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Phase transformation of melamine at high pressure and temperature

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Abstract Pyrolysis experiments of melamine were carried out under high pressure of 5 GPa and different temperatures. The crystal structure, chemical bonding, and composition of the melamine pyrolysate were studied by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray energy-dispersive analysis (EDX), and combustion elemental analysis. A new C–N–H phase was found in the pyrolysate at 5 GPa and 800 °C. The structure is tentatively indexed as a monoclinic symmetry, with the following lattice parameters: $a = 8.5368$ (±0.0009)Å, $b = 9.1153$ (±0.0010)Å, $c = 10.2440$ (±0.0011)Å, $\alpha = \gamma = 90°$, and $\beta = 95.5696$ (±0.0016)°. The photoluminescence behavior of the pyrolysates was investigated. A blue emission at 421 nm for the C–N–H phase was observed under the ultraviolet light excitation of 365 nm.

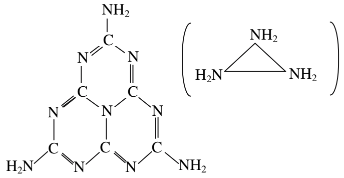
Introduction

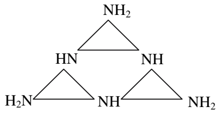
Melamine is a conventional material used as a fire retardant additive for polymeric materials, with a stable heterocyclic structure (triazine). In the early literature, the thermal behavior of melamine was extensively studied [1–3]. The following pyrolytic reactions were reported:

$$2C_3H_6N_6 \xrightarrow{350--400°C} C_6H_6N_{10} \text{ (melamine} \rightarrow \text{melem)}$$

$$3C_6H_6N_{10} \xrightarrow{400--600°C} 3C_6H_3N_9 \text{ (melem} \rightarrow \text{melon)}$$

The structures for melem and melon have been determined [1]:


melem


melon

Melon, which is a kind of brown powder, is considered to be the final thermal condensate from melamine. However, it may be possible that a carbon nitride compound, C_3N_4, can be formed by eliminating ammonia from melon under appropriate conditions, as given by the following reaction:

$$C_6N_9H_3 \longrightarrow 2C_3N_4 + NH_3$$

It has been reported [3] that the pyrolysis of melon is very difficult at ambient pressure due to a large amount of volatile products formed. Hence how to eliminate ammonia from melon is the key to obtaining C_3N_4.

High-pressure technology is considered to be one of the appropriate methods of obtaining C–N compounds. In 1990, Sekine et al. [4] reported the synthesis of a carbon nitride compound from high-pressure pyrolysis of nitrogen-bearing organic materials. The materials employed in their study were telracyanoethylene (C_6N_4) and 1,3,5-triazine ($C_3H_3N_3$) powders. Their experiments were carried out at a pressure of 5 GPa and a temperature of about 1,400 °C, and analyses showed that the product was a carbon nitride substitute with a layered graphite-like structure.

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Maya et al. [5] attempted to prepare carbon nitride by means of pyrolyzing a series of relatively high nitrogen containing organic materials at 700 °C under a pressure of 225 MPa. An amorphous solid was produced with a short-range layered structure containing both trigonal carbon and nitrogen. They postulated that much higher pressures would be required to derive crystalline carbon nitride from the high nitrogen containing organic compounds. Alves et al. [6] suggested that melamine, in a nitridizing environment, may undergo the following reaction:

$$C_3N_6H_6 \xrightarrow[\text{HP, HT}]{NH_2NH_2} C_3N_4 + 2NH_3$$

A brown material with a turbostratic-type structure was obtained in their experiments under 3 GPa and about 800 °C. Montigaud et al. [7, 8] conducted a similar study at 2.5 GPa and 800 °C, and obtained macroscopic samples of C_3N_4 in the graphitic form. Nguyen et al. [9] reported a new crystalline carbon nitride phase synthesized from a mixture of carbon and nitrogen heated to 2000–2500 K at 30(±5) GPa. Terrones et al. [10] claimed that they have successfully prepared C_xN_y nanofibers by pyrolyzing melamine over laser-patterned Fe and Ni substrates. Yao et al. [11] investigated the decomposition of melamine at 4.5 GPa, 800 °C and obtained an intermediate phase with long periodicity along one direction. The above results show that melamine may be an ideal material for synthesizing carbon nitride compounds at high pressure and temperature. However, the detailed polymerization behavior of melamine at high pressure, up to 5 GPa, has been little reported.

