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The second order Raman spectroscopy in carbon crystallinity

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Abstract

Cellulose was heated in the absence/presence of B to determine crystallinity changes due to heat treatment and B doping with the objectives of evaluating the characteristics of the second order Raman spectroscopy in comparison with X-ray diffraction (XRD) and the first order Raman spectroscopy. The crystallinity determined by XRD was similar to those of the first order Raman spectroscopy; crystallinity increases as heat treatment temperature (HTT) increases until 2300 °C. This increase in crystallinity was overturned at 2600 °C in B-doped carbon due to loss of B. But both techniques were not comparative on the determination of crystallite height (L_a) and did not evidently present the crystallinity changes. The second order Raman spectroscopy was used as an alternative technique to clearly quantify the difference in crystallinity. It was confirmed that this new evaluation methodology from the second order Raman spectroscopy is effective for the determination of carbon crystallinity.

1. Introduction

The role of substitutional B in carbons has been extensively investigated due to the use of graphite in nuclear reactors as a moderator [1–3]. Nuclear graphite is a polygranular graphite material with very high chemical purity to avoid absorption of low-energy neutrons and activation of the impurities [4,5]. High dimensional stability is also required for nuclear graphite to withstand the material at high temperatures and in a high flux of neutrons [4]. In the 1950s and 1960s substitutional B has been of great interest to dope into graphite because it has been proved that substitutional B increases the crystallinity of carbon [6–8]; the study of substitutional B in carbon is now motivated by another interest (e.g., oxidation inhibition of carbon materials) [9–12].

Nevertheless, these interests in the effect of substitutional B in carbon materials are also related with an increase in carbon crystallinity; high crystallinity is also preferred to increase oxidation resistance of carbon by reducing active sites [10,13–15]. In general, an increase in carbon crystallinity can be expressed by a decrease in the d-spacing (d_{002}), and an increase in crystallite height (L_c) and width (L_a). Despite it is not clear how substitutional B increases crystallinity, the mechanisms of graphitization enhancement by B incorporation into carbon have been proposed; Hagio et al. [16] argued that electron deficiency of boron with respect to carbon causes a decrease in the repulsive interaction between the π-electron clouds of adjacent graphene layers, allowing these layers to come closer together: a decrease in the d-spacing. In contrast, Hishiyama and Inagaki [17] discussed that the presence of substitutional B decreases the π-electron density in the graphene layers and the resulting decrease in π–π overlap should lead to an increase in d-spacing. Although it should be further discussed to clarify, it is evidently known that

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substitutional B is doped into carbon lattice with the maximum contents of 2.35 at.% at 2350 °C [18].

X-ray diffraction (XRD) has been a major technique to determine carbon crystallinity. As earlier Franklin [19] measured the crystallinity of graphitic carbons by XRD, and Short and Walker [20] also used XRD to determine the crystallite parameters of turbostratic carbons. Since then the determination of carbon crystallinity by XRD has been well established and extensively studied. Raman spectroscopy, a relatively new technique has also been developed and become popular for an alternative technique for XRD to determine carbon crystallinity. Tuinstra and Koenig [21] did first report that the utilization of Raman spectroscopy in carbon crystallinity; they found that the appearance of D and G bands in carbons and established the relationship between the crystallite width and the Raman intensity. The empirical equation [21], $L_a = 43.5/R_I$ and $R_I = I_D/I_G$, derived by the authors, has often been used to validate the crystallinity from XRD [22–24].

But the applications of Raman spectroscopy in the determination of carbon crystallinity have mostly been focused on the first order bands [21–25]; there have been relatively few studies on the second order bands [26,27]. Due to these unbalanced studies the characteristics of the first order Raman spectroscopy are quite well understood but there is still lack of knowledge on the second order despite anomalously sharp features of the second order bands have been reported due to crystallinity changes [26,27]. Therefore, it is necessary to systematically study the properties of the second order Raman spectroscopy in carbon crystallinity.

