Functionalized Inorganic Fluorides

Synthesis, Characterization & Properties of Nanostructured Solids

Edited by

ALAIN TRESSAUD

Research Director CNRS (Emeritus), ICMCB–CNRS,
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Cover images from left to right: *Projection along [001] of the ITQ-33 zeolite structure showing the 18-MRs windows (Chapter 16); Schematic morphology of oxyfluoride glass-ceramics formed by spinodal decomposition (Chapter 9); Crystal structure of* $La_2CuO_{3.6}F_{0.8}$ *[The Cu cations are situated in octahedra; the La cations are shown as large spheres; the F anions are shown as small spheres] (Chapter 13)*

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Preface

Fluorides and fluorinated materials affect various aspects of modern life. The strategic importance of fluoride materials, and the use of adapted fluorination surface treatments, concern many research fields and applications in areas such as energy production, microelectronics and photonics, catalysis, colour pigments, textiles, cosmetics, plastics, domestic wares, automotive technology and building.

Among the issues with which they are concerned [1–4] are:

- the historical importance of fluoride fluxes in the production of metals, in particular aluminium;
- the critical place of fluorine and fluorides in conversion energy processes – for example components of Li-ion batteries and fuel cells, enrichment of ^{235}U through uranium hexafluoride for nuclear energy;
- the etching of silicon wafers for microelectronics;
- the technical revolution of fluoropolymers and fluoride coatings, for example Teflon® and fluorinated plastics, waterproof clothes, biomaterials for cardiovascular or retinal surgeries, kitchen wares, and so forth;
- the beneficial influence of fluoride on dental caries;
- the dominant use of fluorinated molecules in agrochemistry and phytosanitary products;
- the dramatic increase of fluorine-containing molecules for medicine and pharmacy, as efficient imaging products, as dental composites for cariostatic improvement, and so forth;
- the use of ^{18}F-labelled molecules in positron emission tomography (PET) for early diagnosis of cancer and Alzheimer's disease.

In the case of inorganic fluorinated solids, numerous improvements have recently been achieved through the elaboration and functionalization of the materials on a nanometric scale. The present book covers several classes of nanostructured and functionalized inorganic fluorides, oxide-fluorides, hybrids, mesoporous materials and fluorinated oxides such as silica and alumina. The morphologies concerned range from powders or glass-ceramics to thin layers and coatings whereas the applications involved include catalysts, inorganic charges, superconductors, ionic conductors, ultaviolet (UV) absorbers, phosphors, materials for integrated optics, and so forth. Several books have been devoted to the reactivity of carbon-based materials with fluorine (carbon fibres, fullerene, carbon nanotubes, etc) [1,2,5,6], so these types of materials will not be treated in the present book.

The book arose from discussions that took place during the FUNFLUOS project (2004–2008), carried out within the Sixth European Framework Programme. This project involved about ten groups from Germany, France, Slovenia and the UK, all aimed at the synthesis and characterization of fluorinated materials with properties tailored for specific applications.

The topics appearing in the book range from new synthesis routes to physical-chemical characterizations. They address important properties of these materials, including morphology, structure, thermal stability, superconductivity, magnetism, spectroscopic and optical behaviour. Detailed *ab initio* investigations and simulations provide a comparison with experimental results, and potential applications of the final products are also proposed.