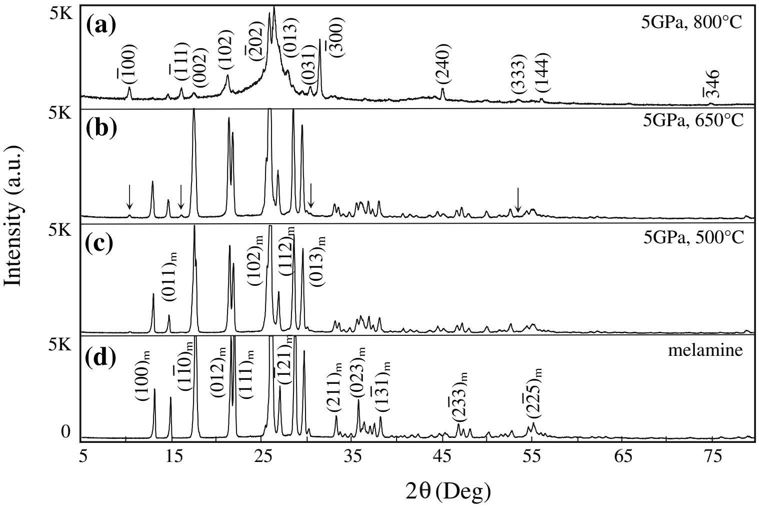
Experimental details

Pure melamine was used as a starting material. Melamine powder was pressed into a cylinder of 8 mm in diameter and 10 mm in length in a steel die under 25 KN and then placed in a high-compression cell. High pressure and temperature experiments were performed in a China-type CS IB –6 × 8,000 KN cubic–anvil apparatus [12] at a pressure of 5 GPa and temperatures of 400–900 °C for 15 min. The pressure was estimated by the hydraulic load, which was calibrated by the pressure-induced phase transitions of bismuth, thallium, and barium [13]. The temperatures were calculated from the relationship between temperature and input electrical power, which had been determined using a Pt10%Rh-Pt thermocouple prior to these experiments. The morphology of the samples was examined by SEM (KYKY 2800) and crystallinity of the pyrolytic products of melamine was characterized by XRD (Rigaku D/Max-rB diffractometer). Chemical composition was determined by EDX (Kevex level 4) attached to the scanning electron microscope and combustion elemental analysis (CHN100). XPS spectra of the samples were recorded using a ESCALAB MarkII spectrometer. The vibrational spectra were obtained by an FTIR spectrometer, and photoluminescence (PL) properties by SPEX FL-2T2 spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source.

Results and discussion

XRD spectra shown in Fig. 1 reveal that melamine is stable to at least 500 °C at 5 GPa. Above 650 °C, several new reflections, such as those at 2θ angles of 10.421°, 16.203°, 30.558°, and 53.749° begin to arise. Simultaneously, most peaks of melamine gradually disappear. When the pyrolysis temperature reaches 800 °C, at 5 GPa, 12 new peaks appear in the XRD spectrum of the sample shown in Fig. 1a, which predicts a possible new C–N–H phase to be formed in the pyrolysis. Careful peak fitting analysis was

Fig. 1 XRD spectra of melamine and its pyrolyzates recovered from 5 GPa and different temperatures



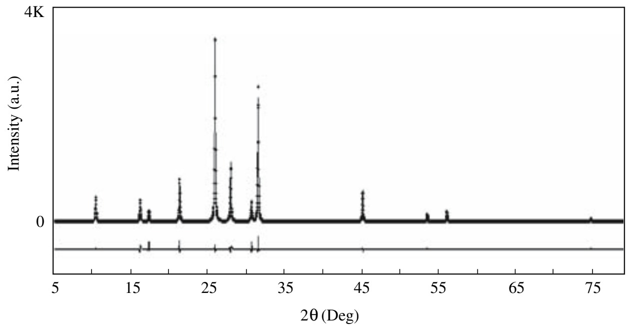


Fig. 2 Pawley refinement plot of the powder diffraction data for the new phase. Upper: experimental (crosses) and calculated (line) powder diffraction profiles; lower: difference between these two patterns

