

Association of broad icosahedral Raman bands with substitutional disorder in SiB_3 and boron carbide

T. L. Aselage and D. R. Tallant

Sandia National Laboratories, Albuquerque, New Mexico 87185-1421

(Received 8 July 1997; revised manuscript received 4 September 1997)

The structure of silicon boride, SiB_3 , is based on 12-atom, boron-rich icosahedra in which silicon atoms substitute for some boron atoms. Raman bands associated with vibrations of icosahedral atoms in SiB_3 are quite broad, reflecting this substitutional disorder. Comparing the Raman spectra of other icosahedral borides with SiB_3 , only boron carbides have similarly broad icosahedral Raman bands. The direct correlation of broad icosahedral Raman bands with substitutional disorder supports the proposition that carbon atoms replace icosahedral boron atoms in boron carbides of all compositions. [S0163-1829(98)05406-X]

Crystal structures of many boron-rich solids can be described as based on 12-atom, boron-rich clusters having the shape of slightly distorted icosahedra. In many of these icosahedral borides, an icosahedron is centered at each vertex of a rhombohedral unit cell (Fig. 1).¹ Atoms within icosahedra occupy two distinct sites distinguished primarily by differences in their external bonding. Six atoms of each icosahedron bond directly to atoms of neighboring icosahedra. These atoms, shown as filled circles in Fig. 1, form triangles at the upper and lower poles of each icosahedron. The remaining six atoms, shown as open circles in Fig. 1, form a hexagonal ring about the equator of an icosahedron. These equatorial atoms can bond to nonicosahedral atoms that belong to two- or three-atom chains lying along the long diagonal of the unit cell. Solids with two-atom chains and all-boron (B_{12}) icosahedra are formed when the intericosahedral chains consist of phosphorus, arsenic, or oxygen atoms: B_{12}P_2 , B_{12}As_2 , or B_{12}O_2 . Alternately, in α -rhombohedral boron, boron atoms in equatorial sites of three adjacent icosahedra bond to one another through weak intericosahedral three-center bonds. The electron densities of intericosahedral three-center bonds in α -rhombohedral boron peak near the locations of the nonicosahedral atoms in Fig. 1.

The crystal structure of boron carbide is derived from Fig. 1 by replacing the two-atom chains with linear three-atom chains.¹ The central position of these three-atom chains is occupied predominantly by boron atoms. The sites at the ends of the chains can be filled by either boron or carbon atoms. In addition, a carbon atom can replace a polar icosahedral boron atom, forming B_{11}C icosahedra. Because of boron and carbon atoms' substitution for one another, the single-phase region of boron carbides extends over a wide composition range: $\text{B}_{12+x}\text{C}_{3-x}$ with $0.15 < x < 1.5$.² The distribution of carbon atoms among different sites in boron carbides as a function of carbon concentration has been extensively debated.³ Since diffraction measurements do not adequately distinguish boron atoms from carbon atoms, this distribution must be inferred from indirect measurements.

Raman spectra of each of the icosahedral borides described above have been measured.⁴⁻¹¹ In our prior analyses, peak assignments were based on comparisons between spectra of different icosahedral borides,⁴⁻⁶ on changes in spectral

features' frequencies with isotopic substitutions,^{6,7} and on changes in features' intensities upon varying a crystal's orientation relative to the exciting laser polarization.⁵⁻⁷ These analyses suggest that stretching motions of intericosahedral chains yield relatively narrow Raman peaks with frequencies below 600 cm^{-1} . Raman peaks with frequencies above 600 cm^{-1} were attributed to vibrations of icosahedral atoms. Icosahedral Raman peaks are relatively narrow in ordered boron-rich solids whose icosahedra contain only boron atoms: α -rhombohedral boron, B_{12}P_2 , B_{12}As_2 , and B_{12}O_2 . Figure 2(a) illustrates the discrete nature of narrow Raman peaks in B_{12}P_2 . Peaks above 600 cm^{-1} in the spectra of α -rhombohedral boron, B_{12}As_2 , and B_{12}O_2 are similarly narrow.

