Preparation and Properties of a New Hard Material of Composition $C_3N_{3.6\text{-}4.5}O_{1.1\text{-}1.2}H_{4.1\text{-}4.2}$

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A new material of composition $C_3N_{3.6-4.5}O_{1.1-1.2}H_{4.1-4.2}$, which is harder than a quartz glass plate and shows ferromagnetism at room temperature, has been prepared by the reaction of $C_3N_3Cl_3$ with Li_3N at 220℃.

Since the hypothetical compound of carbon nitride (β-C_3N_4) was predicted that it might have a high bulk modulus comparable to diamond,[1] considerable effort has been directed toward the synthesis 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 ablation 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.

In this letter, we report the synthesis of a new hard material consisting of carbon and nitrogen as main components by a chemical reaction. 1,3,5-trichlorotriazine ($C_3N_3Cl_3$) and lithium nitride(Li_3N) were chosen as starting materials in this study. After these materials were mixed in a nitrogen atmosphere[8] and set on a SiC crucible in a PTFE vessel, the reaction was carried out at 220℃ for 24 h under N_2 atmosphere, followed by washing with water and acetone to eliminate the unreacted Li_3N, $C_3N_3Cl_3$ and by-product LiCl. The reaction did not proceed completely at a temperature below 220℃.

A new nitrogen-rich material was formed as a creamy white powder. The formation of LiCl as the by-product was observed by X-ray diffraction analysis. The expected reaction was as follows;

$$C_3N_3Cl_3 + Li_3N \rightarrow C_3N_4 + 3LiCl \quad (1)$$

The product was composed of two kinds of materials. One is crystalline particles with the composition $C_3N_{4.5}O_{1.2}H_{4.1}$ (Found: C;28.47, N;49.84, O;15.85, H;3.31 wt%), which shows ferromagnetic properties and can be easily separated by a permanent magnet. The other is non-crystalline particles with the composition $C_3N_{3.6}O_{1.1}H_{4.2}$ (Found: C;30.66, N;42.09, O;19.17, H;3.53). These compositions were determined by usual combustion method, followed by gas chromatography. The oxygen and hydrogen as sub-components could be brought in the material by a side reaction of the product with water, in the forms such as amino group ($-NH_2$) and carboxyl group (>C=O) which were detected by IR spectroscopic analysis. However, the material was stable and the compositions did not change thereafter.

Figure 1 shows the X-ray diffraction pattern for the crystalline particles, which is totally different from that of graphite or diamond. Although some diffractions (d = 0.281, 0.225 and 0.211 nm) coincide with calculated values for β-C_3N_4,[1] the definite structure has not been determined yet. Electron diffraction and TEM observation suggest that the material separated by the magnet was a mixture consisting of several kinds of crystals. Dark field images for the diffractions indicate that the crystallite sizes are around 100 nm. When the reaction was carried out under N_2 containing small amount of air, the main product was non-crystalline particles with amorphous carbon-like structure.

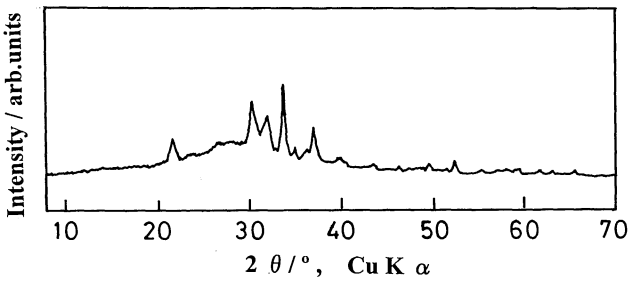

Figure 1. X-ray diffraction pattern of $C_3N_{4.5}O_{1.2}H_{4.1}$ prepared by the reaction of $C_3N_3Cl_3$ with Li_3N under N_2.

The interesting thing is that the crystalline material separated by magnet is harder than quartz glass. The powders were scraped on a quartz glass plate with an automatic polisher and the surface profile was measured by 3-dimensional surface roughness measuring instrument (Kosaka Lab.Ltd., SE-30K).

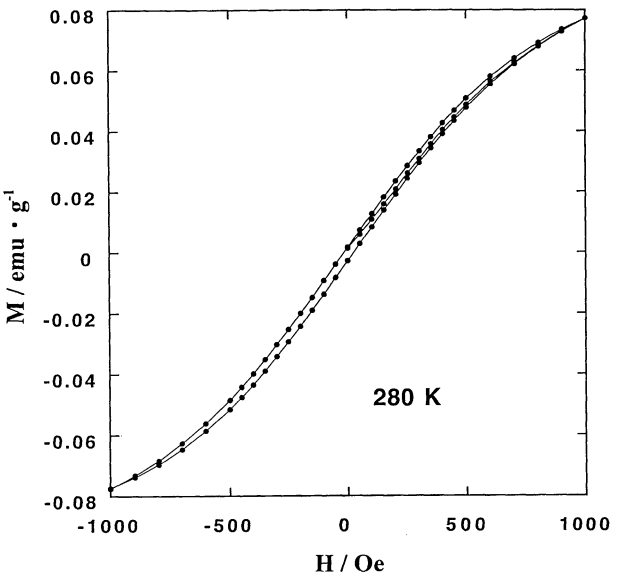

Figure 2. Hysteresis (M versus H) curves at 280 K in the magnetic field range of ±1 kOe for $C_3N_{4.5}O_{1.2}H_{4.1}$ prepared by the reaction of $C_3N_3Cl_3$ with Li_3N under N_2.

The particle was able to make fine scratches on it. The surface profile indicated that the scratches of 1～3 μm in depth and 10 ～20 μm in width were made on the quartz glass, which has a hardness of about 100 (Hv: measured by micro hardness tester, Akashi Co., MVK-G2) with a smooth surface.

As is mentioned before, we have found that the material with high crystallinity shows the stronger ferromagnetism than that with non-crystalline structure. The magnetization curve (the magnetic field dependence of magnetization) was measured by magnetic property measurement system (Quantum Design Co., MPMS-5S) in the magnetic field range of ± 50kOe. Susceptibility was measured as a function of temperature in the range between 2 and 300K. 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. The amount of magnetic metals contained in the material was determined by acid dissolution followed by ICP emission spectrometry: Fe<50ppm, Co <10ppm and Ni<10ppm, which should not be the cause of the ferromagnetism of this material. There have been several reports on the ferromagnetic properties for the material consisting of light elements,[9-11] which have been explained by the interaction between the localized spins on the radicals. We have not succeeded in the complete separation of the amorphous material and the several kinds of crystals. The structural study for the material would be able to explain the origin of ferromagnetism as well as that of hardness.

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