carried out for the XRD spectrum in Fig. 1a using the Pawley fitting technique in the Reflex module of Materials Studio programme [14]. Figure 2 is the Pawley refinement plots for the new phase on the basis of space group $P2_1/c$, in which one obvious amorphous background and two peaks of melamine were subtracted. The refined parameters include the zero point shift of the diffractogram, background parameters, and profile parameters. The new phase can be tentatively indexed as monoclinic structure with the following cell parameters: $a = 8.5368$ (±0.0009)Å, $b = 9.1153$ (±0.0010)Å, $c = 10.2440$ (±0.0011)Å, $\alpha = \gamma = 90°$, and $\beta = 95.5696$ (±0.0016)°. The resulting R factors reached Rwp = 11.78% and Rp = 8.09%. Because the new phase formed is associated with complicated polymeric reaction between melamine molecules, only the cell parameters were fitted in this work. The detailed atoms position in the unit cell need further studies. The experimental XRD data, calculated data related to the new phase, and the errors are listed in Table 1. Melamine is obviously carbonized when the temperature rises to 900 °C under 5 GPa.

It is known that crystalline melamine is a molecular crystal with a monoclinic structure belonging to the space group $P2_1/c$, with lattice parameters $a = 7.27$ Å, $b = 7.48$ Å, $c = 10.57$ Å, $\alpha = \gamma = 90°$, and $\beta = 112.33°$. By comparing the lattice parameters of melamine with the new phase, it can be noticed that a and b values in the new phase lattice are larger than those of melamine, while β of new phase is smaller. On the basis of melamine crystal lattice structure and space group ($P2_1/c$), we know that melamine molecules are linked to each other in the $(10\bar{4})$ plane. Application of 5 GPa forces the melamine molecules to polymerize within the $(10\bar{4})$ plane and causes the $(10\bar{4})$ planes in the melamine crystal lattice to slip along the <401> direction. The extension of the $(10\bar{4})$ interplanar spacing leads to an increase in the lattice constants of a and b. The slip between adjacent $(10\bar{4})$ planes results in a decrease in the β-angle. The phase change is shown in Fig. 3. If the pressure increases further, β might decrease to 90° when the polymeric reaction reaches to such an extent that the layered polymer fragments are large enough and aligned vertical to the c axis. The new phase would possess two possible structures, orthorhombic or hexagonal, depending on the symmetry of the polymeration.

Besides the characteristic reflections of the new crystalline phase, one obvious amorphous peak centered around $2\theta = 26.08°$ also appears in the XRD spectrum shown in Fig. 1a. Radial distribution function (RDF) based on the amorphous peak indicates an average coordination number

Table 1 Reflections in the XRD spectra of the melamine pyrolysate obtained at 5 GPa, 800 °C (indexed according as $a = 8.5368$ (±0.0009)Å, $b = 9.1153$ (±0.0010)Å, $c = 10.2440$ (±0.0011)Å, $\alpha = \gamma = 90°$, and $\beta = 95.5696$ (±0.0016)°)

2θ / °	Experimental interplanar distance	Calculated interplanar distance from new phase		Error $(d_{cal} - d_{exp})/ d_{cal}$
	d_{exp}/Å	d_{cal}/Å	$h\ k\ l$	
10.421	8.482	8.495	$(\bar{1}00)$	0.0015
14.811	5.976, $(001)_{Melamine}$			
16.203	5.471	5.481	$(\bar{1}11)$	0.0018
17.551	5.054	5.096	(002)	0.0082
21.358	4.160	4.159	(102)	–0.0002
25.986	3.426	3.431	$(\bar{2}02)$	0.0015
26.525	3.358, $(200)_{Melamine}$			
28.045	3.179	3.184	(013)	0.0016
30.558	2.923	2.915	(031)	–0.0027
31.623	2.827	2.832	$(\bar{3}00)$	0.0018
45.308	2.001	2.002	(240)	0.0005
53.749	1.704	1.697	(333)	–0.0041
56.326	1.632	1.636	(144)	0.0024
75.162	1.263	1.266	$(\bar{3}46)$	0.0024

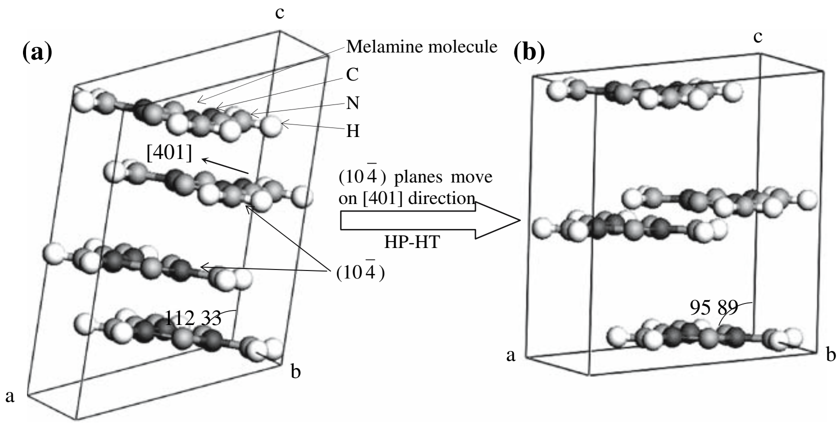


Fig. 3 (**a**) Crystal structure of melamine. (**b**) Crystal structure of the new C–N–H phase formed from melamine pyrolyzates under high pressure