In the first section, two innovative routes toward nanoscaled metal fluorides and hydroxyfluorides are presented: the *fluorolytic* sol-gel synthesis by E. Kemnitz *et al.* and the microwave-assisted route by D. Dambournet *et al.* In a second section, several physical-chemical characterizations are developed in order to understand the mechanisms that are responsible for the improvement of the properties of these materials: investigation of the main characteristics of high-surface-area aluminium fluorides as catalysts by E. Kemnitz and S. Rüdiger; determination of surface acidities (Lewis and Brønsted types) using a large range of probe molecules, by A. Vimont *et al.*; a better knowledge of the environment of the different nuclei using high-resolution solid-state nuclear magnetic resonance (NMR) by C. Legein *et al.* The theoretical investigation of these topics is highlighted by the predictive modelling of aluminium fluoride surfaces by C. Bailey *et al.,* which allows a better understanding of the underlying processes at the molecular and nano levels. An example of industrial application of the inorganic fluorides is given by P. Garcia Juan *et al.* In the following section, some examples of outstanding optical properties of nanostructured fluorides are proposed: nanostructured fluorocompounds as UV absorbers, by A. Demourgues *et al.*; transparent oxyfluoride glass-ceramics by M. Mortier and G. Dantelle; luminescent and antireflective coating of (oxy)fluorinated materials obtained by the sol-gel technique, by S. Fujihara; planar optical waveguides based on fluoride glasses, by B. Boulard. Hybrids, composites and mesoporous fluorides are original materials with great potential and the interesting nature of such materials is illustrated in the next section by the chapters on polyanion condensation in inorganic-organic hybrid fluorides, by K. Adil *et al.*; superconducting/magnetic properties of Cu- and Mn-based oxyfluorides, by E. Antipov and A. Abakumov; ionic conductivity of fluoride-containing phases by E. Ardashnikova *et al.*; intercalation in hybrid compounds containing perfluoroalkyl groups, by Y. Matsuo.

The two following chapters deal with the synthesis of microporous frameworks using the fluoride and F_2-gas routes, respectively. The examples concern either compounds based on silica, germanium, phosphates and clays, by J. L. Paillaud *et al.*, or highly fluorinated silica, by A. Demourgues *et al.* The optical and magnetic properties of oxyfluoride glasses based on rare-earth elements are illustrated by S. Yonezawa *et al.* Finally the chapter by A. Tressaud *et al.* describes the use of surface fluorination of porous alumina for applications in offset technology.

A very wide range of materials, properties, and applications have therefore been gathered in this book, which covers various new fields in which inorganic fluorides are part of the innovating process. Among the information that can bring answers to some crucial questions in materials science, we can quote new synthesis routes towards more efficient and less aggressive catalysts, protection against harmful UV radiation, new integrated lasers and optical amplifiers, antireflective coatings, solid-state ionic conductors, highly hydrophobic silica and switchable coatings for offset technology.

Erhard Kemnitz and Alain Tressaud
Berlin and Bordeaux
September 2009

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The Funfluos European Network (2004): First row (from left to right): D. Menz, B. Žemva, E. Kemnitz (Coordinator), A. Demourgues, A. Tressaud, and J. Winfield. Second row (from left to right): U. Gross, M. Feist (partly hidden), S. Rüdiger, P. Millet (European Commission), N. Harrison, A. Wander, T. Skapin and S. Schröder

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1

Sol-Gel Synthesis of Nano-Scaled Metal Fluorides – Mechanism and Properties

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1.1 Introduction

Sols are dispersions of nanoscopic solid particles in, for example, liquids – i.e., colloidal solutions. The particles can agglomerate forming a three-dimensional network in the presence of large amounts of the liquid thus forming a gel. Inorganic sols are prepared via the sol-gel process, the investigation of which started in the nineteenth century. This process received great impetus from the investigations of Stöber *et al*. [1], who studied the use of pH adjustment on the size of silica particles prepared via sol-gel hydrolysis of tetra-alkoxysilanes.

1.1.1 Sol-Gel Syntheses of Oxides – An Intensively Studied and Widely Used Process

Hydrolysis of alkoxysilanes and later on of metal alkoxides in organic solutions has become an intensively studied and widely used process [2]. The most common products are almost homodispersed nanosized silica or metal oxide particles for, e.g., ceramics or

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glasses, or the aqueous sols are used to prepare different coatings for, e.g., optical purposes. Optical applications depend on differences in the respective indices of refraction of the coated material and the applied layer. The latter has to be of very uniform and thoroughly adjusted thickness.