As mentioned the incorporation of B into carbon will make quite interesting changes of carbon crystallinity and these changes will be interpreted by Raman spectroscopy and XRD in this study. The second order Raman spectroscopy has been used before to measure the crystallinity changes of B-doped carbons [28,29], but B was doped only a selected temperature (e.g., 2350 °C for Ref. [28] and 3000 °C for Ref. [29]). Consequently, the crystallinity changes of B-doped carbons in a broad range of heat treatment temperature (HTT) have not been reported yet or well understood by the second order Raman spectroscopy. The objectives of this study are to evaluate the characteristics of the second order Raman spectroscopy in carbons heat treated at different temperature in the absence/presence of B in comparison with XRD and the first order Raman spectroscopy.

2. Experimental

Before any heat treatment, a carbon precursor, cellulose (Aldrich) was mixed with elemental B (Union Carbide, 99.999%) with the initial content of 1 wt% to prepare B-doped carbons. Cellulose was selected as a carbon precursor due to its availability, high purity and non-graphitizability. Unlike graphite or HOPG (highly oriented pyrolytic graphite), cellulose-derived carbons are expected to well represent the crystallinity changes by different HTT. Elemental B was selected due to its high concentration in comparison with organic compounds [10]. Cellulose in the absence and presence of B was collected in a ceramic boat, and then the boat was placed in a quartz tube within a Lindberg furnace for heat treatment. The furnace was flushed by nitrogen (99.999%) at 250×10^{-6} m^3/min for 30 min before heat treatment to remove residual oxygen, then heated to the desired temperatures up to 1000 °C in nitrogen.

For heat treatment at higher temperature the sample was removed from the furnace and collected in a graphite crucible. A graphitization furnace (Centorr, Inc.) with a graphite crucible was evacuated before heat treatment and argon (UHP, 99.999%) was introduced. This procedure was repeated at least three times to remove the residual oxygen in the furnace. The furnace was heated to the desired temperature and held for 30 min. The selected HTT was 600, 1000, 1600, 1900, 2300 and 2600 °C: total 6 HTTs. B-free carbons were prepared in the same conditions as the counterparts of B-doped carbons.

Raman spectroscopy (Renishaw, RM 1000) was employed to evaluate the relative changes in carbon crystallinity in a back-scattered configuration using Ar$^+$ laser as a source at 488 nm, ranging from 800 to 1800 cm^{-1} band for the first order and from 2400 to 3400 cm^{-1} for the second order. In comparison with Raman spectroscopy, XRD (Rigaku Geiger-Flex) was used to measure the crystallinity changes. The samples were ground and deposited on a glass slide. A scan range was between 10° and 60° (2θ) with 0.5°/min of scan speed. Silicon powder was added as an internal standard. To determine the B concentration in the carbons, an inductively coupled plasma (ICP) emission spectroscopy (Perkin–Elmer P2000) was used with the detection limit of 0.05 wt%.

3. Results and discussion

3.1. Determination of crystallinity by XRD and the first order Raman spectroscopy

The final B retentivity was determined and presented in Table 1; the results indicate that the final B loading in carbons decreases as HTT increases. The X-ray patterns were examined for the samples both in the absence/presence of B, and the crystallite parameters such as d_{002}, L_c from (0 0 2) peak and L_a from (1 0) peak are presented in Table 2.

Crystallinity increases as HTT increases both in the absence/presence of B, as expected: a decrease in d_{002}

Table 1
Final B concentration in cellulose-derived carbon

HTT (°C)	Initial B concentration (wt%)	Final B concentration (wt%)
600	1	0.63
1000	1	0.62
1600	1	0.65
1900	1	0.46
2300	1	0.22
2600	1	0.06

Table 2
Effects of B and HTT on carbon crystallinity determined by XRD

Initial B concentration (wt%)	HTT (°C)	d_{002} (nm)[a]	L_c (nm)[a]	L_a (nm)[a]
0	600	[b]	[b]	[b]
	1000	[b]	[b]	[b]
	1600	0.350	2	2
	1900	0.347	3	3
	2300	0.344	4	4
	2600	0.341	4	4
1	600	[b]	[b]	[b]
	1000	[b]	[b]	[b]
	1600	0.349	3	4
	1900	0.345	3	5
	2300	0.340	5	7
	2600	0.341	4	6

[a] L_c is derived from (0 0 2) and L_a from (1 0) peak, respectively.

