Molecular routes syntheses of graphite-like C–N compounds with various N/C ratios in high pressure and temperature

Taishi HORIBE, Keiji KUSABA, Ken NIWA, Masashi HASEGAWA,[†]
Keisuke YASUDA^{*,††} and Ryoya ISHIGAMI^{*}

Department of Crystalline Materials Science, Nagoya University, Nagoya 464–8603, Japan

^{*}Wakasa Wan Energy Research Center, Tsuruga, Fukui 914–0192, Japan

Graphite-like carbon nitride inorganic compounds were synthesized from molecular 1,2,4-triazole $C_2N_3H_3$ in high pressure and temperature conditions using a DIA-type multianvil large press. It was found that the N/C content ratio of the carbon nitrides can be systematically controlled by changing the heating temperature at 5 GPa. The substitution of nitrogen for carbon in graphene layers results in the low crystallinity of the synthesized C–N compounds. It should be noted that the *c*-axis which is equivalent of the distance between two graphene layers, decreases monotonously with increasing N/C content ratio. This is attributed to both of the smaller atomic size of nitrogen than that of carbon and Van der Waals attraction between C–N graphene layers because of the different electronegativity between nitrogen and carbon.

©2016 The Ceramic Society of Japan. All rights reserved.

Key-words : High pressure synthesis, Carbon nitrides

[Received May 13, 2016; Accepted August 8, 2016]

1. Introduction

The synthesis technique in high pressure and high temperature conditions is useful to synthesize C–N inorganic compounds. The most familiar target materials by using this synthetic technique is C_3N_4 because cubic C_3N_4 has been theoretically expected to be harder than diamond.¹⁾ In addition to researches on hard materials, recent studies also focus on the capability of the C–N compounds for hydrogen storage materials.²⁾ Accordingly, various kinds of molecular substances have been tried as a precursor so as to synthesize the inorganic C–N compounds including cubic C_3N_4 in high pressure and temperature. For example, Bordon et al. reported high pressure syntheses of the carbon nitride imide $C_2N_2(NH)$ from the single-source precursor 1-cyanoguanidine under high-pressure and high-temperature conditions.³⁾

There are numerous reported studies related to inorganic C–N compounds.⁴⁾ In the previous studies, a Laser-Heated Diamond-Anvil Cell (LH-DAC) was often used to synthesize the cubic C_3N_4 and related compounds. The manuscript by Bordon et al. above also employed the synthesis experiments by using LH-DAC.³⁾ Kojima and Ohfui have recently reported an interesting report on structure and stability of carbon nitride by using LH-DAC.⁵⁾ They investigated the crystal structure of carbon nitride under high pressure and temperature up to megabar pressures using graphitic C_3N_4 as a starting material. They reported that it transformed to an orthorhombic phase above 30 GPa and 1600 K which had similar unit cell parameters [$a = 7.6251(19)$, $b = 4.4904(8)$, and $c = 4.0424(8)$ Å at 1 atm] to those of reported hydrogen-bearing carbon nitride phases such as $C_2N_2(NH)^{3)}$ and $C_2N_2(CH_2)^{6)}$. They also determined content the ratio of nitrogen and carbon (N/C) to be 4/3. We have also reported the

organic-to-inorganic conversion from molecular 1,2,4-triazole using LH-DAC in the field of 15 GPa and about 2500 K.⁷⁾ It was found that the synthesized compounds had two kinds of morphology, depending on the synthesis conditions. One was a candy-like morphology of which XRD pattern indicated the amorphous state. The other was a complicated rose-flower-like one and was composed with the network of thin platelet crystals in $\sim$ nm thickness.

Although the synthesis technique in high pressure and high temperature using LH-DAC is useful to synthesize inorganic C–N compounds, as mentioned above, it is difficult to control the heating temperature of a sample in DAC when the LH-DAC is employed for the syntheses. This means the difficulty of the systematic studies concerned with the high pressure synthesis of the C_3N_4 . Therefore, we have studied the synthesis of inorganic C–N compounds as a function of temperature using a multianvil-type large volume press by which we can control the sample temperature precisely. In this study, inorganic C–N compounds have tried to be synthesized from molecular 1,2,4-triazole as a starting material which has a five-membered ring of carbon and nitrogen atoms, and the nitrogen content, morphology and crystal structure of the synthesized C–N compounds were evaluated.

