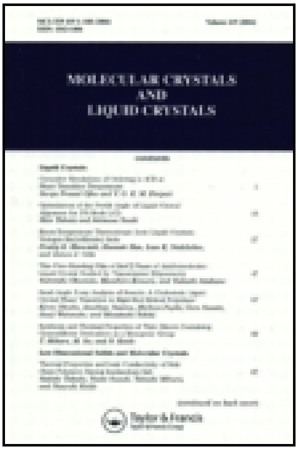

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Nano-Graphites and their Potassium Intercalated Compounds: Structural and Electronic Properties

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Nano-Graphites and their Potassium Intercalated Compounds: Structural and Electronic Properties

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Graphite-nano particles were prepared by the heat-treatment of diamond-nano particles. Various heat-treatment temperatures in the range 900–1600°C were used. X-ray diffraction studies indicate that the onset temperature of diamond-graphite transition is around 1000°C and the complete conversion of diamond to graphite occurs at 1600°C. X-ray diffraction studies on the potassium intercalated compounds of these graphite-nano particles, while indicating the absence of staging phenomenon, show that small neutral potassium clusters are included in these intercalated compounds. The presence of neutral potassium clusters could also explain the observed magnetic susceptibilities and the large deviations in the ESR g-values of these intercalated nano-graphitic systems.

Keywords: Diamond-graphite conversion; Graphite nano-particles; Potassium intercalated graphite

INTRODUCTION

Carbon based nano-scale materials such as fullerenes, nano-tubes and nano-graphites are envisaged to possess novel electronic properties because of their specific sizes and their large specific surface areas. Among these, nano-graphites are characterized by highly disordered stacking of finite-size flat graphene sheets with open edged surfaces and large number of defects quite different from their closed surface counter parts, fullerenes and nanotubes. Recent theoretical reports by Fujita and coworkers[1] suggest that in the case of nano-graphites, non-bonding π-levels of edge origin appear around the Fermi energy, which are dependent on the shape of the nano-graphite edges. Diamond nano-particles subjected to heat-treatment at about 1600°C are completely converted to graphite and show an enhancement[2] in the density of states around the Fermi energy agreeing well with the theoretical predictions. These specific electronic features of nano-graphites are expected to give interesting intercalation compounds that are quite different from the well known bulk graphite intercalation systems. In this paper we report our results on the structural and electronic properties of the potassium intercalated compounds of heat-treated diamond nano-particles. The structural characteristics were investigated by X-ray diffraction studies and the electronic properties were probed by ESR and magnetic susceptibility measurements.[3]

EXPERIMENTAL RESULTS AND DISCUSSION

Diamond-nano particles (typical size ~5nm) were subjected to various heat-treatment temperatures(HTT) viz. 900, 1200, 1400 and 1600°C under argon atmosphere for about 3hrs. Figure 1 depicts the powder X-ray diffraction profiles of the diamond nano-particles in comparison with the profiles of HTT900, 1200, 1400 and 1600 samples. The diamond-nano particles show a peak centered around 43° corresponding to diffraction from the diamond (111) planes. No significant change is observed in the diffraction pattern of the HTT900 sample, but as the HTT is increased a broad-weak peak around 26° starts to appear for the 1200 heat-treated sample. The diamond (111) diffraction peak becomes broader indicating a decrease in the size of diamond particles. For the HTT1400 sample, these features, a broad peak around 26° and increase in the diamond (111) peak width, become much more clear. In case of HTT1600 sample, the peak originating from diamond (111) planes is completely absent; instead new peaks that could be assigned to graphite (100) and (101) appear around 45°. This clearly shows that at 1600°C all the diamond particles are completely converted to graphite. The resulting

HTT1600 nano-particle forms a polyhedron with a hollow inside, whose facets consist of 3-6 graphene sheets with an in-plane size of 7-8nm and an inter sheet distance of 0.353nm.[2] The considerable increase in the inter sheet distance in comparison with bulk graphite evidences a corrugated feature of the graphene sheets in these samples. Diamond surfaces are unstable even at room temperature due to the presence of σ dangling bonds protruding from the surfaces[4]. The as prepared nano-diamond clusters are known to be covered by amorphous graphite on their surfaces due to the easy reconstruction of the diamond (111) planes into graphene planes. Our X-ray diffraction results clearly demonstrate that heat-treatment under inert conditions above ca. 1000°C converts these diamond-nano particles to graphite starting from the cluster surface inwards.

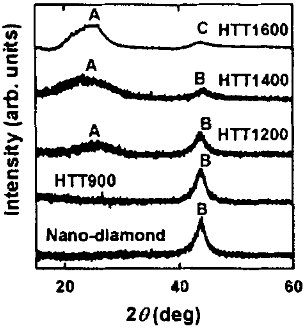

FIGURE 1 X-ray diffractograms of various heat-treated nano-diamond particles. A and C are indexed to (002)and (100),(101) of graphite and B to (111) of diamond.

