A System of B–C–N–O: Synthesis, Characterization and Determination of Unit Cell Parameters

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Boron-rich solids are good candidates to apply instead of diamond. Boron has a unique crystal structure and compounds of it are resistant to heat treatment. These structures have light density, high hardness, and chemically inertness. Also, boron compounds display thermal and electronic properties as a thermoelectric power at high temperatures. A boron, carbon, nitrogen, and oxygen containing compound was synthesized for the first time by classical microwave method using elemental amorphous boron, active carbon, and urea with 1:1:1 molar ratio. The compound is crystallized in monoclinic system with unit cell parameters $a = 12.9575$ Å, $b = 9.3264$ Å, $c = 9.6529$ Å, $\beta = 113.277°$ which are calculated by POWD indexing program. The X-ray diffraction, POWD, the Fourier transform infrared, scanning electron microscopy/energy X-ray diffraction spectroscopy and thermogravimetric/different thermal analysis were achieved.

1. Introduction

Diamond-like semiconductors have a bulk modulus by the reduction of interatomic distance (D), increases with the average periodic number (P) and the degree of covalent character of bonds (C). Therefore, low P and D values and high C value are necessary for high bulk modulus. As a result of this, such materials should be consisting of elements which are located in the area close to the top and center of the periodic table. But, first period elements do not have the electron which is necessary for formation of covalent bonds to create three-dimensional structure. The compounds with high bulk modulus should contain B, C, and N elements that are members of second period elements. Consequently, it is not a coincidence that diamond and cubic boron nitride are super-hard materials [1].

The boron rich solids are good candidates to be superhard materials. They exhibit attractive physical and chemical properties caused by short bond length between atoms and strong covalent characterizations. They also create refractory compounds family with a unique crystal structure [2, 3]. Boron rich phases depend on α-rhombohedral B structure which includes boron carbide and boron super-oxide. On account of having low density, high hardness and chemically inert structure make them useful as an abrasive material [4].

Boron carbide was first synthesized by oxidation of boron trioxide with carbon or magnesium in electric arc furnace by Henri Moissan in 1899 [5]. The reaction of B_4C in excessive carbon occurs by emerging big amount of carbon dioxide in a temperature over the melting point of B_4C [6]. One of the hardest materials is known after the

cubic boron nitride and diamond with 30 MPa Vickers hardness [7]. The boron carbide which chemical composition was unknown certainly, has been known as B_4C until 1940s. It has been obtained as by-product of reactions which include metal borides until 19th century [8]. However, its stoichiometric ratio was accepted as 4:1 practically, it was always known the existing of amount of carbon deficiency [9].

Urea molecule has a planar structure connecting with oxygen center bonded to two hydrogen and nitrogen atoms. The high water resolution of urea is derived from heavy hydrogen bonds between water and urea [10]. Urea can be used as a fuel in microwave reactions due to its high bonding energy and easy inflammability with intensive heat and gas output.

We aim to synthesis a B–C–N–O containing compound which can be used instead of hard materials such as diamond, cBN and BC, by the cheapest, shortest and most applicable microwave method as far as we know. A compound containing B, C, N, and O element not only use in areas needed hard materials, but also the material with all the complicated feature is used in a wide range of field needs in accordance.

2. Experimental procedure

2.1. Synthesis of B–C–N–O compound

The compound containing boron, carbon, nitrogen, and oxygen was synthesized by using amorphous boron, active carbon and urea (as a fuel) with 1:1:1 molar ratio under microwave conditions in a porcelain crucible in open air (250 MHz, 850 W, 10 min). The blackish final product was washed by hot highly pure water for removing excessive material, dried at 70 °C for 2 h and homogenized in an agate mortar.

2.2. XRD, FTIR, DT/TGA and SEM/EDX analyses

Characterization studies were performed by PAN analytical X' Pert PRO Diffractometer (XRD) with Cu K_α

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(1.5406 Å, 45 kV and 30 mA) radiation. FTIR spectrum was taken on a Perkin Elmer Spectrum 100 FTIR Spectrometer from 4000 to 650 cm^{-1}. Thermogravimetric/differential thermal analysis (TG/DTA) was carried out by Perkin Elmer Diamond TG/DTA. Morphological properties and semi-quantitative analysis of the sample were realized by ZEISS Supra 40 VP. Siemens V12 household microwave furnace was used to synthesis of the material.

