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Low-temperature fluorination processes for the synthesis of new materials

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1. Introduction

The exceptional reactivity of fluorine and fluorinating reagents has been illustrated during the past decades by the synthesis of a very large variety of fluorinated inorganic compounds, in particular those based on transition elements with high oxidation states [1,2]. Another aspect of this behaviour is related to the relatively low temperatures at which fluorination reactions may occur, i.e. room temperature or even below. In the following, we give some examples of the low-temperature intercalation of fluorine or metal fluorides into two types of inorganic materials: graphite intercalation compounds (GICs) and layered cuprates. We will focus on structural changes resulting from the intercalation process.

2. Intercalation of fluorine and metal fluorides into graphite

2.1. Experimental procedures

Two main routes can be considered depending on whether a gas–solid reaction occurs, such as the spontaneous (or assisted) intercalation of gaseous metal fluorides, or if the reaction takes place in solution, such as the intercalation of fluorides dissolved in anhydrous HF (AHF) [3,4]. The presence of additives is also necessary to induce the intercalation of fluorine into graphite. Gaseous or anhydrous HF are most generally used, but involatile or volatile fluorides may also be considered [5].

2.2. Determination of the charge transfer

In the charge transfer that occurs during the intercalation of graphite by fluorine or by metal fluorides, the intercalates are expected to function as electron acceptors. The measurement of the thermoelectric power (TEP) allows the determination of the sign of the type of carrier dominating the transport properties. For metal fluoride-based GICs, the temperature dependence of the in-plane TEP follows the general trend observed for acceptor GICs, irrespective of the stage or the intercalate involved, with corresponding positive values of $\alpha \approx 20\ \mu\text{V K}^{-1}$, which corresponds to hole carriers. In electron-acceptor GICs, a contraction of the C–C bond length is also observed because of the contribution of π-antibonding orbitals. An empirical relationship has been proposed between charge transfer and C–C bond length [6]. The charge-transfer coefficient can also be determined from optical reflectivity. In most d-transition metal fluoride-GICs, a metallic reflectivity is observed in the low-frequency region of the spectrum, limited by the plasma edge and followed by a well-defined minimum [7]. The position of the Fermi energy (E_F) can be deduced through the Blinowski–Rigaux model.

2.3. MF_n-GICs

The stage-1 compound with composition $C_{5.2}RuF_{4.5}$ is readily obtained, for example, from powdered graphite and gaseous RuF_5. The value of the *c*-axis rules out the possible intercalation of Ru_4F_{20} tetramers, but fits rather well with RuF_6 octahedra with two faces parallel to the graphene planes. However, the unit cell constant corresponding to the intercalated species is not commensurate with the graphene lattice at 300 K. A possible arrangement of $(RuF_4)_n$ chains formed from RuF_6 octahedra sharing two edges is proposed [6]. A charge transfer of 0.5 electron per $RuF_{4.5}$ unit may be deduced from the variation of the C–C bond length. Between 120 K and 300 K, the intercalated fluoride undergoes several phase transitions. $C_{5.2}RuF_{4.5}$ exhibits metallic

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behaviour and the hysteresis phenomenon occurring in the resistivity variation at 130 K may result from a non-commensurate $\rightleftharpoons$ commensurate transition. The magnetic behaviour differs drastically from that of pure RuF_5 and corresponds to tetravalent Ru present as both isolated $(RuF_6)^{2-}$ octahedra and $(RuF_4)_n$ chains [6].

Stage-1 compounds are readily obtained from RhF_5 and AuF_3 dissolved in AHF. For the rhodium compound, intercalation is associated with a reduction to Rh^{+III} and a co-intercalation with $(HF_2)^-$ species, leading to the composition $C_xRhF_3(HF_2)_{1.3}$ [8]. The +III oxidation state of Rh has been confirmed by magnetic susceptibility and XANES data. The coordination of Rh deduced from a least-square fit of the Fourier-filtered EXAFS spectra is octahedral (6 Rh−F at 1.99 Å) as in RhF_3 [8].

In the case of C_xAuF_y compounds, the EXAFS results lead to four nearest neighbours for the Au atoms, suggesting a square-planar coordination which is usual for Au^{+III} in a low-spin d^8 configuration. From a study of the second neighbour shell, the suggestion of Au_2F_6 dimeric groups consisting of two AuF_4 squares sharing a common edge may be advanced. The dimensions of these groups fit with the hexagonal lattice found for the intercalate from single-crystal precession patterns [9].

2.4. F-GICs in fibres

The intercalation of fluorine in various type of carbon fibres (ex-PAN or ex-pitch, as received or high-temperature treated) has been investigated at room temperature in the presence of gaseous HF. For higher F_2 pressures (10 bar), stage-1 compounds with compositions $C_{2.5}F$ to C_4F are obtained, whereas stage-2 compounds are stabilized at lower F_2 pressures (1 bar). Although in the higher stages (2 to 4) the electrical conductivity may be higher than that of the pristine fibre, in the pure stage-1 compound a drastic increase of resistivity is observed, with ρ being one order of magnitude larger than that of the starting material. The effect of fluorine intercalation on the morphology of the fibre has been followed by high-resolution transmission electron microscopy. Three different types of C−F bonding, an anionic one, a covalent one and a semi-ionic one, have been detected by XPS.

3. Anionic intercalation and superconductivity in La_2CuO_4-type oxides

The effect of halogen-gas treatment (Cl_2 or F_2) on both the structural and physical properties (magnetism and conductivity) of La_2CuO_4 is consistent with the presence of an excess of anionic species. Bulk superconductivity occurs below 32 K and 40 K, for the Cl_2- or F_2-treated sample, respectively. The intercalation of anions between the two (LaO) layers of the structure has been deduced on the basis of chemical analysis, X-ray and neutron diffraction, and EXAFS at the La L_{III} absorption edge [10, 11].

Fluorination of La_2CuO_4 ($P_{F_2} \approx 1$ bar, $T_{F_2} \approx 200$ °C) gives rise to a superconducting oxyfluoride $La_2Cu(O,F)_{4.18}$. An enhancement of the orthorhombic distortion is observed, together with an increase in the *c* parameter. The position of the intercalated anions has been determined by neutron diffraction and EXAFS techniques. The temperature dependence of the unit cell parameters indicates the occurrence of an irreversible orthorhombic → orthorhombic structural transition at ca. 250–300 °C with the disappearance of superconductivity. After annealing at 500–600 °C, the oxyfluoride is further decomposed into stoichiometric La_2CuO_4, LaOF and CuO. Several new superconducting phases have been obtained by fluorination treatments for other K_2NiF_4-derived systems, such as $La_{2-x}M_xCuO_4$ or $La_{2-x-y}RE_xM_yCuO_4$ with $M^{2+} = Sr^{2+}$, Ba^{2+} and RE^{3+} = trivalent rare earth cation.

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