The sol-gel hydrolysis of alkoxysilanes, the most intensively explored one, basically proceeds in two steps. The first step is the hydrolytic replacement of alkoxy groups, OR, by hydroxyl groups, OH, shown schematically in Equation (1.1) for the first alkoxy group:

$$\mathrm{Si(OR)_4 + H_2O \rightarrow (RO)_3SiOH + ROH} \tag{1.1}$$

Because of their relatively high hydrolytic stability, hydrolysis of alkoxysilanes (1.1) has to be catalysed by Brønstedt acids or bases.

In the second step, the primary hydrolysis products undergo condensation reactions under elimination of water (Equation (1.2)) or alcohol (Equation (1.3)).

$$\mathrm{X_3Si\text{-}OH + HO\text{-}SiX_3 \rightarrow X_3Si\text{-}O\text{-}SiX_3 + H_2O(X = OR,\ OH)} \tag{1.2}$$

$$\mathrm{X_3Si\text{-}OH + RO\text{-}SiX_3 \rightarrow X_3Si\text{-}O\text{-}SiX_3 + ROH(X = OR,\ OH)} \tag{1.3}$$

As a result tiny particles with a very open structure are formed. The overall process can be controlled by adjusting the reaction conditions. The colloidal solution of these particles, the sol, can be used as such for, e.g., coating or it can be worked up to yield, eventually, nanoscopic oxide particles. However, metal oxide sols obtained in this way always contain a sometimes remarkable organic part. Its separation demands calcination temperatures of at least 623 K in order to convert the ‘precursors’ into pure metal oxide materials.

Substituting a certain part of the alkoxidic groups by nonhydrolysable ones, such as alkyl groups in the case of alkoxysilanes or phosphonic acid in the case of metal alkoxides, organically modified oxides, i.e. inorganic-organic hybrid materials, have been prepared.

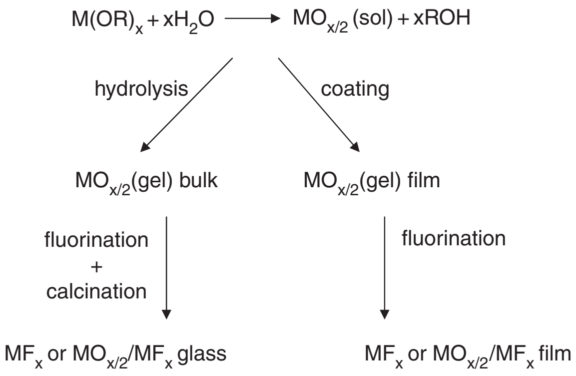
1.1.2 Sol-Gel Syntheses of Metal Fluorides – Overview of Methods

Selected metal fluorides can, in application-relevant fields, outperform metal oxides and silica. Thus, for instance, magnesium fluoride and aluminium fluoride and, in particular, alkali hexafluoroaluminates have both a lower index of refraction and a much broader spectral range of transparency even than silica, making them very interesting for optical layers.

Consequently, several approaches for the preparation of nanoscopic metal fluorides and metal fluoride thin layers have been developed and proposed. Besides physical methods such as milling, laser dispersion or molecular-beam epitaxy, different chemical methods exist. Basically, three approaches can be distinguished:

(i) Postfluorination of a metal oxide preformed via sol-gel route [3].

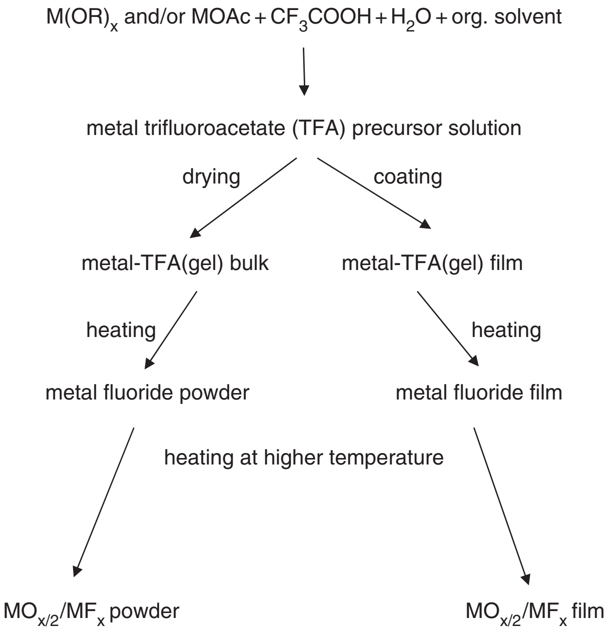
This route is shown schematically in Scheme 1.1. The disadvantages of this route are, to name two, incomplete fluorination of the bulk metal oxides and decrease of surface area in course of the fluorination.