of 2.568 in the amorphous structure. The average bond length is 1.336 Å. The corresponding average coordination number and bond length for the melamine are 2.2 and 1.239 Å, respectively. The rise in average coordination number and bond length indicates that melamine molecules are polymerized. Comparing the data between the pyrolytic products and melamine, we estimate that the polymer contains 13–15 pieces of melamine molecules. During polymerization, a part of H atoms in melamine molecules are eliminated by the formation of NH_3. However, some H atoms on the edge of the polymer may still be retained. The content of H atoms in the polymer is calculated to be about 13–16 at%.

The SEM image given in Fig. 4 shows that the morphology of the sample obtained at 5 GPa and 800 °C is similar to the one given in reference [5]. Many growth steps are present on the surface of particles. These grains may be grown in a mode of step growth. In order to confirm the composition we conducted EDX analyses on ten grains during SEM observation. The result indicates that the average composition of the grains is 42.7 at% C, 54.1 at% N, and 3.2 at% O. The combustion spectrum result shows that the sample contains 35.84 at% C, 46.52 at% N, and 17.52 at% H. Combining both EDX and combustion analyses, the average composition of sample is about 35.51 at% C, 45.1 at% N, 17.09 at% H, and 2.65 at% O. The element of O in the sample is considered to be a surface pollution: some water in air may have been absorbed by the particles because of the more intense chemical affinity between the group –CN– and hydroxyls (–OH). Considering effects of water pollution, the H content of sample is about 11–15 at%, which is close to the above calculating value.

FTIR spectra of melamine and the pyrolytic products at 5 GPa and different temperatures are shown in Fig. 5. The peaks are identified as the following: 3132–3468 cm^{-1}: N–H stretching modes; 2848–2925 cm^{-1}: C–H stretching modes [15]; 2367 cm^{-1}: $-C\equiv N$ stretching mode [16]; 1614 cm^{-1}: $-N{=}C<$ characteristic mode [17]; and 1052–1315 cm^{-1}: C–N stretching mode [18–20]. Comparing the spectra, we can see that the IR spectrum of the sample obtained at 800 °C is different from that of the original melamine IR spectrum. Disappearance of the N–H stretching modes at 3132–3468 cm^{-1} suggests that a majority of N–H bonds in melamine is dissociated at 800 °C under 5 GPa.

The XPS spectra of samples are presented in Fig. 6. The XPS C1s spectrum of melamine is deconvolved into four peaks at 283.44, 284.65, 285.95, and 287.63 eV (Fig. 6a). It is known that the C atoms in a melamine molecule only have one chemical state, which means that there should be only one peak in the XPS C1s spectrum for melamine. However, there are two main peaks centered at 284.65 and 287.63 eV in the spectrum. Dementjev et al. [21] also

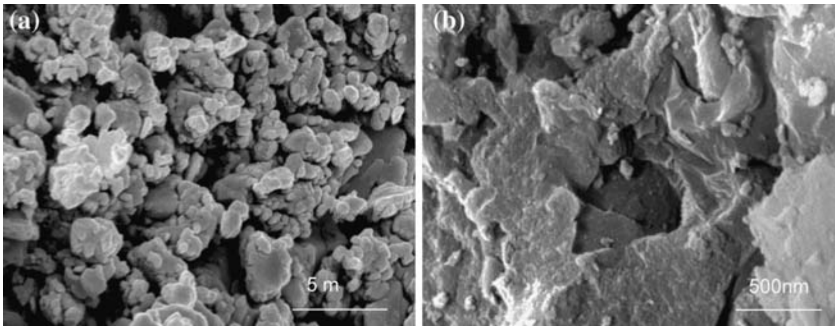


Fig. 4 The morphology of the C–N–H particles obtained from the melamine pyrolyzates

