

Functionalized Inorganic Fluorides

Synthesis, Characterization & Properties
of Nanostructured Solids

Editor
Alain Tressaud



 WILEY

Functionalized Inorganic Fluorides

Synthesis, Characterization & Properties of
Nanostructured Solids

Edited by

ALAIN TRESSAUD

*Research Director CNRS (Emeritus), ICMCB–CNRS,
Bordeaux University, France*



 **WILEY**

A John Wiley and Sons, Ltd., Publication

This edition first published 2010
© 2010 John Wiley & Sons, Ltd

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book. This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The publisher and the author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Functionalized inorganic fluorides: synthesis, characterization & properties of nanostructured solids / edited by Alain Tressaud.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-470-74050-7 (H/B)

1. Fluorides. I. Tressaud, Alain.

QD181.F1F77 2010

546'.731—dc22

2009052139

A catalogue record for this book is available from the British Library.

ISBN: 978-0-470-74050-7 (Cloth)

Set in 10/12pt Times by Integra Software Services Pvt. Ltd, Pondicherry, India
Printed and bound in Great Britain by CPI Antony Rowe, Chippenham, Wiltshire.

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 $\text{La}_2\text{CuO}_{3.6}\text{F}_{0.8}$ [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, ultraviolet (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 F₂-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.

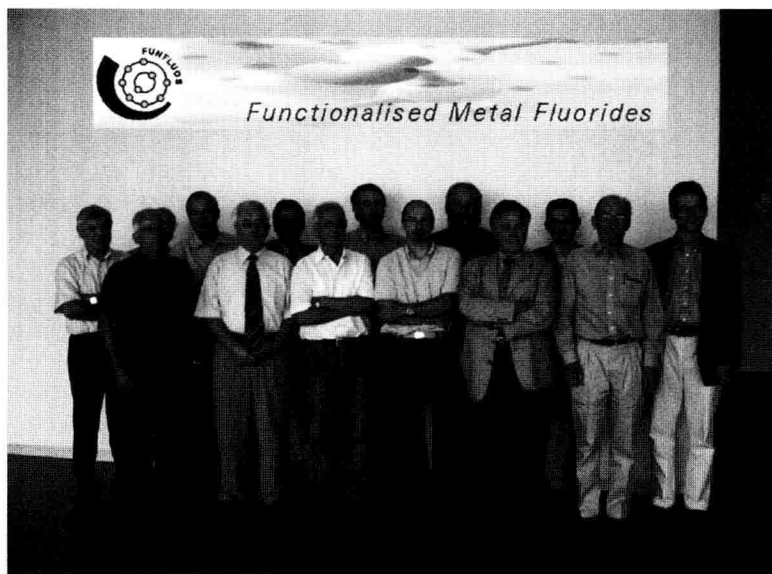
A very wide range of materials, properties, and applications have therefore been gathered in this book, which covers various new fields in which inorganic fluorides are part of the innovating process. Among the information that can bring answers to some crucial questions in materials science, we can 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

References

- [1] *Advanced Inorganic Fluorides*, T. Nakajima, B. Zemva, A. Tressaud (Eds), Elsevier, Amsterdam (2000).
- [2] *Fluorinated Materials for Energy Storage*, T. Nakajima, H. Groult (Eds), Elsevier, Amsterdam (2005).
- [3] *Fluorine and the Environment*, Vol. 1 and Vol. 2, A. Tressaud (Ed.), Elsevier, Amsterdam (2006).
- [4] *Fluorine and Health*, A. Tressaud and G. Haufe (Eds), Elsevier, Amsterdam (2008).
- [5] *Graphite Fluorides and Carbon-Fluorine Compounds*, T. Nakajima (Ed.), CRC Press, Boca Raton, FL (1991).
- [6] 'Fluorofullerenes', in *Dekker Encyclopedia of Nanoscience and Nanotechnology*, O. V. Boltalina, S. H. Strauss, 2nd edition, Dekker, New York (2009).



