

General paper

SYNTHESES AND CHARACTERIZATION OF GRAPHITE-LIKE MATERIAL OF COMPOSITION $\text{BC}_6\text{N}_2(\text{H})$

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Abstract: A new graphite-like layered material of composition $\text{BC}_6\text{N}_2(\text{H})$ is synthesized by the pyrolysis of $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$ adduct, which is prepared by the interaction of acrylonitrile with boron trichloride at room temperature. X-ray diffraction and UV-Visible spectroscopic analysis suggest that the adduct has a cubic or quasi-cubic structure and is gradually polymerized at room temperature. A possible arrangement in a layer of BC_6N_2 has been considered on the basis of ESCA spectra and chemical interactions among the starting materials, being composed of a unit structure N-C-C-C-C-C-C-N-B. $\text{BC}_6\text{N}_{1.5}(\text{H})$ film prepared by CVD reaction ($\text{CH}_2\text{CHCN} : \text{BCl}_3 = 2 : 1$) has a conductivity of $5.31 \times 10^4 \text{ S/m}$ at room temperature and behaves as a semiconductor. The reduction of $\text{BC}_6\text{N}_{1.5}(\text{H})$ with $\text{Li}^+\text{C}_{10}\text{H}_8^-/\text{THF}$ solution has yielded a lithium intercalated compound with a repeat distance of 0.87 nm.

Key words: Graphite-like layered material, B/C/N material, Adduct, Semiconductor, Conductivity, Host material, Intercalation

1. INTRODUCTION

Development of new host materials is of considerable interest for many applications such as lithium secondary battery in these days. The structural similarity and the quite different physical property between graphite and hexagonal boron nitride (h-BN) have motivated the synthesis of new boron/carbon/nitrogen materials (B/C/N materials) based on the graphite network. It is expected that B/C/N materials interact with acids or bases moderately and is a semiconductor [1], because their properties may be intermediate between those of graphite, which is an excellent host material and is a semimetal, and h-BN, which has limited intercalation properties and is an insulator.

The first attempt to prepare a B/C/N material was made by Kosolapova et al. [2] by the solid-gas reaction of boron and carbon powders under a nitrogen or ammonia atmosphere at 1800~2000 °C. Chemical vapor deposition (CVD) was used by Badzian et al. [3] to prepare these hybrid materials and further investigated by Bartlett group [4]. Recently, the stoichiometric compounds BC_2N [5-8], BC_3 [6,9], C_5N [6,9] and BC_4N [7,8] were synthesized by CVD or solid-phase pyrolysis of precursors.

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 forms Li-intercalated compound and behaves as a

semiconductor [10,11]. During the CVD reaction of acrylonitrile with boron trichloride, an adduct of white powders formed at cool zone in the CVD reaction tube [10,11].

In this paper, we investigate preparations and structures of a new adduct $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$ and a new graphite-like material of composition $\text{BC}_6\text{N}_2(\text{H})$. The liquid-gas reaction at room temperature was chosen as the preparation method for the adduct. CVD method and pyrolysis of the adduct were used to synthesize $\text{BC}_6\text{N}_{2-\alpha}(\text{H})$ ($\alpha = 0 \sim 0.5$). Electrical conductivity and Li-intercalation for $\text{BC}_6\text{N}_{2-\alpha}(\text{H})$ are also reported.

2. EXPERIMENTAL PROCEDURE

2.1. Starting Materials

Acrylonitrile (CH_2CHCN , Hayashi Pure Chemical Ind. Ltd., 99 %), boron trichloride (BCl_3 , Sumitomo Seika Co. Ltd., 99.9 %) and nitrogen (N_2 , 99.99 %) were used without further purification.

