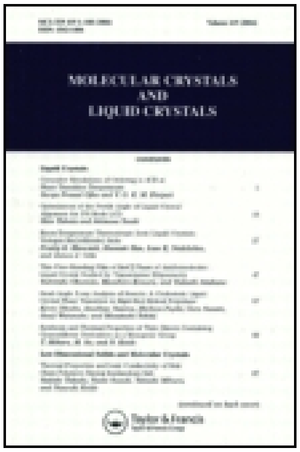

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Intercalation of heavy alkali metals in boron substituted carbons B_xC_{1-x}

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Abstract : First stage intercalation compounds were obtained using vapor reaction of heavy alkali metals (M= K, Rb and Cs) with B_xC_{1-x} platelets (x=0.1 and x=0.25). Depending on the value of x, $M(B_{0.1}C_{0.9})_{8\pm1}$ and $M(B_{0.25}C_{0.75})_{10\pm1}$ compounds were formed. Intensity calculations of the *00l* lines suggested domains of $M(B_xC_{1-x})_5$ first stage dense structure. As formed $B_{0.25}C_{0.75}$ was incompletely intercalated by cesium from its liquid ammonia solution whereas extended intercalation was obtained with heat treated $B_{0.25}C_{0.75}$ host (T=1600°C) giving a first stage $Cs(B_{0.25}C_{0.75})_{12}$ derivative.

Keywords : Boronated carbon, Heavy alkali metals, intercalation, X-ray diffraction, Electrical conductivity, Magnetoresistance, Interstratification.

INTRODUCTION

Boron substituted carbons B_xC_{1-x} (0<x<0.25) are known to intercalate lithium in a larger extent than graphite due to the electron acceptor properties of the boron atoms [1]. Since cristallinity is decreasing when x increases from 0.1 to 0.25 [1], understanding the influence of structure on the reactivity with alkali metals is of great interest. Heavy alkali metals (with K, Rb, or Cs) were intercalated in as prepared $B_{0.25}C_{0.75}$ and $B_{0.1}C_{0.9}$ and in $B_{0.25}C_{0.75}$ heat treated at 1600°C.

EXPERIMENTAL

Platelets of turbostratic B_xC_{1-x} synthesized by CVD at 1100°C were used as host materials; for some experiments further heat treatment was performed at 1600 °C under argon. Oriented platelets were carefully outgassed at 400°C and allowed to react with K, Rb and Cs vapor using the conventional two bulb method. We selected the temperatures of boronated carbon (T_{host}) and alkali metal (T_M) in order to prepare the first stage derivatives. They were respectively T_M=310°C and T_{host}=350°C for cesium derivatives, whereas lower temperatures (typically T_{host}=270°C and T_M=250°C) were used with potassium and rubidium. Particularly with potassium, equilibrium is reached after a long reaction time (more than one week). The alkali metal content was estimated from the weight uptake at the end of the reaction. Elemental analysis were also performed in "Centre d'Analyses, CNRS,Vernaison, France".

Cesium compounds were also prepared by allowing the host to react with a diluted cesium blue solution in liquid ammonia (T=-40°C). After dipping several days into the blue solution, the B_xC_{1-x} platelets were washed with pure liquid ammonia and finally pumped to 10^{-4} mbar in order to remove the ammonia excess.

00l lines and *hk* bands were recorded by X ray diffraction on a rotating crystal, respectively in reflection and transmission modes, with a curve position sensitive detector (INEL CPS 120) at λ=0.70926 Å for the cesium and potassium compounds and λ=1.5406 Å for the rubidium derivatives because of Rb fluorescence with $Mo_{K\alpha 1}$ radiation.

Electrical resistivity and magnetoresistance of a cesium compound synthesized in ammonia solution were measured with a conventional four probe method using silver paste as electrical contacts in the range [4K-300K].

RESULT 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 and Fig. 2) are typical of first stage derivatives.

The amount of alkali metal intercalated in a given host is independent of its nature among K, Rb or Cs. However the content is higher in $B_{0.1}C_{0.9}$ than in $B_{0.25}C_{0.75}$, respectively $M(B_{0.1}C_{0.9})_{8\pm1}$ and $M(B_{0.25}C_{0.75})_{10\pm1}$. It has been suggested that better cristallinity of $B_{0.1}C_{0.9}$ as compared to $B_{0.25}C_{0.75}$ could be explained by a smaller content of interstitial boron. This could be the reason for more extended intercalation of the alkali metal in $B_{0.1}C_{0.9}$. The identity periods (table 1) of $M(B_{0.25}C_{0.75})_{10}$ compounds are slightly smaller than $M(B_{0.1}C_{0.9})_8$ derivatives, but comparable to those of corresponding GIC. Despite intercalation rate in B_xC_{1-x} is comparable to that of GIC, the compounds almost keep a black color instead of being golden. On the other hand, heat treatment of $B_{0.25}C_{0.75}$ at 1600°C prior to cesium reaction results in the formation of a $Cs(B_{0.25}C_{0.75})_8$ golden compound.