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

List of Contributors

Artem M. Abakumov, Department of Chemistry, Moscow State, University, Moscow, Russia

Karim Adil, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Evgeny V. Antipov, Department of Chemistry, Moscow State, University, Moscow, Russia

Elena I. Ardashnikova, Department of Chemistry, Moscow State, University, Moscow, Russia

Christine L. Bailey, Computational Science and Engineering Department, STFC Daresbury Laboratory, Warrington, Cheshire, UK

Monique Body, Laboratoire de Physique de l'Etat Condensé, UMR-CNRS, Université de Maine, Le Mans, France

Brigitte Boulard, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Jocelyne Brendlé, Laboratoire de Matériaux à Porosité Contrôlée, UMR-CNRS, Université de Haute Alsace, Mulhouse, France

Jean-Yves Buzaré, Laboratoire de Physique de l'Etat Condensé, UMR-CNRS, Université de Maine, Le Mans, France

Amandine Cadiau, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Philippe Caullet, Laboratoire de Matériaux à Porosité Contrôlée, UMR-CNRS, Université de Haute Alsace, Mulhouse, France

Damien Dambournet, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Géraldine Dantelle, Laboratoire de Photonique Quantique et Moléculaire (LPQM), UMR CNRS, Cachan, France

Marco Daturi, ENSICAEN, Université de Caen, CNRS, Caen, France

Alain Demourgues, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Etienne Durand, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Johannes Eicher, Solvay Fluor GmbH, Hannover, Germany

Shinobu Fujihara, Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama, Japan

Placido Garcia Juan, Solvay Fluor GmbH, Hannover, Germany

Nicholas Harrison, Computational Science and Engineering Department, STFC Daresbury, Laboratory, Warrington, Cheshire, UK Department of Chemistry, Imperial College London, London, UK

Annie Hémon-Ribaud, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Erhard Kemnitz, Institute for Chemistry, Humboldt University of Berlin, Berlin, Germany

Jae-ho Kim, Graduate School of Engineering, University of Fukui, Fukui, Japan

Ilya B. Kutsenok, Department of Chemistry, Moscow State, University, Moscow, Russia

Christine Labrugère, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Emilie Lataste, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Marc Leblanc, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Christophe Legein, Laboratoire des Oxydes et Fluorures, CNRS, Le Mans, France

Vincent Maisonneuve, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France

Charlotte Martineau, Laboratoire des Oxydes et Fluorures, UMR CNRS, Le Mans, France, Tectospin, Université de Versailles Saint Quentin en Yvelines, Versailles, France

Yoshiaki Matsuo, Department of Materials Science and Chemistry, University of Hyogo, Hyogo, Japan

Michel Mortier, Laboratoire de Chimie de la Matière Condensée de Paris, UMR CNRS, Paris, France

Sanghamitra Mukhopadhyay, Department of Chemistry, Imperial College London, London, UK

Jean-Louis Paillaud, Laboratoire de Matériaux à Porosité Contrôlée, UMR-CNRS, Université de Haute Alsace, Mulhouse, France

Joël Patarin, Laboratoire de Matériaux à Porosité Contrôlée, UMR-CNRS, Université de Haute Alsace, Mulhouse, France

Nicolas Penin, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Vladimir A. Prituzhalov, Department of Chemistry, Moscow State, University, Moscow, Russia

Stephan Rüdiger, Institute for Chemistry, Humboldt University of Berlin, Berlin, Germany

Gudrun Scholz, Institute for Chemistry, Humboldt University of Berlin, Berlin, Germany

Thomas Schwarze, Solvay Fluor GmbH, Hannover, Germany

Barry Searle, Computational Science and Engineering Department, STFC Daresbury Laboratory, Warrington, Cheshire, UK

Gilles Silly, Institut Charles Gerhardt Montpellier, Physicochimie des Matériaux Désordonnés et Poreux, Université de Montpellier II, Montpellier, France

