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Syntheses and Structures of New Graphite-like Materials of Composition BCN(H) and $BC_3N(H)$

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New graphite-like materials of composition $BC_{0.9-1.3}N_{0.8-0.9}H_{0.4-0.7}$ and $BC_{3.0-3.2}N_{0.8-1.0}H_{0.2-2}$, which are described as BCN(H) and $BC_3N(H)$, have been prepared by the interaction of acetonitrile with boron trichloride in a hydrogen and nitrogen atmosphere and acrylonitrile with boron trichloride, respectively. X-ray and electron diffraction analyses indicate that these materials have hexagonal structures similar to that of graphite. ESCA spectra and the possible chemical bonds suggest that the ideal structure of BCN is made of the unit structure of $BC_2N + BN$, while BC_3N is composed of $BC_3N + BNC_3$. A BCN(H) plate has a basal-plane conductivity of 1.28 $(\Omega\ \mathrm{cm})^{-1}$ at room temperature, while a $BC_3N(H)$ plate has that of 88.5 $(\Omega\ \mathrm{cm})^{-1}$. Thermoelectric measurements indicate that both materials behave as p-type semiconductors and a BCN(H) plate has a high Seebeck coefficient of 300 μV/°K at room temperature in air.

Introduction

Since boron, carbon, and nitrogen feature a formation of planar ring systems such as boron nitride and graphite, new B/C/N,[1−10] C/N,[4,11−15] and B/C[4,16] materials[17] have been synthesized by a variety of chemical methods. The B/C/N materials and the precursors used so far are listed in Table 1. The first attempt to synthesize a B/C/N material was made by Kosolapova et al. by the solid−gas reaction of boron and carbon powders under a nitrogen or ammonia atmosphere at 1800−2000 °C.[1] However, the composition of B/C/N was not investigated in detail at that time. Chemical vapor deposition (CVD) was used by Badzian et al.[2] to synthesize these hybrid materials and further investigated by Kaner[3] and Kouvetakis et al.[4] Recently, the stoichiometric compounds BC_2N[4,9] and BC_4N[9] were synthesized by CVD or solid-phase pyrolysis of precursors.

Table 1. B/C/N Materials and Their Precursors

composition BC_XN_Y	precursor	preparation method	ref
unknown	B and C powders, N_2 or NH_3	solid−gas reaction	1
unknown	BCl_3, CCl_4, N_2, H_2	chemical vapor deposition (CVD)	2
$X = 0.06$, $Y = 1$	BCl_3, C_2H_2, NH_3	CVD	3
$X = 0.86$, $Y = 1$	BCl_3, C_2H_2, NH_3	CVD	3
$X = 2$, $Y = 1$	BCl_3, CH_3CN	CVD	4
$X = 5.2$, $Y = 1.8$	$(Me_2N)_3B$, $C_6H_4(NH_2)_2$	precursor pyrolysis	7
$X = 4$, $Y = 1$	BH_3, C_5H_5N	precursor pyrolysis	9
$X = 2$, $Y = 1$	BH_3, $C_4H_{10}N_2$	precursor pyrolysis	9
$X = 3$, $Y = 1$	BCl_3, $(CH_2CHCN)_n$	solid−gas reaction	10
$X = 6$, $Y = 1$	BCl_3, CH_2CHCN	CVD	10

Interest has been focused on these new materials because of their potential characteristics, such as

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semiconductive[3,4,9,10,17,18] and intercalation properties.[3,4,15,17,19,20] These characteristics must depend on the structures of their graphitic networks. Although the structures have been discussed on the basis of theoretical calculations,[21,22] they have not been experimentally investigated in detail.

We have recently synthesized a graphite-like layered material of composition BC_3N by the interaction of poly(acrylonitrile) or acrylonitrile monomer with boron trichloride and found that it behaves as a semiconductor.[10]

In this paper, the synthesis of new graphite-like materials of composition BCN(H) and $BC_3N(H)$ and investigations of their graphitic structure by means of electron diffraction and ESCA measurements are described. Electrical conductivity and thermoelectric properties for these materials are also reported.

Experimental Procedure

Starting Materials. Acetonitrile (CH_3CN, Wako Pure Chemical Ind. Ltd., 99%), Acrylonitrile ($CH_2{=}CHCN$, Hayashi Pure Chemical Ind. Ltd., 99%), boron trichloride (BCl_3, Sumitomo Seika Co. Ltd., 99.9%), hydrogen (H_2, 99.99%), and nitrogen (N_2, 99.99%) were used without further purification.

