Graphite intercalation compounds with BF_3/F_2: preparation and characterization

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Abstract

Graphite intercalation compounds have been prepared by reaction of highly oriented pyrolytic graphite (HOPG) with mixtures of BF_3/F_2. Pure stages I–III have been obtained. ^{19}F NMR measurements indicate that the intercalant consists of mixtures of BF_3 and BF_4^-. Weight uptake measurements combined with charge transfer determined from reflectivity measurements show that the BF_3/BF_4^- ratio in stage I may be as high as 3.

Introduction

The mechanism of conductivity in graphite intercalation compounds (GICs) and its relation to charge transfer and the identity of the intercalated species have been the focus of much research activity [1]. However, there are only a few reports in which the conductivity and charge transfer were measured independently using different techniques (but on the same sample) in the same laboratory. This paper reports on the intercalation of BF_3 into highly oriented pyrolytic graphite (HOPG). Physical measurements, such as transport properties, on these GICs have been previously reported elsewhere [2]. Boron trifluoride alone cannot be intercalated into graphite; an additional oxidizing agent such as fluorine is necessary. In the past, the intercalation of graphite with BF_3 has been achieved using the nitronium ion (NO_2^+) [3, 4], ClF [5, 6] or F_2 [7] as oxidizers. Both first- and second-stage compounds of nominal composition C_7BF_4 [7] and $C_{16}BF_4$ [5] have been reported.

Experimental and results

Graphite in the form of HOPG was supplied by A. W. Moore of Union Carbide Co. (Amoco). Graphite samples were baked out at 300 °C under vacuum prior to use. BF_3 and F_2 were obtained from Matheson Co. The BF_3 was purified by trap-to-trap distillation and the fluorine was freed of HF by contacting with CsF. Infrared spectra attested to the absence of impurities, particularly HF.

Samples of given stage were prepared on a Sartorius Model 4201 magnetic suspension balance. Such a balance has been previously used in the intercalation or deintercalation of graphite [8] but, to our knowledge, this is almost the only use of such a balance with fluorine and/or fluorides, except for one report of its use with AsF_5 [9]. The balance features a stainless-steel reaction chamber which is completely isolated from the balance beam mechanism and thus allows weight change measurement as a function of time in corrosive gases up to a pressure of several atmospheres. The HOPG samples were contained in a platinum cup suspended from a free floating magnet in the BF_3/F_2 atmosphere. This magnet was magnetically coupled through a sapphire window to a magnet suspended from the balance beam. An electromagnetic feedback circuit maintained a constant attractive force and a constant gap between the magnets and thus accurately transmitted weight changes to the balance mechanism (± 0.1 mg). The gas mixtures reacted somewhat with the stainless steel walls (but not with the gold-plated magnet assembly and Pt cup) causing a small continuous decrease in pressure. These pressure changes were monitored with an MKS Baratron to ± 0.1 Torr, and corresponding buoyancy corrections were applied to the weight readings. The reaction could thus be terminated at any desired stoichiometry, and allowed isolation of pure stages. At the end of the run the reaction chamber was evacuated. The difference between the initial and final weights under vacuum usually corresponded within ± 0.2 mg to the continuously recorded weight changes after correcting the latter for buoyancy effects. Samples were removed for other measurements under a strong flow of dry nitrogen (99.999%), and further handling was carried out in a Vac/Atmospheres Dri-Lab.

The intercalation of graphite with BF_3/F_2 mixtures could be followed either by continuous monitoring of the specific conductivity as a function of time or by following weight increases as a function of time. The weight increase of a 22 mg HOPG sample in a 1000 Torr of a 1:1 BF_3/F_2 mixture is shown in Fig. 1. Stoichiometries were labelled as *nominal* in terms of BF_4^-, because NMR data indicated the presence of both BF_3 and BF_4^-. The curves feature reproducibly a change of slope at an approximate stoichiometry C_{14}"BF_4", which may indicate a transition from stage III to stage II. Another, much less pronounced, change of slope appears at $C_{9.5}$"BF_4", which may indicate a transition from stage II to stage I. A plateau is reached at a stoichiometry $C_{7.6}$"BF_4", beyond which there is no further weight uptake. This corresponds to stage I. Pure stages are attained in the ranges indicated in Fig. 1 and mixtures of stages elsewhere. No pure stages higher than III were obtained. Analyses of the weight-uptake measurements (Fig. 1) suggest that at the beginning of the intercalation the weight uptake is proportional to $t^{1/2}$, t being the exposure time. This is consistent with theories [10] and previous experiments on other intercalants [11].

