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TERNARY INTERCALATION COMPOUND OF GRAPHITE WITH ALUMINUM FLUORIDE AND FLUORINE

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Ternary intercalation compound of graphite with AlF_3 and F_2, $C_xF(AlF_3)_y$ was prepared under fluorine atmosphere at temperatures of 20-400 °C. Typical 1st stage compound has a composition of $C_6F(AlF_3)_{0.15}$ with repeat distance 9.40 Å. Rapid progress in the reaction led to the formation of graphite fluoride, $(C_2F)_n$.

No graphite intercalation compound of metal fluoride with high melting and boiling points has been reported. The compounds hitherto prepared are those intercalated by such fluorides as liquid or gas at room temperature. In this paper we report the preparation of a graphite intercalation compound of AlF_3 with high sublimation point.

A mixture of flaky natural graphite and AlF_3 put in a nickel vessel was placed in a nickel reaction tube and the system was evacuated by a rotary pump at 20-100 °C. Fluorine gas was then introduced into the tube to 1 atm. After the reaction was kept at the same temperature for less than 1 hour, temperature of the reaction tube was raised up to 310-400 °C at heating rate of ca. 4 °C/min, being maintained for 24-45 hours at each temperature. To prepare graphite fluoride, $(C_2F)_n$, it was necessary either to leave the reaction system at room temperature for 5-6 hours after introduction of fluorine gas or to heat the reaction tube rapidly up to 400 °C at the rate of 30 °C/min, followed by the reaction for 5 hours at 400 °C.

Table 1 shows the result of elemental and X-ray analyses of the intercalation compound and graphite fluoride. Intercalation compound (2) was blue-black in color, whereas compound (1) into which the intercalant was not fully inserted was slightly bluish black. Compound (3) was such one as slightly decomposed losing some fluorine molecules. These compounds were so stable that their exposure to air for one day or immersion in water overnight could affect no change in their X-ray diffraction patterns. However, they released a trace amount of fluorine, being kept in glass ampul for more than 2 weeks. Furthermore when compound (1) was immersed in KI solution for several days, the color of the solution was changed to yellow.

Table 1. Analytical data for $C_xF(AlF_3)_y$ and graphite fluoride

No.	Compound	Elemental analysis (%)	X-ray diffraction data (Cu-Kα)				
			Int.	2θ(°)	d(Å)	hkℓ	I_c(Å)
(1)	$C_8F(AlF_3)_{0.15}$	C:75.4	m	9.38	9.42	001	
		F:21.5	m,br	16.44	5.39	unknown	
	slightly bluish black	(Al): 3.1	s	18.70	4.74	002	9.44 *
			vs	28.44	3.14	003	±0.04
			vw,br	48.42	1.88	005	
			vw,br	58.90	1.57	006	
(2)	$C_6F(AlF_3)_{0.15}$	C:69.3	w,br	9.72	9.09	001	
		F:26.7	m	18.98	4.67	002	9.40 *
	blue-black	(Al): 4.0	vs	28.32	3.15	003	±0.06
			vw,br	48.7	1.87	005	
			vw	59.26	1.56	006	
(3)	$C_{17}F(AlF_3)_{0.45}$	C:78.4	w,br	9.60	9.20	001	
		F:16.9	m	18.94	4.68	002	9.50 *
	black,	(Al): 4.7	s	27.80	3.21	003	±0.14
	slightly		vw,br	47.4	1.92	005	
	exfoliated		vw,br	58.0	1.59	006	
(4)	Intermediate product	C:73.4	vw,br	11.16	7.92	001	for graphite fluoride
		F:26.8					
			vs	27.40	3.25		
	black, exfoliated		vw,br	56.10	1.64		
(5)	Graphite fluoride	C:47.4	s,br	11.42	7.74	001	
		F:50.7	w,br	41.52	2,17	100	
	gray, exfoliated	$(C_2F)_n$:65%	**				
(6)	Graphite fluoride	C:49.5	s,br	11.10	7.89	001	
		F:50.7	w,br	42.12	2.14	100	
	gray, exfoliated	$(C_2F)_n$:71%	**				

* Repeat distance for $C_xF(AlF_3)_y$ was calculated from (00ℓ) diffraction lines except broad (00ℓ) lines.

** The content of $(C_2F)_n$ was calculated on the assumption that the product contains only $(CF)_n$ as an impurity. By representing the amounts of $(C_2F)_n$ and $(CF)_n$ as x and 1-x respectively, F/C ratio is related with x by the following equation: $F/C = 1 - (1/2)\cdot x$.

