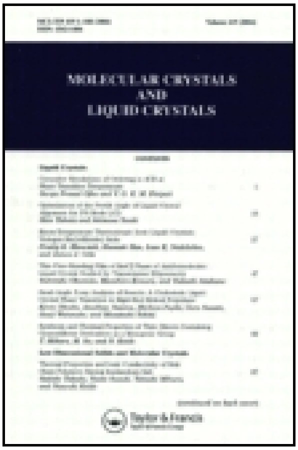

Molecular Crystals and Liquid Crystals

Raman scattering study of graphite fluorides

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RAMAN SCATTERING STUDY OF GRAPHITE FLUORIDES

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Highly fluorinated C_XF samples ($1 < x < 2$), prepared at room temperature and 515°C, were analysed by Raman and IR absorption spectroscopies. The effect of fluorination on structural disordering is analysed by observing both the Raman allowed E_{2g2} phonon mode at $1580\,cm^{-1}$ and the disorder induced phonon mode at $\sim 1360\,cm^{-1}$. Raman spectra suggested the coexistence of C_2F and C_1F phases.

Keywords: graphite; intercalation; fluorine; graphite fluorides

INTRODUCTION

Among the GICs, graphite-fluorine system has unique features because of the high reactivity of elemental fluorine. On one hand fluorine is intercalated into graphite in the presence of fluoride additives at ambient temperature forming C-F ionic or semi-covalent bond with high or semi conducting properties. On the other hand it reacts exothermally with graphite at high temperature ca. > 350°C to form graphite fluorides with C-F covalent bond having insulating properties [1]. In the present study, Raman scattering method and IR spectroscopy have been used to investigate the structure of highly fluorinated graphite phases and the formation process of graphite fluoride.

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EXPERIMENTAL

The details of preparation method of fluorinated graphite samples are described elsewhere [2]. For the preparation of highly fluorinated graphite, natural graphite powder (particle size: 57–74 µm) was fluorinated at room temperature by K_2NiF_6 or $KAgF_4$ and elemental fluorine under pressure in anhydrous HF. For the preparation of graphite fluorides, graphite powder (average diameter: 7 µm) was fluorinated at 515°C by elemental fluorine (1bar) for different fluorination times in the range from 1 min. to 10 hours in a batch type nickel reactor. The fluorinated samples were analyzed for elemental analysis, Raman spectroscopy ($\lambda = 514.5\,\text{nm}$), IR absorption spectroscopy and X-ray diffractometry.

RESULTS AND DISCUSSION

The fluorination condition, composition and XRD data of highly fluorinated graphite samples are compiled in Tables 1 and 2.

As shown in Table 1, C/F ratio was in the range of 1.88–1.25. A small amount of HF was detected in the sample R-1 due to the cointercalation of HF. The samples (R-3 and R-4), prepared using $KAgF_4$, have higher fluorine contents than those prepared by K_2NiF_6 (R-1 and R-2) because of the moderate oxidizing capability of the former. The I_C values are very high suggesting the formation of F double layers between a pair of graphene layer [1,3]. The lattice parameter along the a-axis i.e. a_0, is also larger in all samples than that of original graphite, 0.2461 nm due to the weakening of C-C bond.

TABLE 1 X-ray Diffraction Data and Compositions of C_XF Samples Prepared by K_2NiF_6 or $KAgF_4$ and Elemental Fluorine at Room Temperature [2]

			X-ray diffraction data			
Sample	F_2 (bar)	Fluoride	Stage^a	I_C(nm)	a_0(nm)	Composition
R-1	7.9	K_2NiF_6	1 (2) (3)	0.6435 (0.9334) (1.231)	0.2464	$C_{1.88}F(HF)_{0.58}$
R-2	11.8	K_2NiF_6	1	0.6470	0.2470	$C_{1.64}F$
R-3	11.8	K_2NiF_6	1 (2) (3)	0.6388 (0.9418) (1.240)	0.2466	$C_{1.46}F(HF)_{0.35}$
R-4	11.8	$KAgF_4$	1	0.6280	0.2480	$C_{1.37}F$
R-5	11.8	$KAgF_4$	1	0.6260	0.2474	$C_{1.25}F$

Here R stands for room temperature; ^{a}( ), minor phase.

