Gallium Flux Synthesis of $Tb_{3-x}C_2Si_8(B_{12})_3$: A Novel Quaternary Boron-Rich Phase Containing B_{12} Icosahedra**

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Aluminum, gallium, and indium fluxes provide substantial advantages in the exploratory synthesis of a large class of quaternary and ternary silicides and germanides.[1] We have demonstrated that flux chemistry is a powerful tool for the stabilization of complex aluminide/silicide phases of the type RE/Ni/Si/Al (RE = rare earth metal).[2] Complex intermetallics can have useful properties such as exceptionally high melting points, hardness, chemical inertness, and high-temperature thermoelectric energy conversion.[3, 4] In an attempt to extend this chemistry to the RE/Ni/Si/B systems, as lighter analogues of the Al-based compounds, we have explored the use of liquid gallium in the synthesis of complex silicon borides. We selected gallium because our studies on RE/Ni/Si/Ga showed that it was exceptionally difficult to form corresponding quaternary phases,[5] therefore, competing phases of this type were not expected. We hope to establish a methodology leading to new silicon boride compounds, which today are a relatively unfamiliar class. Liquid Ga may be an ideal solvent for such systems because it has a low melting point of 29.6 °C and does not react with silicon or boron, though both are soluble in it, and boron and silicon dissolved in the flux are highly reactive.[6]

Here we describe the discovery of $Tb_{1.8}Si_8C_2(B_{12})_3$, which was initially found as a minor product of a reaction between Tb, B, Ni, and Si in a 1:6:1:1 molar ratio, respectively, in a 10-fold molar excess of gallium.[7] Similar reactions with early rare earth metals, B, Ni, and Si in a 1:6:1:1 ratio with a 10-fold excess of gallium yielded mainly REB_6, REB_{12}, recrystallized silicon, and $Ni_5Ga_3Si_2$.[8] The formation of $Tb_{1.8}Si_8C_2(B_{12})_3$ was surprising, since we started with a quinary system of boron, gallium, silicon, terbium, and nickel, yet both Ni and Ga were excluded from the final product. Adventitious carbon, presumably present in one of the starting materials, was incorporated into the structure to stabilize the new quaternary boron-rich compound. Quaternary boron-rich systems are quite rare; a thorough search of the literature reveals only $RB_{22}C_2N$ (RE = Y, Ho, Er, Tm, and Lu) and $CrSi_3(B_{12})Se_{12}(B_2Se_3)_{1.33}$.[9] The new compound was initially thought to be a ternary phase. Carbon was determined to be part of the structure only after several failed attempts at a rational synthesis with gallium flux, and close inspection of the bond lengths revealed a 1.695(1) Å bond between a "boron atom" and its symmetry equivalent. This is shorter than a typical *endo* or *exo* boron–boron bond, but is quite reasonable for a carbon–carbon bond.[10, 11] Furthermore a successful high-yield synthesis (ca. 90 %) could be carried out only after carbon was added to the reaction mixture. Analogues with lighter RE atoms could not be synthesized.[12]

The novel compound $Tb_{1.8}(B_{12})_3C_2Si_8$ represents a new structure type, shown in Figure 1 a.[13] There are three salient characteristics of this structure: the B_{12} icosahedral cages, an Si_8 ethane-like cluster, and their mode of connectivity. There are four crystallographically distinct types of boron atoms, all