[b] Peaks too broad for reliable quantification.

and an increase in L_c and L_a. The enhancement of crystallinity by heat treatment is well studied and accepted [19] but the splitting of the (1 0) peak into (1 0 0) and (1 0 1) was not observed due to non-graphitizability of the carbon precursor. The reliable quantifications of the carbons heated at 600 and 1000 °C were not possible due to too broad peaks of (0 0 2) and (1 0).

A comparison of crystallinity between B-free and B-doped samples is interesting here. The d-spacing of the carbon in the absence of B decreases as HTT increases, so that the carbon exposed at 2600 °C has the lowest d_{002}; in contrast, the d-spacing of the B-doped carbons increases at 2600 °C. The very same behaviors can also be observed in crystallite height and width. It seems to be related with the B content: the B concentration of the carbon at 2600 °C does dramatically decrease in comparison with the carbon at 2300 °C (see Table 1).

The B incorporation into carbon lattice, up to 2.35 at.% at 2350 °C [18], results in a decrease in the d-spacing, and an increase in the crystallite height and width [10]. But the concentration of substitutional B decreases above 2350 °C [18], resulting in a decrease in B concentration, as proved in Table 1. Due to this decrease in B content, the crystallite parameters at 2600 °C in the presence of B were changed to a decrease in crystallinity. Despite these changes, crystallinity of the carbons is higher in the presence of B than that of their counterparts. The enhancement of graphitization by substitutional B is well documented [6,9–11]. It is obvious here that the B doping into carbon is beneficial for an increase in crystallinity although the mechanism is not clear yet [16,17].

The ratios of the FWHM (R_ω) and the band intensity (R_I) between the D and G bands, and L_a derived from R_I are presented in Table 3. Unlike single crystal graphite, the samples showed the D- and G-bands at ~1360 and ~1600 cm^{-1}, respectively. The FWHM ratio between the D and G bands is assigned to R_ω (ω_D/ω_G); the relative intensity between the D and G bands is assigned to R_I (I_D/I_G) and L_a is derived from the empirical equation, $L_a = 43.5/R_I$ [21]. The results from the first order Raman spectroscopy seem to be agreed with those of XRD; R_ω and R_I decrease as HTT increases in both B-free and B-doped carbons. But it was overturned at 2600 °C in B-doped carbons; both ratios increase.

But there is a clear discrepancy of L_a between XRD and Raman spectroscopy. Unlike XRD it was possible to determine L_a even at low HTT (600 and 1000 °C) in Raman spectroscopy. But L_a did keep constant until 2300 °C in the absence of B. In the presence of B, L_a did

Table 3
Effects of B and HTT on carbon crystallinity determined by the first order Raman spectroscopy

Initial B concentration (wt%)	HTT (°C)	R_ω (ω_D/ω_G)[a]	R_I (I_D/I_G)[a]	L_a (nm)[b]
0	600	3.203	0.934	5
	1000	2.648	0.886	5
	1600	0.974	0.617	5
	1900	0.764	0.882	5
	2300	0.648	0.923	5
	2600	0.514	0.570	8
1	600	3.199	0.927	5
	1000	2.498	0.911	5
	1600	0.845	0.924	5
	1900	0.627	0.682	6
	2300	0.501	0.571	8
	2600	0.512	0.576	8

[a] R_ω (ω_D/ω_G) is the FWHM ratio between the D and G bands.