Figure 2(b) shows the Raman spectrum of a boron carbide

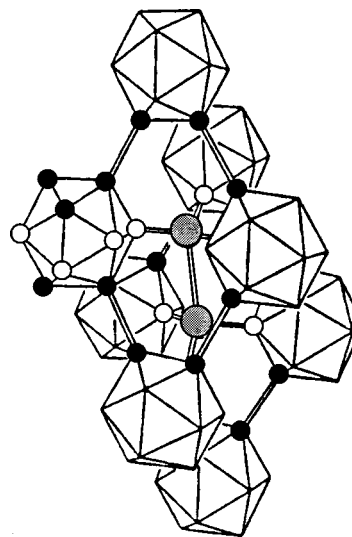


FIG. 1. Representation of the structure of icosahedral borides. Six atoms of each icosahedron bond directly to atoms of neighboring icosahedra. These atoms, shown as filled circles, form triangular rings at the upper and lower poles of the icosahedron. One complete triangle of polar atoms is shown in the upper-left-most icosahedron. The remaining six atoms of the icosahedron form a chair-configuration hexagon at the equator of the icosahedron. These atoms, shown as open circles, bond to nonicosahedral atoms located along the long diagonal of the rhombohedral unit cell.

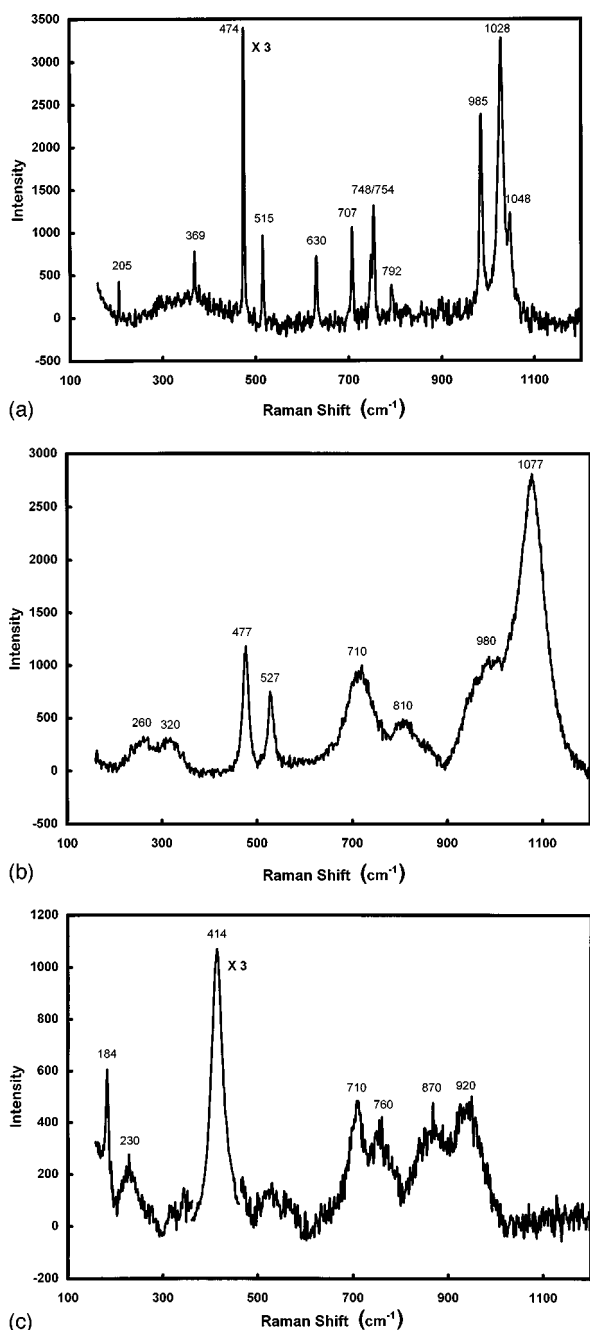


FIG. 2. (a) Raman spectrum of a pressed-powder sample of $^{11}\text{B}_{12}\text{P}_2$. Peaks above 600 cm^{-1} are related to vibrations of boron atoms within B_{12} icosahedra. The peak at 474 cm^{-1} is due to the stretching of the P-P chain (Ref. 7). Boron in this sample was enriched from its natural abundance, 80%, to greater than 99% ^{11}B . (b) Raman spectrum of a pressed-powder sample of $\text{B}_{12.15}\text{C}_{2.85}$. Broad peaks above 600 cm^{-1} have been associated with motions of atoms within B_{11}C icosahedra. The two narrow peaks at 477 and 527 cm^{-1} have been attributed to vibrations of CBC chains and their nearest icosahedral boron neighbors (Ref. 7). (c) Raman spectrum of a pressed-powder sample of SiB_3 . The intensities of the 474 cm^{-1} peak in (a) and the 414 cm^{-1} peak in (c) have been reduced by a factor of 3 to enhance the less intense peaks.

having the composition $\text{B}_{12.15}\text{C}_{2.85}$. With this carbon-rich composition, nearly all of boron carbides' icosahedra contain a carbon atom in a polar site, B_{11}C , and nearly all three-atom chains have carbon atoms at both ends, CBC. The bands at

477 and 527 cm^{-1} in Fig. 2(b) have been associated with the motions of atoms in CBC chains and their boron-atom neighbors in equatorial sites of icosahedra.⁵⁻⁷ The relatively narrow widths of these lines suggest that these vibrations are largely decoupled from the polar icosahedral sites in which carbon atoms substitute for boron atoms.