2.2. Preparation of Adduct $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$ and $\text{BC}_6\text{N}_2(\text{H})$

BCl_3 vapor ($8.3 \times 10^{-7} \text{ m}^3/\text{s}$) and N_2 ($8.3 \times 10^{-7} \text{ m}^3/\text{s}$) were introduced into the flask which contained acrylonitrile liquid (50 g) at room temperature. The liquid-gas reaction was carried out for 3.5 h. The solid of adduct obtained was then set in a quartz tube and heated at a temperature between 500 and 1000 °C by electric furnace under N_2 atmosphere for 1 h.

SYNTHESES AND CHARACTERIZATION OF $\text{BC}_6\text{N}_2(\text{H})$ 2.3. Preparation of $\text{BC}_x\text{N}_y(\text{H})$ by CVD Method

A quartz tube of 22 mm inner diameter and 1000 mm in length was used as a reactor. A quartz glass plate ($30 \times 5 \times 1$ mm) as a substrate was set at the center of the reaction tube. Acrylonitrile vapor (3.3×10^{-7} m³/s) carried by N_2 (2.3×10^{-6} m³/s) and BCl_3 gas (1.6×10^{-7} m³/s) were introduced to the hot zone (1000 °C) of the reactor.

A black plate was deposited on the substrate in the hot zone, while black powders were mainly obtained behind the hot zone. The plate and powders were then heated at 500 °C in a N_2 atmosphere for 1 h.

2.4. 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 $\text{Cu K}\alpha$ radiation. The scan speed was 1° (2θ)/min. The moisture sensitive products such as the adduct and the Li-intercalated compound were covered with polymer films to prevent the sample from the hydrolysis by air.

UV-Visible absorption spectra for solutions (BCl_3 in CH_2CHCN) were measured by using a quartz cell and obtained by an UV-Visible-Near IR spectrometer (Perkin-Elmer Lambda 19). TEM photographs and electron diffraction data were obtained by a transmission electron microscope (JEOL JEM-2000FX). ESCA measurements were carried out by using an electron spectrometer (Shimadzu ESCA 750S) with $\text{Mg K}\alpha$ radiation. The binding energies of the elements were corrected by placing the $\text{Au}_{4f7/2}$ line at 84.0 eV.

2.5. Electrical Conductivity Measurement

Electrical conductivity was measured for the $\text{BC}_x\text{N}_y(\text{H})$ film deposited on the quartz substrate by using a d.c. four-probe technique at 20~700 °C under vacuum.

2.6. Li Intercalation

0.56 g of the powders obtained by CVD was added into a 4.0×10^2 mol/m³ $\text{Li}^+\text{C}_{10}\text{H}_8/\text{Tetrahydrofuran}$ (THF) solution (1.0×10^{-4} m³) and then the mixed solution was stirred for 1 week. The product was filtrated and washed with THF in a dry box.

3. RESULTS AND DISCUSSION

3.1. Adduct $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$ and its Polymerization

When the BCl_3 gas was introduced into the flask,

an exothermic reaction occurred and fine white powders formed in the gas phase as well as on the CH_2CHCN liquid. The white powders could be dissolved in the liquid at the first time and deposited on the liquid in the flask as the reaction proceeded. The color of powders and liquid gradually changed to yellow, when the $\text{CH}_2\text{CHCN} : \text{BCl}_3$ molar ratio was about 10 : 1. All the CH_2CHCN liquid changed to yellow~orange soft solid when the $\text{CH}_2\text{CHCN} : \text{BCl}_3$ molar ratio was 2 : 1.

Figure 1 shows the X-ray diffraction pattern for the adduct $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$. The sharp pattern has a integer relationship suggestive of cubic or quasi-cubic symmetry: $d^{-2}(\text{nm})^{-2}$ (I/I_0): 1.67(w), 6.68(vs), 13.3(vw), 15.0(vw), 41.6(vw).

