



High pressure synthesis of new heterodiamond phase

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ABSTRACT

New heterodiamond phase (structure type of cubic boron nitride) with boron and nitrogen atoms partially substituted by carbon has been synthesized by using high pressure-high temperature treatment of the mixture of boron and C₃N₄ carbon nitride powders. This phase consisted of up to 5 micron-sized individual crystals. The composition of new phase was established with the help of microanalysis and structure refinement.

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1. Introduction

Promising results on synthesis of BCN phases and their characterization have been acquired fairly recently. The formation of ternary cubic phases was observed at pressures as high as 20–25 GPa and temperatures ranging from 2000 to 2500 K [1,2]. Recovered after thermobaric treatment bulk samples had nanocrystalline nature and the volume not larger than 1 mm³. The hardness of c-BC₂N measured by different methods was higher than that of (111) single-crystal cubic boron nitride [3]. The unit cell parameter of ternary cubic BC₂N and BC₄N phases were in agreement with Vegard's law for solid solution of diamond and cubic boron nitride. Nevertheless, experimental results obtained so far by different research groups are contradictory and difficult to reproduce because of yet high parameters for synthesis. Therefore, the goal of present work was to study the possibility for high pressure synthesis of heterodiamond phases at much lower parameters that will enable preparation of large volume samples and scale-up of the material for complex analysis of its structure, physical and mechanical properties and applications.

2. Experimental

We have utilized a spherical modification of carbon nitride powder of C₃N₄ stoichiometry [4,5] which consisted of nano- and submicroscale size polymer particles containing besides C and N up to 15 at.% oxygen and commercial crystalline boron powder of over 99.8% purity. Thermobaric treatment of 5 mm diameter and 3 mm high

pellets obtained from mixed powders was carried out at pressures ranging from 6 to 9 GPa in the high pressure chambers of “toroid” type. A detailed description of the experimental setup is given [6]. After stabilization of applied pressure, samples were heated up to a desirable temperature in the 500–1600 °C range, at which held for 5 to 300 s. Thereupon, the sample was quenched to room temperature followed by pressure release. Phase analysis of the samples was carried out on Bruker AXS diffractometer. X-ray diffraction data for the structure refinement were collected on a Stoe Stadi/P diffractometer with a rotating sample in symmetric transmission mode. The software program package GSAS was used for the Rietveld refinement. Microstructure studies and elemental analysis were done with scanning electron microscope (SEM) JEOL JSM-6390 and transmission electron microscope (TEM) JEM2010.

3. Results and discussion

During the previous study we have found that thermobaric treatment of nanospherical modification of carbon nitride at pressures 7–9 GPa and temperatures 500–1000 °C results in formation of hexagonal phase of carbon nitride (g-C₃N₄) with the embedded tiny crystallites of cubic C₃N₄ phase observed by TEM [7]. Temperature increase to 1200–1300 °C causes a fast decomposition of carbon nitride and formation of graphite. The present studies have shown that the addition of boron powder to carbon nitride creates a prospect for a number of chemical reactions and phase transitions to occur under high pressures. Boron content in the reaction mixture was varied from 20 to 80 wt.%. It was found that high contents of boron lead to predominant synthesis of boron carbides, while low boron contents result in decomposition of the most of carbon nitride. Therefore, in this work we present the results obtained with the mixtures of C₃N₄ and 35–50 wt.% boron.

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It was found that at pressures, ranging from 7 to 9 GPa, and temperatures above 1000 °C boron entirely reacts with the carbon nitride. Treatment times of just a few seconds become sufficient for full conversion of the precursors in the mixture. Treatment at pressures not lower than 8 GPa and temperatures in the range of 1450–1600 °C leads to formation of new cubic phase with the unit cell parameter near 3.650 Å [6]. The highest yield of this phase has been obtained from mixtures which contained approximately equal amounts of boron and carbon nitride. With pressure decrease to 7 GPa and temperature kept within 1400–1600 °C range, dramatical reduction of new cubic phase content in the products and formation of mostly graphite-like modifications has been observed (Fig. 1). Besides peaks of hexagonal boron nitride ($a = 3.32$ Å) and carbon nitride C_3N_4 ($a = 3.28$ Å), X-ray diffraction shows a peak which corresponds to an interplane distance of 3.18 Å. This peak most likely belongs to a hexagonal ternary nitride (h-BCN) phase.

