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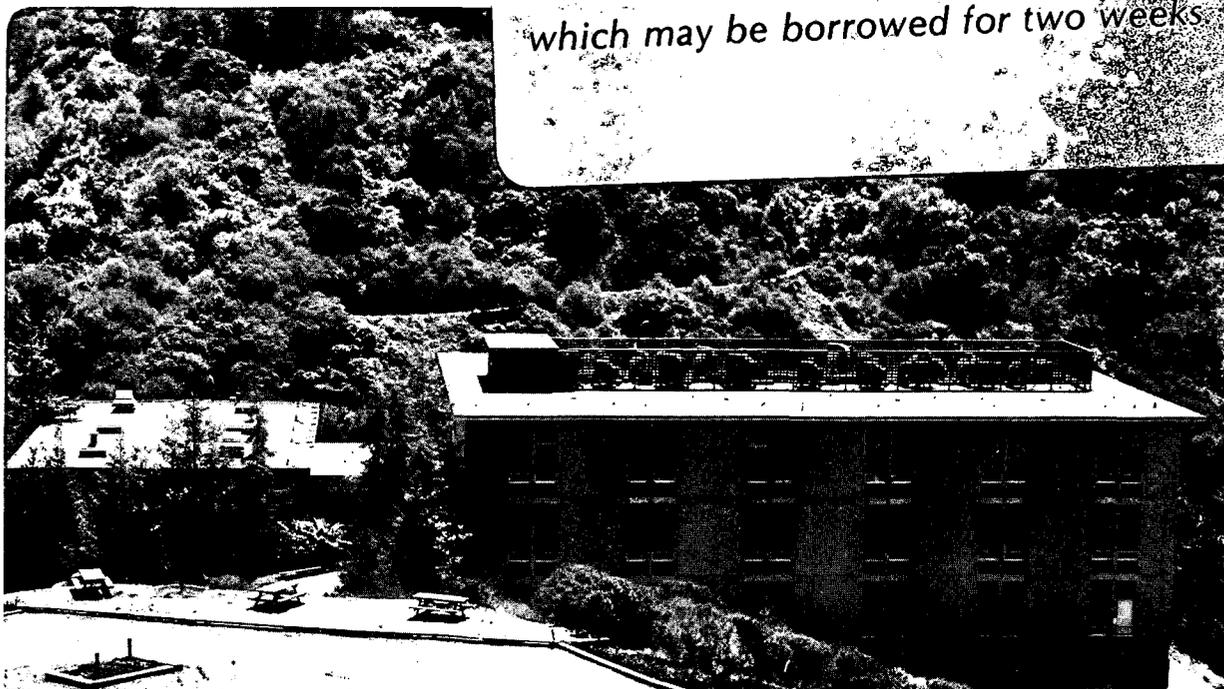
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OF GRAPHITE-LIKE STRUCTURE

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BORON-CARBON-NITROGEN MATERIALS OF GRAPHITE-LIKE STRUCTURE

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ABSTRACT

New structural relatives of graphite with the composition $B_xC_yN_x$ have been synthesized from the interaction of boron trichloride, acetylene and ammonia at 400-700°C. A hexagonal layer structure type is indicated by X-ray and electron diffraction data. Binding energies of 1s electrons (ESCA) for B, C and N indicate that each graphite-like sheet is a composite of all three elements. The material of approximate composition $B_{0.35}C_{0.30}N_{0.35}$ is a semiconductor and is intercalated by both strong reducing and oxidizing agents.

MATERIALS INDEX: boron-carbon-nitrogen graphites.

Introduction

The close dimensional relationship of layer-form boron nitride and graphite invites the possibility that hybrids of these materials might be made. Although there is a slight energy overlap of the valence and conduction bands in graphite (1), the heteroatomicity of boron nitride (2) results in a band gap (3) of >3.8 eV. It is anticipated therefore that substitution of some of the carbon atoms of graphite by both boron and nitrogen atoms will result in materials having band gaps less than that of layer-form boron nitride. The band gap may depend not only upon the composition but also upon the particular atomic arrangements.