The 2 : 1 adduct became brownish hard solid after a storage under N_2 at room temperature for one month. Even the yellowish solution ($\text{CH}_2\text{CHCN} : \text{BCl}_3 = 10 : 1$) became brownish soft solid after one month. The UV-Visible spectra (Fig.2) for the solution ($\text{CH}_2\text{CHCN} : \text{BCl}_3 = 10 : 1$) changed smoothly over a one month period with strong absorption shifting from a 400 nm in fresh

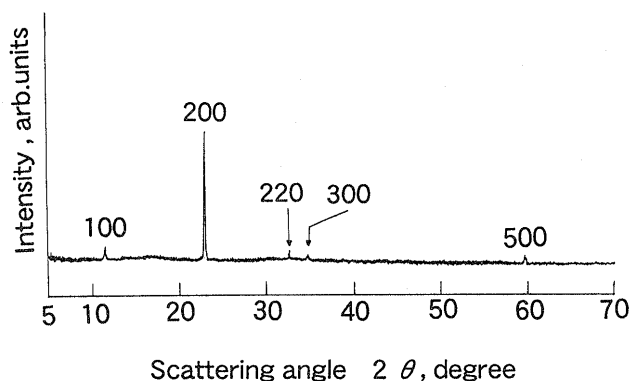


Fig.1. X-ray diffraction pattern of $(\text{CH}_2\text{CHCN})_2\text{BCl}_3$ adduct.

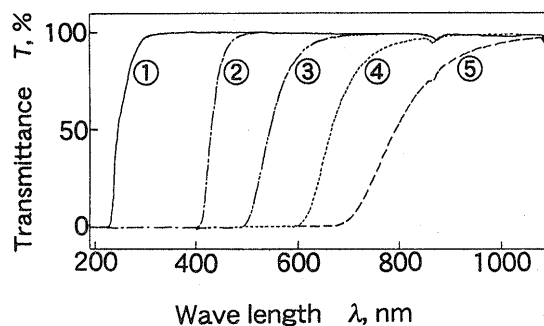


Fig.2. Change in UV-Visible spectrum of $\text{CH}_2\text{CHCN} : \text{BCl}_3 = 10 : 1$ solution. ① CH_2CHCN ② $\text{CH}_2\text{CHCN} + \text{BCl}_3$ (just after preparation) ③ 2 days later ④ 6 days later ⑤ 1 month later.

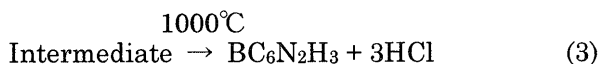
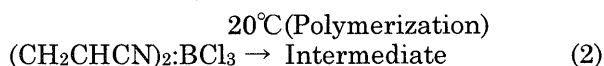
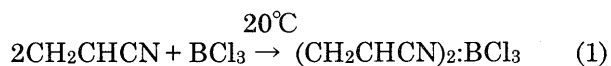
solution to 800 nm in aged solutions. These results suggest that the conjugated double bonds in the 2 : 1 adduct and the 10 : 1 solution increased with time. In other words, CH_2CHCN gradually polymerized at room temperature by the interaction with BCl_3 .

In this reaction, each BCl_3 molecule can act as a Lewis acid for one Lewis base of a nitrogen of $-\text{CN}$ group in the CH_2CHCN . The composition $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$ can be interpreted by the interaction of each BCl_3 molecule with half of the available nitrogen in the dimerized $(\text{CH}_2\text{CHCN})_2$. The observed polymerization of the CH_2CHCN and the hardening of the 2 : 1 adduct also suggest that the initial 2 : 1 adduct is a CH_2CHCN dimer adduct with BCl_3 .

3.2. $\text{BC}_6\text{N}_2(\text{H})$ Prepared by Pyrolysis of Adduct and the Reaction Process

Black powders were obtained by the pyrolysis of the adduct $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$ at 500~1000 °C. HCl gas was eliminated during the pyrolytic reaction. The elemental analyses indicated the black powder obtained by the pyrolysis at 1000 °C had a composition $\text{BC}_{5.8-6.2}\text{N}_{1.8-2.0}\text{H}_{2-4}$ which is described as $\text{BC}_6\text{N}_2(\text{H})$ in this paper.

