An Oxidation-Resistant Semiconductor

Stabilization of β-SiB_3 from Liquid Ga: A Boron-Rich Binary Semiconductor Resistant to High-Temperature Air Oxidation**

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Liquid metals can be powerful solvents for the exploration of novel refractory solid-state materials ranging from intermetallic compounds to silicides, carbides and borides. Recently we have discovered, from liquid Al and Ga, a large variety of ternary and quaternary phases of the type RE/TM/Si or Ge, RE/TM/Al or Ga, RE/TM/Al/Si or Ge, and RE/TM/Ga/Ge or Si (RE = rare earth La–Lu, and TM = 1st, 2nd, or 3rd row transition metal).[1,2] Many of these phases cannot be formed by conventional high temperature solid-state synthetic techniques such as direct combination reactions with arc melting or radio-frequency (rf) induction furnace heating.[3] We have extended the flux methodology to include RE/TM/B/Si (borosilicides) in an attempt to produce lighter analogues of the RE/TM/Al/Si compounds, and we chose liquid gallium as the reaction medium because both Si and B are soluble in it and do not form binaries.[4] Also from previous work we learned that RE/TM/Ga/Si phases do not form readily, and so competing phases of this type are not anticipated.[1] Boron-containing solids have acquired renewed interest because quaternary borocarbides are superconducting,[5] and MgB_2 is a high temperature nonoxidic superconductor.[6]

Borosilicides are an unfamiliar class of compounds. Specifically boron-rich borosilicides are rare with only a handful of examples are known: $CrSi_3(B_{12})Se_{12}(B_2Se_3)_{1.33}$, $REB_{41}Si_{1.2}$ (RE = Y, Tb), $Sc_{0.83-x}B_{10.0-y}C_{0.17+y}Si_{0.083-z}$,[7] SiB_3, SiB_4 and SiB_6[8] to name a few. We have recently shown that liquid gallium can provide an excellent route to complex quaternary silicon borides such as $Tb_{1.8}Si_8C_2(B_{12})_3$ that cannot be formed by using high-temperature techniques such as arc melting.[9] Herein, we present an illustration of the ability of liquid Ga to stabilize boride phases inaccessible by conventional synthetic routes. Namely, we describe a novel B-rich, refractory, semiconducting binary phase β-SiB_3.

β-SiB_3 is a surprising discovery because a phase with a similar formula, $Si_{1-x}B_{3+x}$ with a compositional spread of x = 0–0.2,[10] that has a rhombohedral structure has been known for decades.[11] We will henceforth refer to this phase as α-SiB_3. Instead β-SiB_3 is orthorhombic *Imma*, representing a new structure type.[12] Despite the similarity in stoichiometry and the presence of B_{12} icosahedra the structural features and electronic properties of the α and β phases are very different. Rhombohedral α-SiB_3 forms from direct combination of the elements with prolonged isothermal heating at 1225 °C or by arc melting, in contrast β-SiB_3 was produced from a lower temperature reaction (1000–850 °C) in Ga flux. Additionally, in α-SiB_3, some Si atoms are randomly distributed in the B_{12} cages resulting in very distorted icosahedra.[13] In contrast, Si atoms in β-SiB_3 are rigorously excluded from the cages, thus resulting in more regular icosahedra. To the best of our knowledge this is the first Si–B binary phase that is fully crystallographically ordered without any Si/B mixed sites or disorder. This exclusion of Si from the cages has a profound influence on the thermal stability of the orthorhombic form.

β-SiB_3 was originally found as a minor product in reactions aimed to produce $Er_{1.8}Si_8C_2(B_{12})_3$ from the Ga flux. The new phase forms as distorted rectangular plates that are translucent and amber in color. Energy dispersive spectroscopy (EDS) on several crystals of the title compound detected only Si and B.[14] The presence of C in β-SiB_3 was detected by combustion elemental analysis which showed the carbon concentration to be ~0.4% by weight.[15] Similar combustion analysis on α-SiB_3 (a phase known to contain no C) showed a C concentration of 0.16% by weight. We originally thought that there was a small amount of C present

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in β-SiB_3, and that it was statistically distributed over the B_{12} cages resulting in the stoichiometry $Si_4B_{12-x}C_x$ ($x \sim 0.4$). The yield of β-SiB_3 was observed to increase when carbon was included in the preparation (from 40% to 60%). Although it is possible that a small amount of carbon is accommodated in the structure, we believe that it is not needed to prepare the compound. The issue of adventitious carbon inclusion is discussed below.