The stage of the compound was identified by X-ray (001) diffractograms using Cu $K\alpha$ radiation. Figure 2 shows typical diffractograms obtained for stages I–III.

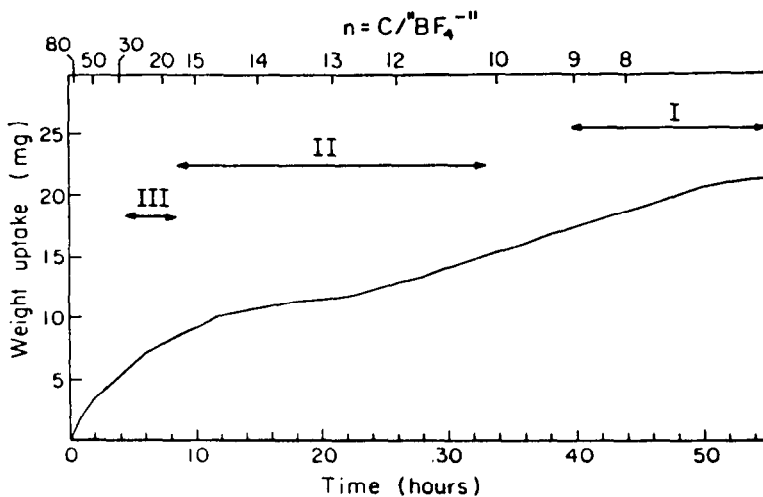Fig. 1. Weight increase as a function of time of a 22 mg sample of HOPG exposed to a 1:1 mixture of BF_3/F_2. Note the ranges in stoichiometry ratios where pure stages can be isolated.

The d-spacings were obtained from the slopes of least-square linear plots of the l-values $vs.$ $2\lambda^{-1}\sin\theta$. The average repeat distances were: stage I, $I_c = 7.69(2)$ Å (in agreement with Rosenthal et $al.$ [7]); stage II, $I_c = 10.95(2)$ Å; stage III, $I_c = 14.21(2)$ Å. If these values are fitted to the standard equation $I_c = (n-1)3.35 + d_s$ then the filled layer spacings, d_s, contract from 7.69 Å (stage I) to 7.60 Å (stage II) to 7.52 Å (stage III).

In-plane resistivity measurements

The a-plane resistivity, ρ_a, was measured by the a.c.-contactless technique [12]. The resistivity as a function of nominal stoichiometry and stage is shown in Fig. 3. These results differ from the compounds obtained with NO_2BF_4, because the latter contain co-intercalated CH_3NO_2, and no stage I is obtained. Moreover, the present compounds show a minimum resistivity of $3\,\mu\Omega$ cm at stage III, and stage I has a resistivity of $100\,\mu\Omega$ cm; $i.e.$ 2.5 times that of HOPG. The in-plane resistivity $vs.$ temperature for the three stages has been reported previously [2].

