SYNTHESIS AND PROPERTIES OF A NEW CARBON/NITROGEN MATERIAL OF COMPOSITION $C_3N_{3.6\sim4.5}O_{1.1\sim1.2}H_{4.1\sim4.2}$

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Introduction

Since Liu and Cohen [1] predicted β-C_3N_4 could have bulk moduli comparable to diamond, considerable effort has been directed toward the growth of C_3N_4. So far there have been several reports on the deposition of small crystalline C_XN solids which were synthesized by using physical methods such as laser abration of graphite under an atomic [2] or an ionic nitrogen beam [3] or rf diode sputtering [4]. Although the graphitic C_XN materials have been synthesized by chemical vapor deposition [5], precursor-pyrolysis reaction [6], or solid-gas reaction[7], the chemical method has never given the hard C_XN solid having 3-dimensional structure.

In this paper, we report the synthesis of a new carbon/nitrogen material having 3-dimensional structure by chemical reaction. Several properties such as hardness, ferromagnetism and photoluminescence are also reported.

Experimental

Synthesis of carbon/nitrogen compound: 1,3,5-trichlorotriazine($C_3N_3Cl_3$) and lithium nitride(Li_3N) were mixed under nitrogen atmosphere [8] and set in a pressure vessel. The reaction was carried out at 220℃ under N_2 atmosphere, followed by treatment with water and acetone, to eliminate the unreacted Li_3N, $C_3N_3Cl_3$ and by-product LiCl.

The obtained powders were scraped on a quartz glass plate with an automatic polisher. The surface profile was measured by 3-dimensional surface roughness measuring instrument.

The magnetization curve (the magnetic field dependence of magnetization) was measured in the magnetic field range of $\pm$ 50kOe. Susceptibility was measured as a function of temperature in the range between 2 and 300K.

The photoluminescence spectrum was measured for the powder by a spectrophotometer at room temperature.

Results and Discussion

A new nitrogen-rich solid is formed as a creamy white powder. The formation of LiCl as a by-product was observed by X-ray diffraction analysis. The expected reaction is as follows, see eqn.(1).

$$C_3N_3Cl_3 + Li_3N \rightarrow C_3N_4 + LiCl \quad (1)$$

Usual combustion method, followed by gas chlomatography was used to determine the composition $C_3N_{3.6\sim4.5}O_{1.1\sim1.2}H_{4.1\sim4.2}$. The oxygen and hydrogen could be introduced by water treatment after the reaction. However, the material was stable and the composition did not change any more after exposure to air.

Figure 1 shows the X-ray diffraction pattern for the obtained material, which is totally different from that of graphite or diamond. Although some diffractions (d = 0.281, 0.225 and 0.211 nm) coinside with calculated values for β-C_3N_4 [1], the definite structure have not been found yet. Electron diffraction and TEM observation indicate that this 3-dimensinal crystallite size was around 100 nm. When the reaction was carried out under N_2 containing small amount of air, the material with amorphous carbon-like structure was obtained.

The interesting thing is that a part of the material obtained in this study is harder than quartz glass which has a hardness of about 100 (Hv). The particle was able to make fine scratches on it. The surface profile indicated that the scratches of 1$\sim$3 μm in depth and 10 $\sim$20 μm in width were made on the quartz glass with a smooth surface.

Incidentally, we have found that this material shows ferromagnetic behavior at room temperature. Figure 2 shows a hysteresis (M versus H) curve at 280K with a coercive field of about 20 Oe. The saturation magnetization at room temperature is estimated to be 0.12 emu/g. The hysteresis curves are not so different in the temperature range between 5K and 300K. There are almost no change in magnetic susceptibility (χ) in this temperature range. These results suggest that the sample is in a ferromagnetic state even at room temperature. There have been several reports on the ferromagnetic properties for the material consisting of light elements [9], which have been explained by the interaction between the localized spins on the radicals. In this study, we have observed that the material with high crystallinity shows the ferromagnetic properties stronger than that with amorphous structure. We are now under investigation about the relation between the crystal structure and the ferromagnetism.

