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Inorganic fluorinated materials in France: recent developments

Alain Tressaud*

Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB-CNRS, Université Bordeaux 1, Avenue Dr. A. Schweitzer, 33608 Pessac, France

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Abstract

The purpose of this very short review is obviously not to give an extensive image of the activities carried out in France these last years in various domains related to inorganic fluorine chemistry. At the turn of the century, it will rather focus on a few examples obtained in French research groups, mostly this last decade, in the fields of the synthesis and discovery of some outstanding chemical and physical properties of inorganic fluorinated materials. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The following examples have been selected from chapters of the book "Advanced Inorganic Fluorides", which will appear in 1999 (T. Nakajima, A. Tressaud, B. Žemva (Eds.)), to be published by Elsevier Science.

2. Synthesis of new inorganic fluorides [M. Leblanc, Laboratoire des Fluorures, University Maine, Le Mans]

Various original routes have been proposed to synthesize new series of fluorides, in particular main group transition metal, aluminium and rare-earth fluorides: for instance "chimie douce", decomposition, exchange or insertion reactions, precipitation from aqueous solutions in sub- or super-critical conditions, epitaxy.

The influence of the experimental conditions (temperature, pressure, reducing or oxidising atmosphere, particle size) has been carefully examined and correlated with the formation of stable or metastable phases, such as:

- new three-dimensional framework in fluorophosphates (e.g. $SrAl_2(PO_4)_2F_2$) prepared by hydrothermal synthesis;
- new family of rare-earth fluorides with open structures δ-$(H_3O)Ln_3F_{10}$, H_2O obtained from HF solutions and exchange reactions between H_3O^+ and alkaline ions (Li^+, Na^+), Cu^{2+} or Mn^{2+};
- stabilization of HF_2^- groups in the solid state (i.e. $Ba_5Nb_3O_3F_{18}(HF_2)$).

Finally, the importance of the accurate control of the dimensions and properties of the materials has been strongly emphasised. The elaboration of films for sensors, nanoparticles for catalysis and layers for planar waveguides or coatings appears to be important breakthrough for fluoride materials, together with the growth of large crystals for laser applications which illustrate the outstanding optical properties of fluorides.

3. Oxyfluorinated open frameworks [G. Ferey, T. Loiseau, D. Riou, Institut Lavoisier, University Versailles]

There is now an increasing demand for new porous materials with higher selectivity in separation technologies, higher rates of conversion in fine chemicals and catalysis industry. That means a strategy for designing new compounds with new structures and enhanced performances.

In the field of open frameworks, an important change was provided by Guth, Kessler and Wey in 1986 (Mulhouse, France) who introduced the fluoride method in the synthesis of microporous solids. The fluoride ion is a mineralizing agent but can also participate to the reaction and the structure for providing new topologies as shown mainly by Kessler and Ferey's groups. Another breakthrough concern the mesoporous compounds with pore sizes in the 20–100 Å range by using surfactant micellar templates. Very recently, the concept of microporous frameworks, which was primarily reserved to inorganic skeletons took a new dimension by the discovery of porous mixed inorganic–organic frameworks.

*Corresponding author. Fax: +33-556-842761

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The only attempts to propose a description of the mechanism of formation of these phases concern exclusively fluorinated phosphates. The strategy previously developed for the systems containing Al and Ga has been applied to the V_2O_5–P_2O_5–HF–diamine–H_2O and lead to V_2PO_8F, en, the first fluorovanadophosphate with an open structure. In the systems Fe_2O_3–P_2O_5–HF–diamine–H_2O the first porous fluorinated iron(III) phosphates ever isolated were obtained. Beside the well known ULM-3 and ULM-4 structure types (ULM for University Le Mans), new open-structure fluorophosphates were characterized: $Fe_4(PO_4)_4F_2(H_2O)_3$, DABCO (ULM-12), its anhydrous variant $Fe_4(PO_4)_4F_2$, DABCO (ULM-19), and $Fe_4(PO_4)(HPO_4)_4F_3(H_2O)_4$, $H_3N(CH_2)_3NH_3$ (ULM-15). On the other hand, the titanium family has provided the first example of a mixed valence compound, $Ti^{III}Ti^{IV}F(PO_4)_2$, $2H_2O$ in the series of oxyfluorinated solids with an open framework.

4. Optical properties of fluoride glasses [J.L. Adam, J. Lucas, Laboratoire des Verres et Céramiques, University Rennes 1]

Since two decades, fluoride glasses have generated a growing interest due to exceptional optical properties combined with a relative ease of preparation. Based on heavy metals such as zirconium, barium, indium or gallium and on fluorine anions, the fundamental vibration modes of fluoride glasses are at lower frequencies than that of silica glass. This results in an extended optical transmission domain up to 6–10 μm in the infrared, depending on the glass composition. Another major consequence is the lower probability of non-radiative mechanisms in rare-earth-doped fluoride glasses. Thus, several radiative emissions of rare-earth ions, which are weak or absent in silica, can be observed in fluoride glasses.

