

S<sub>6</sub>

## NEW SYNTHESIS OF FIRST STAGE GRAPHITE INTERCALATION COMPOUNDS WITH FLUORIDES

A. Hamwi\*, S. Mouras, D. Djurado and J. C. Cousseins

Université de Clermont-Ferrand-II, Laboratoire de Chimie des Solides, U.A. 444, B.P. 45, 63170 Aubière (France)

Until now, it was well known that first stage graphite intercalation compounds with most of inorganic fluorides were not easily obtained. For example, the preparation of the first stage MoF<sub>6</sub> graphite required very long reaction times (about 10 days) ; CrO<sub>2</sub>F<sub>2</sub> reacts with graphite to form only a third-stage compound whereas it has been reported that pure ReF<sub>6</sub> did not react with graphite.

In other cases, the intercalation was possible only if reaction was carried out under Cl<sub>2</sub>, HF or F<sub>2</sub> atmosphere. IF<sub>5</sub> and WF<sub>6</sub> intercalated only in the presence of HF, a first and a second stage respectively had been obtained at room temperature. In the same way, first stage TaF<sub>5</sub> or NbF<sub>5</sub>-graphite and a third stage TiF<sub>4</sub>-graphite had been prepared under a chlorine pressure superior to two atmospheres !

The studies of the reaction of inorganic fluorides with graphite in the presence of fluorine atmosphere have been limited to few compounds. In this paper, we show it is possible to extend these studies to a large number of fluorides. Indeed, under elemental fluorine current, the fluoride MF<sub>x</sub> is formed from the element M and reacts directly with graphite. By this way, first stage graphite intercalation compounds with MF<sub>6</sub> (M = W, Mo, Re), CrO<sub>2</sub>F<sub>2</sub>, MF<sub>5</sub> (M = Nb, Ta), TiF<sub>4</sub> and BF<sub>3</sub> have been easily obtained in few hours. Typical results are collected in the next table :

Fluoride	MF <sub>5</sub> M=Nb,Ta	MF <sub>6</sub> M=W,Mo,Re	CrO <sub>2</sub> F <sub>2</sub>	BF <sub>3</sub>	TiF <sub>4</sub>
Formula C <sub>n</sub> (MF <sub>x</sub> ) I <sub>C</sub> Å	n=6 to 8 8.30	n=8 to 10 8.18	n=8 to 10 8.18	n=7 7.75	n=7 8.20

Composition of final products was deduced from mass uptake measurements and elemental analysis. IR spectra of all compounds showed that MF<sub>x</sub><sup>-</sup> (x = 4, 6 or 7) or MF<sub>x</sub><sup>2-</sup> (x = 6 or 8) species were predominantly intercalated. However, in all cases, the eventuality for graphite lattice to be partially fluorinated cannot be discarded (confirmed by IR). Further improvement of experimental procedure would be able to limit this phenomenon.

It must be noticed that n<sup>th</sup> stage intercalation compounds (with n > 1) can also be prepared by adjusting reaction times and temperatures.