Angélique Simon-Masseron, Laboratoire de Matériaux à Porosité Contrôlée, UMR-CNRS, Université de Haute Alsace, Mulhouse, France

Laetitia Sronek, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Hans-Walter Swidersky, Solvay Fluor GmbH, Hannover, Germany

Masayuki Takashima, Graduate School of Engineering, University of Fukui, Fukui, Japan

Alain Tressaud, Institute of Condensed Matter Chemistry of Bordeaux (ICMCB-CNRS), University Bordeaux 1, Pessac, France

Alexandre Vimont, ENSICAEN, Université de Caen, CNRS, Caen, France

Adrian Wander, Computational Science and Engineering Department, STFC Daresbury Laboratory, Warrington, Cheshire, UK

John M. Winfield, Department of Chemistry, University of Glasgow, Glasgow, UK

Susumu Yonezawa, Graduate School of Engineering, University of Fukui, Fukui, Japan

Contents

<i>Preface</i>	xvii
<i>List of Contributors</i>	xxi
1 Sol-Gel Synthesis of Nano-Scaled Metal Fluorides – Mechanism and Properties	1
<i>Erhard Kemnitz, Gudrun Scholz and Stephan Rüdiger</i>	
1.1 Introduction	1
1.1.1 Sol-Gel Syntheses of Oxides – An Intensively Studied and Widely Used Process	1
1.1.2 Sol-Gel Syntheses of Metal Fluorides – Overview of Methods	2
1.2 Fluorolytic Sol-Gel Synthesis	4
1.2.1 Mechanism and Properties	5
1.2.2 Insight into Mechanism by Analytical Methods	8
1.2.3 Exploring Properties	27
1.2.4 Possible Fields of Application	29
References	35
2 Microwave-Assisted Route Towards Fluorinated Nanomaterials	39
<i>Damien Dambournet, Alain Demourgues and Alain Tressaud</i>	
2.1 Introduction	39
2.2 Introduction to Microwave Synthesis	40
2.2.1 A Brief History	40
2.2.2 Mechanisms to Generate Heat	40
2.2.3 Advantages of Microwave Synthesis	41
2.2.4 Examples of Microwave Experiments	41
2.3 Preparation of Nanosized Metal Fluorides	42
2.3.1 Aluminium-based Fluoride Materials	42
2.3.2 Microwave-assisted Synthesis of Transition Metal Oxy-Hydroxy-Fluorides	61

2.4	Concluding Remarks	64
	Acknowledgements	64
	References	65
3	High Surface Area Metal Fluorides as Catalysts	69
	<i>Erhard Kemnitz and Stephan Rüdiger</i>	
3.1	Introduction	69
3.2	High Surface Area Aluminium Fluoride as Catalyst	71
3.3	Host-Guest Metal Fluoride Systems	74
3.4	Hydroxy(oxo)fluorides as Bi-acidic Catalysts	78
3.5	Oxidation Catalysis	84
3.6	Metal Fluoride Supported Noble Metal Catalysts	88
3.6.1	Hydrodechlorination of Monochlorodifluoromethane	90
3.6.2	Hydrodechlorination of Dichloroacetic Acid (DCA)	94
3.6.3	Suzuki Coupling	95
	References	97
4	Investigation of Surface Acidity using a Range of Probe Molecules	101
	<i>Alexandre Vimont, Marco Daturi and John M. Winfield</i>	
4.1	Introduction	101
4.1.1	Setting the Scene: Metal Fluorides versus Metal Oxides	102
4.1.2	Some Examples of the Application of FTIR Spectroscopy to the Study of Surface Acidity in Metal Oxides	103
4.1.3	A Preview	107
4.2	Characterization of Acidity on a Surface: Contrasts with Molecular Fluorides	108
4.2.1	Molecular Brønsted and Molecular Lewis Acids	108
4.2.2	A Possible Benchmark for Solid Metal Fluoride, Lewis Acids: Aluminium Chlorofluoride	109
4.3	Experimental Methodology	110
4.3.1	FTIR Spectroscopy	110
4.3.2	Characteristic Reactions and the Detection of Adsorbed Species by a Radiotracer Method	112
4.4	Experimental Studies of Surface Acidity	117
4.4.1	Using FTIR Spectroscopy	118
4.4.2	Using HCl as a Probe with Detection via [³⁶ Cl]-Labelling	123
4.4.3	Metal Fluoride Surfaces that Contain Surface Hydroxyl Groups: Aluminium Hydroxy Fluorides with the Hexagonal Tungsten Bronze Structure	129
4.4.4	Possible Geometries for HCl Adsorbed at Metal Fluoride Surfaces: Relation to Oxide and Oxyfluoride Surfaces	135
4.5	Conclusions	136
	References	137