^{19}F NMR identification of the intercalant species

^{19}F NMR measurements were performed on a Bruker WH-300. The intercalated HOPG samples were cut to fit the inside diameter of standard 5 mm NMR tubes and stacked on top of each other with the c-axis parallel to the length of the tube and the magnetic field axis. This geometry was
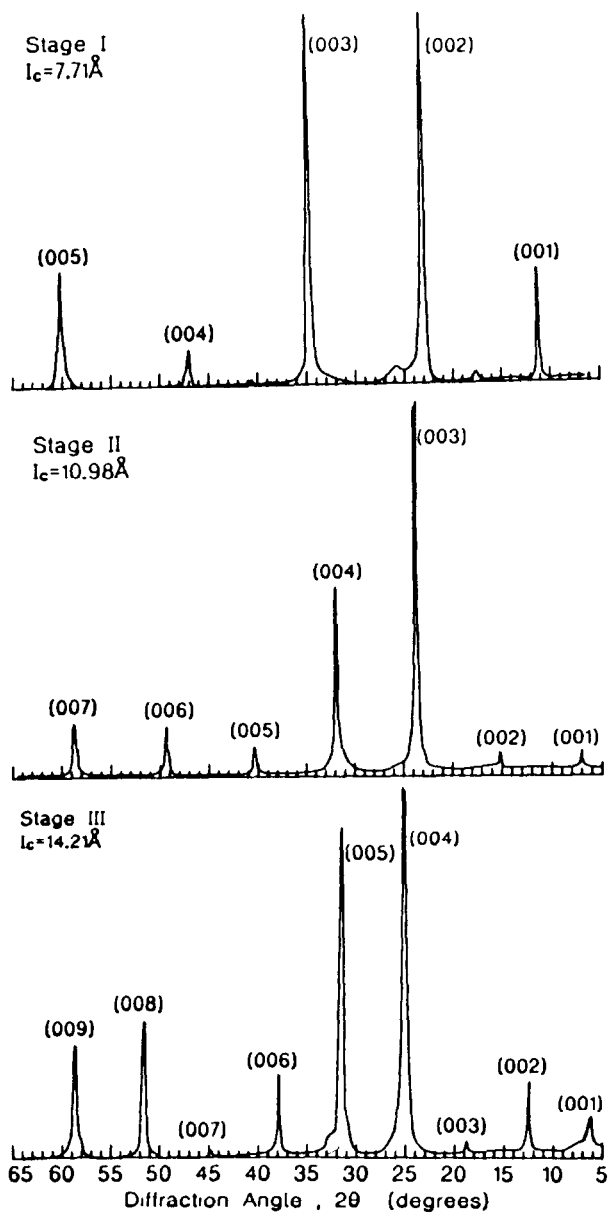
Fig. 2 X-ray diffractograms of pure stages I–III

required to overcome skin depth effects and took advantage of the low conductivity along the c-axis (large skin depth along the a-axis).

We have used the chemical shifts of the different species (BF_4^-, BF_3, F^-) for the identification. The NMR spectra for H $\parallel$ c are shown in Fig. 4. The chemical shifts observed (measured $vs.$ C_6F_6) are
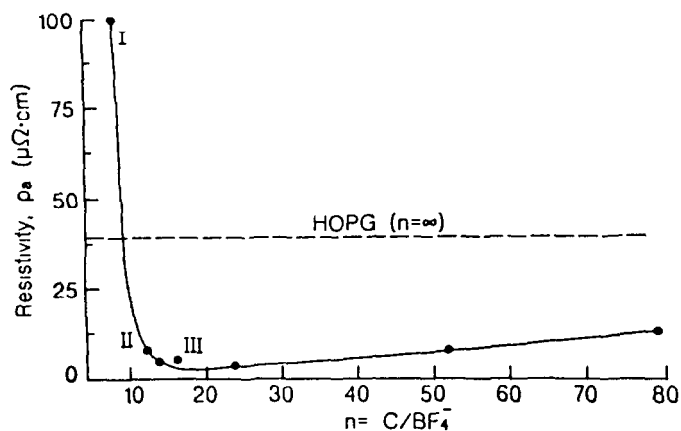
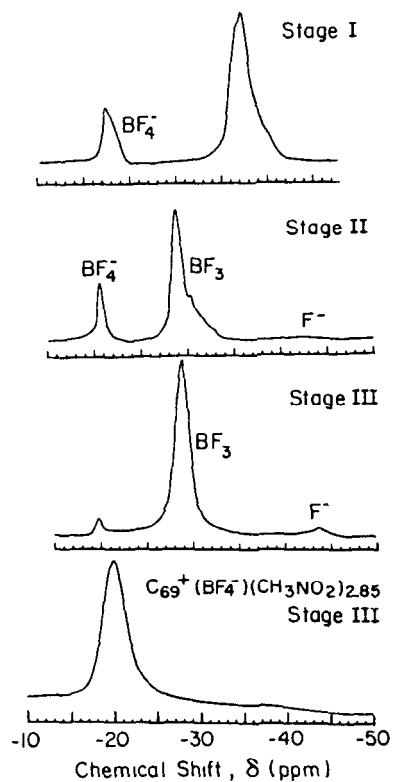Fig 3 Resistivity of HOPG as a function of time of exposure to BF_3/F_2 mixtures Roman numerals indicate stage numbers