[b] R_I (I_D/I_G) is the intensity ratio between the D and G bands, and L_a is derived from $L_a = 43.5/R_I$ [21].

little increase as HTT increases but a decrease in crystallinity at 2600 °C was not noticed unlike XRD. Despite the carbon precursor was non-graphitizable, it does not seem to be rational if the carbons heated at 600 and 2300 °C have the same crystallite width. Especially, it is known that an increase in L_a is greater than that of L_c in the presence of B [6,10], but L_a at 2600 °C is identical regardless the presence of B from Raman spectroscopy.

This determination of L_a from Raman spectroscopy has been extensively used and often compared with that of XRD [22–24]. Gruber et al. [24] used several types of carbon blacks to determine the crystallite parameters by XRD and Raman spectroscopy and reported that a comparison of L_a from both techniques is agreed within 10%. Cuesta et al. [22] selected a total number of 45 carbon materials ranging from natural graphite to coals and compared their crystallinity by XRD and Raman spectroscopy. The authors did find a quite discrepancy between two techniques up to 100% and suggest the use of XRD whenever it is possible. The use of Raman spectroscopy is definitely practical, but as notice from both studied above, the relative intensity from the first order Raman spectroscopy seems to have a restriction to evaluate the crystallinity changes and should be used in great care.

Unlike the first order, the second order Raman spectroscopy seems to be ignored although its interesting behavior in carbon crystallinity has been noticed. Therefore, it would be noteworthy to pay attention to the second order Raman spectroscopy for evaluation of carbon crystallinity.

3.2. Determination of crystallinity by the second order Raman spectroscopy

The second order Raman spectroscopy of cellulose-derived carbon in the absence/presence of B is presented in Figs. 1 and 2, respectively. Three bands are observed: ~2700, ~2950 and ~3250 cm^{-1}. The band at ~2700 cm^{-1} is assigned to G′ which is a merged band of G'_1 and G'_2 bands [28,30]; the band at ~2950 cm^{-1} is D″, a combination of D and G bands [27,28,30]; the band at ~3250 cm^{-1} is 2D′, a counterpart in the second order spectrum of D′ band [28]. The general features of these

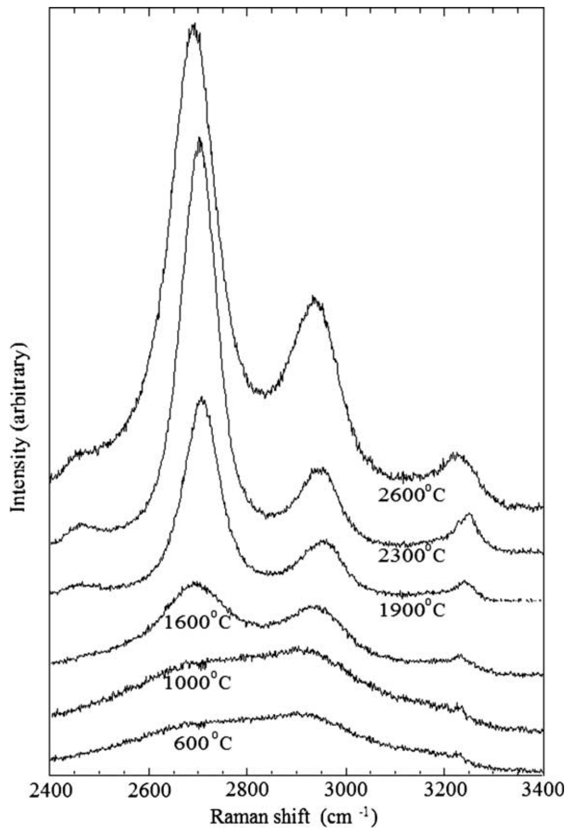

Fig. 1. The second order Raman spectroscopy of cellulose-derived carbon in the absence of B.

