

# INTERCALATION COMPOUNDS OF ALKALI METALS IN BORON SUBSTITUTED CARBONS $B_xC_{1-x}$

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## Introduction

It was previously shown that crystallinity of boron substituted carbons  $B_xC_{1-x}$  ( $0 < x < 0.25$ ) is decreasing when  $x$  increases from 0.1 to 0.25 [1]. This property was attributed to the presence of boron atoms in interstitial sites. Due to substitution of carbon by boron, these materials intercalate successfully lithium at a larger content than graphite. In order to better understand the influence of the structure of host on the intercalation process, we prepared intercalation compounds of heavy alkali metals (K, Rb, Cs), for two different compositions  $B_{0.25}C_{0.75}$  and  $B_{0.1}C_{0.9}$ .

## Experimental

Oriented platelets were allowed to react in the vapor phase with K, Rb and Cs using the conventional two bulb method in a Pyrex glass tube carefully evacuated at  $10^{-6}$  mbar. We selected the temperatures of boronated carbon ( $T_{\text{host}}$ ) and alkali metal ( $T_M$ ) in order to reach the first stage derivatives. They were respectively  $T_M=310^\circ\text{C}$  and  $T_{\text{host}}=350^\circ\text{C}$  for cesium derivatives, whereas lower temperatures (typically  $T_{\text{host}}=270^\circ\text{C}$  and  $T_M=250^\circ\text{C}$ ) were used with potassium and rubidium in order to avoid the reaction of the alkali metal with Pyrex glass. Alkali metal content was estimated from weight uptake at the end of the reaction.

Cesium compounds were also prepared by the reaction of the host with a cesium solution in liquid ammonia. Cesium dissolves in liquid ammonia at  $T < 35^\circ\text{C}$  giving a blue paramagnetic solution containing solvated  $\text{Cs}^+$  cations and electrons. After dipping  $B_xC_{1-x}$  platelets several days into the blue solution, they were washed with pure liquid ammonia and finally pumped to  $10^{-5}$  bar in order to remove excess ammonia.

The  $00l$  lines and the  $hk$  bands were recorded by X ray diffraction on a rotating crystal, respectively in the reflection and transmission modes, with a curve position sensitive detector (INEL CPS 120) at

$\lambda=0.70926 \text{ \AA}$  for the cesium and potassium compounds and  $\lambda=1.5406 \text{ \AA}$  for the rubidium derivatives due to Rb fluorescence with  $\text{Mo}_{K\alpha 1}$  radiation.

Electrical resistivity and magnetoresistance of the cesium compound synthesized in ammonia solution were measured with a conventional dc or ac four probe method using silver paste as electrical contacts. A classical cryostat enabled to perform the studies in the range [4K-300K].

## Results and discussion

### Vapor phase intercalation :

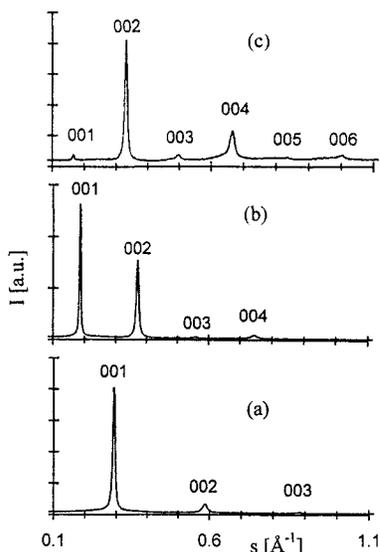
The intercalation process is comparable to that of graphite, and stages are formed. In the selected conditions of temperature, the  $00l$  diffractograms of the intercalated compounds (Fig. 1) are typical of first stage derivatives.

Whatever the alkali metal among K, Rb or Cs, the compositions of the first stage intercalation compounds are almost similar, respectively  $M(B_{0.1}C_{0.9})_{8\pm 1}$  and  $M(B_{0.25}C_{0.75})_{10\pm 1}$ , showing that the alkali content is higher in  $B_{0.1}C_{0.9}$  than in  $B_{0.25}C_{0.75}$ . This could be explained by a larger content of interstitial boron in  $B_{0.25}C_{0.75}$  than in  $B_{0.1}C_{0.9}$ , preventing more extended intercalation of the alkali metal. The identity periods  $I_c$  (table 1) of  $M(B_{0.25}C_{0.75})$  compounds are comparable to those of GIC, whereas they are slightly higher for  $M(B_{0.1}C_{0.9})$  derivatives.

