

# XRD Analysis of Boron Doped Glassy Carbon

A. Devečerski<sup>1</sup> and B. Matović<sup>1</sup>

<sup>1</sup>Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro,  
drak@vin.bg.ac.yu

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**Abstract.** Glassy carbon samples containing boron are produced via two different procedures. Boron was introduced into the glassy carbon precursor in order to avoid commonly used high temperature doping process and also to obtain the samples of glassy carbon with boron uniformly distributed throughout the bulk of a material. Structural analysis of specimens treated under different temperature-pressure conditions shows that boron enhances the structural ordering of all samples but not in the same extent, clearly indicating that boron in different samples occupies different structural positions.

## Introduction

Glass-like carbons are usually obtained by pyrolysis of thermosetting resins around 1273 K. Due to their unique combination of properties including isotropy, chemical inertness, gas impermeability, high hardness and wear resistance, they have been used in a wide variety of applications: medical implants, high performance materials for aerospace industry, electrochemical electrodes, fuel cell components and as essential material for silicone wafer processing equipment used in the manufacture of semiconductor devices [1,2]. Boron has a unique property as a substitutional element in the carbon structure. It can replace carbon atom in the graphene layer thus altering many properties of original carbon material: structure, thermal and electrical conductivity, oxidation stability etc [3-7]. One of the major disadvantages [8] of employing doping as a route to the introduction of boron into carbon material is the necessity for high temperatures [3-7] for the doping reaction (usually around 3000 K). The other disadvantage of this widely employed boron doping strategy is the existence of a concentration gradient, i.e. the boron content in carbon material decrease with the depth of material.

The aim of this work was to examine the possibilities for introducing the boron atoms into the glassy carbon precursor in order to avoid high temperature doping process and also to obtain the samples of glassy carbon with boron uniformly distributed through the bulk of a material.

## Experimental

Materials used in this investigation were as follows: resol type phenol-formaldehyd resin (»Latex«, Yugoslavia); boric acid ( $H_3BO_3$ ) p.a.; amorphous boron metal powder, p.a.; ethyl-alcohol ( $C_2H_5OH$ ), p.a.

Boron was added into the matrix precursor (resin) via two procedures:

(i) Boron oxide ( $B_2O_3$ ) obtained from thermal degradation of  $H_3BO_3$ , in amount sufficient to obtain 4 wt% of boron in a resulting glassy carbon (GCB1 in the further text),

was dissolved in  $C_2H_5OH$  and this solution was then mixed with the resin which was also previously dissolved in  $C_2H_5OH$ .

(ii) in the form of amorphous boron metal powder in amount sufficient to obtain 4 wt% of boron in a resulting glassy carbon (GCB2).

Undoped glassy carbon is marked as a GC.

All samples were then heat treated at 350 and 420 K in order to achieve the complete polymerization of resin. Samples were then carbonized under an inert atmosphere of a flowing nitrogen up to 1270 K, with heating rate of 12 K/hour. In the next step carbonized samples were exposed to two different treatments: at 2073 K in an atmosphere of flowing argon (HTT), at 2073 K in an atmosphere of a flowing argon with the simultaneous application of uniaxial pressure of 25 MPa (HTT+P).

Structural analysis of powdered samples was carried out by a Siemens D-500 powder diffractometer.  $CuK\alpha$  radiation was used in conjunction with a  $CuK\beta$  nickel filter.

