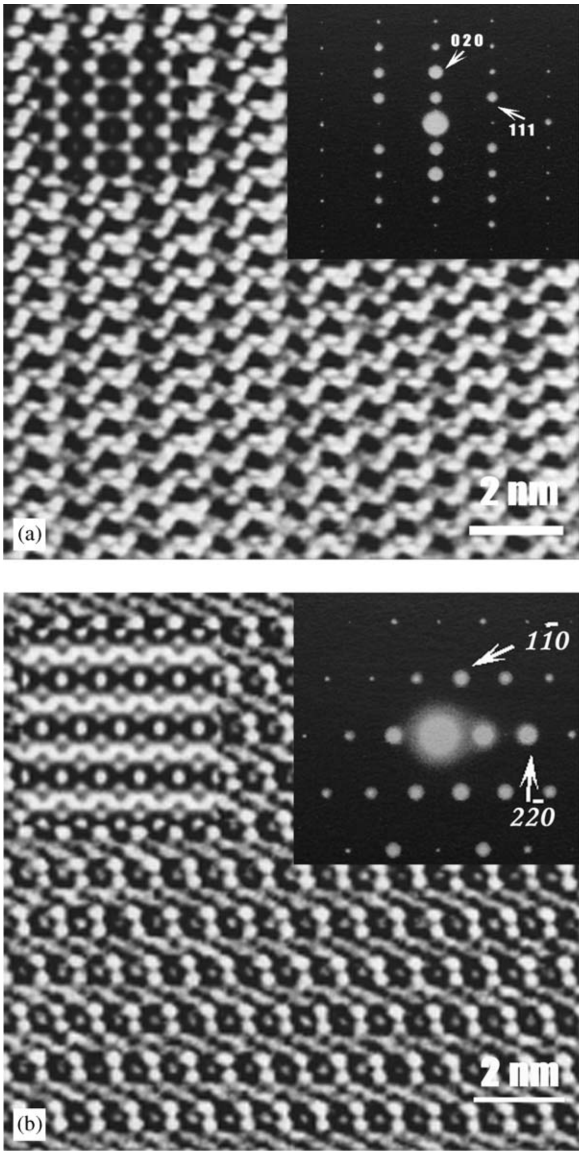

Fig. 4. HRTEM images of the grown crystals project along the (a) [101] direction and (b) [111] direction, the inserted are the corresponding SAED patterns and the simulated HRTEM images.

The selected area electron diffraction pattern along the [101] axis show a pseudo six-fold symmetry (Fig. 4a). In real space, if we neglect the Be atoms, the boron icosahedron clusters interconnected in six-fold symmetry (Fig. 3b). That may be the reason why our crystal shows a hexagonal habit in shape.

The composition of single crystals was analyzed by electron energy loss spectrum (EELS). Be and B signals were clearly observed in the spectrum (Fig. 5). No carbon atom was observed in the single crystals. The semi-quantity analysis reveled that the Be:B ratio in the crystals is 1:11–16, which is in good agreement with the calculated composition (1:15.6) from the XRD data.

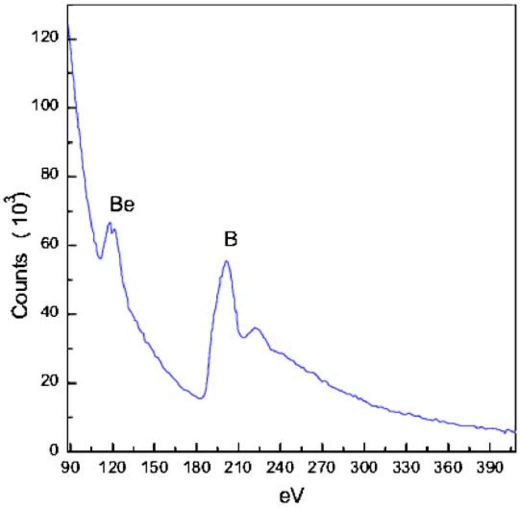

Fig. 5. The electron energy loss spectrum (EELS) for $Be_{8(1-x)}(B_{48})B_2$ crystals. The quantitative analysis gave a composition of Be:B = 1:(11–16), which is in good agreement with the calculated composition (1:15.6) from XRD.

4. Conclusions

A binary single crystal with formula of $Be_{8(1-x)}(B_{48})B_2$ ($x \sim 0.6$) was found in Be–B system with copper solution growth method. Single crystal XRD analysis reveled that the boron icosahedral framework in the crystal is similar with that of $TiB_{24}C$ reported before, but Be occupies a different site. The structure was also confirmed with HRTEM observations and selected area electron diffraction analysis method.

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