High-Temperature High-Pressure Synchrotron X-Ray Diffraction Study of C_3N_4 *

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Abstract Pure beta-C_3N_4 with symmetry group P63/M (176) and cubic C_3N_4 were synthesized in laser heated diamond anvil cell under high pressure and high temperature conditions. The precise XRD analysis ($R_{wp} = 2.8$) was successfully performed to refine the structures of graphite C_3N_4 and beta-C_3N_4. Moreover, the structural transition from beta-C_3N_4 to cubic C_3N_4 was monitored by In-situ high pressure synchrotron X-ray diffraction analysis.

Key words C_3N_4, laser heated diamond anvil cell, high pressure, synchrotron, X-ray diffraction

1 Introduction

By means of combination of an empirical model and an ab initio calculation, the theorist Marvin L. Cohen had predicted in 1985 that carbon nitrides should be candidates for superhard materials[1, 2]. After that, Liu and Wentzcovitch refined the structure of beta-C_3N_4 and investigated two other structural phases with composition C_3N_4 using an ab initio VCS MD algorithm[3]. In 1996, Teter and Hemley performed a more systematic study of the properties of carbon nitrides using first-principles calculations[4]. The equilibrium structural parameters, bulk moduli and total energies for graphite C_3N_4, alfa-C_3N_4, beta-C_3N_4, cubic C_3N_4 and pseudocubic C_3N_4 were presented. The vibrational and many other properties of C_3N_4 have also been studied by J. Widany et al.[5]

Motivated by these results in theory, scientists have paid more attention to synthesize covalent C-N solids as a kind of dense and hard materials for many years. Another goal of these efforts is to verify if one can design a material beginning with theories to select candidates for laboratory synthesis, as is pointed out by Wang[6, 7]. Various physical and chemical methods have been adopted, such as high pressure high temperature; sputtering; plasma; chemical vapor deposition etc.[8—11]. Several different types of carbon nitrides with composition C_xN_y have been synthesized. As yet, however, pure samples with single phase of beta-C_3N_4 or cubic C_3N_4 have not been observed.

In this paper, we present our new progress in synthesis of carbon nitrides. Samples with single phase of beta-C_3N_4 were produced under high pressure and high temperature conditions. The X-ray diffraction patterns together with Rietveld refinement were presented. Furthermore, the phase transition from beta- to cubic C_3N_4 was interpreted by In-situ high pressure synchrotron X-ray diffraction analysis.

2 Experimental

The original material used for synthesis is the graphite C_3N_4, which was prepared by Ma[12], using Multi-cell high-pressure high-temperature synthesis technique, detailed procedure of the experiment

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was described in Ref. [12]. The chemical composition was analyzed by bulk elemental analysis on a Perkin-Elmer 240C Elementa Analyzer, showing that C/N ratio of the product is 3/3.94. X-ray diffraction pattern of the graphite C_3N_4 is presented in Fig. 1. Rietveld refinement confirmed that the graphite C_3N_4 forms a hexagonal structure with space group P-6M2, the lattice parameter is: $a = b = 4.74281$Å, $c = 6.42763$Å, unit cell volume is 125.214 Å^3. The criterion for the agreement between the simulated and experimental diffraction pattern is the factor R_{wp}, Our Rietveld refinement yielded the R-factors with $R_{wp} = 3.42$, $R_p = 2.64$, which indicated that the simulated is very precise. Therefore, considering the elemental analysis and X-ray diffraction result, we confirmed that the sample is graphite C_3N_4, Compared with the c value calculated by Hemley[4], our result is slightly smaller, possibly resulting from the residual stress in the bulk materials.

High-pressure high-temperature experiments were performed to synthesize beta-C_3N_4 using laser heating diamond anvil cell technique on an in-situ HPHT Raman scattering system. The system is described detailedly elsewhere[13]. The graphite C_3N_4 was loaded into a 200μm sample chamber drilled in the center of a 250μm thick T301 steel foil. Diamonds with culet diameters of 500μm were used to compress the sample. No pressure medium or heat isolator was used to keep the sample clean. The pressure was increased up to 6.6GPa and then heated by 1053nm laser to 1800K. After that, the sample was annealed at 1350K for ten minutes. The product in the DAC was then picked out carefully from the gasket for X-ray scattering experiment.

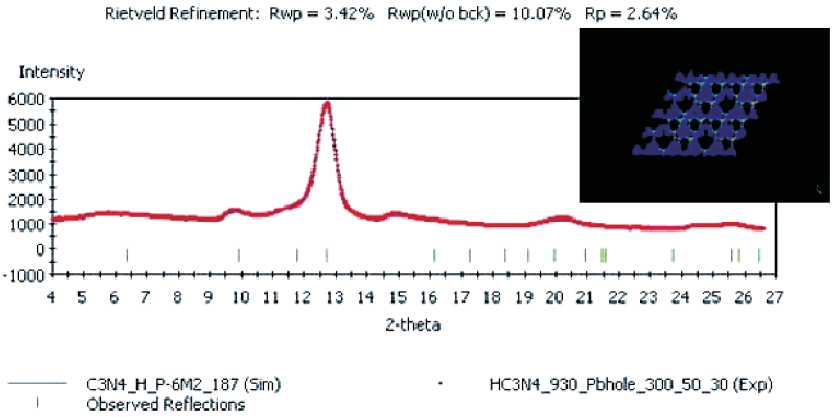

Fig. 1. X-ray diffraction pattern of the graphite C_3N_4.