Synthesis of BCN(H). A quartz tube of 40 mm inner diameter and 1000 mm in length was used as a reactor.

Acetonitrile vapor (50 cm^3/min) carried by N_2 (430 cm^3/min), BCl_3 (50 cm^3/min) gas and H_2 (250 cm^3/min) were introduced into the hot zone (1000 °C) of the reactor. This gas-phase reaction was carried out for 9 h. Black plates were deposited in the hot zone, while dark brown powders were obtained behind the hot zone. The plates and powders were then heated at 1000 °C in a N_2 atmosphere for 1 h.

Synthesis of $BC_3N(H)$. Acrylonitrile vapor (50 cm^3/min) carried by N_2 (310 cm^3/min) and BCl_3 (50 cm^3/min) gas were introduced to the hot zone (1000 °C) of the reactor. The gas-phase reaction was carried out for 8 h. Black plates were deposited in the hot zone, while black powders were obtained behind the hot zone. The plates and powders were then heated at 1000 °C in a N_2 atmosphere for 1 h.

Characterization of the Products. The chemical compositions of the products were established by the usual combustion in oxygen followed by gas chromatography for carbon, hydrogen, and nitrogen; by alkali melting followed by ICP atomic absorption spectrum for boron.

X-ray diffraction data were obtained by using a diffractometer (Shimadzu XD-3A) with Ni-filtered Cu Kα radiation. The scan speed was 1° (2θ)/min.

TEM photographs and electron diffraction data were obtained by a transmission electron microscope (JEOL JEM-2000FX). SEM observations were performed by a scanning electron microscope (JEOL JSM-T200).

ESCA measurements were carried out by using an electron spectrometer (Shimadzu ESCA750S) with Mg Kα radiation. The binding energies of the elements were corrected by placing the $Au_{4f7/2}$ line at 84.0 eV.

Electrical Conductivity and Thermoelectric Property Measurements. Electrical conductivity and thermoelectric force were measured simultaneously for specimens of the BCN(H) and $BC_3N(H)$ plates at 20−700 °C in air or under vacuum. Electrical conductivity was measured using a d.c. four-probe technique. For the thermoelectric force measurement, a temperature gradient was generated by heating one end of the specimen. The temperature difference between the two ends was controlled to be 5−10 K. Plots of thermoelectric force versus temperature difference gave rise to a straight line in all cases, and the Seebeck coefficient was calculated from its slope.

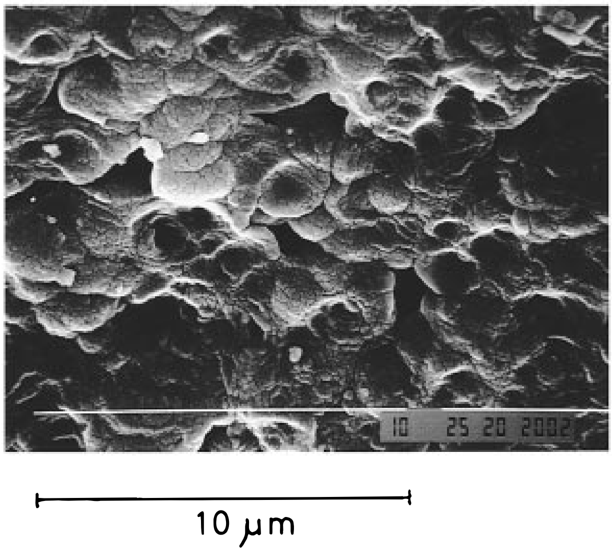

Figure 1. SEM photograph of BCN(H) plate synthesized by the interaction of acetonitrile with BCl_3 in a hydrogen and nitrogen atmosphere.