Importantly, no traces of the known black rhombohedral α-SiB_3 phase were found by powder X-ray diffraction, nor visual inspection in the flux reactions. As the crystal habit and color of the two species are quite different, they are easily distinguished by looking. An inspection of other reactions of the type TM/B/C/Si (TM = Fe, Co, Ni, Cu, Zn) in a Ga flux showed large amounts of β-SiB_3, particularly when TM = Cu.

The formation of β-SiB_3 is exclusive to flux synthesis. Several attempts were made to produce the phase by direct combination of the elements with arc-melt alloying, rf induction heating and prolonged heating at 1000 °C for two weeks. The induction furnace and the two-week 1000 °C isothermal synthesis both yielded starting material, presumably because the temperatures reached by these methods were insufficient to bring about a reaction. Arc-melt alloying Si and B in a 1:3 ratio yielded the α-SiB_3 structure. EDS analysis was also performed on crystals produced from this reaction and found on Si and B present in similar ratios to the title compound. These results may explain why β-SiB_3 was not discovered previously, as flux routes to borosilicides are a new synthetic strategy.

The structure of β-SiB_3 has two building blocks: infinite Si_4 chains and B_{12} cages (Figure 1a and 1b respectively). The B_{12} cages are linked together forming a layer, Figure 1c. The Si_4 chains contain two base-fused triangle units forming a rhombus. The rhombi are linked to one another to form a sinusoidal chain that propagates along the *a* axis, Figure 1a. There are two crystallographically distinct Si atoms one at the apex of the fused triangles (Si(1)) and one that forms the base with its symmetry equivalent (Si(2)). The Si(1)–Si(1) bond from apex to apex is 2.3336(8) Å. The other Si–Si bonds in the structure are substantially longer with Si(1)–Si(2) being 2.5967(4) Å and Si(2)–Si(2) (base of the triangle) at 2.3970(8) Å. To the best of our knowledge, the infinite Si_4 chain is a novel structural feature, although it has a slight similarity to the Ge_4 chains of $BaGe_2$. However, in the latter compound the Ge_4 chains are anionic and are well rationalized by the Zintl concept.[16] In contrast, the Si_4 chains of β-SiB_3 are not anionic and are not regarded as Zintl species.

The four crystallographically distinct boron atoms are arranged in the B_{12} cages that form a sheet structure extending over the *ac* plane, which results in a regular four-sided ring of cages Figure 1c. The cages are bound through symmetry-generated B(4)–B(4) bonds at 1.717(2) Å. Intracage distances range from 1.934(2) Å for B(4)–B(4) to 1.756(2) Å for B(1)–B(3) with an average of 1.792 Å. The Si zig-zag chains insert between the B_{12} icosahedral sheets forming B–Si bonds and a three-dimensional framework along the *b* axis (Figure 2). The B–Si bond distances are 2.027(1) Å for Si(1)–B(1), 1.973(2) Å between Si(2) and B(3), and 2.009(2) for Si(2)–B(2).

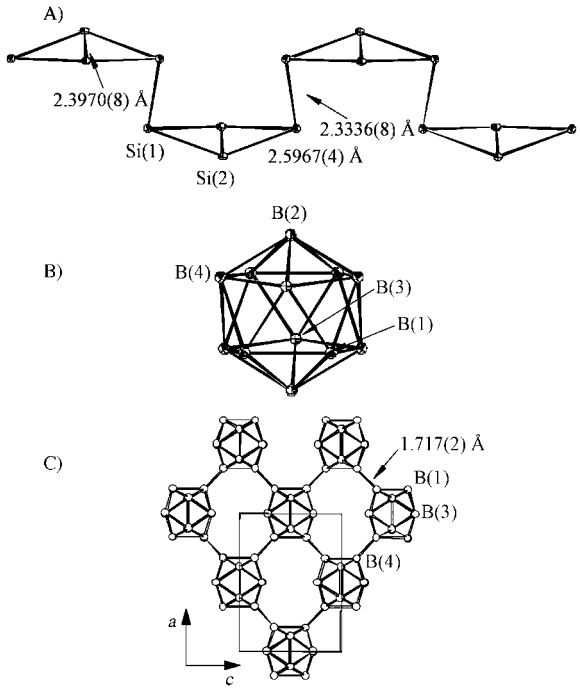

Figure 1. a) A segment of the infinite Si_4 ribbon as it extends down the *a* axis, a motif reminiscent of red phosphorous, thermal elipsoids are set at the 50% probability level. Selected bond angles Si(1)-Si(1)-Si(2) = 91.85(2)°, Si(1)-Si(2)-Si(1) = 121.53(2)°, Si(2)-Si(1)-Si(2) = 54.97(2)°, Si(2)-Si(2)-Si(1) = 62.513(9)°. b) B_{12} icosahedral unit, thermal elipsoids are set at the 50% probability level. c) The arrangement of B_{12} cages in the *ac* plane.