3. Results and discussion

The X-ray powder diffraction pattern and data of the sample are displayed in Fig. 1 and Table I, respectively. When we compared the pattern to database of inorganic crystal structure data (ICSD), there were no corresponds to any crystal structure. Hence, we determined the crystal system and calculated the unit cell parameters of the material by POWD indexing program. As a result of this, the compound is crystallized in monoclinic system with unit cell parameters $a = 12.9575$ Å, $b = 9.3264$ Å, $c = 9.6529$ and $\beta = 113.277°$.
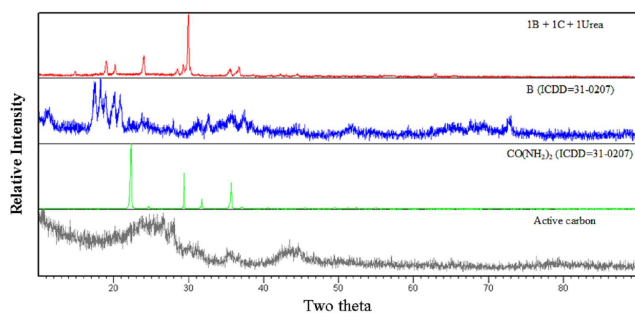

Fig. 1. Powder XRD pattern of B–C–N–O system.

TABLE I

Powder X-ray diffraction data of B–C–N–O system.

I/I_0	d_{obs} [Å]	d_{calc} [Å]	$\sin^2 \Theta_{obs}$	$\sin^2 \Theta_{calc}$	$h\ k\ l$	Difference
6.26	5.9514	5.9514	0.0168	0.0167	2 0 0	0.000
22.71	4.6632	4.6632	0.0273	0.0273	0 2 0	0.000
18.09	4.4336	4.4336	0.0302	0.0302	0 0 2	0.000
30.67	3.7035	3.7035	0.0433	0.0433	1 0 2	0.000
11.83	3.1300	3.1324	0.0606	0.0605	2 2 1	0.023
16.76	3.0507	3.0543	0.0638	0.0636	-4 1 1	0.035
100.00	2.9793	2.9757	0.0669	0.0670	4 0 0	-0.037
13.81	2.9541	2.9557	0.0680	0.0679	0 0 3	0.017
9.45	2.5286	2.5273	0.0928	0.0920	-3 2 3	-0.021
16.03	2.4438	2.4463	0.0994	0.0992	4 1 1	0.039

Figure 2 and Table II show the FTIR spectra and vibration data of the product, respectively. After the comparison of vibrations between final product and starting materials, there is change about all the peaks listed in Table II which are characteristic peaks of BO_3 group, respectively [11–13].
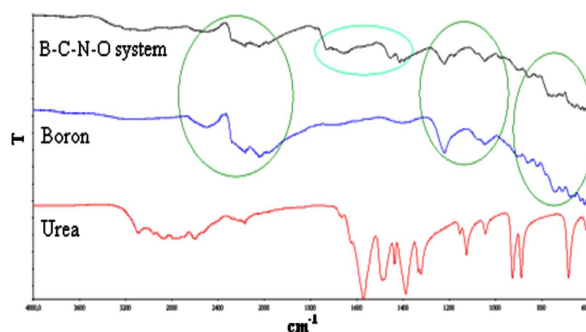

Fig. 2. FTIR spectrum of B–C–N–O system.

TABLE II

FTIR spectrum data of B–C–N–O system.