Fig 4 ^{19}F NMR spectra of stages I–III as well as of a graphite/BF_4^- salt co-intercalated with nitromethane

TABLE 1

^{19}F NMR shifts of GIC with BF_3/F_2 [a]

Stage	$\delta(BF_3)$	$\delta(BF_4^-)$	$\delta(F^-)$
I	− 37.3	− 22.5	—
II	− 29.2	− 20.8	− 42.0
III	− 29.1	− 19.8	− 43.7
A [b]	—	− 20.0	
Lit. [13]	− 29.6	− 13.0	− 40.0

[a] $vs.$ C_6F_6.
[b] $A = C_{69}^+(BF_4^-)(CH_3NO_2)_{2.85}$.

summarized in Table 1, together with the literature values [13]. The use of chemical shifts alone to identify the intercalated species must be treated with caution, especially in an anisotropic medium where shift anisotropies may play a role. The plausibilities of the assignments for stages II and III are strengthened by the fact that the intensity ratios BF_4^-/BF_3 increase with time, indicating the release of neutral BF_3 from the lattice. Furthermore, authentic intercalated BF_4^- obtained from the reaction of HOPG with NO_2BF_4 in nitromethane [3, 4] gives only *one* signal, essentially the same as that assigned here to BF_4^- in $HOPG/BF_3/F_2$, although the absolute shifts differ from the literature value. This may be due to different environments. The presence of $B_2F_7^-$ has been postulated to account for the quadrupole splitting in the ^{11}B NMR spectra [6]. For stage I, the chemical shifts not only differ significantly from the literature values, but are also shifted considerably as a function of time. Hence, the assignments to BF_4^- and BF_3 are somewhat questionable. Perhaps at the high concentrations of BF_3 present in stage I the presence of $B_2F_7^-$ may account for the shifts from the literature values. The tetrafluoroborate salt was identified as stage III with $I_c = 14.56$ Å, identical to that reported by Billaud *et al.* [4].

Because part of the BF_3 is evolved spontaneously, calculation of the BF_3/BF_4^- ratio from relative peak heights is unreliable. This ratio can be estimated from a combination of weight uptakes and the degree of charge transfer per carbon atom obtained from reflectivity measurements [2]. The latter show that the charge transfer per carbon atom is about 0.032 for stage I; *i.e.* the graphene layers are not over-oxidized by the intercalant [2]. It is thus reasonable to assume that the charges transferred to the graphene layers are free with a mean free path of at least 5 Å. Based on this assumption and that stage I contains no observable concentration of F^-, the degree of charge transfer per intercalated species is about $7.6 \times 0.032 = 0.24$; *i.e.* about a quarter of the intercalated BF_3 appears as BF_4^-. Thus, the stoichiometry for stage I would be $C_{32}^-(BF_4^-)(BF_3)_3$. The *caveat* regarding the identity of the species in stage

I should be borne in mind, however. Nevertheless it is evident that, contrary to previous assumptions [7], the intercalated species is not exclusively BF_4^-.

It is of interest to compare the filled layer spacing ($d = 7.69$ Å) with that calculated from $r(B-F)$, the bond length of BF_4^-, for different geometries. This bond length, as determined from crystal-structure analyses of various structures containing the BF_4^- moiety, ranges from 1.29 Å to 1.40 Å with a trend to shorter bond lengths for larger cations [14]. If we take $r(B-F) = 1.34$ Å and assume that the BF_4^- lies between the graphene layers with its C_2 axis parallel to the graphite c-axis, the calculated repeat distance would be 7.49 Å. With the C_3 axis of BF_4^- parallel to the c-axis, the calculated repeat distance is 7.73 Å, *i.e.* in reasonable agreement with the measured one of 7.69 Å. The second structure is therefore to be preferred.

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