From these results, we consider that the reaction proceeded as follows (See reaction 1~3): two molar (or dimer) of CH_2CHCN as the Lewis base reacted with the Lewis acid BCl_3 at room temperature and formed the new adduct $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$, which gradually polymerized at room temperature and formed graphite-like material of composition $\text{BC}_6\text{N}_2(\text{H})$ by the pyrolysis reaction at 1000 °C.



The yield of the final product $\text{BC}_6\text{N}_2\text{H}_3$, described as $\text{BC}_6\text{N}_2(\text{H})$ in this paper, was about 50 % on the basis of the above reaction (1)~(3). The material of composition $\text{BC}_6\text{N}_2(\text{H})$ was obtained by the pyrolysis reaction (3) within two days after the reaction (1) had finished. Too much polymerization (Reaction 2) gave different materials which had larger carbon content than $\text{BC}_6\text{N}_2(\text{H})$.

3.3. Structure of $\text{BC}_6\text{N}_2(\text{H})$

Figure 3 shows the X-ray powder diffraction pattern of $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of the adduct at 1000 °C. Broad peaks at 24.3° and 43.3° (2θ) are similar to those of (002) and (10)

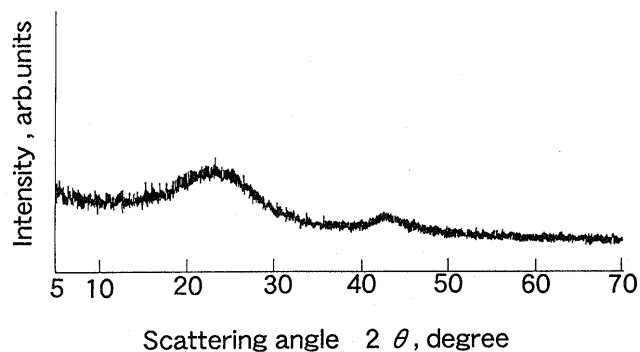


Fig.3. X-ray powder diffraction pattern of $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of adduct at 1000°C.

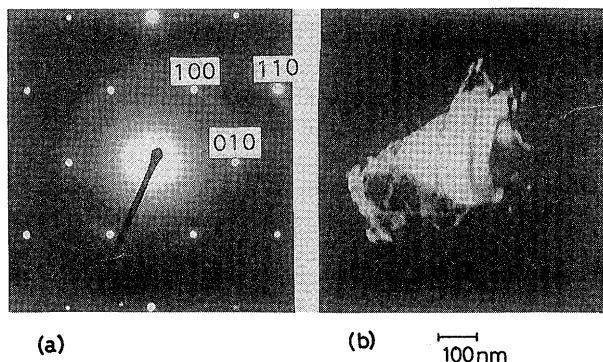


Fig.4. Electron diffraction pattern (a) and dark field image (b) from (100) diffraction for $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of adduct at 1000°C.

diffractions of non crystalline carbon such as a petroleum coke heat-treated at 1000 °C. The interlayer spacing is 0.37 nm, calculated from the (000) diffraction at 24.3° (2θ). The crystallite size in the direction of c-axis is very small (ca. 1 nm), which can be estimated from the half width (8.9° in 2θ) of the diffraction peak at 24.3° (2θ) by using the Scherrer's equation.

Six symmetrical spot pattern was partly observed on the electron diffraction analysis (Fig.4(a)) only for the micro region of $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis at 1000 °C, although ring diffraction was mostly observed. The d spacing of observed (100) diffraction (d_{100}) is 0.208 nm which is slightly smaller than that of graphite (0.210 nm). Dark field image resulted from the (100) diffraction (Fig.4(b)) indicates the crystalline particle of ~100 nm. From these X-ray and electron diffraction results, $\text{BC}_6\text{N}_2(\text{H})$ is composed of very small single crystals which has the graphite-like layered structure.

