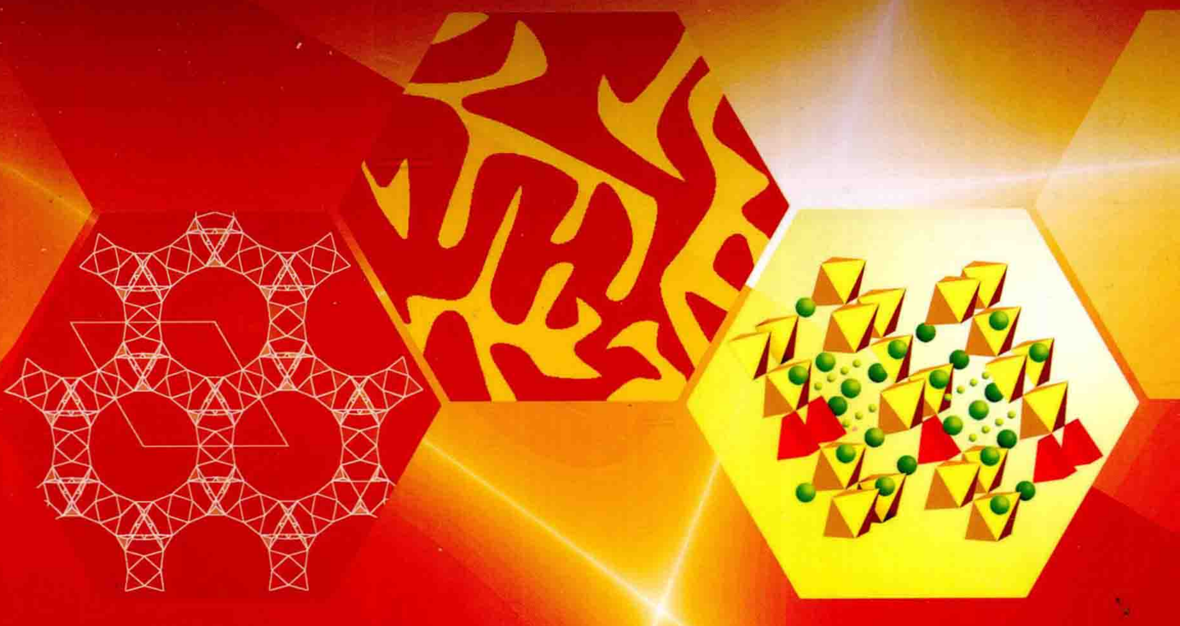
Functionalized Inorganic Fluorides

Synthesis, Characterization & Properties of Nanostructured Solids

Editor
Alain Tressaud



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Synthesis, Characterization & Properties of Nanostructured Solids

Edited by

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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)*

Functionalized Inorganic Fluorides

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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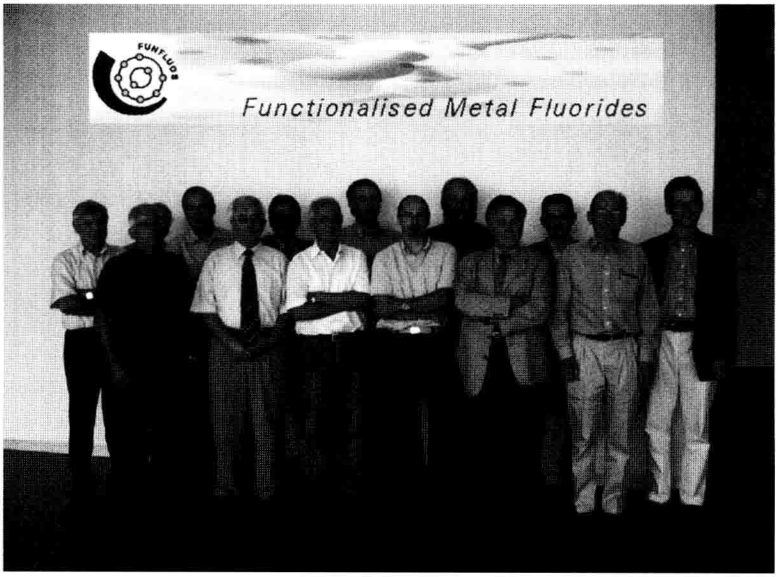

The Funfluos European Network (2004): First row (from left to right): D. Menz, B. Žemva, E. Kemnitz (Coordinator), A. Demourgues, A. Tressaud, and J. Winfield. Second row (from left to right): U. Gross, M. Feist (partly hidden), S. Rüdiger, P. Millet (European Commission), N. Harrison, A. Wander, T.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

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