Synthesis of New Carbon-Nitride-Related Materials at High Pressure and Temperature

M Sougawa¹, T Sumiya¹, K Takarabe¹, Y Mori¹, T Okada², H Gotou² and T Yagi²

¹Okayama University of Science, 1-1 Ridai, Okayama, 700-0005, Japan
²The Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Chiba, 277-8581, Japan

E-mail. s05sm06@std.das.ous.ac.jp

Abstract. Low-compressive new carbon-nitride-related materials were synthesized with a high-pressure and high-temperature treatment of CNHO nanoparticle prepared with an atmospheric nitrogen plasma. New phases were recovered at ambient conditions and the most prominent new phase is tentatively assigned to be an orthorhombic unit cell with the lattice parameters; a = 7.635 Å, b = 4.487 Å, and c = 4.040 Å.

1. Introduction
Dense carbon nitrides consisting of a C-N single bond are expected to have a high bulk modulus exceeding that of diamond. In 1989, Liu and Cohen first predicted the hard carbon nitride of β-C3N4 [1] and Teter and Hemly subsequently predicted in 1996 α-, cubic-, and pseudocubic-C3N4 for the hard and polymorphic carbon nitride [2]. Furthermore, Mattesini and Mater predicted in 2002 that β- and α-C11N4 also have a high bulk modulus exceeding that of diamond [3]. All these theoretical studies have long intrigued us with researches on the new hard materials. In the last two decades, many synthetic studies have been reported and some papers claim that they have synthesized the carbon nitride of β- or α-C3N4. However there seems no consensus for the reproducible synthesis of the carbon nitride [4],[5].

E Horvath-Borden et al have reported the synthesis of crystalline C2N2(NH) at high pressure and high temperature with the use of the precursor C2N4H4 having partly the double C=N bond [6]. Their chemical bond analysis shows that C2N2(NH) consists mainly of the C-N single bond and the calculated bulk modulus of C2N2(NH) is 277 GPa, but no experimental bulk modulus was reported for C2N2(NH).

In this paper we report on the high-pressure and high-temperature synthesis of the carbon-nitride-related materials with the precursor CNHO nanoparticle prepared by the use of the atmospheric nitrogen plasma.

2. Experimental
A Mao-Bell-type diamond anvil cell (DAC) was used for the high-pressure and high-temperature synthesis. Each cell has a pair of diamond culet of 350 μm and a rhenium gasket with a hole of 120 μm in diameter served as the sample chamber. The sample was mixed with absorbent materials (Pt, Au) for a laser to subject CNHO to high temperature. Heating was carried out with a YAG laser at the pressure of 40 GPa for about ten minutes. The temperature was between 1200 K and 1700 K evaluated
from the radiation spectrum. The pressure was determined by a ruby fluorescent method and the absorbent materials scale. The X-ray diffraction measurements were carried out using the synchrotron radiation facility at the National Institute for High Energy Physics (KEK), Tsukuba and SPring-8, Aioi. The preparation of precursor CNHO was reported elsewhere [7]. While the composition of synthesized precursor varies within certain limits, the typical composition is C$_3$N$_4$H$_2$O. H$_2$O arises partly from the absorption of water in air.

3. Result and discussion

Figure 1a shows the X-ray diffraction (XRD) pattern of the precursor with Pt in DAC subjected to the pressure of 40 GPa. In Figure 1a, the open circle at 2.32 Å is the XRD line from the precursor and the other XRD lines are from Pt as the laser heat absorber embedded in the gasket hole. As the precursor was heated to the temperature of 1700 K at the pressure of 40 GPa, the new XRD lines appeared and are indicated by the dot circle in the middle XRD pattern (b). All these new XRD lines move to larger d-spacing as decreasing pressure and remain at the atmospheric pressure as shown in the upper XRD pattern (c). Thus the new phase is quenchable. The similar experiment was conducted using a gold Au as the laser heat absorber. Figure 2 shows the XRD patterns of the sample at the pressure of 40 GPa after heating at 1200 K (a) and 1700 K (b). These XRD patterns are identical with Figure 1b.

![Figure 1](image_url)

**Figure 1.** XRD patterns of the precursor at the pressure of 40 GPa before heating (a), after heating at the temperature of 1700 K (b), and the recovered sample outside the DAC (c). The open circle (○) indicates the XRD line from the precursor and the dots (●) indicate the XRD lines of a new phase.
Figure 2. XRD patterns of the sample at the pressure of 40 GPa after heating at the
temperature of 1200 K (a) and 1700 K (b). The open circle (○) indicates the XRD line from
the precursor and the dots (●) indicate the XRD lines of a new phase.