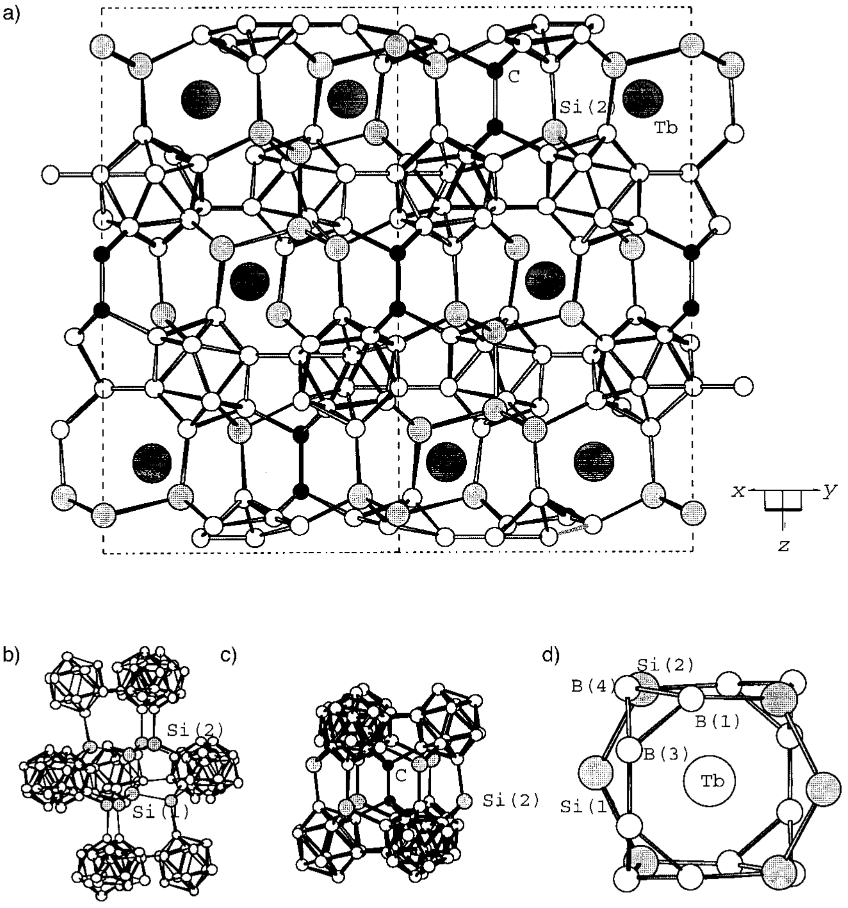

Figure 1. a) View of the unit cell of $Tb_{3-x}C_2Si_8(B_{12})_3$ showing the boron cage and the connectivity of the Si and C atoms. b) View of the ethane-like Si_8 cluster and its linking motif to the B_{12} cages. c) View of the C–C fragment and its connectivity to the B_{12} units. Shown also is the Si(2)–B_{12} bonding. d) Coordination environment of the rare earth metal site, caged by Si(1), Si(2), B(1), B(4), and B(3). Tb–B(3) 2.764(4), Tb–B(4) 2.783(4), Tb–Si(2) 2.8391(7) Å.

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of which are contained in the B_{12} cluster. The B_{12} cluster itself is distorted from ideal geometry and has boron–boron bond lengths of 1.785(7)–1.831(8) Å (av 1.803 Å). This is reasonable for the electron-deficient bonding in the B_{12} icosahedron. The structure contains two crystallographically distinct silicon atoms. The eight Si atoms are clustered together in an ethane-like staggered configuration with a central Si(1)–Si(1) bond length of 2.329(5) Å. Each Si(1) atom is bound to three Si(2) atoms (Si–Si 2.360(2) Å), which in turn form bonds to the B_{12} clusters. The tetrahedral coordination environment of Si(1) is compressed along the Si(1)–Si(1) bond axis, and this results in Si(2)-Si(1)-Si(2) bond angles of 114.25° instead of the ideal tetrahedral angle of 109.5°. The remaining bonds involving Si(2) are to B(1) and B(4) of three separate B_{12} cages (Figure 1b). Each C atom bonds to a symmetry-equivalent atom to give a C–C bond of length 1.695(1) Å in a similarly compressed staggered ethane-like unit with sp^3 hybridization. The carbon atoms form three additional bonds to B(2) of three separate boron cages (B(2)–C 1.820(7) Å, B(2)-C-C 115.5°; Figure 1c).

The B_{12} cage clusters are linked to each other through symmetry generated B(3)–B(3) bonds (1.726(8) Å) and are arranged in a trigonal layer extending over the *ab* plane (Figure 2). The one crystallographically distinct Tb site refined to 60% occupancy, which is in good agreement with the measured atomic ratios from EDS. The Tb ion is situated on a 3d Wyckoff site and is coordinated by four Si(2) atoms at 2.839(7) Å, two Si(1) atoms at 3.315 Å, and 12 boron atoms at 2.764(4)–2.930(4) Å (Figure 1d).