The repeat distance of $C_xF(AlF_3)_y$ was 9.40-9.50 Å, which is by ca. 1 Å larger than other 1st stage compounds of fluorides.[1)] ESCA spectra (Fig. 1) for $C_xF(AlF_3)_y$ shows that the chemical bond between intercalated fluorine and carbon of graphite layer is similar to that for graphite fluoride, $(C_2F)_n$. This means that intercalated fluorine atom is situated in contact with carbon atom of graphite. Provided that intercalated AlF_3 is sandwiched in two sheets composed of fluorine atoms, the dimension of the intercalant becomes ca. 6 Å, which is well consistent with the observed value 6.05 Å(=9.40-3.35 Å). If the intercalation compound prepared is a second stage one, it is difficult to accomodate aluminum fluoride between narrow graphite layers of 2.70 Å. It is therefore reasonable that $C_xF(AlF_3)_y$ in Table 1 is regarded as a first stage compound.

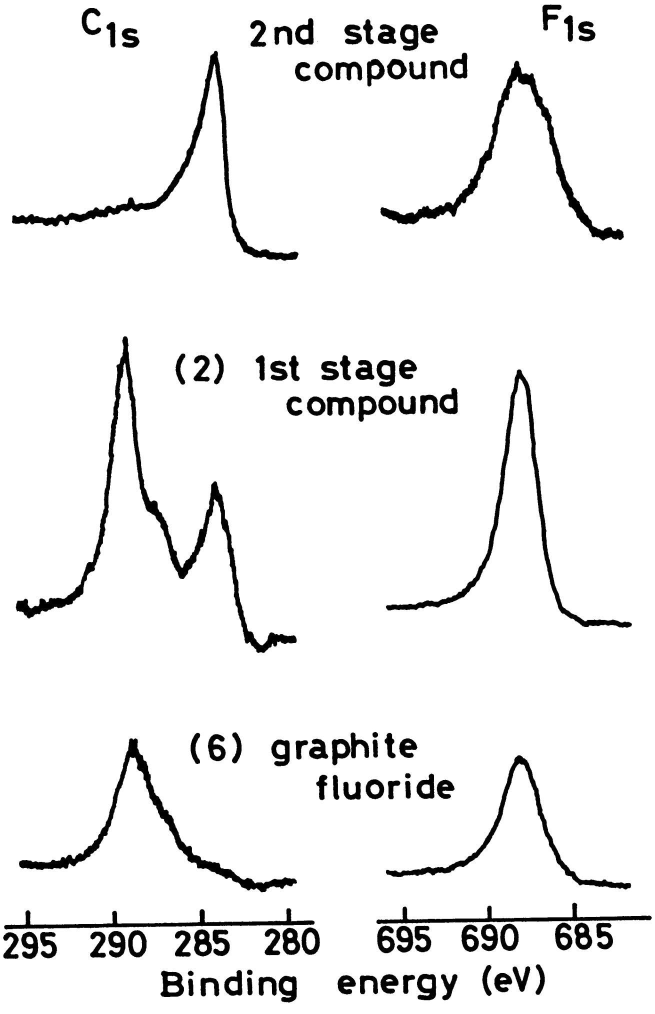

Fig. 1 ESCA spectra for $C_xF(AlF_3)_y$ and graphite fluoride, $(C_2F)_n$

Graphite fluoride, $(C_2F)_n$ prepared in this study has the same appearance in shape as exfoliated graphite. Exfoliation of graphite is caused by release of an intercalant with increase in temperature. It is considered that graphite fluoride is formed through the decomposition of the intercalation compound and subsequent fluorination of exfoliated residue.

$$\text{Graphite} + AlF_3 + F_2 \longrightarrow C_xF(AlF_3)_y \xrightarrow[300\text{-}400\ ^\circ C]{F_2} (C_2F)_n + AlF_3$$

We investigated the fluorination of exfoliated graphite with elemental fluorine and obtained such results that graphite fluoride, $(C_2F)_n$ could be prepared with high reaction rate in comparison with natural graphite.$^{2)}$ According to the above method, $(C_2F)_n$ is prepared with more simple process and higher reaction rate.

The reaction of AlF_3 with F_2 was performed using thermobalance and weight change was monitored. When fluorine gas was introduced into the reaction tube to 1 atm at room temperature, the weight decrease was clearly observed. However, the weight was recovered to original value in proportion to fluorine pressure when it was reduced stepwise to less than 0.1 atm. From this result, it was considered that a gaseous species of $(AlF_3)_m\cdot(F_2)_n$ was formed by the reaction of AlF_3 with fluorine gas.

$$mAlF_3(s) + nF_2(g) \rightleftharpoons (AlF_3)_m\cdot(F_2)_n\ (g)$$

Gaseous species $(AlF_3)_m\cdot(F_2)_n$ would be intercalated into graphite.

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