

BORONATED CARBONS: CHARACTERIZATION OF DISORDERED SOLID SOLUTIONS

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Introduction

It has appeared that the chemical preparations of mixed compositions consisting of carbon, boron and nitrogen atoms lead to modulate the electronic structure and the associated physical properties of carbon materials. In the present work we are only interested by the more stable phase i.e. the graphitic one. The influence of boron doping on the layered carbon structure has been tested since forty years, and in order to summarize, the preparation of such binary compounds (B,C) can be dispatched in two categories:

i) Chemical reactions at, or near, thermodynamic equilibrium which lead to low boron content materials. Lowell [1] has thus shown that the thermodynamic solubility of boron in carbon could not exceed 2.35 at%, and Marchand [2] has summarized various usable techniques to dope carbons and graphites with boron (0,1 to 1 at%).

ii) Chemical reactions which are not at equilibrium and give non-crystalline solids with various boron contents. The values of the boron content is a function of the nature of the experimental process and of the initial phases.

Numerous techniques and precursors are used with in particular thermal chemical vapour deposition (CVD) which has been widely developed and we will now focus on these results.

Kouvetakis [3], starting from benzene and boron trichloride obtained for the first time the so called BC₃ formula compound at 800°C under reduced pressure. At higher deposition temperatures, 800 to 1100°C, we were using acetylene instead of benzene to synthesize also BC₃ and other compositions with lower boron content [4].

Boron rich materials of B_xC_{1-x} type are not yet satisfyingly described and the aim of this paper is to better characterize some specific boron rich compositions obtained by CVD. Both structural and physical properties have been investigated: in particular low temperature d.c. conductivity and dynamic and static magnetic susceptibility. The final purpose is to correlate the structural disorder, both positional and substitutional, with the particular electronic and vibrational structures evidenced by low temperature physical experiments.

Experimental

These B_xC_{1-x} materials are made by low pressure chemical vapor deposition technique [4]. The total pressure in the alumina reactor is 30 mbar, the alumina substrate temperature is 1100°C and the gases used for these manipulations are boron trichloride (5 to 10 Scm³ mn⁻¹), acetylene (11 Scm³ mn⁻¹) and hydrogen (477 Scm³ mn⁻¹).

All the compositions have been determined either by electron probe micro analysis (EPMA) or occasionally by RBS (Rutherford back scattering) or by a chemical analysis. The comparison we have made between those different techniques gave a good agreement.

Results and discussion

1. Structural properties

On figure 1 are reported X-ray diffraction results of pure carbon (obtained at 1100°C) BC₉ (10 at%), BC₅ (17 at%), BC₄ (20 at%) and BC₃ (25 at%). The full width at half-maximum (FWHM) of d₀₀₂ line for BC₃ and BC₄ samples is, as expected, less than that of pure carbon due to the boron presence, but it is more than that of BC₅ and BC₉. This matter of fact is confirmed by the position of the (002) diffraction line which is greater for BC₃ and BC₄ than for BC₅ and BC₉. Figure 1 clearly shows the existence of a minimum of d₀₀₂ and FWHM lying around 10-15 at%. This result is confirmed by the analysis of density measurements.

The XPS analysis have been obtained from reference compounds (HOPG, elemental boron, a B₁₃C₂ film obtained by CVD, and a B₄C commercial powder) and from different samples near the BC₃ stoichiometry, respectively. The comparison seems to indicate that BC₃ samples have specific B-C binding energies which are not the same for B₄C or B₁₃C₂. It denotes the presence of boron atoms with very strong electropositive surroundings in some interstitial position.

2. Electronic and magnetic properties

The measurements of d.c. electrical resistivity from liquid helium to room temperature of BC₃, BC₅ and BC₉ have been carried out. Consistently with the fact of having the better texture, BC₉ compound has the weakest resistivity and moreover it has a weak temperature dependence which corresponds to a quasi metallic behaviour whereas in the BC₃ case we can notice a weak localization phenomenon [4].

The magnetic properties of B_xC_{1-x} compounds were probed using super conducting quantum interference device (SQUID magnetometer) and electron spin resonance (ESR spectrometer). The main results observed on these paramagnetic compounds is the coexistence of Curie law and a constant term which is attributed to a Pauli paramagnetism.

3. Comparison between theory and experiments

On table 1 are presented and compared the values of the density of states at the Fermi level $N(\epsilon_F)$ obtained by different experimental techniques. We note that the $N(\epsilon_F)$ values given by specific heat measurements [5] are always greater than that calculated from SQUID and ESR measurements: this is possible because of the contribution of defects to the linear specific heat term which is due to localized phonons [6]. Besides a comparison with Slonczewski-Weiss-Mc Clure model based on extended Hückel theory [7] and used for slightly doped graphites exhibit large differences. This is the proof that a rigid band approximation does not apply for these doped samples which are non-crystalline solids.

Conclusion

B_xC_{1-x} compounds have been prepared by thermal CVD techniques and characterized by several structural and physical methods. We have to distinguish two classes of materials: the boron poor ones seem to be single phases with relatively well defined bidimensional texture, while the boron rich ones are more disorganized but are still metastable solid solution of boron into a pregraphitic carbon.

Such a constatation implies the existence of a critical boron concentration which separates the two zones. A value around 17 at% B appears reasonable. It corresponds to the presence of one boron atom per benzene cycle, which could destroy entirely the aromaticity of the graphitic planes and permit more easily their deformation and the defect formation. This is a new class of non-crystalline solid solutions with interstitial boron which present very promising physical properties.

References

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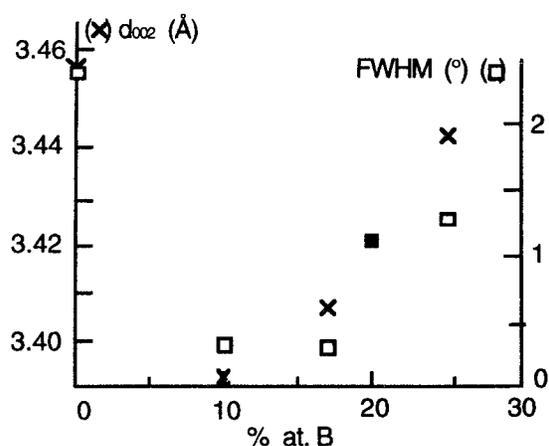


Figure 1: X-ray diffraction results of pure carbon (deposited at 1100°C) BC₉, BC₅, BC₄ and BC₃ samples.

	Theoretical calculations	Experimental data		
	SWMc C model	SQUID Magnetometer	ESR Intensity line	Specific heat linear term [5]
BC ₃	74.23	47.6	10.9	141.1
BC ₅	63.56	108.7	no signal	—
BC ₉	48.42	111.3	no signal	277.8
Graphite	4.6	—	4.64	5.85

Table 1: Density of States at the Fermi level $N(\epsilon_F)$. Comparison between theory and experiments.