## Results

X-ray diffraction patterns of samples carbonized at 1273 K are given in Fig. 1. All samples have two broad maxima corresponding to (002) and (10) reflections of a turbostratic carbon structure, which are typical for GC structure [1]. (002) reflection for GC sample is very broad (value of full width at half maximum - FWHM  $\approx 7^\circ$ ) and became even wider in the case of GCB1 and GCB2 samples ( $\approx 7.7^\circ$  and  $7.5^\circ$ ). Observed changes in  $2\Theta$  (i.e.  $d_{002}$ ) values are less than corresponding standard deviations, and we cannot unambiguously confirm the decrease of the  $d_{002}$  spacing in boron containing samples as it was reported in the Ref [1]. Nevertheless, some important observations can be made: for GCB2 sample there is a sharp reflection at  $2\Theta = 28^\circ$  corresponding to crystalline  $B_2O_3$  (and/or  $H_3BO_3$ ) which does not appear in GCB1 sample, nor in the GCB sample in the Ref [1]. Small peak at  $14.5^\circ$  also belongs to  $B_2O_3$ . Obviously,  $B_2O_3$  was formed in GCB2 during the sample preparation, probably as a result of the reaction of boron with released co-products of polymerization and carbonization ( $H_2O$  etc.). Insert in the upper right corner of Fig. 1, shows magnified encircled area of GCB2 sample, with the arrow pointing to peak at  $17.5^\circ$  that belongs to strongest reflection of added elemental boron. This indicates that boron in GCB2 sample is partly present as  $B_2O_3$  and partly as elemental boron. Absence of  $B_2O_3$  or elemental boron reflections in GCB1 sample demonstrates that there is a difference in the nature between boron present in this sample and boron in GCB2 sample. It seems that boron in GCB1 sample was not formed as separate phase and it was efficiently protected from reaction with above-mentioned co-products. It should be mentioned that no reflections which may originate from  $H_3BO_3$  or  $B_2O_3$  could be observed in the X-ray diffraction patterns of polymerized GCB1 sample. This suggests that boron is uniformly distributed throughout the bulk of the material and presumably that is chemically bonded to the polymer cross-linked structure.

Table 1. Structural parameters obtained from X-ray diffraction patterns presented in Fig 1.

Sample	$2\Theta$ ( $^\circ$ )	$d_{002}$ (nm)	FWHM ( $^\circ$ )	$L_c$ (nm)	n
GC	$\approx 23.7$	$\approx 0.375$	7.0	1.2	4
GCB1	$\approx 23.4$	$\approx 0.380$	7.7	1.1	4
GCB2	$\approx 23.9$	$\approx 0.370$	7.5	1.1	4

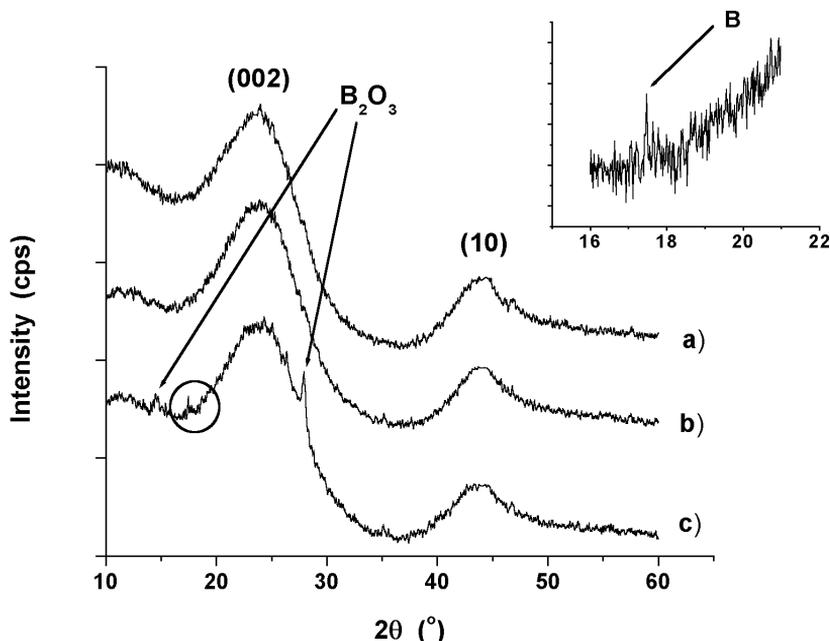


Fig 1. X-ray diffraction patterns of samples carbonized at 1273 K.  
a) GC; b) GCB1; c) GCB2.