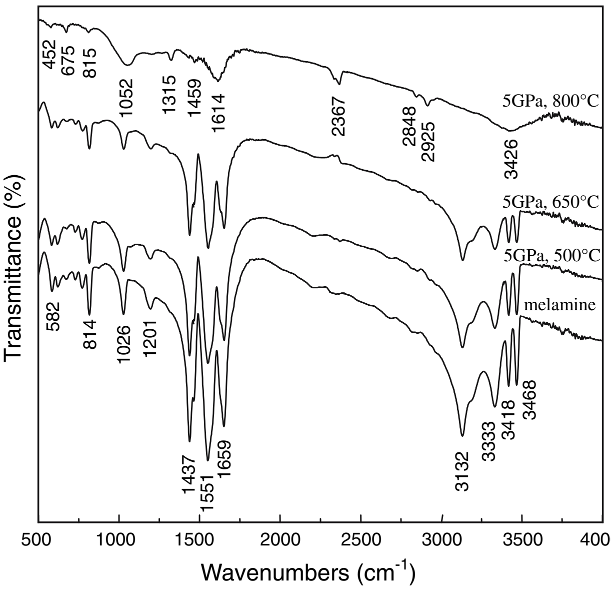


Fig. 5 FTIR spectra of melamine and its pyrolyzates obtained after high pressure and temperature treatment at 5 GPa and different temperatures

obtained the same result in their XPS spectra studies of a compressed melamine powder. They have not been able to explain this result. Generally, incorporation of the carbon impurity is unavoidable in the XPS experiment. Wagner and Bird et al. [22, 23] have reported that a C1s peak from the carbon impurity usually appears in the range of 284.62–285.58 eV. Therefore, we consider the peak at 284.65 eV to be originated from carbon impurity. Two weaker peaks, at 283.44 and 285.95 eV, are satellite peaks corresponding to a π–π* bond of the C network. The peak at 287.63 eV corresponds to the C atoms in melamine. After melamine has been treated at 5 Gpa and 800 °C, the peak of 287.63 eV split into two at 286.12 and 287.69 eV (Fig. 6b). The peak at 286.12 eV is considered to be a reflectance of the sp^{2}C=N bands in carbon nitride substance [24–26]. From the above XRD and FTIR analyses, we propose that melamine undergoes polymeric reaction, forming larger fragments consisting of 10–20 triazines under our experiment condition. Some C atoms near the edge of fragments have a chemical surrounding similar to melamine, which causes the appearance of the peak at 287.69 eV in the XPS C1s spectrum. C and N atoms in the center region of the fragments bond each other like that in graphite-like carbon nitride, resulting in 286.12 eV. The XPS N1s spectrum of melamine is composed of the two peaks, at 398.3 and 399.65 eV (Fig. 6c). The peak at 398.3 eV is ascribed to nitrogen inside the aromatic heterocycles. The peak of 399.65 eV corresponds to the amine-type nitrogen, NH$_2$. The decrease of the peak value at 399.65 eV in Fig. 6d signifies that some N–H bonds in the melamine molecule are broken under the condition of 5 Gpa and 800 °C. The peak at 401.26 eV originates from the sp^{2}C=N double bonds produced by the N atoms transposing C atoms in the graphite ring. It should be noted that there is not any information about the sp^{3}C–N bond in