⁵ In contrast with the narrow bands of B_{12}P_2 [Fig. 2(a)], boron carbides' Raman bands in the frequency range of vibrations involving icosahedral atoms, above 600 cm^{-1} , are quite broad. We have attributed this broadness to disorder introduced by the substitution of carbon atoms for boron atoms among polar icosahedral sites.⁵ Significantly, broad icosahedral Raman bands are observed in boron carbides whose compositions span the whole single-phase region, suggesting that carbon atoms are preferentially retained within icosahedra even at the lowest carbon concentrations.⁵⁻⁷

Our analysis of boron carbides' Raman spectra thus suggests that boron atoms preferentially replace carbon atoms within chains rather than within icosahedra as the carbon concentration of boron carbide is reduced.⁵⁻⁷ This interpretation, however, is in disagreement with electronic structure calculations, which conclude that retention of carbon atoms within chains is energetically favorable to their retention within icosahedra.¹² Furthermore, there are alternative interpretations of the vibrational spectra of boron carbides.^{10,11,13-16} In particular, many analyses presume bonding within boron carbides' CBC chains to be so stiff and strong as to preclude carbon atoms being removed from them. Additionally, boron carbides' Raman bands have been described as being relatively distinct and narrow, typical of a largely ordered solid.¹⁰ It has been suggested¹¹ that any unusual breadth present in boron carbides' Raman peaks arises from electronically induced distortions and from statistical distortions (e.g., differences in chain composition¹⁴) that are not present in other icosahedral borides. However, our new results show that broadening of icosahedral Raman bands is associated with substitution of a heteroatom for an icosahedral boron atom. This conclusion is drawn from the similarity of the Raman spectra of SiB_3 and boron carbides.

The structure of SiB_3 is described by 12-atom icosahedra and two-atom chains, as shown in Fig. 1. The two chain sites are occupied by silicon atoms. Additionally, silicon atoms statistically replace 1.5 of the six polar boron atoms in each icosahedron.¹⁷ The structure of SiB_3 may thus be represented as $(\text{B}_{10.5}\text{Si}_{1.5})\text{Si}_2$. Unlike boron carbides, the presence of silicon atoms within icosahedral sites is clearly confirmed by x-ray diffraction measurements.¹⁷ Also unlike boron carbides, the chains of SiB_3 are uniform in their two-silicon-atom composition.