2. Experimental procedure

Samples were synthesized by a high-pressure and high-temperature method using a DIA-type multianvil press apparatus. The starting material was a white powder of 1,2,4 triazole ($C_2N_3H_3$; 98% purity, ALDRICH). The sample cell assembly for the high-pressure and high temperature treatments is shown in Fig. 1. The powder was encased in a BN capsule. The treatment pressure was fixed at 5 GPa and the heating temperatures were 300–1000°C. The pressure was increased up to 5 GPa for about 20 min, and then the temperature was increased at a rate of 100°C/min up to the target temperature. The sample was heated for 30 min and then cooled down rapidly to room temperature in a few seconds by turning off the heater. After these treatments the

[†] Corresponding author: M. Hasegawa; E-mail: hasegawa@numse.nagoya-u.ac.jp

^{††} Present address: Kyoto Prefectural University, Japan

^{†††} Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.124.P10-1>

Fig. 1. Sample cell assembly for the high-pressure and high temperature treatments.

Fig. 2. SEM image of the recovered sample synthesized at 5 GPa, 700°C.

pressure was decreased to ambient pressure.

After the samples were recovered at ambient pressure, they were subjected to the powder X-ray diffraction (X-ray source; Cu-K α) and Raman spectroscopy (Excitation laser; 514.5 nm, 100 mW) experiments in order to be identified. They were also inspected by a Scanning Electron Microscopy (SEM)-Energy Dispersive X-ray spectroscopy (EDX) analyses for observation of morphology and analysis of nitrogen and carbon ratio N/C. The N/C content ratio was also measured by the Rutherford backscattering spectroscopy (RBS) at the Wakasa Wan Energy Research Center.⁸⁾ In this measurement, 2-MeV He²⁺ ions from a tandem accelerator were used for the incident beam, and scattered ions were detected at 150 degree. The obtained RBS spectra were analyzed using SIMNRA code⁹⁾ and then the N/C ratio was evaluated based on these analyses.

3. Results and discussion

All recovered samples were black. It is interesting that they were not sintered and quite brittle to be easily broken by a tweezers although they were heated at 5 GPa, as shown in Fig. 2 (SEM image). This is clearly different from the general results of hard sintering syntheses of inorganic compounds in GPa range pressures. This suggests that some gas or fluid such as H₂, N₂ and NH₃ was probably produced during the treatment of 1,2,4 triazole under high pressure and temperature.

Figure 3 shows the heating temperature dependence of the XRD patterns of the recovered samples after heating at high pressures and temperatures. All XRD patterns show a diffraction

Fig. 3. Heating temperature dependence of XRD patterns of recovered samples after heating at 5 GPa. The triangular symbols represent the diffraction peak derived from the synthesized inorganic C–N compounds while the circular symbols correspond to the diffraction peaks from NaCl which was used as internal standard material.

Fig. 4. *d*-value of the 002 reflection equivalent of the distance between graphene layers as a function of heating temperature at 5 GPa. Solid line is guide for eye.

around 26° which corresponds to the 002 reflection line of the graphite structure. This indicates that all recovered samples have a graphite-like structure. It should be noted that the reflection angle depends systematically on the heating temperature. Since the *d*-value of the 002 reflection is equivalent to the distance between graphene layers, the inter-layer distance also changes systematically depending on the heating temperature, as shown in Fig. 4. The *d*-value increases rapidly with increasing heating temperature and then almost saturates above about 600°C. The saturated *d*-value is close to that of pure graphite and suggests that most of nitrogens are removed by heating temperature above 600°C at 5 GPa.

It should be also noted that the 002 reflection of all samples are broad, indicating low crystallinity, i.e. bumpy graphene layers in the graphite-like structure of the recovered samples. Figure 5 shows the Raman spectrum of the recovered sample heated at 500°C and 5 GPa. The peaks basically corresponding to the D and G bands of the graphite in this spectrum are also broad, which is consistent with the broad reflection peak of the XRD pattern. This is attributable to the substitution of nitrogens for carbons in the graphene layers. Two types of the substituted nitrogen state can be proposed as shown in Fig. 6. One is shown in Fig. 6(a), i.e.

Fig. 5. Raman spectrum of the recovered sample heated at 500°C, 5 GPa. The left and right peaks correspond to the D and G bands, respectively.