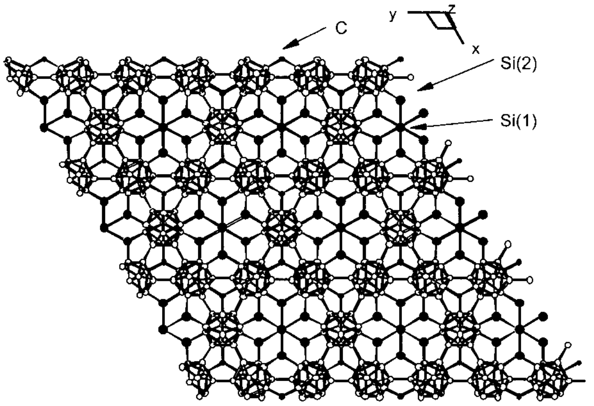

Figure 2. View down the *c* axis of the layer of B_{12} units and the staggered Si(1)/Si(2) network and their bonding relations. The rare earth metal atoms are omitted for clarity. The B_{12} cages are joined by B(3)–B(3) bonds.

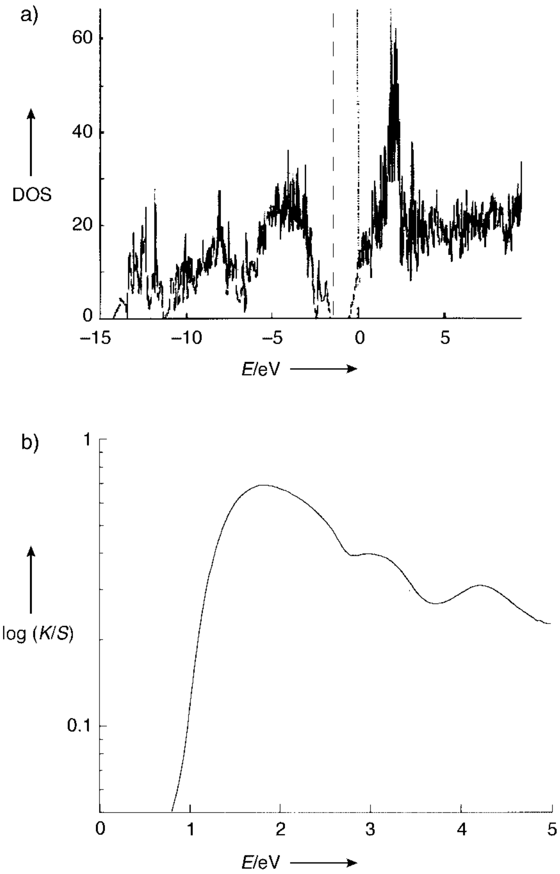

Figure 3. a) Total density of states (DOS) plot for the hypothetical $La_3C_2Si_8(B_{12})_3$. Solid black line is the Fermi level when the rare earth site is fully occupied, and the dotted line is the hypothetical Fermi level for 60% occupancy, which results in a band gap of about 1 eV. b) Experimental optical absorption spectrum of $Tb_3C_2Si_8(B_{12})_3$ showing a band gap of about 0.9 eV.

To better understand the origin of the vacancy at the rare earth metal site, an ab initio band-structure calculation was carried out.[14] Due to the difficulty in treating partially filled f levels and vacancies, Tb was modeled by fully occupied La. The resulting band structure and density of states (DOS) suggests that the driving force for the vacancy is valence precision, which consequently establishes a large band gap (ca. 1.0 eV) in the compound (Figure 3a). When the rare earth site is fully occupied, there is nonzero electron density at the Fermi level (i.e., a metal). However, integrating the DOS from –0.5 eV to the Fermi level yields 3.2 electrons, which corresponds well with the removal of approximately 35% of the rare earth metal ions from the compound. The solid line represents the Fermi level with a fully occupied rare earth metal site, and the dotted line is the Fermi level of the species with 65% occupancy. Experimentally we observe 40% removal. The extra 5% may originate from the presence of carbon atoms in the B12 cages. This is not unreasonable given the existence of carboranes, and it corresponds to about 5 carbon atoms distributed over 105 boron sites. It is curious that this compound creates vacancies to attain valence precision and a wide band gap, while other compounds such as LaB_6 (the trivalent analogue of the valence-precise compound CaB_6) do not. Instead, the extra electron results in metallic behavior.[15]

The presence of an optical semiconductor band gap in $Tb_{1.8}(B_{12})_3C_2Si_8$ was confirmed experimentally with near-IR/UV/Vis diffuse reflectance measurements to be about 0.9 eV, in good agreement with the DFT band calculations (Figure 3b).