Observed wave numbers [cm^{-1}]	Vibration type
2519	CO_2 [11]
3450, 1579	H_2O [11]
1331	υ (BO_3) [11]
1223	BO_3 [3–11]
1110	υ_{as} (BO_3) [12]
1032	υ (BO_3) [13]
908	υ_s (BO_3) [13]
891	δ_{dd} (BO_3) [12]
690	υ (BO_3) [11]

Thermal analysis results of B–C–N–O system is given in Fig. 3. There is a significant mass loss about 25% nearly 350 °C which is related to crystal water settled in the structure subsequently. This mass loss which is related to only crystal water displays that the compound is quite stable in the range of 400–1200 °C.
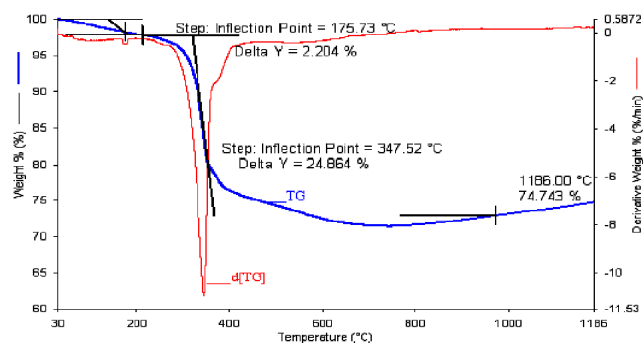

Fig. 3. TG/DTA curves of B–C–N–O system.

Figure 4 is SEM micrograph of B–C–N–O system. The investigation of the micrograph shows a homogeneous distribution of the sample with particle size 0.1–1 μm.

The results of EDX analysis and percentages of composition of the sample are given in Fig. 5 and Table III, respectively. Purple, pink, blue, and green lines correspond with B, C, N, and O, respectively. In consequence, this compound contains B, C, N, and O elements with a suggested empirical formula $B_{26}C_{20}N_8O_4 \cdot (H_2O)$.
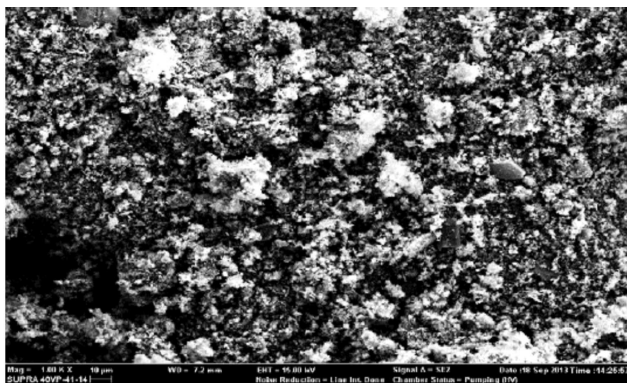
Fig. 4.   SEM micrograph of B–C–N–O system.

Fig. 5.   EDX results of B–C–N–O system.

TABLE III

Elemental composition ratio of B–C–N–O system.

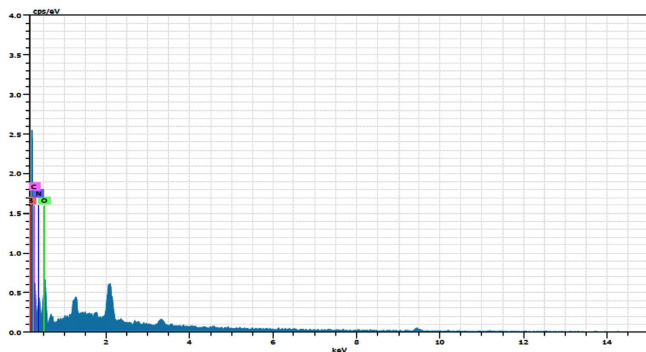| Element	Percent by mass
B	38.54%
O	10.75%
N	16.87%
H	0.28%
C	33.56%

4. Conclusion

A boron, carbon, nitrogen, and oxygen containing compound was synthesized for the first time by classical microwave method using elemental boron, active carbon and urea with 1:1:1 molar ratio. The compound is crystallized in monoclinic system with unit cell parameters $a = 12.9575$ Å, $b = 9.3264$ Å, $c = 9.6529$ Å, $\beta = 113.277°$ which are calculated by POWD indexing program. The XRD, POWD, FTIR, SEM/EDX and TG/DTA analysis were achieved.

Acknowledgments

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