Fig. 6. Two types of the substituted nitrogen state in inorganic C-N compounds. (a) type 1: the substituted nitrogen has three bonds with neighboring three carbons, (b) type 2: the nitrogen have two bonds with neighboring two carbons in the layer. (c) schematic illustration of the nitrogen-substituted graphene layers containing types 1 and 2.

the substituted nitrogen has three bonds with neighboring three carbons. This atomic arrangement in the layer is basically the same as that of the graphite. The other is shown in Fig. 6(b), in which the nitrogens have two bonds with carbons in the layer.

Teter and Hemly proposed a structural model of the graphite-type C_3N_4 .¹⁰⁾ In their model there are two types of nitrogen as shown in Fig. 6. We have calculated the bond distance between carbon and nitrogen using their structural data; 1.44 Å for the former type in Fig. 6(a) and 1.32 Å for the latter in Fig. 6(b). In addition, the distance between two carbons in the pure graphite is calculated to be 1.42 Å using the reported structural data.¹¹⁾ Therefore, when nitrogens are substituted for carbons in the graphene layers, the layers are curved and bumped because of the difference among C-C and two C-N bond distances mentioned above. As a result, the layered C-N structure has lower crystallinity than pure graphite one and results in the broad 002 reflection in the XRD pattern in Fig. 3.

It should be noted again that the 2θ scattering angle and broadness of the 002 reflection depend systematically on the heating temperature at 5 GPa. This suggests that the nitrogen content of these recovered samples also changes depending on the heating temperature. Accordingly, we have analyzed their nitrogen content by two methods, i.e. RBS spectroscopy and SEM-EDX. The RBS spectra are shown in Fig. 7 as a function of the heating temperature. The nitrogen/carbon content ratio (N/C) of all samples estimated by the two methods are listed in Table 1 and also shown in Fig. 8 as a function of the heating temperature. It is found that the N/C, i.e. nitrogen content decreases rapidly with increasing heating temperature and almost become constant above about 600°C. However, it should be noted that nitrogen still remain even after heating at 1000°C.

Since the d -value of the 002 reflection may be related to the

Fig. 7. RBS spectra as a function of the synthesis heating temperature at 5 GPa.

Table 1. Analysis results of nitrogen/carbon (N/C) content ratio of the synthesized samples by Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX)

RBS		SEM-EDX	
Heating Temperature	N/C	Heating Temperature	N/C
400°C	0.46	400°C	0.57
400°C	0.27	500°C	0.33
500°C	0.046	600°C	0.036
700°C	0.067	700°C	0.098
900°C	0.12	800°C	0.049

Fig. 8. Synthesis heating temperature dependence of nitrogen/carbon (N/C) content ratio analyzed by RBS and SEM-EDX. Blue and red colored circles correspond to the data of RBS and SEM-EDX measurements, respectively. Solid line is guide for eye.

nitrogen content, it is interesting to plot the relationship between the N/C ratio and d -value of the 002 reflection. Figure 9 shows the d -value as a function of the ratio of carbon and nitrogen, N/C. It should be noted that the d -value decreases monotonously with increasing N/C ratio, i.e. being substituted by nitrogen for carbon. Two main reasons for this relationship can be expected. One is the difference of atomic size between carbon and nitrogen. Since nitrogen atom is smaller than carbon one, the substitution by nitrogen for carbon results in the decrease of the distance between graphene layers. The other is the Van der Waals attrac-

Fig. 9. Relationship between the N/C ratio and d -value of the 002 reflection equivalent of the distance between graphene layers. Blue and red colored circles correspond to the data by RBS and SEM-EDX measurements, respectively.

Fig. 10. Schematic illustrations to explain the Van der Waals attraction between C–N graphene layers. (a) graphene layers of pure graphite. (b) nitrogens are electrified by substitution for carbon to be negative locally (gradated red part) and the other part are to be positive. (c) Van der Waals attraction between C–N graphene layers.

tion between graphene layers, as shown in **Fig. 10**. Carbon atoms in pure graphene layer is formed by a strong sp^2 hybridized bondings. On the other hand, the inter-layer interaction is a weak Van der Waals force. When nitrogen is substituted for carbon, the nitrogens slightly attract electrons around neighboring carbons because of the difference of the electronegativity between nitrogen and carbon, i.e. nitrogen has higher electronegativity than carbon. Therefore, nitrogens are charged to be negative locally and the other part are to be positive, as shown in Fig. 10(b). As a result, the negatively charged part (δ^-) and positively one (δ^+) are attracted with each other between two layers, as shown in Fig. 10(c). This results in the decrease of the inter-layer distance with increasing nitrogen content, i.e. N/C ratio.