Magnetic susceptibility measurements were performed on the title compound to establish the oxidation state and the occupancy of the Tb site. Curie–Weiss behavior was observed for the compound down to 20 K, where small deviations indicative of antiferromagnetic interactions were observed.

The calculated effective magnetic moment of 9.60 μ_B per mole of rare earth metal, assuming the site is 60 % occupied, is in good agreement with the calculated value of 9.72 μ_B.[16] The Weiss temperature of -17 K is consistent with a small antiferromagnetic interaction of the Tb atoms. The large Tb–Tb distances of 5 Å and the presence of vacancies explain the weak interactions between the Tb sites.

We have demonstrated here the utility of liquid gallium for the synthesis of the novel quaternary boron silicon carbide $Tb_{1.8}Si_8C_2(B_{12})_3$. We also have evidence for isostructural analogues with Y, Sc, Er, Dy, and Tm.[17] The existence and stability of such complex metal silicide carbide boride compounds should encourage additional exploratory research in this relatively unfamiliar area.

Experimental Section

The optimized synthesis used boron (0.0195 g, 1.80 mmol), amorphous silicon (0.0112 g, 0.4 mmol), graphitic carbon (0.002 g, 0.2 mmol), terbium metal (0.0143 g, 0.09 mmol), and gallium metal (1.5 g, 21 mmol). All reagents were used without further purification and were combined in an alumina tube, which was flame sealed under a vacuum of 7.0×10^{-5} mbar. The reaction mixture was heated to 1000 °C over 12 h, held at 1000 °C for 96 h, and cooled to 500 °C over 60 h. The reaction product was isolated by warm centrifugation to remove excess gallium, and further isolation was effected by 5 M I_2 in dimethylformamide. Total yield after isolation was generally 90 % with approximately 95 % purity. Unconsumed boron and recrystallized silicon are the main side products. Magnetic measurements were performed on a Quantum Design super conducting quantum interference device (SQUID) with MPMS software. Temperature-dependent measurements were performed at 500 G.

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[1] a) J. D. Bryan, G. D. Stucky, *Chem. Mater.* **2000**, *13*, 253; b) R. R. Urbano, C. Rettori, Z. Fisk, S. B. Oseroff, *Phys. Rev. B* **2001**, *63*, 2406.

[2] a) B. Sieve, X. Z. Chen, R. Henning, P. Brazis, C. R. Kannewurf, J. A. Cowen, A. J. Schultz, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2001**, *123*, 7040; b) X. Z. Chen, S. Sportouch, B. Sieve, P. Brazis, C. R. Kannewurf, J. A. Cowen, R. Patschke, M. G. Kanatzidis, *Chem. Mater.* **1998**, *10*, 3202; c) X. Z. Chen, P. Small, S. Sportouch, M. Zhuravleva, P. Brazis, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **2000**, *12*, 2520; d) X. Z. Chen, P. Brazis C. R. Kannewurf, J. A. Cowen, R. Crosby, M. G. Kanatzidis, *Angew. Chem.* **1999**, *111*, 695; *Angew. Chem. Int. Ed.* **1999**, *38*, 693.

[3] B. Aronsson, T. Lundstrom, S. Rundqvist, *Borides, Silicides, Phosphides*, Wiley, New York, **1965**, pp. 20–32.

[4] a) T. Nakayama, J. Shimizu, K. Kimura, *J. Solid State Chem.* **2000**, *154*, 13; b) Y. Ishizawa, T. Tanaka, *J. Solid State Chem.* **2000**, *154*, 229.

[5] X. Z. Chen, P. Larson, S. Sportouch, P. Brazis, S. D. Mahanti, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1999**, *11*, 75.

[6] T. B. Massalski, *Binary Alloy Phase Diagrams*, *Vol. 1*, 2nd ed., ASM International, New York, **1990**, p. 484; T. B. Massalski, *Binary Alloy Phase Diagrams*, *Vol. 2*, 2nd ed., ASM International, New York, **1990**, p. 1856.