Figure 3 shows the photoluminescence spectrum for the obtained material. The material exhibits strong lumi-

nescence in the range 350～550nm with a peak at 408nm, which is efficiently excited by UV-light of 343nm. There are two possibilities to explain this luminescent characteristics. One is owing to the π - π * transition of the triazine ring (C_3N_3) in this material, which is also observed for the starting material (1,3,5-trichlorotriazine). The other is due to some defects in the material. We think that the latter might be the reason, because strong photoluminescence was observed for the material with amorphous structure, which is in opposition to the case of ferromagnetism.

Conclusions

A new material of composition $C_3N_{3.6\sim4.5}O_{1.1\sim1.2}H_{4.1\sim4.2}$ has been prepared by the reaction of $C_3N_3Cl_3$ with Li_3N at 220℃. The material can make fine scratches on a quartz glass plate, having a structure different from the hypothetical β-C_3N_4 which is predicted to be the hard material no less than diamond. The material with high crystallinity exhibits ferromagnetic behavior even at room temperature, while the material with amorphous structure shows stronger photoluminescence in the range 350-550 nm and have a peak at 408 nm.

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References and Notes

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8. Caution!: This mixture sometimes violently reacted with fire even under nitrogen atmosphere.
9. For example: Kinoshita, M., Jpn.J.Appl.Phys., 1994, 33, 5718.

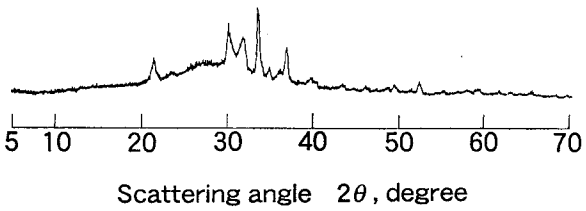

Figure 1. X-ray diffraction pattern of $C_3N_{3.6}O_{1.1}H_{4.2}$ prepared by the reaction of $C_3N_3Cl_3$ with Li_3N under N_2.

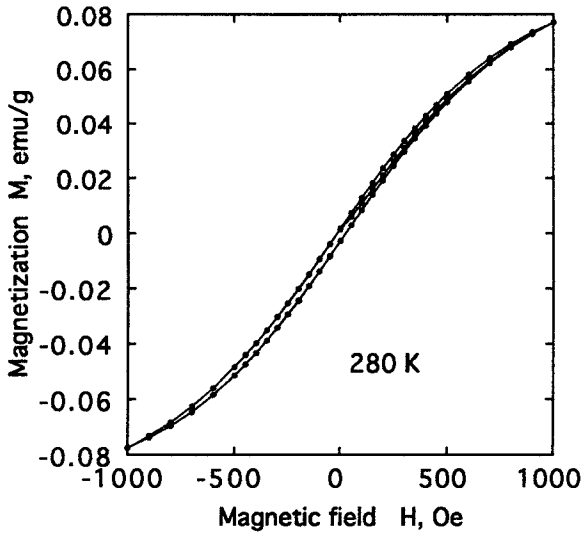

Figure 2. Hysteresis (M versus H) curves in the magnetic field range of ±1 kOe for $C_3N_{3.6}O_{1.1}H_{4.2}$ prepared by the reaction of $C_3N_3Cl_3$ with Li_3N under N_2 containing a small amount of O_2.

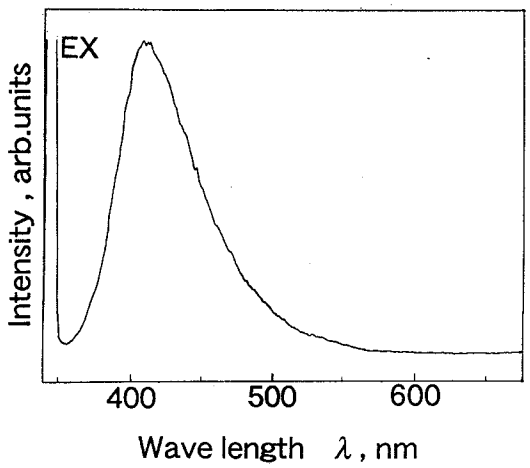

Figure 3. Photoluminescence spectrum at 300K for $C_3N_{3.6}O_{1.1}H_{4.2}$ prepared by the reaction of $C_3N_3Cl_3$ with Li_3N. EX indicates the excitation light of 343nm.