The spectroscopic properties of rare-earth-activated fluoride glasses have been extensively investigated with emphasis on radiative transitions specific to low-phonon-energy materials. Various preparation methods of fluoride glass fibers have been proposed. Rare-earth-doped fluoride glass lasers operate at discrete wavelengths from the blue to the mid-IR. From a practical point of view, several visible lasers can be pumped via efficient up-conversion processes by means of commercially available laser diodes. In the long-wavelength side, radiative transitions are reported in the eye-safe domain, above 1.4 μm, and in transparency domains of the atmosphere, around 2 μm and in the 3–5 μm window. Fluoride glass optical amplifiers for the three telecommunication windows, at 0.8, 1.3 and 1.55 μm, have received special attention, especially praseodymium and erbium-doped amplifiers. Permanent Bragg gratings have been induced in zirconium-based ZBLAN optical fibers, evidencing the definitive advantage of compact, all-solid-state fluoride glass fiber lasers. Recently, Nd^{3+}-doped ZBLA channel waveguides have appeared to be a promising technology for low-cost integrated optics and complementary components of optical fibers.

5. Magnetic properties of Usovite-type and Jarlite-type fluorides: isolated trimers, homonuclear-, bimetallic- and lozenge chains [J. Darriet and R. Georges, ICMCB-CNRS, University Bordeaux 1)]

Large interest in the thermodynamics of one-dimensional (1D) systems has been stimulated by the engineering of new materials of this type, as for instance ferrimagnetic chains made up of two non-equivalent spin sublattices spreading in a 1D network. Very often, their peculiar topological features allow an accurate theoretical description of their behaviour, so that one can hope to get fundamental insights into the underlying physics of magnetic phenomena. In particular, bimetallic chains have been encountered in fluorides with usovite-type [$Ba_2CaMgAl_2F_{14}$] and jarlite-type [$Sr_6Na_2MgAl_6F_{32}(OH)_2$] structures. Despite the large differences between the sizes of the alternating sites offered, some compounds are disordered, making irrelevant any description in terms of regularly alternating chains. New theoretical treatments have been proposed, in order to account for the magnetic behaviour.

6. Luminescent properties of fluorides [C. Fouassier, ICMCB-CNRS, University Bordeaux 1]

Due the high optical quality of crystals and their wide transmission range, fluorides are well suited for the study of spectroscopic properties. These compounds have brought a major contribution to the knowledge of luminescence processes since they possess specific characteristics which influence luminescent properties. Four domains have attracted considerable attention in recent years:

Laser crystals. Because of the wide transmission range and the high number of emitting levels, consequence of the low phonon energies, a considerable amount of laser emissions have been obtained from fluoride crystals with wavelength ranging from the ultraviolet (Ce^{3+}-doped $LiLuF_4$) to the infrared (Cr^{3+}-doped $LiSrAlF_6$, V^{2+}-doped MgF_2 and $KMgF_3$, Ni^{2+}-doped $BaLiF_3$).

Scintillator crystals. Because under excitation by X or γ radiations or particles, the number of emitted photons decreases with increasing bandgap, fluorides have lower efficiencies than oxides or other halides. However the high optical quality, chemical stability and radiation hardness make them well suited for application in fast detectors for high energy particles, for example Ce-activated crystals of $BaThF_6$ and LuF_3.

Ionisation processes, hole burning. Photoionisation is responsible for the quenching of the luminescence of cations with reducing character in some lattices and two-step ionisation affects the efficiency of lasers. Ionisation of Sm^{2+} in alkaline-earth fluorides CaF_2, SrF_2, BaF_2 can be used for obtaining high capacity optical memories (hole burning).

Energy storage phosphors. Photostimulable phosphors are key-materials for digital X-ray imaging systems. Most of them contain halides and in particular fluorine which brings the chemical stability required for application (e.g. BaFCl:Eu, BaFBr:Eu, $Ba_7Cl_2F_{12}$:Eu).

7. Surface modifications of materials by fluorination treatments [A. Tressaud, ICMCB-CNRS, University Bordeaux 1; C. Cardinaud, G. Turban, Institut des Matériaux Jean Rouxel, CNRS, University Nantes]

The surface characteristics of materials dominate the performance of the final products in many applications. Surface treatments by exposure to very reactive atmospheres show several advantages when compared to more conventional methods: (i) the chemical modification is limited to surface only and does not perturb the bulk properties, (ii) reaction temperature is very low and avoid thermal degradation of the material, (iii) non-equilibrium reactions are possible.

Surface fluorination has been proposed for modifying and/or protecting the surface of various materials such as polymers, metal surfaces (Al), carbon-based compounds (exfoliated graphite, carbon blacks, diamond-like carbon films, diamond), inorganic ceramics (high T_c superconducting cuprates: $YBa_2Cu_3O_{7-\delta}$; cathode materials: $LiMO_2$; pigments: rare earth sulphides), intermetallic compounds for hydrogen storage ($LaNi_5$ and $MgNi_2$ types). Depending on the expected properties of the treated materials, the fluorination can be carried out in plasma-enhanced conditions, for instance in radiofrequency plasmas of CF_4, NF_3, SF_6, or in F_2 or fluorinating gases under atmospheric pressure. In particular, the processing of materials by plasma techniques is being increasingly used in various areas of production and manufacturing. This allows chemical reaction to occur at temperatures that are considerably lower than for thermal reactions taking place at thermodynamic equilibrium.

The decisive parameters defining a cold plasma, some diagnostic techniques for plasma processing, and elements of fluorine-based plasma chemistry have been extensively investigated by different groups, in particular in Nantes, and have finally allowed to describe mechanisms of plasma fluorination of inorganic materials.