A Novel Graphite-Like Material of Composition BC_3, and Nitrogen–Carbon Graphites

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Interaction of benzene with boron trichloride at 800 °C yields a graphite-like metallic solid of composition BC_3, and chlorine–pyridine mixtures at 800 °C give a nitrogen–carbon also having a graphite-like structure.

Although planar boron in threefold co-ordination commonly occurs and is a feature of the ring systems of boron nitride and borazine, there appears to have been no report of boron having been substituted extensively for carbon in the graphite structure. Lowell has shown that the maximum substitution of boron for carbon in graphite at 2350 °C is 2.35 atom %.[1] Nor has nitrogen been extensively substituted for carbon in graphite. Boron–carbon graphites offer the possibility of greater electrical conductivity relative to graphite because the electron deficiency of each boron atom creates a 'hole-carrier' in the valence band. A similar enhancement of the conductivity is expected for nitrogen–carbon graphites, since the additional electrons contributed by the nitrogen atoms provide 'electron-carriers' for the conduction band. Different intercalation chemistry from that of graphite is also expected for boron and nitrogen carbons. In this communication the first examples of boron–carbon and nitrogen–carbon are described.

The boron–carbon, BC_3, is formed as a lustrous film of metallic appearance, from interaction of BCl_3 with benzene at 800 °C: $2\ BCl_3 + C_6H_6 \rightarrow 2\ BC_3 + 6\ HCl$. The chemical composition was established by combustion in fluorine to give BF_3 and CF_4, the relative proportions of which, in the gaseous mixture, were determined by i.r. absorption spectrometry. This indicated a C : B atomic ratio of 3 : 1. Hydrogen fluoride and chlorine fluorides were absent from the combustion product. Electron micrographs show that BC_3 is a homogeneous product, with sheet-like character. The sheets are seen to be 3—4 Å apart, the preferred orientation being well defined. The material is otherwise randomly laid down and the individual grains have dimensions only ~50 Å across in the *ab* plane. Electron diffraction from this material confirms the graphite-like symmetry. As is to be expected for nonepitaxially grown materials, deposited at such moderate temperatures, the electron-diffraction patterns reveal no general *hkl* reflections (because sheet-to-sheet registry does not occur), but the 00*l* and *hk*0 reflections establish the graphite-like character, as does the pseudo-graphite unit cell c/a ratio of 2.76 (graphite $c/a = 2.72$). Because the individual layers in BC_3 exhibit little or no registry with respect to one another, there is properly no true unit cell (except the possible two-dimensional one). Since the *X*-ray and electron scattering is not markedly different for B and C, superlattice effects are weak and at the present level of crystallinity not discernible. For comparison purposes a graphite unit cell has been invoked although for the BC_3 and also for C_xN, described below, this involves two unregistered layers. That the boron is truly a constituent of the sheet, and not an amorphous component of a mixture with graphite, is established by the products of interaction at 300 °C with chlorine: $2\ BC_3$ (polycrystalline) + $3\ Cl_2 \rightarrow 6$ C (amorphous) + $2\ BCl_3$. (Under comparable conditions high purity polycrystalline graphite shows no change in crystallinity or weight on treatment with chlorine.) *X*-Ray powder photographs of BC_3 are of broad-line character and exhibit only *hk0* and 00*l* features, but show that the *a* dimension and the interlayer spacing are similar to those of graphite itself. The synthetic approach, the analysis, and the structural findings, together indicate that the atomic arrangement within the sheets may be as illustrated in Figure 1. The crystallinity is improved by hot pressing at 1200 °C, but at higher temperatures, graphite and the boron carbide $B_{12}C_3$ are formed: $12\ BC_3 \rightarrow 33\ C + B_{12}C_3$.

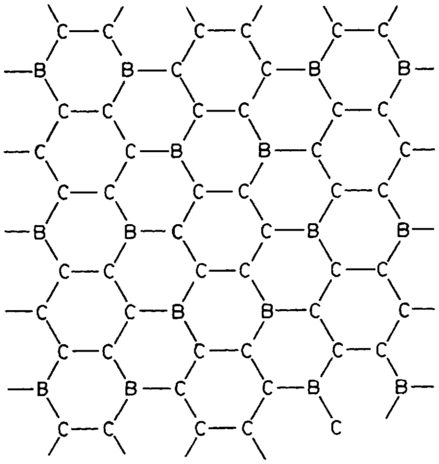

Figure 1. The probable atomic arrangement in a layer of the boron–carbon hybrid BC_3.

The measured density of BC_3 (by flotation) as prepared, indicates approximately 10% voids, since D(obs.) = 2.00; D(calc.) = 2.21 g cm^{-3}. Four-probe basal-plane resistivity measurements made on five separate flakes of the material, as prepared, indicated that the basal plane conductivity of such BC_3 was approximately 10% greater than that of similar pieces of highly oriented pyrolytic graphite (H.O.P.G.) which, at 298 K, have a basal-plane specific conductivity $\sigma\ (ab) \approx 2 \times 10^4$ ohm^{-1} cm^{-1}.

BC_3 is intercalated by both strongly oxidizing and strongly reducing species. Treatment with sodium naphthalide in tetrahydrofuran gave a bronze first-stage material with an interlayer spacing (I_c) of ~4.3 Å. Similar treatment of polycrystalline graphite (Union Carbide SPI) did not result in intercalation of the graphite. Sodium is the least effective alkali guest for graphite intercalation. This has been rationalized by Hérold.[2] Oxidation with $(SO_3F)_2$ gave a deep blue first-stage material with $I_c = 8.1$ Å, the gravimetry for which indicates the composition $(BC_3)_2SO_3F$. This is similar to the oxidation of layer-form BN and graphite by this powerful oxidizer.[3,4] It has been established[4] that the limiting composition is $BN(SO_3F)_{0.33}$ for the boron nitride salt, for which $a = 2.50(1)$, $c = 8.06(1)$ Å; $U = 43.7(1)$ Å^3. For BN, $a = 2.50_4$, $c = 3.33_0$; $U = 18.08$ Å^3, hence the effective volume of $(SO_3F)_{0.33}$ is 25.6 Å^3. The effective packing volume of SO_3F^- in KSO_3F and NH_4SO_3F[5] is ~75 Å^3. This implies that the ligands of the SO_3F guests must be in two close-packed layers between the enclosing BN sheets. This kind of close packing must be approached in the $(BC_3)_2SO_3F$ material. Liquid bromine with

BC_3 rapidly gave a deep blue solid of composition $(B_{0.25}C_{0.75})_{15}Br$ which has greater vacuum stability than its graphite relatives. Intercalation of graphite by bromine has been discussed by Hérold[2] and Hooley.[6]

Interaction of gaseous pyridine and chlorine, flowing within a hot silica tube, produced a silvery deposit on the cooler silica when the hot zone was at ~800 °C. Material produced at this temperature, when burned in fluorine, yielded only carbon fluorides, nitrogen trifluoride, and nitrogen (HF and chlorine fluorides were absent) and had an approximate composition C_5N. Deposits of this material on silica have superior electrical conductivity to comparable deposits of carbon. Electron diffraction patterns of the C_5N are similar to those given by BC_3. Higher reaction and heat treatment temperatures lead to loss of nitrogen. A sample heated to 1400 °C, at 4000 lb in^{-2} in a graphite die, has a composition $C_{57}N$ (Found: C,98; N,2%). This gave fair quality X-ray powder patterns consistent with an interlayer spacing of 3.42(1) Å (graphite, 3.35_4 Å), with $a =$ 2.44(1) Å being slightly smaller than that of graphite ($a = 2.47_1$ Å).

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