Results and Discussion

Product BCN(H). The plates and powders obtained from several parts of the CVD reaction tube gave compositions in the range $BC_{0.9-1.3}N_{0.8-0.9}H_{0.4-0.7}$, which is described as BCN(H) in this paper. This result indicates that almost no distribution was observed for the compositions of products in this reaction system. Without hydrogen gas in this system, that is, in the reaction system of acetonitrile and BCl_3 a material of composition BC_2N[4] can be obtained by the reaction according to the following equation:

$$BCl_3 + CH_3CN \xrightarrow{1000\ ^\circ C} BC_2N + 3HCl \qquad (1)$$

The composition BCN(H) of the product obtained in the present reaction system under hydrogen and nitrogen atmosphere suggests that some side reaction such as that in eq 2 might occur together with the reaction in

$$BCl_3 + {}^3/_2H_2 + {}^1/_2N_2 \xrightarrow{1000\ ^\circ C} BN + 3HCl \qquad (2)$$

eq 1. The reaction in eq 2 can proceed thermodynamically because of a large negative ΔG value (−110 kJ/mol) at 1000 °C, which is calculated by using the JANAF thermochemical tables.

Figure 1 shows a SEM photograph for the cross section of the BCN(H) plates deposited inside the reaction tube. The plates look like sintered ceramics made of small particles.

Structure of BCN(H). Figure 2 shows X-ray powder diffraction pattern of the pulverized BCN(H) plates. The broad diffraction lines observed for the (00*l*) $\{2\theta = 24.5°\}$ and (100) $\{2\theta = 43°\}$ planes suggest that the crystallite sizes for BCN(H) are small, and there are some defects in the layered structure. A lot of edge planes and the defects probably contain hydrogen atoms derived from

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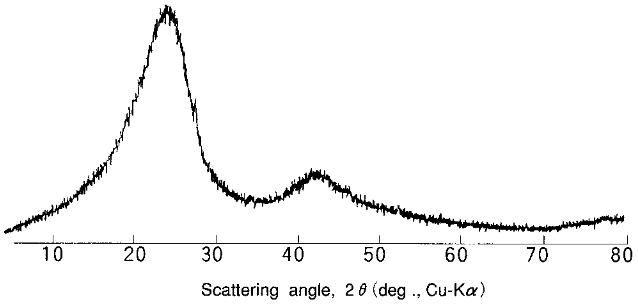

Figure 2. X-ray powder diffraction pattern of BCN(H) synthesized by the interaction of acetonitrile with BCl$_3$ in a hydrogen and nitrogen atmosphere.

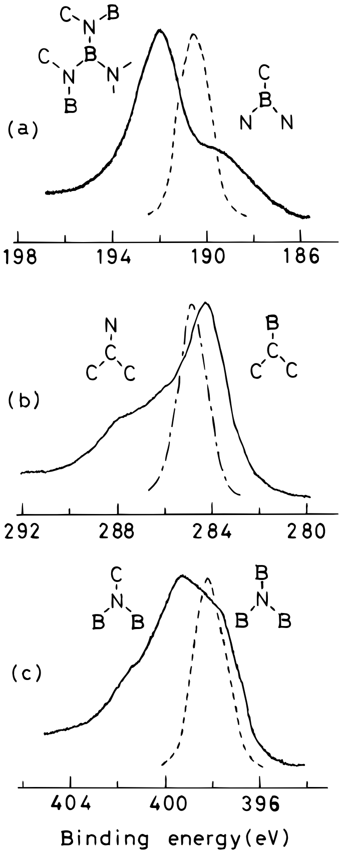

Figure 3. ESCA spectra of BCN(H) plate synthesized by the interaction of acetonitrile with BCl$_3$ in a hydrogen and nitrogen atmosphere. (- - -) h-BN, (—•—) graphite.

−CH$_3$, −NH$_2$, etc., groups. The *d* spacing in the direction of the *c* axis was 0.36 nm, which is similar to the *d* spacing of noncrystalline graphite such as a petroleum coke heat-treated at 1000 °C.

Figure 3 shows the ESCA spectra for the BCN(H) plate. The reproducible spectra were obtained only by eliminating the surface of the plate with a blade just before the ESCA measurements.

The B$_{1s}$ spectrum in Figure 3 suggests that two kinds of boron atom exist in the graphite-like BCN(H) network. The peak at 192.1 eV is at a higher binding energy than that for h-BN (190.1 eV). This indicates that some of the boron atoms in the BCN(H) network are more electropositive than that in h-BN. However, the nitrogen atom is the most electronegative atom in this system. Therefore, the chemical shift can be explained by a boron surrounded by three nitrogen atoms which partly connect with carbon atoms (see upper left in Figure 3). On the other hand, a shoulder at 189.5 eV suggests that other boron atoms in the BCN(H) network connect with rather electropositive atoms, that is, carbon atoms in this case (see upper right in Figure 3).