A nearly single-phase sample of SiB_3 was produced in a recent study of the Si-B system.¹⁸ This sample of SiB_3 was prepared by solid-state reaction of silicon and boron powders at $1225\text{ }^\circ\text{C}$ under gettered argon. The silicon and boron powders each had their respective natural abundance of isotopes. Powder x-ray diffraction showed the sample to be nearly single-phase SiB_3 , with trace levels of Si and SiB_6 impurities (see Fig. 2 of Ref. 18). High-resolution, quantitative electron-energy-loss spectra obtained from individual grains of the powdered SiB_3 sample gave a B:Si ratio of approximately 3:1, in accord with the bulk stoichiometry of the sample.¹⁹ The Raman spectrum of SiB_3 has not

previously been reported. We measured the Raman spectrum of our SiB_3 powder sample using the 514.5-nm argon-ion laser line for excitation and a triple spectrometer equipped with holographic gratings and charge-coupled-device detector for dispersion and detection of the Raman-shifted scatter. The spectrum was stripped of background fluorescence and Rayleigh scatter by an empirical fitting procedure.

The Raman spectrum of SiB_3 is shown in Fig. 2(c). We note that the crystalline silicon impurity in the SiB_3 sample was not present in sufficient concentration to produce an observable peak at its characteristic Raman frequency, 520 cm^{-1} .²⁰ The Raman spectrum of SiB_3 bears a strong resemblance to that of $\text{B}_{12.15}\text{C}_{2.85}$ [Fig. 2(b)]. In particular, peaks in the frequency range associated with vibrations of icosahedral atoms, above 600 cm^{-1} , are similarly broad in both SiB_3 and boron carbides. Since each chain of SiB_3 has two silicon atoms, disorder in SiB_3 is produced only by the substitution of silicon atoms for icosahedral boron atoms. This correlation of substitutional disorder in icosahedral sites with broad icosahedral Raman bands in SiB_3 thus supports our prior contention that the substitution of carbon atoms for icosahedral boron atoms is responsible for boron carbides' broad icosahedral Raman bands. We now discuss the features of the SiB_3 spectrum in more detail.

Consistent with our mode assignments in other icosahedral borides, we associate the intense feature at 414 cm^{-1} in the Raman spectrum of SiB_3 with the stretching motion of its two-silicon-atom chain. This frequency is lower than observed in crystalline silicon,²⁰ at 520 cm^{-1} , or in amorphous silicon,²⁰ at $460\text{--}470\text{ cm}^{-1}$. This lower vibrational frequency is consistent with relatively weak and soft intrachain bonding implied by the Si-Si distance in SiB_3 , 2.46 \AA ,¹⁷ being greater than the interatomic separation in crystalline silicon, 2.35 \AA . Additionally, the frequency of the Si-Si stretch will be lowered if silicon atoms' icosahedral boron neighbors are carried along by their motion, as will occur when intrachain bonding is relatively soft compared to chain-icosahedron bonding.⁷

The highest-frequency Raman-active modes of icosahedral boron-rich solids are thought to be related primarily to motions of atoms within the polar triangles of icosahedra.^{4-7,21,22} The frequencies of these modes in SiB_3 , $850\text{--}950\text{ cm}^{-1}$, are somewhat lower than those of boron carbide or other icosahedral borides. Silicon atoms substitute for icosahedral boron atoms only within the polar triangle sites in SiB_3 .¹⁷ Because a silicon atom is substantially larger than a boron atom, the average intra-icosahedral separations are larger in SiB_3 than in the other icosahedral borides. Lower vibrational frequencies of polar atoms in SiB_3 can then be rationalized as being due to (1) the greater mass of the silicon atoms, and (2) the decreased stiffness associated with increased intra-icosahedral separations. The icosahedral modes of SiB_3 at about $700\text{--}800\text{ cm}^{-1}$ are closer in frequency to those of boron carbide. Lower-frequency icosahedral vibrations are believed to involve larger participation by equatorial boron atoms.

In summary, the Raman spectrum of SiB_3 shows evidence of its known substitutional disorder in icosahedral sites through its broad icosahedral Raman bands. Of icosahedral borides with structures related to Fig. 1, only SiB_3 and boron carbides have similarly broad icosahedral Raman bands. It follows that boron carbides' broad icosahedral Raman bands arise from similar substitutional disorder: carbon atoms substituting for boron atoms. Broad icosahedral Raman bands in boron carbides of all compositions provide strong evidence that carbon atoms are preferentially retained in icosahedral sites.