M	$M(B_{0.25}C_{0.75})_{10}$ I_c [Å]	$M(B_{0.1}C_{0.9})_8$ I_c [Å]	MC_8 GIC I_c [Å]
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 (I_c) of $M(B_{0.25}C_{0.75})_{10}$, $M(B_{0.1}C_{0.9})_8$ and MC_8 GIC.

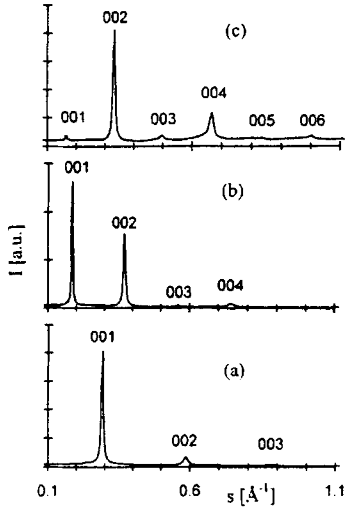

Figure 1 : *00l* diffractograms of $B_{0.1}C_{0.9}$ (a) and its intercalation compounds with K (b) and Cs (c).

Broadening and "wings" of the *00l* lines with increasing diffraction angle, either for host or for the intercalated compounds can be explained by the presence of random fluctuations in the layer positions (along the c axis) [2].

Details of the diffractograms of cesium and rubidium intercalation compounds presented asymmetric *00l* lines particularly at large angle. This effect could not be due to fluctuations in the positions of the layers but is rather explained by interstratification of another structure in the main first stage structure. The profiles of *00l* lines of $Cs(B_{0.25}C_{0.75})_{10}$, $Cs(B_{0.1}C_{0.9})_8$, and $Rb(B_{0.25}C_{0.75})_{10}$ were temptatively reproduced by ab-initio calculations. In all the cases the best fits were obtained if a conventional first stage $M(B_xC_{1-x})_{9\pm1}$ structure is interstratified with a dense first stage $M(B_xC_{1-x})_{5\pm1}$ structure. For example, in the case of the first stage $Cs(B_{0.1}C_{0.9})_{8\pm1}$ compound (I_c=6.02Å), intensity calculations[2] showed good agreement with the experimental data for if this derivatives is interstratified with 16% of a first stage $Cs(B_{0.1}C_{0.9})_5$ phase (I_c=6.3 Å) (Fig. 2). Interstratification of a dense structure was also pointed out in the $Cs(B_{0.25}C_{0.75})_8$ golden compounds from $B_{0.25}C_{0.75}$ heat treated at T=1600°C. 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 as compared to pure carbons.

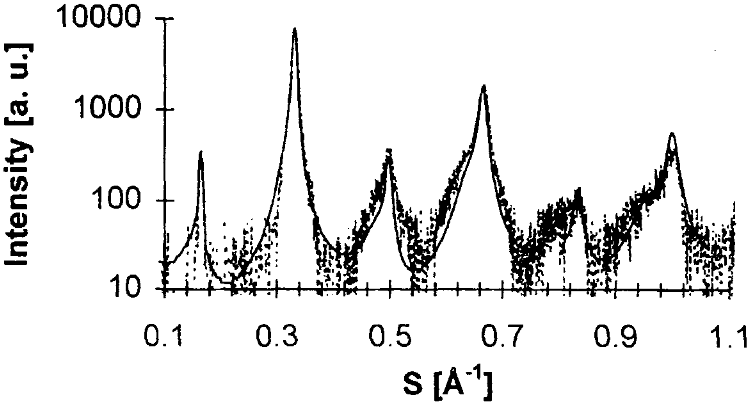

Figure 2 : Experimental *00l* scan of $Cs(B_{0.1}C_{0.9})_{8\pm1}$, (dashed lines). The continuous line is the result of a model in which 84% of the first stage $Cs(B_{0.1}C_{0.9})_8$ (layer A, I_c=6 Å) is interstratified with 16% of $Cs(B_{0.1}C_{0.9})_5$ (layer B, I_c=6.3 Å). The positions along the c axis are supposed to follow a Gaussian law. The mean square deviation $<\delta^2>$ is equal to 0.0036.