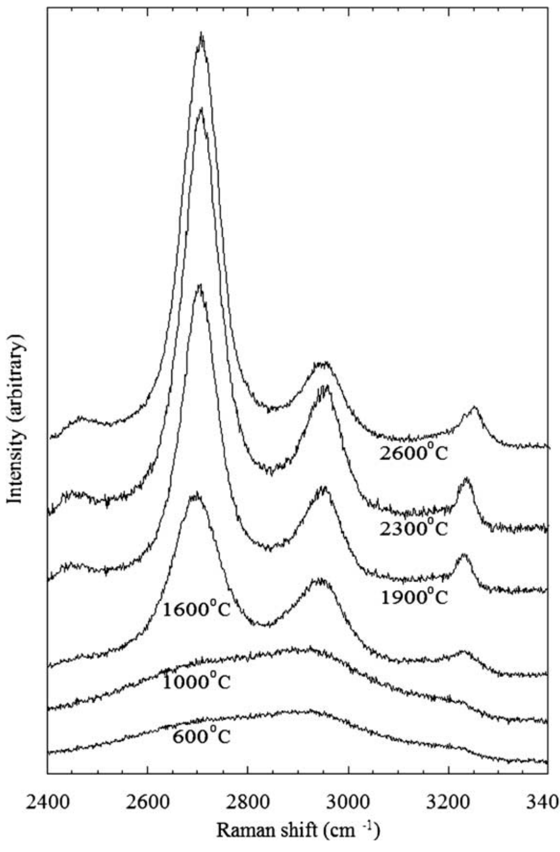

Fig. 2. The second order Raman spectroscopy of cellulose-derived carbon in the presence of B.

bands are following; the intensities of the three bands increase as HTT increases, and the carbons heated at low temperature (600 and 1000 °C) do not show any band development unlike the first order Raman spectroscopy.

Hishiyama et al. [28] stated that the appearance of the D′ band is a characteristic of the disordered graphite structure and observed an increase in the intensities of the G′ ($I_{G'}$) and 2D′ ($I_{2D'}$) bands, and a disappearance of D″ band as crystallinity increases in the presence of B. Endo et al. [29] also observed the vanishing of D″ band in the incorporation of B but also noticed a decrease in $I_{G'}$ and a disappearance of 2D′. Another inconsistent result is presented by Chieu et al. [31]; the authors observed an increase in $I_{G'}$ and $I_{2D'}$, and a decrease in $I_{D''}$ as HTT increases. These related but conflicting results in comparison with the results here seem to be due to carbon precursors: graphite fibers and HOPG vs. non-graphitizable carbons. Unlike non-graphitizable carbons here, graphite fibers and HOPG do already have high crystallinity and are expected to behave in different manner in the presence of B.

Sato et al. [27] heated disordered carbons up to 2400 °C and observed the pattern changes of the second Raman spectroscopy. Their observation is quite interesting here; the G′ band is sensitive to structure, its intensity and the FWHM increases and decreases, respectively, as HTT increases, and the 2D″ band is still distinct at high HTT. Bearing their observation in mind, the changes of the bands in Fig. 1 suggest the intensity and the FWHM of the G′ and D″ increases and decreases, respectively, as crystallinity increases. But these changes are clearly overturned at 2600 °C in the presence of B in Fig. 2; the intensity and the FWHM of the bands decreases and increases, respectively, suggesting a decrease in crystallinity. This behavior is well matched with the findings in XRD and the first order Raman spectroscopy.

To quantify these changes in the absence/presence of B, the relative intensity and the FWHM of the G′ and D″ bands are calculated and presented in Figs. 3 and 4, respectively. For the calculation of the relative intensity, the intensity of the band was divided by that of the band at 2600 °C. Fig. 3 presents the relative intensity and the FWHM of the G′ band in the absence/presence of B. In the absence of B the relative intensity and the FWHM continuously increases and decreases, respectively. But in the presence of B the relative intensity has a maximum at 2300 °C; the intensity of the band at 2300 °C is almost 30% greater than that of 2600 °C. The change of the FWHM shows a very similar trend: a minimum at 2300 °C. But the B-doped samples do always have lower FWHM than their counterparts, suggesting the incorporation of B is beneficial for graphitization.