The authors would like to acknowledge the experimental assistance of George Sartor and Regina Simpson. This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, United States Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

¹B. Morosin, A. W. Mullendore, D. Emin, and G. A. Slack, in *Boron-Rich Solids*, edited by D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, AIP Conf. Proc. No. 140 (AIP, New York, 1986), p. 70.

²M. Bouchacourt and F. Thevenot, *J. Less-Common Met.* **82**, 227 (1981); K. A. Schwetz and P. Karduck, in *Boron-Rich Solids*, edited by D. Emin, T. Aselage, A. Switendick, B. Morosin, and C. Beckel, AIP Conf. Proc. No. 231 (AIP, New York, 1991), p. 405.

³Discussions of different models of carbon atoms' locations in boron carbides are found in the volumes of Refs. 1 and 2 and in many of the papers listed below.

⁴J. A. Shelnett, B. Morosin, D. Emin, A. Mullendore, G. Slack, and C. Wood, in *Boron-Rich Solids* (Ref. 1), p. 312.

⁵D. R. Tallant, T. L. Aselage, A. N. Campbell, and D. Emin, *Phys. Rev. B* **40**, 5649 (1989).

⁶D. R. Tallant, T. L. Aselage, and D. Emin, in *Boron-Rich Solids* (Ref. 2), p. 301.

⁷T. L. Aselage, D. R. Tallant, and D. Emin, *Phys. Rev. B* **56**, 3122 (1997).

⁸Y. Kumashiro, H. Yoshizawa, and K. Shirai, in *Proceedings of the 11th International Symposium on Boron, Borides, and Related Compounds*, edited by R. Uno and I. Highashi [Jpn. J. Appl. Phys. **10**, 166 (1994)].

⁹P. V. Huong, *Diamond Relat. Mater.* **1**, 33 (1991).

¹⁰U. Kuhlmann and H. Werheit, *Phys. Status Solidi B* **175**, 85 (1993).

¹¹U. Kuhlmann and H. Werheit, *J. Alloys Compd.* **205**, 87 (1994).

¹²D. M. Bylander, L. Kleinman, and S. Lee, *Phys. Rev. B* **42**, 1394 (1990); D. M. Bylander and L. Kleinman, *ibid.* **43**, 1487 (1991); L. Kleinman, in *Boron-Rich Solids* (Ref. 2), p. 13.

¹³K. Shirai and S. Emura, *J. Phys.: Condens. Matter* **8**, 10 919 (1996).

¹⁴U. Kuhlmann, H. Werheit, and K. A. Schwetz, *J. Alloys Compd.* **189**, 249 (1992).

¹⁵H. J. Becher and F. Thevenot, *Z. Anorg. Allg. Chem.* **410**, 274 (1974).

- ¹⁶B. S. Abbott and C. L. Beckel, in *Boron-Rich Solids* (Ref. 2), p. 344.
- ¹⁷B. Magnusson and C. Brosset, *Acta Chem. Scand.* **16**, 449 (1962); T. Lundstrom and H. Bolmgren, in *Proceedings of the 11th International Symposium on Boron, Borides, and Related Compounds*, edited by R. Uno and I. Higashi [*Jpn. J. Appl. Phys.* **10**, 1 (1994)].
- ¹⁸T. L. Aselage, *J. Mater. Res.* (to be published).
- ¹⁹T. J. Headley, J. R. Michael, S. M. Myers, G. A. Peterson, and T. L. Aselage, in *Microscopy and Microanalysis*, edited by G. W. Bailey *et al.* (Springer, New York, 1997), p. 455.
- ²⁰F. H. Pollack, *Test Meas. World*, May, 1985, p. 2.
- ²¹C. L. Beckel, M. Yousaf, M. Z. Fuka, S. Y. Raja, and N. Lu, *Phys. Rev. B* **44**, 2535 (1991).
- ²²C. L. Beckel and M. Yousaf, in *Boron-Rich Solids* (Ref. 2), p. 312.