The observed d-spacing and XRD intensity of the new phase are compiled in Table 1. Those from
the precursor and the laser absorber are excluded. We propose that the prominent new phase is the
orthorhombic unit cell of the space group Cmc2_1 with the three lattice constants of a = 7.635 Å, b =
4.487 Å, and c = 4.040 Å. The overall coincidence of d-spacing among them is good in agreement
except the doublet lines at 2.10 Å and 2.12 Å. The ratio of the XRD intensity of this doublet to that of
the main doublet at 3.81 Å and 3.87 Å varies strongly on each high-pressure and high-temperature
runs. However those ratios for the other XRD lines are almost constant. We can expect that the
relative XRD intensities are kept at a constant in the certain crystal structure, so the large variation of
those on the synthetic run implies the coexistence of the different phase. The proposed cell for the
prominent phase does not agree with any of the theoretically proposed hard C_3N_4 [1], [2]. The atomic
position in the proposed unit cell and the determination of the composition are on progress.

The pressure dependence of the proposed cell parameters for the prominent new phase was
determined by the measurement of the XRD patterns up to 40 GPa. The result is shown in Figure 3
and the bulk modulus $B_0$ is calculated with the use of the linear equation (1). The calculated bulk
modulus is about 374 GPa by the Ruby scale and, if we use Pt scale embedded in the gasket hole, the
estimation is about 435 GPa.

$$B_0 = -V_0 \left( \frac{dP}{dV} \right)$$

(1)
Table 1. Comparison of d-spacing for the new phase and the proposed cell. The experimentally overlapped XRD lines are bracketed right in the d-spacing. The asterisks in the integrated intensity show the overlapped XRD lines. The doublet at 2.10 Å and 2.12 Å belongs to the different phase. See the text for this.

| Experimental result | Proposed cell |  
|---------------------|---------------|
| d (Å)               | a = 7.635 Å, b = 4.487 Å, and c = 4.040 Å |
| 3.87                | 3.81          |
| 100*                | 3.818         |
| 3.81                | 3.818         |
| 2.8                 | 2.794         |
| 32                  | 2.244         |
| 2.24                | 2.214         |
| *2.21               | 2.214         |
| *2.12               | 2.214         |
| 2.02                | 2.020         |
| 18                  | 18            |
| 1.96                | 1.961         |
| 13*                 | 1.941         |
| 1.94                | 1.941         |
| 1.94                | 1.934         |
| 1.91                | 1.909         |
| 1                   | 1.909         |
| 1.79                | 1.790         |
| 1                   | 1.790         |
| 1.75                | 1.785         |
| 2                   | 1.785         |
| 1.50                | 1.501         |
| 2                   | 1.501         |
| 1.49                | 1.492         |
| 2                   | 1.492         |
| 1.49                | 1.468         |
| 2                   | 1.468         |
| 1.40                | 1.454         |
| 1                   | 1.454         |
| 1.39                | 1.446         |
| 1                   | 1.446         |
| 1.38                | 1.397         |
| 4*                  | 1.397         |
| 1.38                | 1.379         |
| 4*                  | 1.379         |
| 1.37                | 1.368         |
| 4*                  | 1.368         |
| 1.36                | 1.361         |
| 510                 | 1.361         |
| 1.29                | 1.289         |
| 4*                  | 1.289         |
| 1.27                | 1.272         |
| 113                 | 1.272         |
4. Summary
Low-compressive carbon-nitride-related orthorhombic phase has been synthesized with the high-pressure and high-temperature treatment of CNHO nanoparticle. This result implies the existence of the low-compressive carbon-nitride-related materials other than $\beta$-C$_3$N$_4$ and its polymorph. A lot of studies remain to understand the nature of synthesized carbon-nitride-related materials and the synthetic process, but we believe that this report shows experimentally the hard carbon-nitride-related materials with the bulk modulus of some range of 400 GPa.

Acknowledgement
The author, M Sougawa, thanks to Dr. Kusaba of Tohoku University for a detail introduction of the DICVOL program to deduce the space group of the synthesized material.

References
[1] Liu A Y and Cohen M L 1989 Science 245 841
[2] Teter D M and Hemly R J 1996 Science 271 53
[3] Mattesini M and Mater S F 2002 Phys. Rev. B 65 075110
[4] Sung S, Tsai T, Huang K, Huang J and Shih H C 1998 Jpn. J. Appl. Phys. 37 L148
[5] Yamamoto K, Koga Y, Yase K, Fujiwara S and Kubota M 1997 Jpn. J. Appl. Phys. 36 L230
[6] Harvath-Bordon E, Riedel R, McMillan P F, Kroll P, Miehe G, van Aken P A, Zerr A, Hoppe P, Shebanova O, McLaren I, Lauterbach S, Kroke E and Boehler R 2007 Angew. Chem. Int. Ed. 46 1476
[7] Tabuchi H, Sougawa M, Takarabe K, Sato O and Ariyada O 2007 Jpn. J. Appl. Phys. 46 1596

Figure 3. Pressure dependence of three lattice constants a (■), b (●), c (▲), and the volume (◊) derived from the tentative orthorhombic cell for the new phase. The pressure was estimated by the Ruby scale.