[7] Electron microprobe energy dispersive spectroscopy (EDS) was performed on several crystals of the compound and indicated that boron, silicon, and terbium were present in the trigonal antiprismatic crystals (20 kV accelerating voltage, 120 s acquisition time; the ratio of terbium to silicon was 1:4). EDS data were also acquired at low accelerating voltages of 8 kV and a high magnification of 2500 × to quantify boron and carbon. High magnification was used to ensure exclusion of carbon tape. It was found that B and C were present in a ratio of 17:1, which is in good agreement with the expected ratio of 18:1. EDS analyses were performed with a JEOL JSM-35C scanning electron microscope equipped with Noran Vantage Energy Dispersive Spectroscopy (Si:Li) detector and Norvar window suitable for the standardless quantization of light elements ($Z = 4$).

[8] M. El-Boragy, T. Rajasekharan, K. Schubert, *Z. Metallkd.* **1982**, *73*, 193.

[9] a) M. Sugimori, H. Fukuoka, H. Imoto, T. Saito, *J. Organomet. Chem.* **2000**, *611*, 547; b) F. Zhang, A. Leithe-Jasper, J. Xu, T. Mori, Y. Matsui, T. Tanaka, *J. Solid State Chem.* **2001**, *159*, 174.

[10] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1999**, p. 132.

[11] Consideration of its coordination environment added further credence to the assignment of this site as carbon. This situation was quite similar to the discovery of carbon in the valence-precise compound $NaCB_5$, though in this case bond lengths were indistinguishable: B. Albert, K. Schmitt, *Chem. Commun.* **1998**, 2373.

[12] Synthesis of $(RE)_{3-x}C_2Si_8(B_{12})_3$ (RE = La, Ce, Pr, Nd, Sm, Gd) attempted by combining 1.8 mmol boron, 0.4 mmol silicon, 0.2 mmol graphite, and 0.09 mmol rare earth metal with 21 mmol of gallium metal was unsuccessful. The reaction heating profile and isolation are identical to those described for the synthesis of the title compound. The products were REB_6, REB_{12}, and recrystallized silicon; no quaternary phases were found.

[13] Crystal data for $Tb_{1.8}C_2Si_8(B_{12})_3$: $M_r = 923.96$; rhombohedral, space group $R\bar{3}m$, $a = 10.1171(9)$, $c = 16.397(2)$ Å, $V = 1453.4(3)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.583$, $\mu = 3.515$ mm^{-1}, $R1/wR = 2.69/5.75$ % for all 417 unique reflections, 7648 total reflections ($R_{int} = 2.81$ %), and 49 parameters. X-ray diffraction data were collected at room temperature on a Bruker SMART CCD diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined with the SHELXL suite of programs (G. M. Sheldrick, SHELXL, Structure Determination Programs, Version 5.0. Siemens Analytical X-Ray Instruments Inc., Madison, WI, **1995**). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412170.

[14] Band-structure calculations were performed with the self-consistent full-potential linearized augmented plane-wave method (LAPW) within density functional theory (DFT) with the generalized gradient approximation (GGA) for the exchange and correlation potential. Scalar relativistic corrections were added, and spin–orbit interaction (SOI) was incorporated by using a second variational procedure. The calculations were performed with the WIEN97 program.

[15] V. I. Matkovich, *Boron and Refractory Borides*, Springer, New York, **1977**, p. 145.

[16] C. Kittel, *Introduction to Solid State Physics*, 7th ed., Wiley, New York, **1996**, p. 425.

[17] Crystal data for $Er_{1.8}C_2Si_8(B_{12})_3$: $M_r = 938.96$; rhombohedral, space group $R\bar{3}m$, $a = 10.0994(9)$, $c = 16.354(2)$ Å, $V = 1444.6(3)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.619$, $\mu = 4.153$ mm^{-1}, $R1/wR = 2.10/5.23$ % for all 413 unique reflections, 3807 total reflections ($R_{int} = 3.51$ %), and 49 parameters. Crystal data for $Y_{1.8}C_2Si_8(B_{12})_3$: $M_r = 904.64$; rhombohedral, space group $R\bar{3}m$, $a = 10.101(2)$, $c = 16.441(2)$ Å, $V = 1452.7(5)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.551$, $\mu = 4.713$ mm^{-1}, $R1/wR = 3.90/9.14$ % for all 417 unique reflections, 2829 total reflections ($R_{int} = 7.28$ %), and 49 parameters.