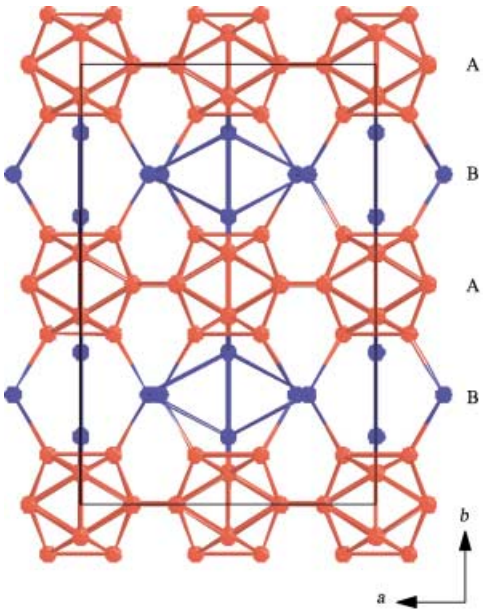

Figure 2. A view of the overall structure of β-SiB_3 showing the way two structural moieties stack along the *b* axis. Si atoms: blue; B atoms: red.

β-SiB_3 is a semiconductor with an energy band gap of ≈2.0 eV, (Figure 3a).[17] This wide gap is in sharp contrast to that of the α-SiB_3, which is only ≈0.2 eV, (Figure 3b), and points to the dramatically different electronic properties of

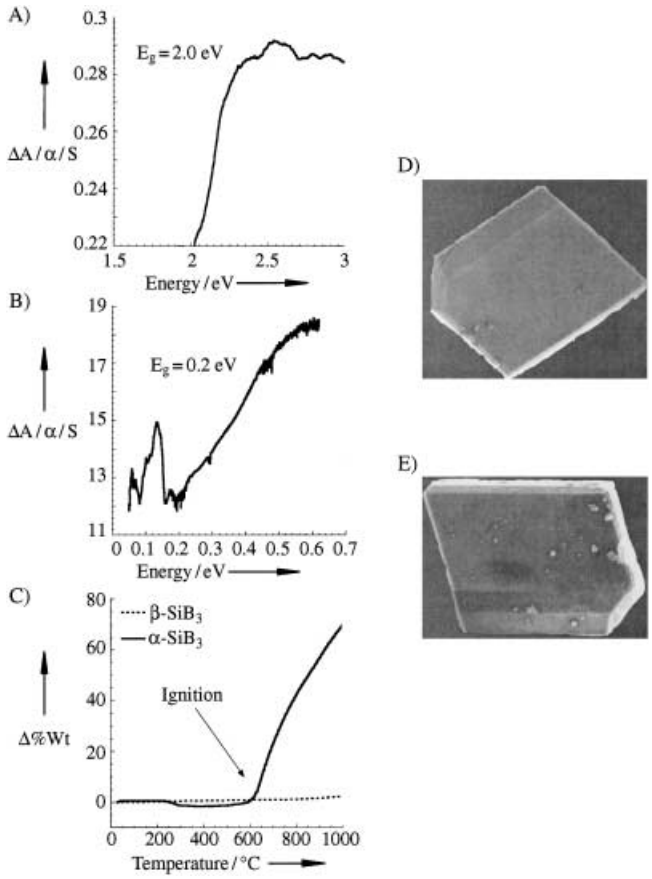

Figure 3. A) A comparative plot of the optical absorbance versus energy (eV) for β-SiB_3 and B) α-SiB_3. (α = absorption coefficient, S = scattering) C) Thermal gravimetric analysis of α-SiB_3 and β-SiB_3 in air. Percent relative weight gain (Δ %Wt) is defined as [(Weight − $Weight_{initial}$)/$Weight_{initial}$] × 100. D) Scanning electron micrograph of β-SiB_3 before heating at 700 °C. E) Scanning electron micrograph of same β-SiB_3 crystal after heating at 700 °C.