The broad IR absorption band at $3.2 \times 10^5 \sim 3.4 \times 10^5 \text{ m}^{-1}$ for $\text{BC}_6\text{N}_2(\text{H})$ suggests that the hydrogen atoms attached to the edge part of the small

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crystalline of $\text{BC}_6\text{N}_2(\text{H})$ in such forms as $-\text{NH}_2$ and $-\text{NH}-$. The hydrogen in $\text{BC}_6\text{N}_2(\text{H})$ may disturb the production of large-particle pseudo-graphitic BC_6N_2 . The hydrogen, however, could not be easily removed by the heat-treatment at 1500°C or the following additional reaction with BCl_3 : $\text{BC}_6\text{N}_2\text{H}_3 + \text{BCl}_3 \rightarrow 2\text{BC}_3\text{N} + 3\text{HCl}$. The hydrogen in $\text{BC}_6\text{N}_2(\text{H})$ must be introduced by the deformation of the structure, which was caused by the fast pyrolytic reaction under atmospheric pressure as well as the configuration of the hetero-atoms. The large-particle BC_6N_2 could be prepared if the reaction could be made by well controlled method such as low pressure CVD.

3.4. Atomic Arrangement in a Layer of BC_6N_2

Figure 5 shows the ESCA spectra for the $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of the adduct at 1000°C . The B_{1s} spectrum indicates the peak (191.1 eV) at higher binding energy than that for h-BN (190.1 eV). This indicates that the boron atoms in the $\text{BC}_6\text{N}_2(\text{H})$ 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 (see upper left in Fig.5). The C_{1s} spectrum has a peak at 284.8 eV which is almost the same as that of graphite. This indicates that the major part of the carbon atoms in $\text{BC}_6\text{N}_2(\text{H})$ network have a structure similar to that of graphite. The spectrum, however, is distributed to the higher binding energy, which is due to the carbon partly connected to the electronegative nitrogen atom (see the middle part of Fig.5). The N_{1s} spectrum has a peak at higher binding energy (398.9 eV) than that for h-BN (398.1 eV), which suggests nitrogen atoms connected with carbon atoms as well as boron atoms in $\text{BC}_6\text{N}_2(\text{H})$ network (see the lower left in Fig.5).

Figure 6 indicates a possible atomic arrangement in the layer of BC_6N_2 , which is derived from the interpretation of ESCA spectra and the following assumptions deduced by reaction (1)~(3): (a) The original monomer chain C-C-C-N of acrylonitrile can remain in the BC_6N_2 network, (b) A B-N bond can be made from the coordinate bond of B-N caused by the formation of the adduct $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$, (c) B-B and N-N bonds cannot be easily made, because of the thermodynamically implausible reaction of B-Cl and B-Cl $\{\Delta G = 340 \text{ kJ/mol}$ for the reaction $\text{BCl}_3 \rightarrow \text{B} + 1.5\text{Cl}_2$ at $1000^\circ\text{C}\}$ and a repulsion of lone-pair electrons between nitrogen atoms, respectively. The structure can be generated by repetition of a unit structure NCCCCCNB, which could reflect the main framework of the adduct $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$ as the precursor.

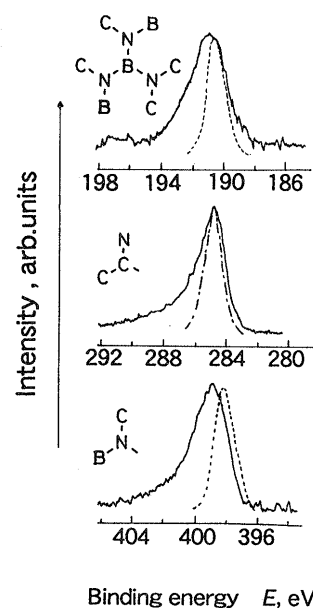


Fig.5. ESCA spectra of $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of the adduct at 1000°C .
..... : h-BN, — — — : graphite