After the pure beta-C_3N_4 phase was acquired, we loaded the beta-C_3N_4 into a 70μm sample chamber drilled in the center of a T301 steel foil gasket, which is pre-compressed to 30μm thick. A pair of diamond with culet diameter of 200μm was used to generate high pressures up to 50GPa. No pressure medium was used but a small crystal ruby was added as pressure calibrant. In-situ high pressure synchrotron X-ray diffraction measurements were carried out at the Beijing Synchrotron Radiation Facilit (BSRF). The electron energy of storage ring worked at 2.2GeV, electron beam current was 95—70mA. The energy dispersive X-ray diffraction spectra were collected for 800s at each pressure interval with a solid Si-Li detector at a fixed 2θ angle of 23.94.

3 Results and discussions

Fig. 2 shows the X-ray diffraction pattern of pure beta-C_3N_4 derived from graphite C_3N_4[12]. Rietveld refinement was performed to optimize the lattice parameter, and the refinement result is also very precise with a precision of $R_{wp} = 2.81$, $R_p = 1.98$. The obtained beta-C_3N_4 forms the hexagonal structure with space group P32/M, the lattice parameter is: $a = b = 6.32586$Å, $c = 2.44752$Å, which is also smaller than the value calculated by Hemley[4].

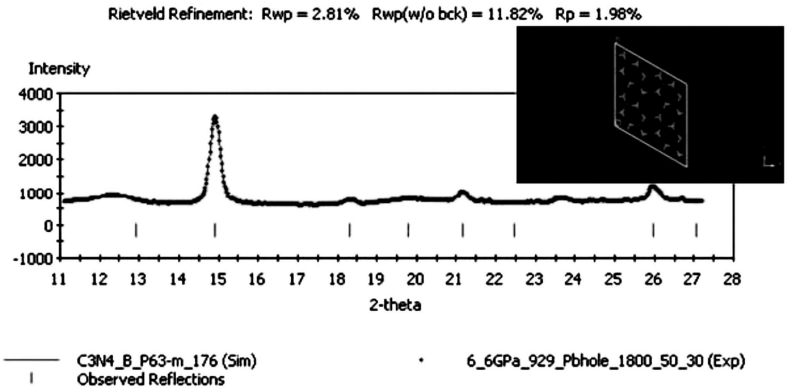

Fig. 2. X-ray diffraction pattern of the beta-C_3N_4.

The energy dispersive X-ray diffraction patterns of C_3N_4 at different pressures and ambient temperature were presented in Fig. 3. It is obvious to note that the characteristic peak of beta-C_3N_4 which locates at 16keV at ambient pressure became weakened and two other peaks which belong to cubic C_3N_4 as calculated by Hemley[4], emerged when pressure is increased to 6GPa. It is remarkable that both of the two phases of cubic C_3N_4 and beta-C_3N_4 are all have these two peaks, so the phase transition pressure should be point that the characteristic peak of beta-C_3N_4 is disappear. From Fig. 3 we can see that two phases of beta- and cubic C_3N_4 coexist between 6GPa and 19GPa. Then the pure cubic C_3N_4 was obtained when the pressure is higher than 19GPa. During the process of continue compression, no major change of the diffraction peaks happens except that all lines move towards high energy direction. The energy dispersive X-ray diffraction pattern of cubic C_3N_4 has been indexed with the hkl Miller indices of (211), (220), (321) and (420), which are shown in Fig. 3. The cubic C_3N_4 is stable up to 55GPa, the highest pressure this experiment could reached. A more complete study of the transition from beta-C_3N_4 to cubic C_3N_4 and other properties is in progress and will be reported elsewhere.

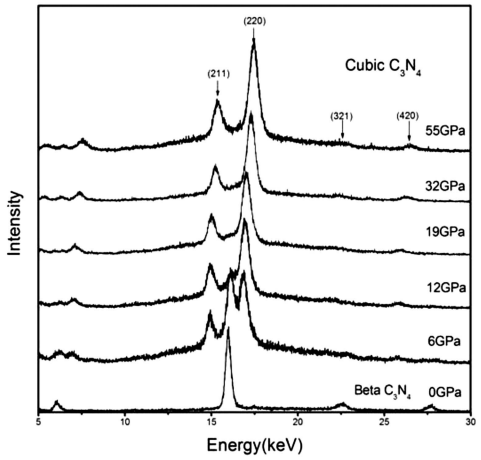

Fig. 3. Energy dispersive X-ray diffraction pattern of C_3N_4 at different pressures and ambient temperature.

4 Conclusions

In summary, we first report the synthesis of pure beta-C_3N_4 and cubic C_3N_4 in laser heated diamond anvil cell under high pressure and high temperature conditions. The obtained beta-C_3N_4 and cubic C_3N_4 was characterization successfully by XRD Analysis ($R_{\rm wp} = 2.8$). Furthermore, in-situ high pressure synchrotron X-ray diffraction analysis indicated that the structural conversion from beta-C_3N_4 to cubic C_3N_4 began at pressure of 6GPa and the pure cubic C_3N_4 was obtained when the pressure is higher than 19 GPa.

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C_3N_4的高温高压同步辐射研究*

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摘要 利用激光加热金刚石对顶砧技术在高温高压条件下合成了纯beta相和立方相C_3N_4, beta相C_3N_4所属对称群为P63/M (176). 对石墨相与beta相C_3N_4的X射线衍射结果进行了精确分析, 得到优化晶胞参数. 原位高压同步辐射X射线衍射分析表明, 在6GPa时由beta相到立方相C_3N_4的相转变已经发生, 之后两相共存直到19GPa时相变结束得到纯立方相C_3N_4.

关键词 C_3N_4 激光加热金刚石对顶砧 高压 同步辐射 X 射线衍射

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