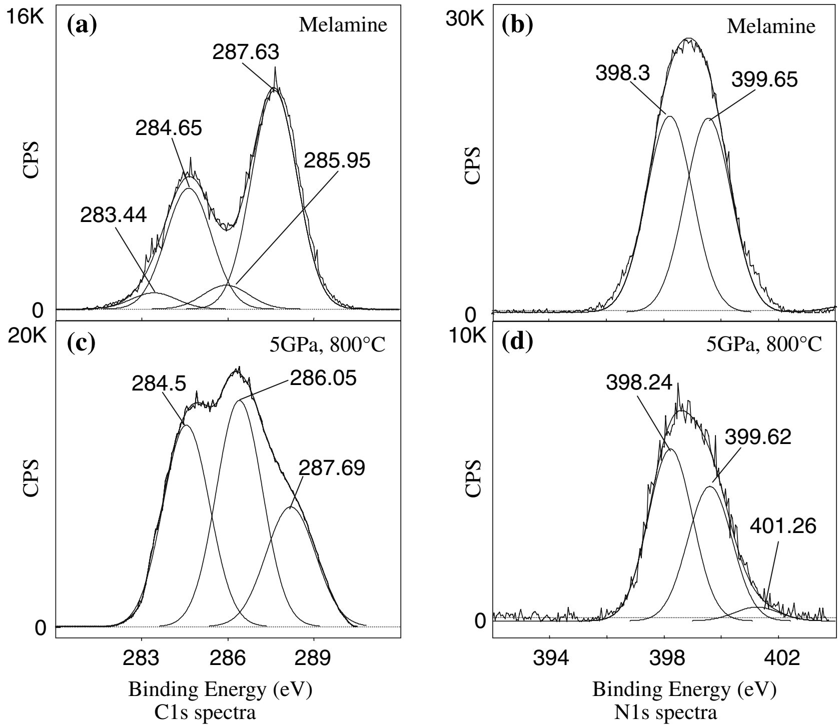


Fig. 6 XPS spectra of melamine and its pyrolysis product obtained after high pressure and temperature treatment at 5 GPa and 800 °C

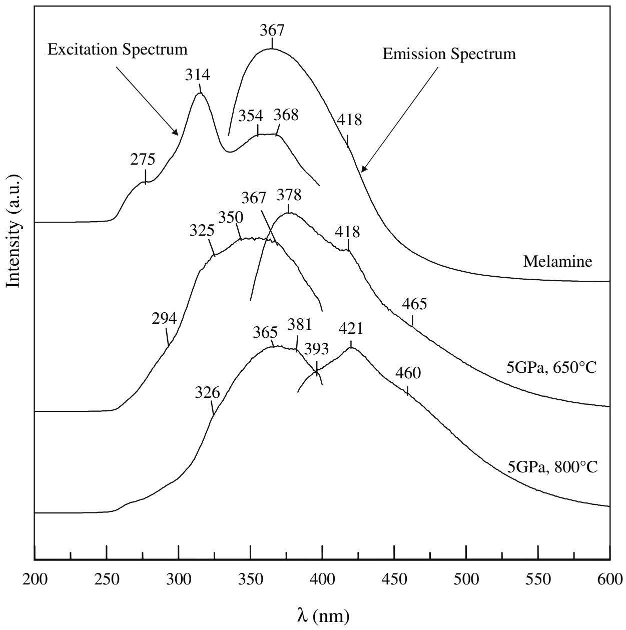


Fig. 7 PL spectra of melamine and its pyrolysates obtained under high pressure and different temperatures

the results of XPS. This indicates that the new phase still belongs to a layered crystal with low hardness.

Figure 7 shows the PL spectra of the melamine and its pyrolysates obtained under the conditions of 5 GPa, 650 °C and 800 °C. From the PL spectra we can see that the main emission peak appeared at 367 nm with an excitation wavelength of 314 nm, which is in accord with that reported in the literature [27]. The emission at 367 nm comes from the triazine moieties in the melamine molecule. A small excitation peak at 418 nm is considered to be derived from the electronic ground state associated with the forms in the triazine polymer. This indicates that a small amount of the triazine polymer already existed in the raw melamine powder. When melamine is heated at 5 GPa to different temperatures, a large number of the triazine polymers is formed, leading to the strongest excitation moving into the range of 350–381 nm. Correspondingly, the center of dominating emission peak changes from 357 nm to 418–421 nm. This result agrees well with the information obtained from the XRD and FTIR analyses where a new carbon nitride phase is formed by means of the polymerization between the melamine molecules (or 1, 3, 5-triazines).

Conclusion

A C–N–H crystalline phase with a monoclinic structure has been obtained from the pyrolyzate of melamine at 5 GPa and 800 °C. XRD analysis shows that the lattice parameters of the phase are $a = 8.5368$ (±0.0009)Å, $b = 9.1153$ (±0.0010)Å, $c = 10.2440$ (±0.0011)Å, $\alpha = \gamma = 90°$, and $\beta = 95.5696$ (±0.0016)°. The average composition of sample is about 35.51 at% C, 45.1 at% N, 17.09 at% H, and 2.65 at% O. XPS and FTIR results indicate that most of the N–H bonds in the pyrolytic product are broken under 5 GPa and 800 °C. PL analysis reveals that the monoclinic carbon nitride phase possesses properties of blue emission at 421 nm under ultraviolet light excitation. Our experiments indicate that at a pressure below 5 GPa, melamine can be transformed into another kind of monoclinic molecule crystal consisting of the triazine polymers with sp^{2}C=N bonding. Higher pressure above 5 GPa is necessary to obtain compact carbon nitride structure with sp^{3}C–N bonding.

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