X-ray diffraction patterns for samples treated at 2073 K under ambient pressure are presented in Fig 2. Samples containing boron clearly shows enhanced structural ordering and crystal formation indicated by appearance of higher and narrower (002) reflections. Width of the (002) reflection (*FWHM*) is proportional to crystallite size i.e. crystallite thickness ( $L_c$ ) and number of graphene layers ( $n$ ) present in the corresponding crystallite. As one can see from the data presented in Tables 1 and 2, temperature treatment at 2073 K significantly increases  $L_c$  and  $n$  values for all samples when compared with the values of the same samples treated at 1273 K.

Table 2. Structural parameters obtained from X-ray diffraction patterns presented in Fig 2.

Sample	$2\Theta$ (°)	$d_{002}$ (nm)	<i>FWHM</i> (°)	$L_c$ (nm)	$n$
GC	25.560	0.3482	4.3	1.9	6
GCB1	25.920	0.3435	1.0	8.2	25
GCB2	26.120	0.3409	1.0	8.2	25

X-ray diffraction patterns for samples treated at 2073 K under high pressure (25 MPa) are presented in Fig 3. *GCB1* and *GCB2* samples are obtained as solid pellets while *GC* sample remain powdered although grains are increased in size. It is obvious that pressure influences more efficiently structural ordering of the *GCB1* sample than the *GC* and *GCB2* sample. This is clearly illustrated in Fig 3, by height and width of the (002) reflection and also by the data presented in Table 3, i.e. *GCB1* sample exhibits smallest  $d_{002}$  value and highest  $L_c$  and  $n$  values. It may also be seen that only *GCB1* sample possesses clearly developed (004) reflection positioned at  $2\Theta \approx 54.2^\circ$ , while (10) reflection ( $2\Theta \approx 43^\circ$ ) of

glassy carbon is completely diminished. It is also important to observe that only in the X-ray diffraction pattern of *GCB1* sample, reflections presumably originated from the presence of  $B_4C$  appeared. The appearance of these reflections implies: 1) that when amount of boron in the carbon sample exceeds the substitutional solid solubility limit for a given temperature ( $\approx 1$  wt.% at 2073 K) [10],  $B_4C$  reflections appears indicating that excess of boron is present in the interlamar positions [9] between graphene layers, and 2) it is possible that solution-precipitation mechanism [9] involving  $B_4C$  plays an important role in enhancing structural ordering of glassy carbon by forming graphite domains in disordered glassy carbon structure.

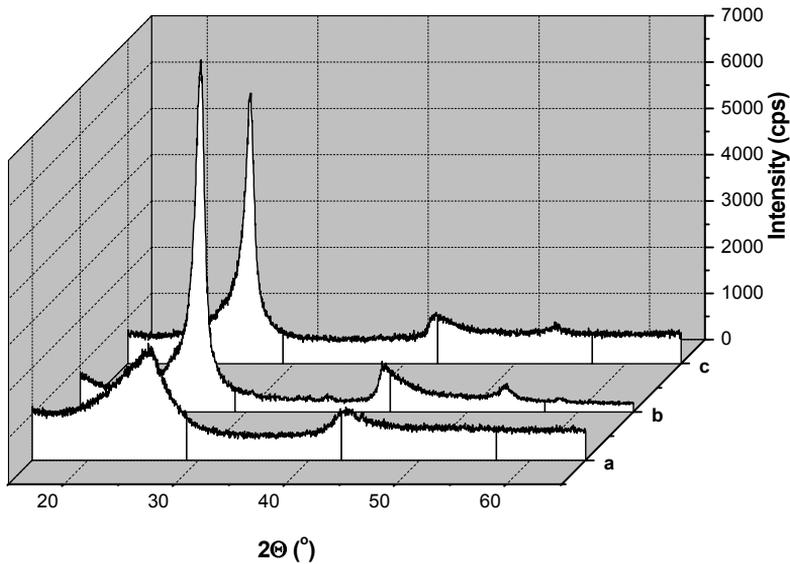


Fig 2. X-ray diffraction patterns of samples treated at 2073 K. a) GC; b) GCB1; c) GCB2.