these two phases.[18] Thermopower measurements on β-SiB_3 showed a small positive room temperature Seebeck coefficient of $+20\ \mu V K^{-1}$, which decreased approximately linearly to $+10\ \mu V K^{-1}$ at 400 K. The positive value indicates holes as the dominant charge carriers as is typically the case for boron-rich compounds with B_{12} icosahedra.[19]

Ab initio band-structure calculations were carried out for β-SiB_3 to probe for the existence of an energy band gap and to see if the compound were stable without the inclusion of carbon.[20] The calculations show an indirect band gap of ~1.5 eV, which indicates valence precision. This result demonstrates that C atoms are not needed in the B_{12} cages to satisfy any electronic requirements of β-SiB_3. Based on this result, we believe that C atoms are not present in the structure and that β-SiB_3 is truly a new Si–B binary phase. The theoretically determined band gap is in reasonably good agreement with the optically determined value of 2.0 eV.

A remarkable property of this phase is the extreme inertness to chemical attack by concentrated sulfuric acid, aqua regia, and a 5 M solution of NaOH for > 24 h. Thermal gravimetric analysis (TGA) showed β-SiB_3 did not oxidize under a pure oxygen atmosphere below approximately 600 °C. When the experiment was repeated in air instead of oxygen, there was no evident ignition point and only a nominal relative weight gain of ≈2 % was observed up to 1000 °C. In contrast, α-SiB_3 shows an ignition point of 600 °C in air, Figure 3c. We attribute the lack of stability in α-SiB_3 to the nature of the Si–B disorder within the B_{12} icosahedra, which causes the weakening of bonds. To test more realistically the thermal stability of the title compound, several single crystals were placed in open fused silica tubes and heated to 700 °C and held there for 12 h. β-SiB_3 remained intact at this temperature. Scanning electron micrographs of a β-SiB_3 single crystal before and after heating can be seen in Figure 3d and 3e respectively. Only when the experiment was repeated at 1000 °C was there evidence of thermal degradation.

The resistance to air oxidation at high temperature is impressive for a nonoxidic compound. As it also has a wide band gap of 2.0 eV, this new material might be useful as a refractory p-type semiconductor capable of operating in extreme environments. Currently the leading material for such applications is SiC, however, it suffers from the major drawback of having nearly 200 polytype structures, all of which have different electronic properties.[21] The compound presented here has no other polytypes, and β-SiB_3 can be made independently from α-SiB_3.

It is significant that the synthesis of β-SiB_3 requires metallic flux conditions, which permit the total bypass of the rhombohedral compound α-SiB_3. The results reported herein warrant future investigations of the electrical properties of β-SiB_3.

Experimental Section

Optimized flux synthesis of β-SiB_3 was carried out by combining B (43 mg, 4 mmol; 99.995 % submicron amorphous, Aldrich), Si (28 mg, 1 mmol; 99.999 % −325 mesh, Cerac), Cu (64 mg, 1 mmol; 99.9 % 325 mesh, Cerac), and Ga (1.394 g, 20 mmol; 99.99 % 2–5 mm pieces, Plasmaterials) into an Al_2O_3 ceramic tube. The ceramic tube was placed in a fused silica tube that was flame-sealed under a vacuum of ~10^{-5} mbar. The reactants were heated up to 1000 °C over 12 h, then held at 1000 °C for 96 h. The reaction system was then cooled to 150 °C over 48 h. Isolation of the product was accomplished by a warm centrifugation, which removed the excess Ga. Further purification was carried out by adding the product to a solution of I_2 (5 M) in dimethylformamide, and subjecting the mixture to ultrasound for 30 min to remove remaining Ga. Small shiny amber colored plates were obtained approximately 0.5–1 mm at the widest point. Typical yields were 40 %.

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[15] Combustion analysis was carried out by selecting single crystals of the title compound (sample size 2.272 mg) and α-SiB_3 (sample size 3.730 mg) and rinsing them in aqua regia and "piranha" solution (75 vol% conc. H_2SO_4/25 vol% 30% H_2O_2) to minimize surface carbon contamination. Elemental analysis was performed with a Perkin Elmer series II CHNS/O analyzer 2400.
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[18] Band-gap measurements for rhombohedral SiB_3 were made with a Nicolet Magna IR 750 FTIR spectrophotometer in reflectance mode. The data was processed with the Kubelka-Munk equation.
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