4. Conclusions

High pressure synthesis of inorganic C–N compounds has been investigated as a function of temperature using a DIA-type multi-anvil press apparatus by which we can control the sample temperature precisely. The inorganic C–N compounds have tried to be

synthesized from molecular 1,2,4-triazole $C_2N_3H_3$ systematically as a starting material which is an organic compound having a five-membered ring of carbon and nitrogen atoms, and be investigated from the viewpoints of nitrogen content and crystal structure.

Graphite-like carbon nitride inorganic compounds have been successfully obtained in high temperatures above 400–1000°C at 5 GPa. The N/C content ratio of the carbon nitrides can be systematically controlled by the heating temperature. The substitution of nitrogen for carbon in graphene layers results in the low crystallinity of the synthesized C–N compounds because of the difference of C–C and C–N bond lengths. Furthermore, it should be noted that the distance between two C–N graphene layers increases monotonously with increasing N/C content ratio, i.e. being substituting by nitrogen for carbon. One of the reasons for this relationship is the larger atomic size of nitrogen than that of carbon. The other is the Van der Waals attraction between C–N graphene layers which results from the different electronegativity between nitrogen and carbon.

Acknowledgements This work is partially supported by both of the JSPS Grants-in-Aid for Scientific Research and the Collaborative Research Project of the Wakasa Wan Energy Research Center.

References

- 1) A. Y. Liu and M. L. Cohen, *Science*, **245**, 841–842 (1989).
- 2) X. D. Bai, D. Zhong, G. Y. Zhang, X. C. Ma, S. Liu and E. G. Wang, *Appl. Phys. Lett.*, **79**, 1552–1554 (2001).
- 3) E. H.-Bordon, R. Riedel, P. F. McMillan, P. Kroll, G. Miehe, P. A. Van Aken, A. Zerr, P. Hoppe, O. Shebanova, I. McLaren, S. Lauterbach, E. Kroke and R. Boehler, *Angew. Chem., Int. Ed.*, **46**, 1476–1480 (2007).
- 4) for example of recent reviews, Y. Zheng, L. Lin, B. Wang and X. Wang, *Angew. Chem. Int. Ed.*, **54**, 12868–12884 (2015). J. Zhang, Y. Chen and X. Wang, *Energy Environ. Sci.*, **8**, 3092–3108 (2015).
- 5) Y. Kojima and H. Ohfuji, *Diamond Relat. Mater.*, **39**, 1–7 (2013).
- 6) M. Sougawa, T. Sumiya, K. Takarabe, Y. Mori, T. Okada, H. Gotou, T. Yagi, D. Yamazaki, N. Tomioka, T. Katsura, H. Kariyazaki, K. Sueoka and S. Kunitsugu, *Jpn. J. Appl. Phys.*, **50**, 095503 (2011).
- 7) K. Niwa, M. Hasegawa, Y. Jin, T. Tanaka, K. Kusaba and T. Yagi, 3rd International Congress on Ceramics (ICC3), Osaka, S2B008 (2010).
- 8) S. Hatori, T. Kurita, Y. Hayashi, M. Yamada, H. Yamada, J. Mori, H. Hamachi, S. Kimura, T. Shimoda, M. Hiroto, T. Hashimoto, M. Shimada, H. Yamamoto, N. Ohtani, K. Yasuda, R. Ishigami, M. Sasase, Y. Ito, M. Hatashita, K. Takagi, K. Kume, S. Fukuda, N. Yokohama, G. Kagiya, S. Fukumoto and M. Kondo, *Nucl. Instrum. Methods Phys. Res. B*, **241**, 862–869 (2005).
- 9) M. Mayer, Computer simulation of RBS, ERDA and NRA, <http://home.mpcdf.mpg.de/~mam/>.
- 10) D. M. Teter and R. J. Hemley, *Science*, **271**, 53–55 (1996).
- 11) Y. X. Zhao and I. L. Spain, *Phys. Rev. B*, **40**, 993–997 (1989).