TABLE 2 Compositions of C_XF Samples Prepared by Elemental Fluorine at 10^5 Pa at 515°C [2]

Sample	Fluorination time (min)	Composition	Color
H-1	1	$C_{1.90}F$	Black
H-2	2	$C_{1.45}F$	Black-Brown
H-3	3	$C_{1.27}F$	Brown
H-4	15	$C_{1.21}F$	Gray-Brown
H-5	30	$C_{1.19}F$	Gray
H-6	600	$C_{1.06}F$	White

As shown in the Table 2, samples prepared at 515°C, were fluorinated to $1 < x < 2$ (in C_XF). The color also changed from black to white with increasing fluorine content. Samples H-1 and H-2 had graphite phase along with the graphite fluoride phase. X-ray diffractogram of sample H-1 showed a strong (0 0 2) diffraction line of graphite along with a weak (0 0 4) line, whereas sample H-2 showed a very weak (0 0 2) line suggesting that

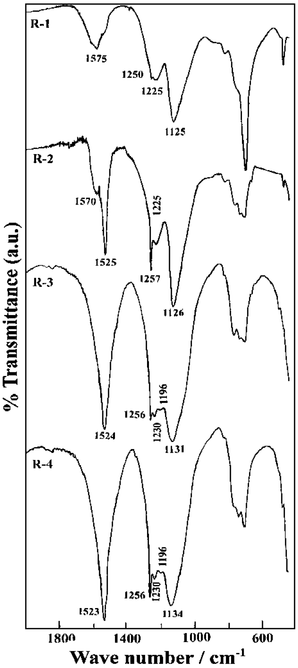

FIGURE 1 IR spectra of samples fluorinated at RT as given in Table 1.

graphite phase still remains. Samples H-3, H-4, H-5 and H-6 had brown, gray brown, gray and white colors, respectively, indicating that these samples are graphite fluorides with puckered graphene layers. No (0 0 *l*) diffraction line was observed for these samples, which may be due to highly disordered stacking of puckered graphene layers along the c-axis, because the original graphite is fine powder of small particle size of 7 μm. On the other hand, (1 0 0) line was observed in all the samples because two dimensional graphene layers were still maintained after fluorination.

Figures 1 and 2 show typical IR absorption spectra of samples prepared at room temperature and 515°C, respectively. As shown in Figure 1, all samples have similar characteristics. The main band comprises semi-covalent C-F bond at $1125 \sim 1134\,\mathrm{cm}^{-1}$ with two weak bands at $1230\,\mathrm{cm}^{-1}$ and $1256 \sim 1257\,\mathrm{cm}^{-1}$. The band at $1230\,\mathrm{cm}^{-1}$ is covalent C-F bond. The peak at $1196\,\mathrm{cm}^{-1}$ is stronger than that observed for C_2F ($1100\,\mathrm{cm}^{-1}$) suggesting that these samples contain C_1F phase. The strong bands at $1575 \sim 1523\,\mathrm{cm}^{-1}$ are due to the A_{2u} mode of graphite lattice indicating that the planarity of graphene layers is preserved. Figure 2 shows the IR spectra of samples prepared at 515°C. A strong band at $1218\,\mathrm{cm}^{-1}$ together

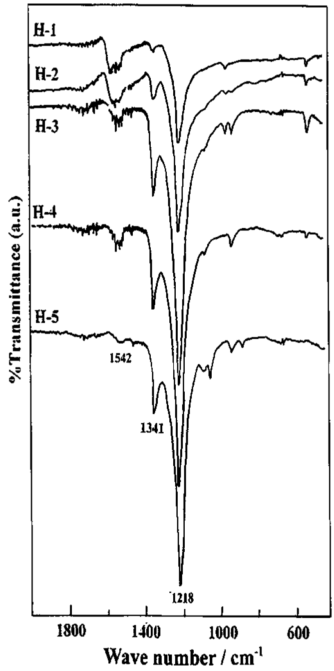

FIGURE 2 IR spectra of samples fluorinated at 515°C as given in Table 2.

with a weak band at 1341 cm^{-1} are due to covalent C-F bond and asymmetric stretching vibrations of peripheral CF_2 groups, respectively. A weak band at 1542 cm^{-1} is attributed to graphite with sp^2 character.