According to SEM/EDX elemental analysis, all synthesized samples contained oxygen in the amount which correlated with the oxygen content in the initial carbon nitride powder. It was reasonable to expect that only boron can bind oxygen to form a stable compound. For removal of boron oxide, samples have been grinded and boiled in water. The presence of well-known boron carbide $B_{13}C_2$ was revealed in a cleaned sample which was obtained from nanosize carbon nitride and had the highest content of new cubic phase. This identification gave an opportunity for conducting a refinement of B–C–N phase parameters by Rietveld method (Fig. 2). In the X-ray diffraction of cubic phase, a reflection from (200) plane typical of F-43 m space group is present. In this type of unit cell, atoms take two four-fold positions, 4a (0,0,0) and 4c (0.25,0.25,0.25). In the course of calculations, the atomic coordinates and thermal parameters for $B_{13}C_2$ have been fixed. The results on BCN compound structure refinement are given in Table 1. According to refinement results, unit cell parameter for ternary cubic phase is 3.65515(3) Å, which exceeds by 1% the unit cell parameter for cubic boron nitride. The calculated composition of the new phase is $B_{0.918}C_{0.139}N_{0.943}$. However, if margin of error is taken into account, the maximum content of carbon in the ternary phase can be in accordance with the $B_{0.863}C_{0.250}N_{0.887}$ formula.

According to X-ray diffraction analysis, use of submicron size carbon nitride does not significantly effects the yield of ternary cubic phase which is always maintained at 70–80% level. The refinement of BCN phase unit cell parameters conducted for three samples prepared from different powder mixtures of carbon nitride and boron yielded the parameters, 3.64037(11), 3.63753(21) and 3.63567(8) Å, respectively, which are lower than those for the BCN phases synthesized from nanosize carbon nitride. SEM/EDX analysis shows that BCN phase crystallites located near the edge of the sample have submicron sizes, but those in the central part are much larger (up to 5 µm). The morphology of the crystals formed in the central part of the sample is presented by SEM image in Fig. 3a. It can be seen that some crystallites exhibit features typical for cubic phases while some particles appear as plates. The average atomic composition, determined for twelve crystals, was found to be 42.8% B, 37.1% N, 11.9% C, and 8.2% O. Similar results have been also obtained by using TEM microscopy. EDS elemental microanalysis on TEM imaged specimen (Fig. 3b) was carried out only after phase identity of individual crystals, which was established through the examination of their electron microdiffraction patterns by SAED. The average data, taken on seven crystals with cubic structure, were 45.3%B, 36.5%N, 11.6%C, and 6.6%O. Phases with the symmetry other than cubic (such as boron carbide) were found to be present in the analyzed sample as well.

Since local EDS and EDX microanalyses of chemical composition of cubic phase crystals revealed the presence of oxygen, the structure refinement by partial substitution of boron and nitrogen atoms in their positions by oxygen has been attempted. According to this refinement, oxygen does not substitute boron. This is indicated by the negative occupancy factor of oxygen in position (0,0,0), so that the refinement does not converge. In case of nitrogen substitution oxygen content in the BCN structure is 4 at.%. The presence of oxygen in crystals of BCN phase, established by microanalysis of individual particles, seems to be responsible for the increase of the unit cell parameter relatively to c-BN. At the same time, it is reasonable to believe that part of oxygen is located not only in the structure cell but both on the particle surface. As the result, on basis of structure refinement, an unambiguous conclusion on oxygen content in BCN phase is difficult to make because of large standard deviations.

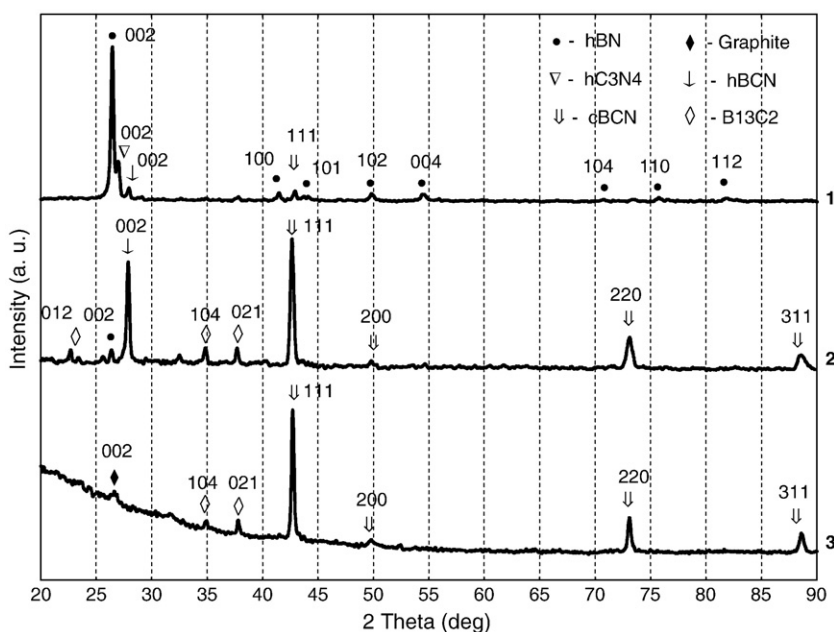


Fig. 1. X-ray ($Cu K\alpha_1$) diffraction patterns obtained after thermobaric treatment of different C_3N_4/B mixtures at variable P,T-parameters: 1–7 GPa, 1450 °C; 2–7.5 GPa, 1600 °C; 3–8 GPa, 1500 °C.

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