The changes in the D″ band are even more noticeable in Fig. 4. The intensity of the band at 2300 °C is almost 40% greater than that of 2600 °C, and the extent of the difference in FWHM of the carbons between 2300 and 2600 °C is close to that of the G′ band. It is evident from Figs. 3 and 4 that substitutional B enhances the graphitization of carbons up to 2300 °C, and the changes of the relative intensity and the FWHM in the second order Raman spectroscopy do well signify the crystallinity changes: the second order Raman spectroscopy is effective for the determination of crystallinity changes even in non-graphitizable carbons.

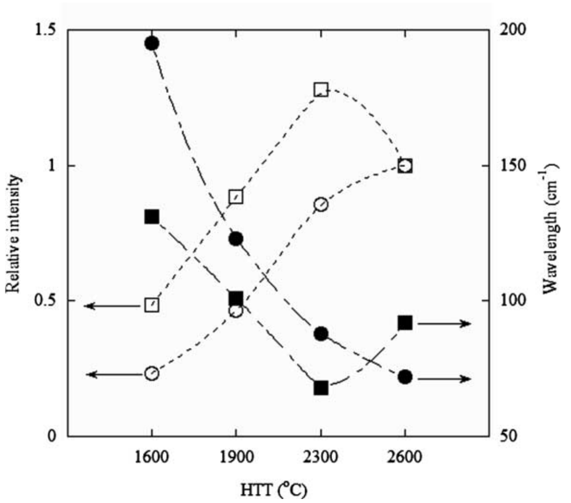

Fig. 3. The relative intensity and the FWHM of the G′ band in the absence/presence of B (circles represent B-free carbons; squares represent B-doped carbons).

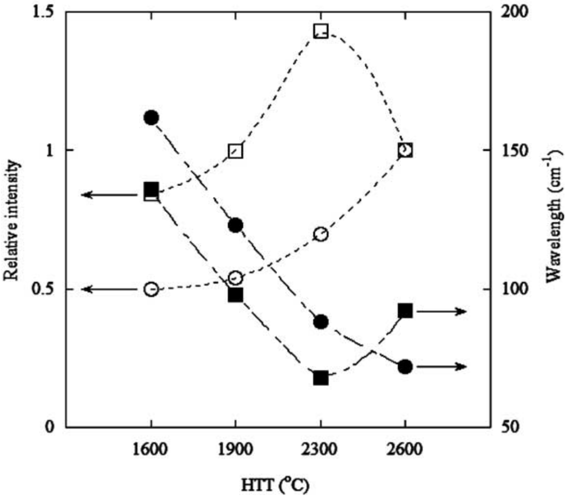

Fig. 4. The relative intensity and the FWHM of the D″ band in the absence/presence of B (circles represent B-free carbons; squares represent B-doped carbons).

4. Conclusions

Carbon crystallinity increased as HTT increased and the presence of B was beneficial for the enhancement of graphitization, as expected. But the crystallinity of the B-doped carbon at 2600 °C decreased due to loss of B. These results were confirmed by XRD and were generally similar to those of the first order Raman spectroscopy. But the discrepancy in carbon crystallinity between two techniques was relatively noticeable; the values of L_a were quite different.

The second order Raman spectroscopy was measured to quantify the extent of difference in crystallinity. The relative intensity and the FWHM of the G' and D'' bands were determined and found to be strongly effective to signify the crystallinity changes even in non-graphitizable carbons. Unlike B-free carbons, the relative intensity of B-doped carbons in the G' and D'' bands had a maximum at 2300 °C and that of the carbon was as much as 40% lower at 2600 °C than at 2300 °C.

It is evident that the second order Raman spectroscopy has anomalously sharp features in the change of carbon crystallinity. These ignored but important characteristics of the bands in the second order Raman spectroscopy should be further examined in great care to evaluate the relationship with XRD and the first order Raman spectroscopy.

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