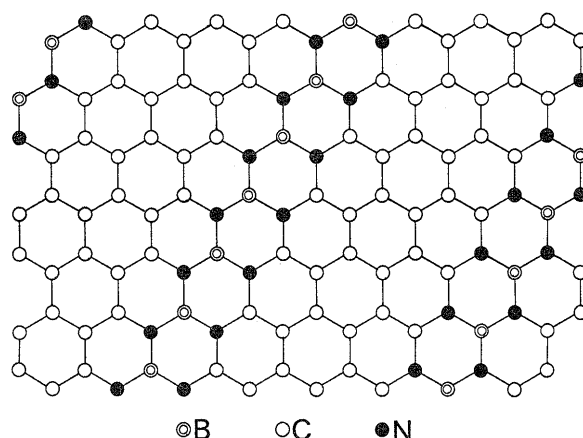


Fig.6. Possible atomic arrangement of BC_6N_2 synthesized by the pyrolysis of the adduct $(\text{CH}_2\text{CHCN})_2:\text{BCl}_3$. The structure can be generated by repetition of a NCCCCCNB unit.

3.5. $\text{BC}_6\text{N}_{1.5}(\text{H})$ Prepared by CVD

Black shiny film (thickness : $26 \mu\text{m}$) deposited on the quartz substrate. The thin film adhered on the substrate so firmly that it could not be easily removed from the substrate. The elemental analyses indicated the powders obtained near the substrate had a composition $\text{BC}_{5.8-6.0}\text{N}_{1.4-1.5}\text{H}_{0.1-0.2}$ [12] which is described as $\text{BC}_6\text{N}_{1.5}(\text{H})$ in this paper. We consider the composition of the film is almost the same as that of the powders obtained near the substrate because of the same ESCA spectra. The

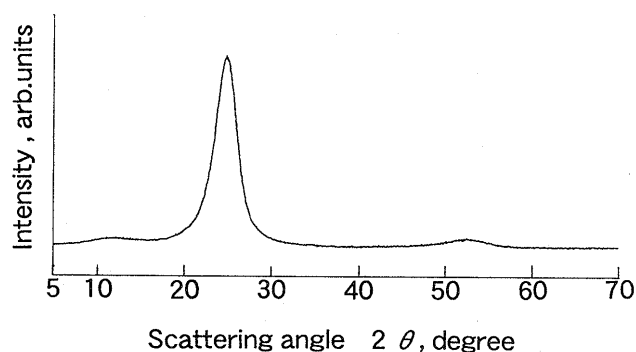


Fig.7. X-ray diffraction pattern of $\text{BC}_6\text{N}_{1.5}(\text{H})$ film prepared by CVD.

Table 1. Comparison of interlayer spacing and crystallite size for $\text{BC}_6\text{N}_{1.5}(\text{H})$ film, powders prepared by CVD and $\text{BC}_6\text{N}_2(\text{H})$ powders synthesized by the pyrolysis of adduct.

Material	$\text{BC}_6\text{N}_{1.5}(\text{H})$ Film	$\text{BC}_6\text{N}_{1.5}(\text{H})$ Powder	$\text{BC}_6\text{N}_2(\text{H})$ powder
Peak pos. degree in 2θ	24.8	25.7	24.3
d spacing nm	3.59	3.46	3.7
Half width degree in 2θ	1.40	2.82	8.9
Crys. size nm	63	31	10

nitrogen and hydrogen contents were smaller than that of $\text{BC}_6\text{N}_2(\text{H})$ obtained by the pyrolysis of adduct, probably because the nitrogen was eliminated in stable forms such as NH_3 or N_2 in the gas phase during the CVD reaction.

Figure 7 shows the X-ray diffraction pattern of $\text{BC}_6\text{N}_{1.5}(\text{H})$ film deposited on the substrate. Although (00 ℓ) diffraction peaks corresponding to those for graphite ($\ell = 2$ and 4) were observed, no (10 ℓ) diffraction was observed. On the other hand, $\text{BC}_6\text{N}_{1.5}(\text{H})$ powders obtained near the substrate showed the (10 ℓ) diffraction as well as (00 ℓ) one. These results suggest that the basal plane of the deposited film oriented parallel to the substrate.