Figures 3 and 4 show Raman spectra of graphite samples fluorinated at room temperature and 515°C. As can be seen in Figure 3 the original graphite phonon mode at 1580 cm^{-1} splits into two modes. i) The mode at $1593 \sim 1583\ \text{cm}^{-1}$ is induced by charge density redistribution accompanying the contraction of C-C bond length as a result of an electron transfer from carbon to fluorine. This is a usual phenomenon observed in acceptor type GICs [1–4]. ii) a novel mode is observed at $1553 \sim 1549\ \text{cm}^{-1}$ with increase in the C-C bond length as confirmed by XRD data (see Table 1). All the samples in Figure 3 show well ordered phonon peaks which indicate the existence of planar graphene layers in these compounds inspite of high fluorine concentration. The planarity of graphene layers is confirmed by IR spectroscopy (see Fig. 1). The phonon mode at $\sim$1360 cm^{-1} is also broa-

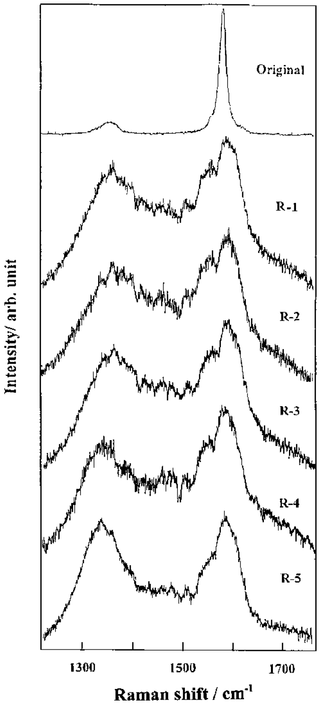

FIGURE 3 Raman spectra of original graphite and samples fluorinated at room temperature (as given in Table 1) [2].

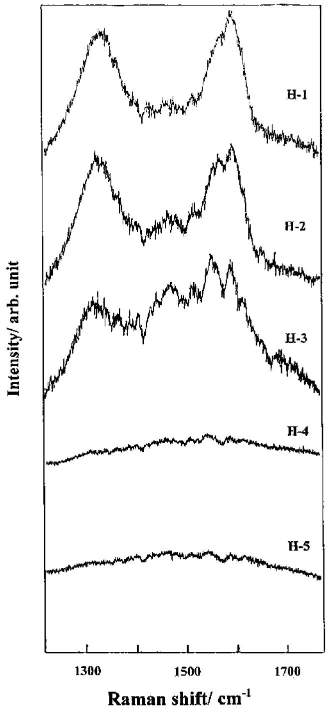

FIGURE 4 Raman spectra of graphite samples fluorinated at 515°C (as given in Table 2) [2].

dened and was in the range $1556 \sim 1337\,\text{cm}^{-1}$, which may be due to the increased level of disorder.

Interestingly, samples H-1 and H-2 (see Table 2) prepared at 515°C show similar Raman spectra as those of C_XF samples prepared at room temperature as shown in Figure 4. This is in agreement with the fact that graphene layers keep the planarity in these two samples. Raman spectrum of sample H-3 shows that graphite skeleton is not completely destroyed by fluorine, but the process is in the transition stage. For samples H-4 and H-5 prepared for 15 min. or more, all Raman modes completely disappeared due to the high level of disorder induced by the change of graphene layer from sp^2 to sp^3 hybridization. As a result, crystalline size of C_XF becomes much less than the optical wavelength. This breaks the translation symmetry and relaxes the conservation law of wave vector. So all phonon modes in principle can contribute to the Raman scattering process. Consequently usual Raman active phonon modes in the Brillouin zone is replaced by multiple small Raman active phonons at the center of the mini-zone [4].

Figure 4 reveals the formation mechanism of graphite fluoride at high temperatures. First the fluorine atoms are intercalated into graphite, forming graphite intercalation compound C_XF and planer C_XF layers are immediately changed to puckered graphite fluoride layers.

CONCLUSION

The Raman spectra of highly fluorinated graphite samples gave two adjacent Raman phonon modes suggesting the coexistance of C_2F and C_1F phases. The formation process of graphite fluoride consists of two steps, namely formation of planer C_XF layers and subsequent puckering of the fluorinated graphene layers.

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