The first claim to synthesis of BCN graphites appears to be that of Badyan, et al. (4). They prepared small particle (250 Å) aggregates from the interaction of boron trichloride, carbon

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tetrachloride, nitrogen and hydrogen at the surface of a hot carbon rod. Their product (optimal yield at 1950°C) showed {hk} and {00l} diffraction lines typical of graphite-like materials with little or no sheet-to-sheet registry. Compositions were not quantitatively specified but the authors assumed that the compositions lay on the BN to C tie line of a ternary BCN phase diagram. The authors also pointed to the possibility of the band gap being intermediate between that of BN and C and mentioned that the conductivity of their "BCN" was several orders of magnitude lower than in crystalline graphite. It was also pointed out that the "BCN" was unstable above 2000°C with respect to boron carbide (B_4C), graphite and nitrogen.

In this report an effective lower temperature route to boron-carbon-nitrogen materials is described. Evidence is presented for their graphite-like structure and semiconductive character. The synthetic method described here can be used to produce a large class of new graphite relatives.

Methods

The starting materials used for each synthesis were anhydrous ammonia (99.99%), boron trichloride (99.9%) and purified acetylene (99.6%), all from Matheson Gas Products. Acetone (employed in the acetylene storage tank) was removed from the acetylene by bubbling the gas through concentrated sulfuric acid. Subsequently the gas was passed through 50 cm stacks of potassium hydroxide pellets and phosphorus pentoxide powder to remove water. A fused silica tube (1.6 cm diameter) was used as the reactor and was heated by a clam-shell furnace. The tube was connected, via Swagelock fittings and Teflon tubing, at one end to the gas tanks and at the other end to a metal vacuum system. The entire apparatus was evacuated and purged with nitrogen prior to each synthesis. Nitrogen was used as a carrier gas to ensure forward flow of the reactants. It had no effect upon the composition of the $B_xC_yN_x$ product. Each gas was regulated with a mass flowmeter to a controlled rate of 10-50 cm^3/min . The acetylene and boron trichloride were mixed before the hot zone of the reactor. Ammonia was introduced in the hot zone. This prevented formation of ammonium chloride before the reaction zone.

X-ray powder photographs were obtained from powdered samples held in glass capillaries (Charles Supper Co.) with a General Electric Precision camera of nominal 45 cm circumference using nickel-filtered $CuK\alpha$ radiation. A JEOL 200CX high resolution electron microscope (200kV accelerating voltage) with biaxial goniometer $\pm 10^\circ$ tilt stage was used to obtain electron diffraction patterns and transmission electron micrographs. Photoelectron spectra were obtained using a GCA/McPherson ESCA 36 spectrometer.

Flat pieces of oriented pyrolytic boron nitride (Union

Carbide Corp.) were used to receive deposits of $B_xC_yN_x$ for conductivity measurements. For this, two boron nitride pieces were cut so that they interlocked at right angles. These crosses were placed in the silica tube near the end of the hot zone. Following deposition of $B_xC_yN_x$, the coated, flat boron nitride pieces were separated and the conductivity of the $B_xC_yN_x$ deposits on the insulating boron nitride was assessed by d.c. four-probe measurements.

Analysis for carbon was carried out in a conventional manner with a V_2O_5 catalyst. Found (sample preparation temperature in parentheses): C (400°C) 3%; (700°C) 30%. In addition, $B_xC_yN_x$ samples were burned in fluorine (2 atmos. at 25°C) at 500°C in a Monel bomb and the products were identified by infrared spectroscopy to be BF_3 , CF_4 and NF_3 . Elemental nitrogen was also present. IR spectrometry provided for the determination of the relative abundances of BF_3 and CF_4 and hence for the x:y ratio in $B_xC_yN_x$. The B:N ratio was determined from the integrated intensity of the ESCA 1s peaks using the 1s peaks of boron nitride for calibration and in all cases it was found to be not significantly different from 1:1.