Table 1 indicates (00 ℓ) peak position, inter-layer spacing, half width of the (00 ℓ) peak and crystallite size for both the $\text{BC}_6\text{N}_{1.5}(\text{H})$ film and the powders prepared by CVD, compared with $\text{BC}_6\text{N}_2(\text{H})$ powders synthesized by the pyrolysis of adduct.

3.6. Electrical Conductivity of $\text{BC}_6\text{N}_{1.5}(\text{H})$ Film

Figure 8 shows the basal-plane conductivity versus temperature curve for $\text{BC}_6\text{N}_{1.5}(\text{H})$ film

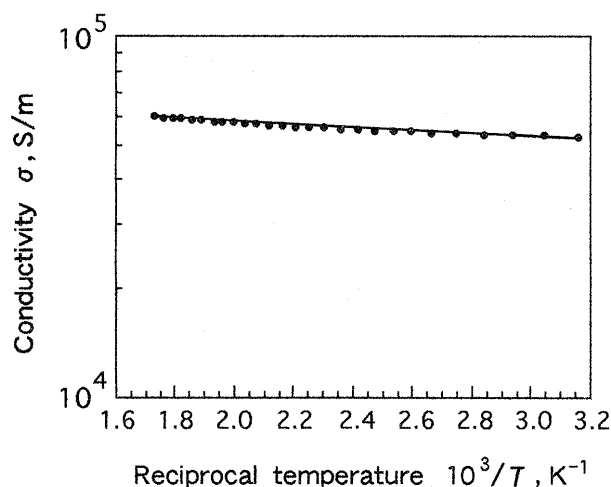


Fig.8. Log conductivity vs reciprocal temperature plot for $\text{BC}_6\text{N}_{1.5}(\text{H})$ film prepared by CVD.

measured in N_2 atmosphere. The conductivity at room temperature is 5.31×10^4 S/m, which is larger than that of $\text{BC}_3\text{N}(\text{H})$ plate prepared by CVD (88.5×10^4 S/m, gas molar ratio; $\text{CH}_2\text{CHCN} : \text{BCl}_3 = 1 : 1$) [11]. Activation energy calculated from the Arrhenius plot shown in Fig.8 is 2.72×10^{-2} eV.

3.7. Intercalation of Li into $\text{BC}_6\text{N}_{1.5}(\text{H})$ Matrix

The reduction with $\text{Li}^+\text{C}_{10}\text{H}_8/\text{THF}$ solution for $\text{BC}_6\text{N}_{1.5}(\text{H})$ yielded a Li intercalated compound. Almost no change in color was detected. The X-ray diffraction analysis indicated that the compound had a d -spacing of 0.87 nm in the direction of c -axis. This compound may be assigned as a first stage with THF as well as Li in the interlayer spacing, which was reported for graphite in the similar case [13]. Because the observed weight increase is more than the amount of Li dissolved in the solution and second stage does not have the capacity for the size of THF as follows: Size of THF whose 5-membered ring oriented parallel to the basal-plane of $\text{BC}_6\text{N}_{1.5}(\text{H})$; 0.19 nm, Van der Waals radii of hydrogen atoms attached to the basal-plane; 0.24 nm (0.12×2), Expected interlayer spacing for first stage; 0.78 nm ($0.35 + 0.19 + 0.24$ nm), for second stage; 1.13 nm ($0.35 \times 2 + 0.19 + 0.24$ nm). The difference between the expected value for the first stage (0.78 nm) and the observed one (0.87 nm) is probably due to the configuration of THF molecule in the interlayer spacing of $\text{BC}_6\text{N}_{1.5}(\text{H})$.

It was reported that BC_2N is one of the candidates for the anode matrix of rechargeable Li battery [14]. The possibility of moderate interaction between B/C/N materials and Li should be further investigated. Electrochemical behavior of

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$\text{BC}_6\text{N}_{1.5}(\text{H})$ in several electrolyte solutions is now studied.

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