The profiles of the *10.* and *11.* bands of the boronated carbon substrate 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 by a 2×2 R 0° 2D cesium superlattice. In Rb and K derivatives, the only bands (*10., 20.*) of the alkali corresponds nearly to a 2×2 R 0° structure, but with a very short range order. Stronger interactions of cesium atoms with the host compared to other alkali metals could explain this different 2D structure. Cesium atoms are to placed above the potential holes of the boron carbide honeycomb though adjacent planes are not correlated as indicated by the absence of *10.l* and *11.l* lines.

Intercalation in NH_3 solution :

Cesium intercalation was performed on as deposited $B_{0.25}C_{0.75}$, and also after annealing under argon at =1600 °C. Heat treatment at T=1600°C enabled to improve the cristallinity and very few impurities of B_4C appeared.

Intercalation in as deposited $B_{0.25}C_{0.75}$ in NH_3 solution was more developed with increasing reaction time. Actually the mass uptake increase from 48 % to 79 % when the reaction time was respectively one day and four days but the complete intercalation was never reached. The compositions deduced from chemical analyses were respectively $Cs(NH_3)_{0.04}(B_{0.25}C_{0.75})_{35}$ and $Cs(NH_3)_{0.16}(B_{0.25}C_{0.75})_{17}$. In the best cases, cesium content is lower than in the first stage $Cs(NH_3)_{2.2}C_{12.8}$ graphite compound prepared in the same conditions [3]; moreover with boronated carbons NH_3 content is negligible. Considering that the compound is a first stage, the identity period deduced from *00l* diffractogram is 6.05 Å (no *001* peak). Intensity calculations show that the experimental pattern cannot be reproduced by a pure first stage but rather with 30% of pure $B_{0.25}C_{0.75}$ (I_c=3.4 Å) interstratified in the first stage $Cs(B_{0.25}C_{0.75})_9$ (I_c=6.05 Å). Consequently only partial intercalation occurred in $B_{0.25}C_{0.75}$ probably as a consequence of two short reaction time.

The rate of intercalation was improved through the reaction of heat treated $B_{0.25}C_{0.75}$ (1600°C) in NH_3-Cs solution during one day. A 96% mass uptake was observed giving the composition $Cs(B_{0.25}C_{0.75})_{11.8}$ on the hypothesis of a negligible NH_3 content. The *00l* diffraction pattern is characteristic of a first stage derivative with I_c=6.28 Å and the lines were correctly fitted by a 1/1 mixture of first stage $Cs(B_{0.25}C_{0.75})_8$ and $Cs(B_{0.25}C_{0.75})_{12.5}$.

Cesium intercalation compounds prepared from as deposited $B_{0.25}C_{0.75}$ was washed in ethanol. The *00l* diffractogram is modified but it does not correspond to that of pristine $B_{0.25}C_{0.75}$. It indicates only a partial deintercalation and the formation of a residual compound which remains. Therefore, transport measurements could be performed.

Electrical resistivity increases as the temperature decreases from 300 K to 4 K. The resistivity of the $B_{0.25}C_{0.75}$ host and of its intercalation compound does not follow 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

Vapor reaction of alkali metals (K, Rb or Cs) with as deposited $B_{0.25}C_{0.75}$ and $B_{0.1}C_{0.9}$ hosts leads to $M(B_{0.1}C_{0.9})_{8\pm1}$ and $M(B_{0.25}C_{0.75})_{10\pm1}$ first stage intercalation compounds (M= K, Rb and Cs). The amount of metal intercalated is depending on the cristallinity and it can be increased by heat treatment of the host up to 1600°C. Evidence of dense $M(B_x\ C_{1-x})_5$ domains interstratified in the first stage structure, showed that in spite of bad cristallinity of the host, boron acts as an electron acceptor and improves partly the intercalation of alkali metals as compared to pure carbons. Intercalation in liquid ammonia solution of cesium is incomplete with $B_{0.25}C_{0.75}$ but it is improved with heat treated $B_{0.25}C_{0.75}$ host (T=1600°C) so that a first stage $Cs(B_{0.25}C_{0.75})_{12}$ is obtained. The cesium content is however lower than in the vapor phase method. This is probably due to ammonia cointercalation during the preparation.

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