Results and Discussion

The interaction of boron trichloride, acetylene and ammonia mixtures in the temperature range 400-700°C deposits a coherent dark gray to black solid on the walls of the silica reactor tube. This deposit occurred in the downstream end of the hot zone and usually extended several cm beyond it. The carbon analyses of the preparations (at 400°C, C ≈ 3% and at 700°C, C ≈ 30%) indicate that higher carbon incorporation requires higher reaction temperatures. This is because of the high activation energy for $C\equiv C$ to $C=C$ bond conversion or C-H bond cleavage either of which must occur before C-B or C-N bond formation can take place. In contrast, formation of B-N bonds can occur with little or no activation energy because of the Lewis acid-base interaction of BCl_3 and NH_3 . The absence of hydrogen fluoride and chlorine fluorides from the fluorine combustion products indicates that all hydrogen and chlorine from the reactants have been eliminated as hydrogen chloride.

X-ray photoelectron spectra illustrated in Figure 1 show that the $B_xC_yN_x$ materials are not simply mixtures of boron nitride and graphite. The spectra compare $B_xC_yN_x$ ($y \approx 0.30$) to a physical mixture of 70% BN (synthesized under similar conditions to $B_xC_yN_x$ and of comparable particle size) and 30% graphite. The boron 1s binding energies (Figure 1a) for the $B_xC_yN_x$ are on the average lower than for BN in the physical mixture, whereas the reverse is the case for the nitrogen 1s binding energies (Figure 1b). This is in harmony with the boron having some carbon atom neighbors as well as nitrogen and the nitrogen having carbon atom neighbors as well as boron. The carbon 1s spectra (Figure 1c) of the $B_xC_yN_x$

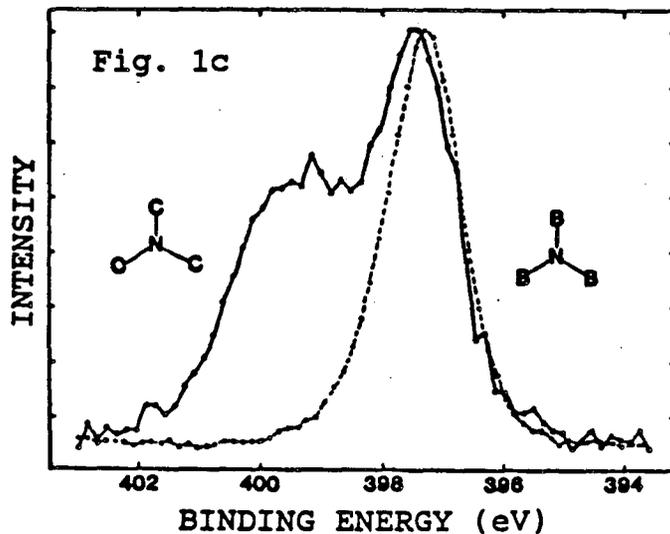
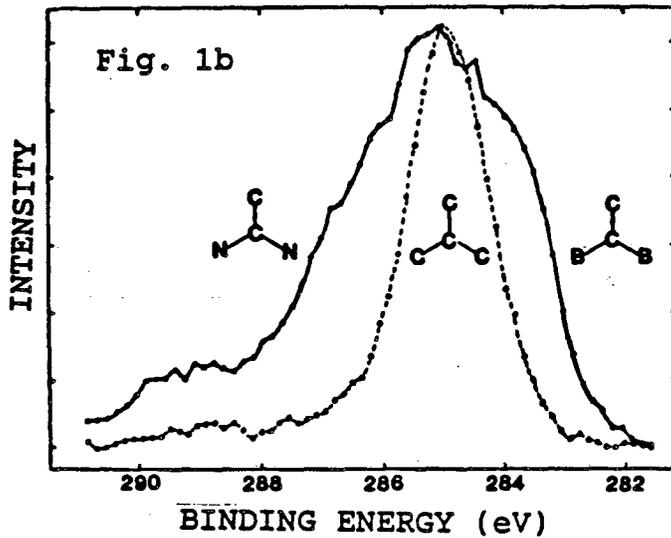
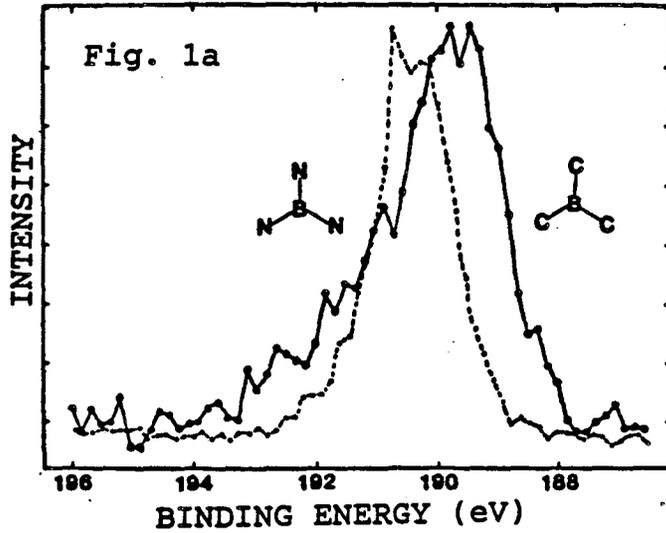