M	$M(B_{0.25}C_{0.75})_{10}$ $I_c [\text{\AA}]$	$M(B_{0.1}C_{0.9})_8$ $I_c [\text{\AA}]$	$MC_8$ GIC $I_c [\text{\AA}]$
K	5.34	5.37	5.35
Rb	5.64	5.66	5.65
Cs	5.94	6.02	5.93

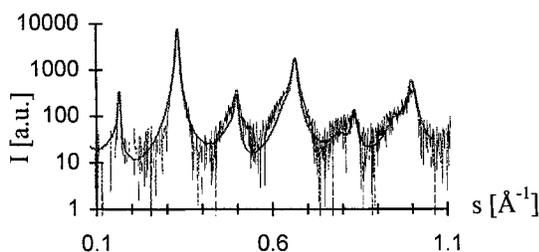
Table 1 : Identity periods of  $M(B_{0.25}C_{0.75})_{10}$ ,  $M(B_{0.1}C_{0.9})_8$  and  $MC_8$  GIC.

The broadening and the wings of the  $00l$  lines with increasing diffraction angle, either for the host or for the intercalated compounds (Fig. 1), are due to the fluctuations in the positions of the layers [2].



**Figure 1** :  $00l$  diffractograms of  $B_{0.1}C_{0.9}$  (a) and its intercalation compounds with K (b), and Cs (c).

Details of the diffractograms of the cesium and rubidium intercalated compounds presented asymmetric  $00l$  lines particularly at large angle. This effect which is not due to fluctuations in the positions of the layers could be explained by interstratification of another structure in the main first stage structure. For example, ab-initio calculations of the intensities [2] show good agreement with the experimental data for the first stage  $Cs(B_{0.1}C_{0.9})_{8\pm 1}$  compound ( $I_c=6.02\text{ \AA}$ ) if it is interstratified with 16% of a first stage  $Cs(B_{0.1}C_{0.9})_5$  ( $I_c=6.3\text{ \AA}$ ) (Fig. 2).



**Figure 2** : Experimental  $00l$  scan of  $Cs(B_{0.1}C_{0.9})_{8\pm 1}$  (dashed lines). The continuous line is the result of a model in which 84% of the first stage  $Cs(B_{0.1}C_{0.9})_8$  (layer A,  $I_c=6\text{ \AA}$ ) is interstratified with 16% of  $Cs(B_{0.1}C_{0.9})_5$  (layer B,  $I_c=6.3\text{ \AA}$ ). The positions along the  $c$  axis are supposed to follow a Gaussian law. The mean square deviation  $\langle \delta^2 \rangle$  is equal to 0.0036.

The first stage dense structure identified in Cs and Rb derivatives confirms that boron acts as an electron acceptor and improves partly the intercalation of alkali metal. We suggest that this particular structure

is due to the interactions of alkali metal with interstitial boron.

The profiles of the  $10.$  and  $11.$  bands of the boronated carbon substrate on the transmission patterns are characteristic of a turbostratic arrangement of the layers. In cesium compounds, the  $hk.$  bands ( $10., 11., 20., 21.$ ) of the intercalate can be interpreted as due to a  $2 \times 2 R 0^\circ$  2D cesium superlattice. In Rb and K derivatives, the only band of the alkali present ( $10.$ ) corresponds nearly to a  $2 \times 2 R 0^\circ$  structure, but with very short range order. Stronger interactions of cesium atoms with the host compared to other alkali metals could explain this difference in the 2D structure.

#### Intercalation in $NH_3$ solution :

The identity period ( $I_c=6.3\text{ \AA}$ ) and the mass uptake (50%) are lower than the values which were previously observed for the first stage  $Cs(NH_3)_{2.2}C_{12.8}$  graphite compound prepared in the same conditions [3]. After washing the specimens in ethanol, we observed a change in the  $00l$  lines, probably due to partial desintercalation. After this treatment, the compound remained stable in air for a long time and transport measurements could be realized.

Electrical resistivity increases as the temperature decreases from 300K to 4 K. The variation of resistivity in the host ( $B_{0.25}C_{0.75}$ ) and its intercalated compound is not a logarithm function of temperature as it would be expected for a weak localization effect in a turbostratic pyrocarbon structure. Similarly, the magnetoresistance becomes positive at low temperature whereas it is usually negative for turbostratic carbon. Usual theories are unable to account for this phenomenon already reported in other studies [4].

## Conclusion

The fact that  $B_xC_{1-x}$  compounds do not intercalate larger amount of heavy alkali metals as compared to graphite is due to the bad crystallinity of the host. In order to improve the intercalation capacity and the conductivity of the materials we plan to intercalate heat treated boronated carbons.

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