Scheme 1.1 *Metal fluoride preparation via post fluorination of sol-gel prepared metal oxides (Reproduced from [4] by permission of Elsevier Publishers)*

(ii) Preparation of a precursor containing a metal compound with organically bound fluorine such as trifluoroacetate, which is calcined to decompose the fluoroorganic component under formation of metal fluoride [5].

This route, shown in Scheme 1.2, also starts from metal alkoxides, which are reacted in solution with, e.g., trifluoroacetic acid to form metal trifluoroacetate sol. This can be



Scheme 1.2 *Metal fluoride preparation via metal fluoroacetate sol-gel formation and following thermal decomposition. (Reproduced from [4] by permission of Elsevier Publishers)*

used for coating experiments. The decisive final step is the thermal decomposition of the fluoro-organic constituent, because of which thermolabile materials cannot be coated. Another disadvantage is the probability that oxidic components can be formed as admixtures or oxofluorides.

(iii) Fluorolytic sol-gel process as counterpart to the hydrolytic one.

The fluorolytic sol-gel route follows rather strictly the 'classical' hydrolytic one by reacting metal alkoxides in anhydrous solution with hydrogen fluoride instead of the hydrogen oxide of the 'classical' process. Consequently, it results eventually in metal fluorides instead of metal oxides.

The fluorolytic sol-gel process, its execution, mechanism, scope as well as properties and possible fields of application of its products are the subjects of this chapter.

1.2 Fluorolytic Sol-Gel Synthesis

Metal alkoxides can be regarded as metal salts of alcohols, where the latter are very weak Brønstedt acids. Acids that are stronger than the respective alcohol can therefore replace alkoxy groups attached to the metal ion under liberation of the alcohol and formation of the metal fluoride according to Equation (1.4).

$$\mathrm{M(OR)_n + x\ HF \rightarrow M(OR)_{n-x}F_x + x\ ROH\ (M = metal\ ion)} \tag{1.4}$$

In fact, starting with aluminium isopropoxide [6], a broad range of metal alkoxides have been subjected to a sol-gel-like liquid-phase fluorination with hydrogen fluoride in organic solution [4, 7]. Although Equation (1.4) closely resembled Equation (1.1) there is an important difference in that condensation reactions like those of Equations (1.2) and (1.3) are not possible in the fluorolysis system. On the other hand, the fluorolysis reactions typically result in the formation of a sol-gel. The formation of a gel was already mentioned in the first paper on metal alkoxide fluorolysis, reporting the reaction of aluminium isopropoxide in alcoholic solution with an ethereal solution of hydrogen fluoride [6]. The gel formation is obviously due to an important consequence of the replacement of alkoxy groups by fluoride, i.e., the Lewis acidity of the metal ion increases leading to a strengthening of the interaction between (liberated) alcohol molecules and metal ions. As a result alcohol molecules that can occupy ligand positions might establish a loose net between (partly) fluorinated metal ions resulting eventually in metal fluoride sol or even gels. Surprisingly, attempts to isolate pure $\mathrm{AlF_3}$ by drying and calcining the gel were not successful; the product obtained had an understoichiometric amount of fluorine even when the primary reaction has been carried out with an overstoichiometric amount of HF [8]. An additional fluorination of the dried gel under gentle conditions (see below) has proved to be a suitable way to remove the attached organic components resulting in X-ray amorphous, highly Lewis acidic aluminium fluoride with unusual large specific surface area, named HS-$\mathrm{AlF_3}$ [9].