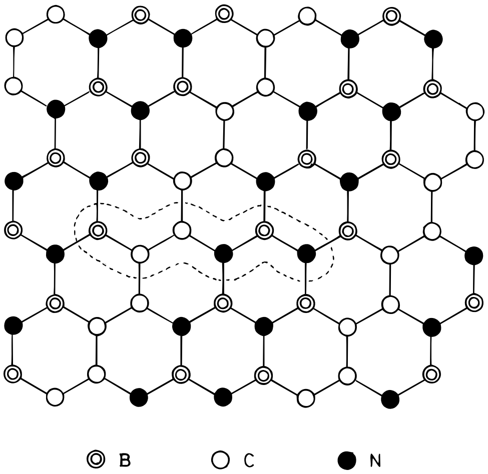

Figure 4. Possible atomic arrangement of BCN synthesized by the interaction of acetonitrile with BCl$_3$ in a hydrogen and nitrogen atmosphere. B−C−C−N and B−N units, from which the structure can be generated by repetition, are shown surrounded by a dashed line.

The C$_{1s}$ spectrum in Figure 3 has a peak at 284.4 eV which is close to that of graphite (284.9 eV). This indicates that the major part of the carbon atoms in BCN(H) network have a structure similar to that of graphite. The spectrum, however, is distributed over a wide range (282−290 eV), which suggests the existence of several kinds of carbon atoms in the BCN(H) network. The distribution to lower binding energy is due to the chemical shift of a carbon connected to boron, while that at higher binding energy is due to the carbon connected to nitrogen (see the middle part of Figure 3).

The N$_{1s}$ spectrum in Figure 3 suggests the existence of two or more kinds of nitrogen atoms in the BCN(H) network. The peak at lower binding energy is in the similar position to that in h-BN (398.1 eV). In other words, some of the nitrogen atoms in the BCN(H) network are surrounded by three boron atoms (see lower right in Figure 3). Another peak at higher binding energy (399.3 eV) is due to nitrogen atoms partially connected to carbon atoms (see lower left in Figure 3).

Figure 4 indicates a possible atomic arrangement in the layer of BCN, which is derived on the basis of the interpretation of the ESCA spectra and the following assumptions deduced by the reactions 1 and 2: (a) The original monomer chain C−C−N of acetonitrile remains in the BCN network, (b) B−C and B−N bonds can be made by the elimination of HCl from the reaction of Cl−B and H−C and a coordinate bond of B−N caused by formation of a CH$_3$CN:BCl$_3$ adduct in the initial reaction of 1 or a direct B−N bond in reaction 2, respectively, (c) B−B and N−N bonds cannot be easily made, because of the thermodynamically implausible reaction of Cl−B and Cl−B {ΔG = 340 kJ/mol for the reaction $BCl_3 \rightarrow B + 1.5Cl_2$ at 1000 °C} and a repulsion of lone-pair electrons between nitrogen atoms, respectively. An unit structure BCCNBN is shown by a broken line, which is constituted by a pair of BC$_2$N and BN monomers produced by the reactions in eqs 1 and 2, respectively.

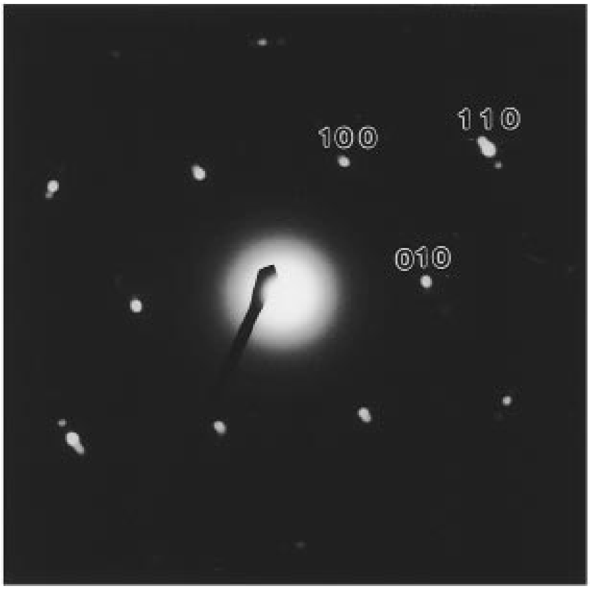

Figure 5. Electron diffraction of $BC_3N(H)$ powder pulverized from the $BC_3N(H)$ plate.

