A Novel B-C-N Compound Derived from Melamine Diborate

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A new B-C-N compound has been synthesized by thermal decomposition of melamine diborate mixed metal Mg powder in Ar at 1273 K. XRD revealed that the product had turbostratic structure and approximate composition of that was $B_{1.1}C_{1.1}N_{1.0}$. Properties of the B-C-N compound obtained are discussed.

Recently, interest in B-C-N compounds, which have the potential applications as semiconductors and host materials, have increased.[1] Various B-C-N compounds were synthesized by chemical vapor deposition or solid-phase pyrolysis of precursors.[2] In most of the conventional research, chemical compounds without oxygen such as BH_3, BCl_3, NH_3, CH_4, melamine, and pyridine etc have been chosen as starting materials in order to prevent the contamination of the oxygen to the B-C-N product. Though nitrogen-rich B-C-N materials have been prepared by the reaction between melamine and boron trichloride, the material considerably contained hydrogen.[3] The B-C-N compound have been prepared by thermal decomposition of the system of boric acid, saccharose, and urea by Hubacek and Sato.[4] They reported that saccharose and boric acid were reduced by the coexisting urea in this system. Melamine diborate (MDB) is the representative material which forms turbostratic BN by the thermal decomposition in N_2 over 873 K.[5] Since BN is thermodynamically stable, B-C-N compound can not be obtained simply by heating of MDB.

We have now found that B-C-N compound with an empirical formula $B_{1.1}C_{1.1}N_{1.0}$ can be produced in high yields by the thermal decomposition of MDB mixed a metal Mg powder, which works deoxidation material, in Ar at 1273 K.

In a typical experiment, MDB, which was precipitated by cooling a hot solution of melamine and boric acid, and metal Mg powder were mixed in the Mg-B mole ratio of 3 or 1, and heated for 1 h in Ar at 1273 K. In this procedure, MgO, Mg_3BN_3, $Mg_3B_2O_6$, Mg_3N_2, and MgB_{12} were formed as by-products. It was considered that the deoxidation of MDB was mainly caused by oxidation of Mg. Since the B-C-N compound was stable for acid, the by-products could be removed by washing with dilute nitric acid.

The crystal shape of the B-C-N compound was the same as MDB and the crystal size hardly changed (Figure 1). By controlling the temperature in synthesizing MDB precisely, it is possible to increase the crystal size of MDB. Unlike the case in which other precursor is used, it is possible to obtain the crystal of large size over mm order by this method.

X-ray powder diffraction of the B-C-N compound was consistent with turbostratic structure. The diffraction pattern revealed (hk0) and (00l) reflections, which were typical for boron nitride precursor obtained by pyrolysis of MDB in N_2.[5] The chemical analytic data in combination with the EDX analysis confirmed that an approximate composition of the B-C-N compound was $B_{1.1}C_{1.1}N_{1.0}$.

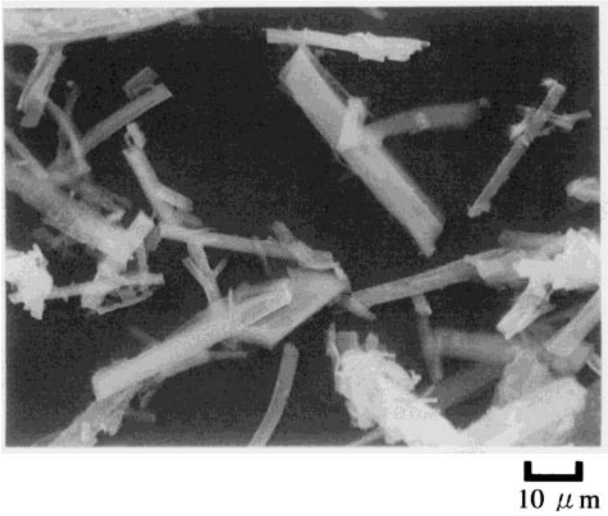

Figure 1. SEM images of the B-C-N compound.

The solid-state ^{13}C MAS NMR spectrum of the B-C-N compound exhibited a broad peak with a maximum at about $\delta = 120$ ppm with respect to tetramethylsilane (Figure 2). The chemical shift was in the range of sp^2-hybridized carbon reported by Jarman et al.[6] The large line width might be due to the disorder of the carbon structure and to the random distribution of C-B, C-C, and C-N bonds, as reported by Riedel et al.[7]

The B-C-N compound had a density of $1.97\ g\,cm^{-3}$ and specific surface area of $215\ m^2\,g^{-1}$. By other method, the B-C-N

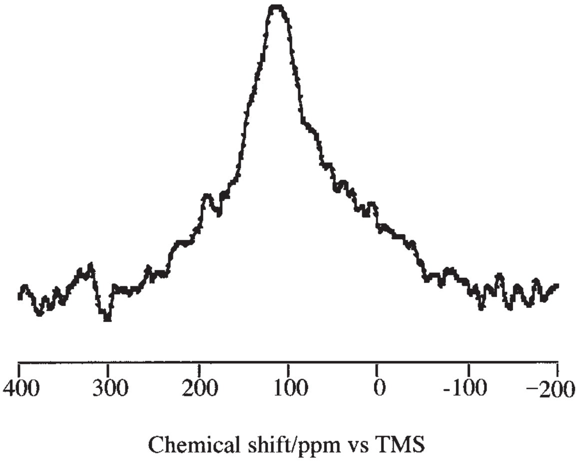

Figure 2. ^{13}C MAS NMR spectrum of the B-C-N compond at a Larmore frequency of 75.468 MHz.

compound with comparatively large specific surface area has not been prepared. The utilization as catalyst and adsorbent may be feasible for the obtained B-C-N compound.

The logarithm of electrical resistance of the B-C-N compound was proportional to reciprocal of temperature, suggesting the semi-conducting properties of the material (Figure 3). The electrical resistance of B-C-N compound obtained in this work was about 2000 times higher than that of the filmy BC_6N prepared by CVD using CH_2CHCN and BCl_3.[8] It was considered that this difference occurred by the difference of the content of carbon and the number of void in the crystal.

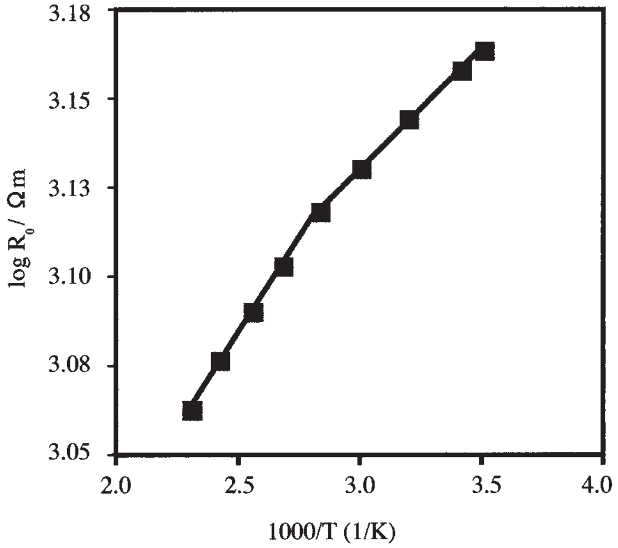

Figure 3. Temperature dependence of electrical resistance for the B-C-N compound.

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