Potassium intercalation into the heat treated diamond nano-particles was carried out utilizing the standard two-zone vapor transport method used for the preparation of bulk-graphite intercalation compounds (K-GIC's).[5] The compositional ratios were estimated from the weight uptake measured under inert argon atmosphere in a glove-box. Potassium could be intercalated only for the samples heat treated above 1200°C, suggesting that in the samples prepared at lower HTTs the diamond (111) planes are not well graphitized to be able to accommodate the potassium in the inter sheet galleries. However, for HTT1600 sample various concentrations of potassium could be intercalated, leading to the approximate compositions of C_9K, $C_{29}K$ and $C_{36}K$, when the same reaction conditions to those for bulk stage –1, 2 and 3 K-GIC's, were employed respectively. The X-ray diffraction profiles revealed the presence of broad shoulders around 30-35°, in addition to the graphite (002) peak. Here we discuss the structure and electronic properties of C_9K in detail. The presence of graphite (002) peak clearly indicates that still large portions of nano-graphite is intact even after the intercalation of potassium. After corrections for the Lorentz polarization factor and atomic form factor, we could fit these broad features to three Lorentzian functions (Figure 2), at 2θ values of 25.4°, 29.1° and 32.3°, corresponding to the graphite (002), II stage (003) and I stage (002) of bulk K-GIC. Formation of such a mixed stage compounds is understandable since the HTT1600 sample is known to have a poly-hedral cage like structure.[2] Hence, it will be difficult for the potassium to penetrate deep into the cages and form a perfectly ordered staging structure as observed in bulk GICs. From the ratios of corrected X-ray intensities and the weight uptake measurements we determined the molar ratio of each component in C_9K to be 0.36 (nano-graphite), 0.33 (C_8K), 0.26 ($C_{24}K$) and 0.05 (neutral potassium). The observed magnetic susceptibility at room temperature for C_9K is 1.33×10^{-5} emu/1C mole. We assumed the observed susceptibility of C_9K as a sum of susceptibilities of individual components[6] multiplied by their molar ratio; and the estimated value at room temperature is 1.91×10^{-5} emu/1C mole, which agrees well with the observed value. However it should be noted that

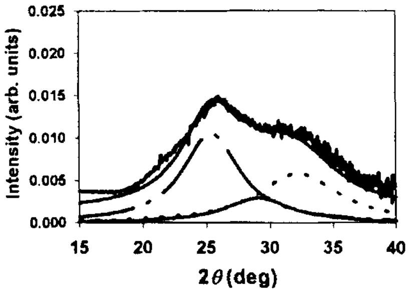

FIGURE 2 Observed and deconvoluted powder X-ray profile for C_9K. The diffraction pattern was fitted for contributions from (002) of graphite (_ _ _), (002) of C_8K (---) and (003) of $C_{24}K$(—).

the observed susceptibility at room temperature for bulk C_8K is 1.41×10^{-5} emu/1C mole, which is also very close to our experimentally observed value. The absence of enhancement in the spin susceptibility in C_9K, could be explained in terms of the charge transfer from potassium to graphite, which makes an upward shift in the Fermi energy from the position where the edge-inherited non-bonding π-states are located.

ESR studies show asymmetric line shapes. Figure 3 shows the temperature dependence of g-values. The temperature dependence of g-values suggests the presence of two kinds of spin species interacting with each other. One of the spin species which have a g-value of g = 2.0013, show Curie type temperature dependent susceptibility and are associated with the localized spins of defect origin. The other spin species showing large shifts in g-value (g =1.9981) is characterized as Pauli spins from the temperature independent susceptibility. The g-values of potassium intercalated bulk graphite do not deviate much from the free electron g-values (Fig. 3). Hence the large g-deviations observed in C_9K should be originating from the *included* neutral potassium clusters. Indeed, such large deviations of g-values were observed in the case of neutral potassium clusters included in zeolites[7], where the host zeolite matrix does not have strong interaction with the included alkali metal clusters. Thus the large shifts in g-values confirm the presence of neutral potassium clusters in intercalated nano-graphite.

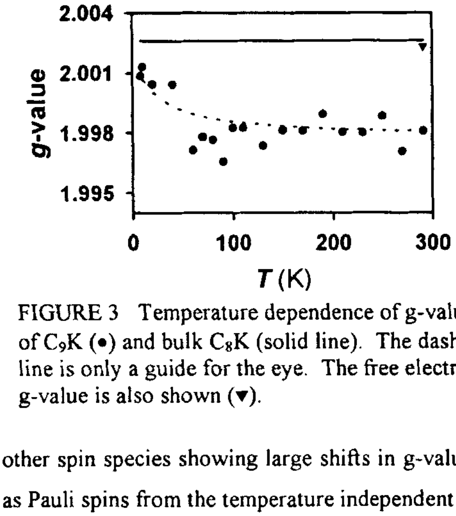

FIGURE 3 Temperature dependence of g-values of C_9K (•) and bulk C_8K (solid line). The dashed line is only a guide for the eye. The free electron g-value is also shown (▼).

CONCLUSIONS

Diamond nano-particles when heat-treated above ca. 1000°C are converted to graphite from the cluster surface inwards and the complete conversion takes place at about 1600°C. Potassium intercalation into these nano-graphites was carried out using the standard two-zone vapor transport method. In case of HTT1600 sample, where different concentrations of potassium could be intercalated, X-ray diffraction studies reveal the formation of mixed stage compounds, apart from the presence of neutral potassium clusters. The observed magnetic susceptibility and the large shifts in ESR g-values also support the presence of neutral potassium clusters. Further analysis like electron microscopy and Raman studies are underway to clearly understand the electronic structure and discern the interaction path ways between Pauli type spins of the potassium clusters and the conduction and localized spins of the nano-graphite.

Acknowledgements
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