FIGURE 1

Photoelectron spectra of $B_xC_yN_x$ ($y \approx 0.30$), indicated with solid lines and a mixture of 70% boron nitride and 30% graphite, indicated with dotted lines. The boron 1s spectra are shown in Fig. 1a, the carbon 1s in Fig. 1b and the nitrogen 1s in Fig. 1c. In each diagram a formula on the left depicts the B, C and N atoms in their most electronegative environment. The formula to the right depicts the B, C and N atoms in their most electropositive environment.

are broad relative to the graphite in the physical mixture. This must arise because the carbon atoms in $B_xC_yN_x$ are in a wide variety of atomic environments.

The ratio of boron to nitrogen in the $B_xC_yN_x$ samples examined by ESCA is approximately one to one. This indicates that NH_3 must also be acting as a nitriding agent (with H_2 elimination). In addition, the boron to carbon ratios are given by the infrared spectrometry of the fluorine combustion products. On this basis the compositions of the 400°C and 700°C products are respectively, $B_{0.485}C_{0.03}N_{0.485}$ and $B_{0.35}C_{0.30}N_{0.35}$. The overall reaction stoichiometry being approximately as follows:



Annealing at 900°C in vacuo for 5 days sharpens the X-ray diffraction pattern of $B_xC_yN_x$ (for $y \approx 0.03$, $a_o = 2.50 \text{ \AA}$ and the interlayer spacing $I_c = 3.34 \text{ \AA}$; for $y \approx 0.30$, $a_o = 2.49 \text{ \AA}$ and $I_c = 3.35 \text{ \AA}$) and confirms a layered hexagonal structure comparable to poorly registered sheets of graphite ($a_o = 2.46 \text{ \AA}$ and $I_c = 3.35 \text{ \AA}$) or boron nitride ($a_o = 2.50 \text{ \AA}$ and $I_c = 3.33 \text{ \AA}$). High resolution transmission electron micrographs show that $B_xC_yN_x$ are layered materials and that the product is homogeneous with an approximate grain diameter of 100 Å. The deposits show marked preferred orientation and electron diffraction patterns obtained with the incident beam perpendicular to the layers show the $\{hk\}$ reflections characteristic of a poorly crystallized graphite or boron nitride.

A $B_xC_yN_x$ ($y \approx 0.30$) hybrid deposited on insulating BN has a room temperature conductivity, $\sigma = 6(1) \times 10^{-4} \text{ S cm}^{-1}$. Moreover, the logarithm of the conductivity shows a linear relationship to the inverse of the absolute temperature as shown in Figure 2. This implies a thermal band gap of 0.2 eV.