Table 3. Structural parameters obtained from X-ray diffraction patterns presented in Fig 3.

Sample	$2\Theta$ (°)	$d_{002}$ (nm)	FWHM (°)	$L_c$ (nm)	n
GC	26.125	0.3408	3.8	2.1	7
GCB1	26.377	0.3376	0.4	20.4	61
GCB2	26.183	0.3401	1.0	8.2	25

Absence of  $B_4C$  reflections in the X-ray diffraction pattern of *GCB2* sample indicate that formation of  $B_4C$  phase is clearly connected with the differences in the procedures conducted when preparing the boron containing samples. Namely, when dissolving  $B_2O_3$  in the  $C_2H_5OH$ , a highly reactive boron alkoxide  $B(OEt)_3$  is produced [11]. It is possible that boron alkoxide chemically interacts with the resin thus incorporating boron uniformly throughout the non-polymerized and polymerized sample. This could be also a possible explanation for the appearance of  $B_4C$  only in the *GCB1* sample. Boron chemically bonded to the polymer can easily form B-C bond during the processes of carbonization, HTT and HTT+P treatments, while HTT and HTT+P treatments are clearly not sufficient to produce the  $B_4C$  in the *GCB2* sample, where boron is present in the form of metal and/or  $B_2O_3$ .

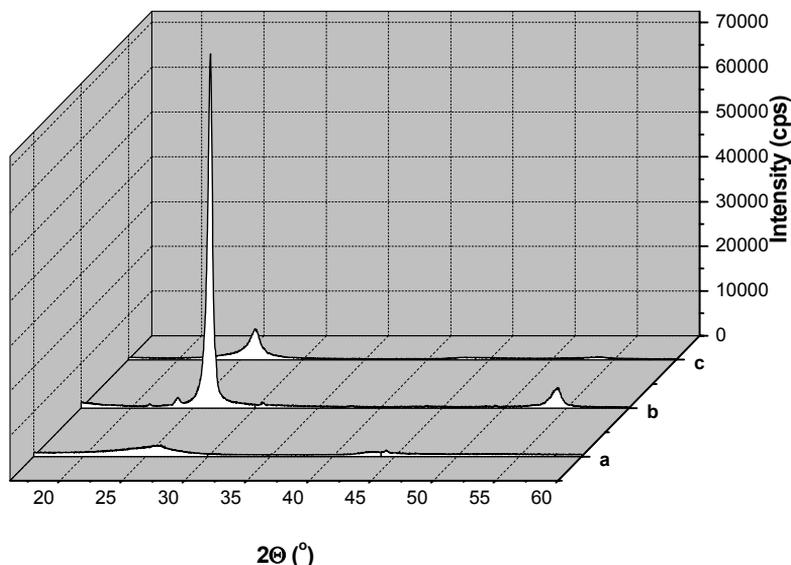


Fig 3. X-ray diffraction patterns of samples treated at 2073 K and 25 MPa pressure. a) GC; b) GCB1; c) GCB2.

### Summary

It was shown that a substantial degree of structural ordering (i.e. graphitization) of glassy carbon could be obtained by adding boron into the glassy carbon precursor (resin). This approach avoids two major disadvantages of commonly used high temperature doping process: need for high temperature (usually 3000 K and above) and non-uniform distribution of boron throughout the bulk of the sample. Structural ordering of glassy carbon sample obtained by adding ethanol solution of  $B_2O_3$  into the resin is especially efficient when high pressure is applied simultaneously with high temperature. This procedure can be used for relatively simple synthesis of graphitic materials and carbon/carbon composites with higher oxidation stability, taking into account that graphite is more resistant to reaction with oxygen than glassy carbon.

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