Product of $BC_3N(H)$. The plates obtained at several positions around the center of the reaction tube gave compositions in the range $BC_{3.0-3.2}N_{0.8-1.0}H_{0.2-2}$, which is described as $BC_3N(H)$ in this paper. This result suggests that the CVD reaction proceeded as follows:[10]

$$\mathrm{CH_2CHCN + BCl_3 \xrightarrow{1000\ ^{\circ}C} BC_3N + 3HCl} \tag{3}$$

The fine black powder obtained, however, showed a composition of $BC_{5.8-6.0}N_{0.8-1.0}H_{0.2-2}$, probably due to a hybrid of $BC_3N(H)$ and carbon produced by thermal decomposition of acrylonitrile.

Structure of $BC_3N(H)$. X-ray diffraction of the $BC_3N(H)$ plates was almost the same as that of BCN(H) shown in Figure 2, suggesting that $BC_3N(H)$ macroscopically also has a noncrystalline graphitic structure.

An electron diffraction pattern for the $BC_3N(H)$ plate, however, showed six symmetrical spots, which are shown in Figure 5. This pattern indicates that the $BC_3N(H)$ microscopically has a hexagonal structure similar to that of a graphite single crystal. The d spacing calculated from the 100 diffraction on Figure 5 is 0.208 nm which is value similar to that of graphite ($d_{100} = 0.213$ nm). Most of the small particles pulverized from the $BC_3N(H)$ plate showed this kind of spot pattern. Therefore, the $BC_3N(H)$ plate is composed of very small single crystals.

Figure 6 shows ESCA spectra of the $BC_3N(H)$ plate. The surface of the plate was removed before the ESCA measurements in the same way as the BCN(H) plate.

The B_{1s} spectrum in Figure 6 suggests the existence of two kinds of boron atoms in the $BC_3N(H)$ network, in a similar manner to that of the BCN(H). The relative intensity of the peak at 189.4 eV is stronger than that for the BCN(H). This suggests that boron atoms connected with carbon atoms are more dominant in $BC_3N(H)$ than in BCN(H).

The C_{1s} spectrum of $BC_3N(H)$ is similar to that of BCN(H), suggesting the existence of graphite-like carbon atoms and several other kinds of carbon atoms connected to boron and nitrogen.

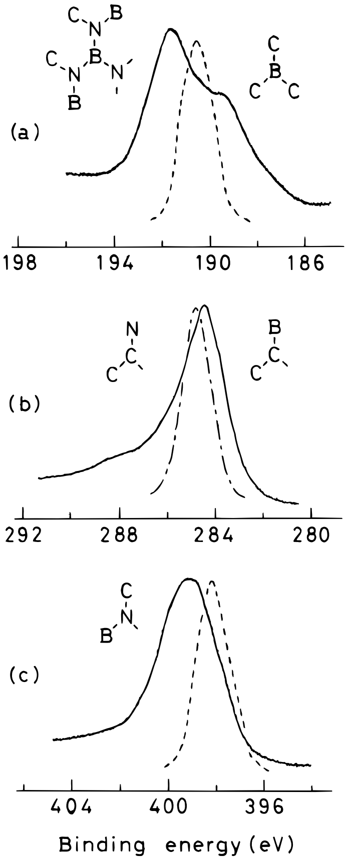

Figure 6. ESCA spectra of $BC_3N(H)$ plate synthesized by the interaction of acrylonitrile with BCl_3. (- - -) h-BN, (—•—) graphite.

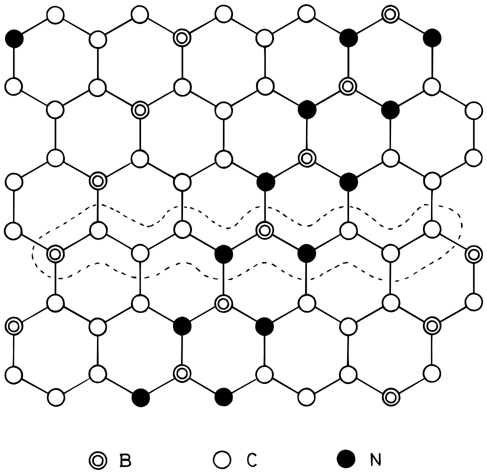

Figure 7. Possible atomic arrangement of BC_3N synthesized by the interaction of acetonitrile with BCl_3. B−C−C−C−N and B−N−C−C−C units, from which the structure can be generated by repetition, are shown surrounded by a dashed line.