Layered $B_xC_yN_x$ can be both oxidatively and reductively intercalated. When $B_xC_yN_x$ ($y \approx 0.30$) reacts with liquid $S_2O_6F_2$ an oxidative intercalation occurs which produces a gallery expansion of $\sim 4.7 \text{ \AA}$. A material is formed with $c_o \approx 8 \text{ \AA}$, similar to the graphite salt C_7SO_3F and the boron nitride salt $(BN)_3SO_3F$ (5,6). Reductive intercalation of $B_xC_yN_x$ ($y \approx 0.30$) has been accomplished using a 0.5 M solution of sodium naphthalide in tetrahydrofuran. The insertion of sodium between the layers of $B_xC_yN_x$ causes a gallery expansion of $\sim 1.8 \text{ \AA}$.

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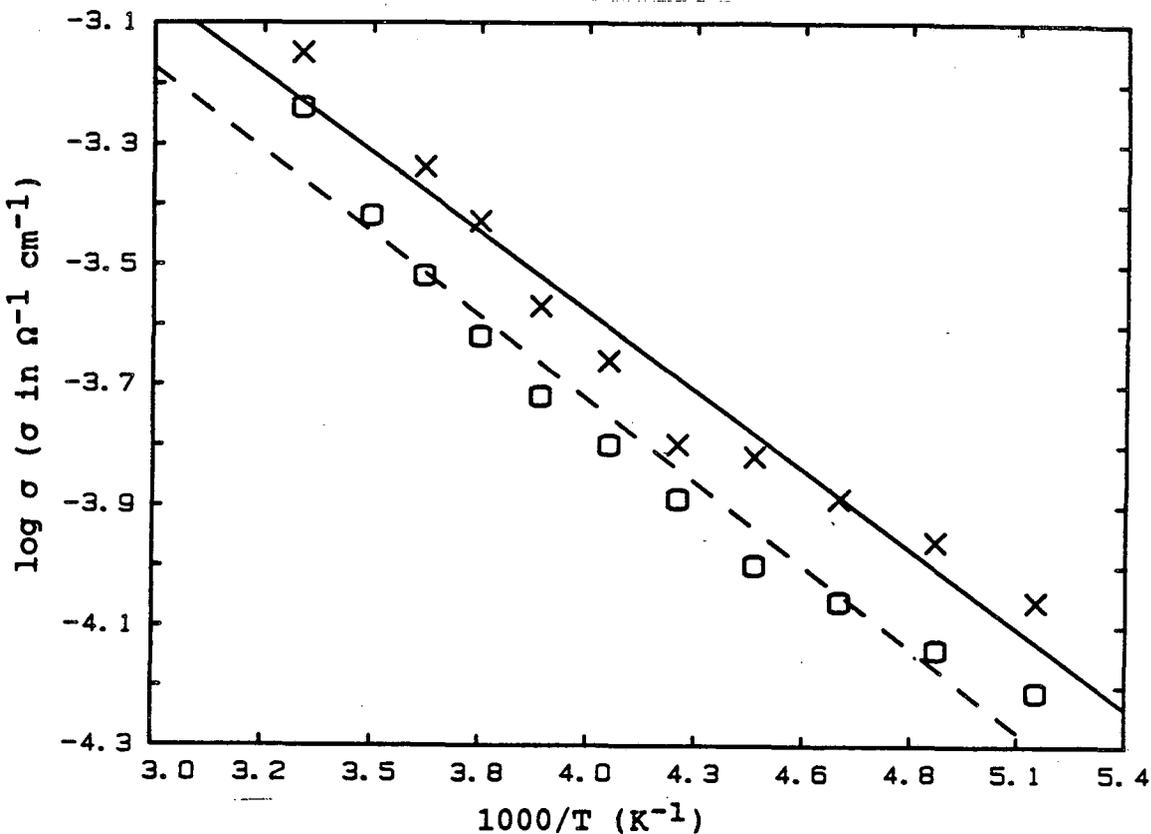


FIGURE 2

Log conductivity vs inverse temperature plot for $B_{0.35}Co_{0.30}Ni_{0.35}$. D.c. four probe measurements were made on two separate samples deposited on boron nitride chips.

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