The N_{1s} spectrum of $BC_3N(H)$ is different from that of BCN(H). No peak at lower binding energy (398.1 eV: nitrogen in h-BN) was observed. The peak observed at higher binding energy (399.1 eV) than that for h-BN is due to nitrogen atoms connected not only with boron atoms but also with carbon atoms.

Figure 7 indicates a possible atomic arrangement in the layer of BC_3N, which is derived from the interpretation of ESCA spectrum and the following assumptions deduced by reaction 3: (a) The original monomer chain C−C−C−N of acrylonitrile can remain in the BC_3N

network, (b) B−C and B−N bonds can be made in ways similar to those for BCN; in this case from a CH_2CHCN:BCl_3 adduct formed in the initial reaction of 3, (c) B−B and N−N bonds cannot be easily made, as is described for BCN. An unit structure BCCCNBNCCC is shown by the broken line, which is constituted by two pairs of BC_3N monomers produced by the reaction in eq 3.

An interesting observation is that nitrogen atoms always connect with boron atoms in the arrangements for both BCN and BC_3N. This result suggests that nitrogen can be stabilized not by carbon but by boron. In fact, the C/N graphitic materials[4,15] are not as thermally stable as the h-BN, B/C/N materials,[17,20] and B/C materials.[4]

Electrical Conductivity of BCN(H) and BC_3N(H)

Figure 8 shows the basal-plane conductivity versus temperature curves for BCN(H) and BC_3N(H) plates measured under vacuum. The conductivity at room temperature for the BCN(H) plate was 1.28 $(\Omega\ cm)^{-1}$, while that for the BC_3N(H) plate was 88.5 $(\Omega\ cm)^{-1}$. The high conductivity for BC_3N(H) might be due to the dominant conjugated C−C bonds in the planar sheet of BC_3N (Figure 7). Activation energies calculated from the Arrhenius plots shown in Figure 8 are 1.99×10^{-2} eV for BCN(H) and 6.29×10^{-3} eV for BC_3N(H), on the assumption that the carriers are only holes(p-type).

Thermoelectric force measurements under vacuum indicated that BCN(H) and BC_3N(H) plates behave as p-type semiconductors. A low N:B ratio results in an overall electron deficiency (excess hole carriers) in the valence band of BCN(H) or BC_3N(H). Though small Seebeck coefficients (10−20 μV/K) were observed under vacuum for BCN(H) and BC_3N(H) at room temperature, a large Seebeck coefficient (300 μV/K) was observed in air only for BCN(H). The oxygen in air could interact with the surface of BCN(H) to generate a large number of hole carriers. These thermoelectric properties will be further investigated.

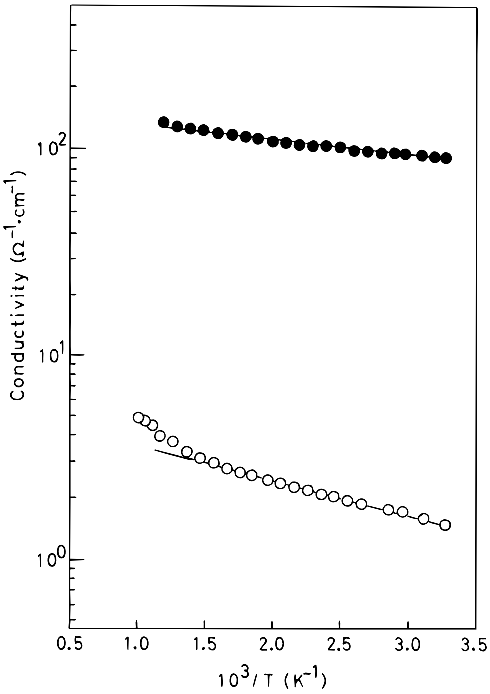

Figure 8. log conductivity vs reciprocal temperature plot for BCN(H) and BC_3N(H) plates. The conductivity was measured by the d.c. four-probe method under vacuum: (●) BC_3N(H) plate; (○) BCN(H) plate.

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