5	Probing Short and Medium Range Order in Al-based Fluorides using High Resolution Solid State Nuclear Magnetic Resonance and Parameter Modelling	141
	<i>Christophe Legein, Monique Body, Jean-Yves Buzaré, Charlotte Martineau and Gilles Silly</i>	
5.1	Introduction	141
5.2	High Resolution NMR Techniques	142
5.2.1	Fast MAS and High Magnetic Field	142
5.2.2	^{27}Al NMR	145
5.2.3	High Resolution Correlation NMR Techniques	148
5.3	Application to Functionalized Al-Based Fluorides with Catalytic Properties	153
5.3.1	Crystalline Aluminium Fluoride Phases	153
5.3.2	^{19}F Isotropic Chemical Shift Scale in Octahedral Aluminium Environments with Oxygen and Fluorine in the First Coordination Sphere	153
5.3.3	Fluorinated Aluminas and Zeolites, HS AlF_3	157
5.3.4	Aluminium Chlorofluoride and Bromofluoride	158
5.3.5	Pentahedral and Tetrahedral Aluminium Fluoride Species	158
5.3.6	Nanostructured Aluminium Hydroxyfluorides and Aluminium Fluoride Hydrate with Cationic Vacancies	159
5.3.7	δ_{iso} Scale for ^{27}Al and ^{19}F in Octahedral Aluminium Environments with Hydroxyl and Fluorine in the First Coordination Sphere	160
5.4	Alkali and Alkaline-earth Fluoroaluminates: Model Compounds for Modelling of NMR Parameters	160
5.4.1	^{19}F NMR Line Assignments	161
5.4.2	^{27}Al Site assignments, Structural and Electronic Characterizations	164
5.5	Conclusion	167
	References	168
6	Predictive Modelling of Aluminium Fluoride Surfaces	175
	<i>Christine L. Bailey, Sanghamitra Mukhopadhyay, Adrian Wander, Barry Searle and Nicholas Harrison</i>	
6.1	Introduction	175
6.2	Methodology	176
6.2.1	Density Functional Theory	176
6.2.2	Surface Free Energies	177
6.2.3	Molecular Adsorption	178
6.2.4	Kinetic Monte Carlo Simulations	179
6.3	Geometric Structure of α and β - AlF_3	180
6.3.1	Bulk Phases	180
6.3.2	Surfaces	180

6.4	Characterization of AlF_3 Surfaces	185
6.5	Surface Composition under Reaction Conditions	188
6.5.1	The $\alpha\text{-AlF}_{3-x}$ (01–12) Termination	189
6.5.2	The $\alpha\text{-AlF}_3$ (0001) Termination	192
6.6	Characterization of Hydroxylated Surfaces	193
6.7	Surface Catalysis	196
6.7.1	Molecular Adsorption	197
6.7.2	Reaction Mechanisms and Barriers	198
6.7.3	Analysing the Kinetics of the Reaction	200
6.8	Conclusions	201
	Acknowledgements	203
	References	203

7 Inorganic Fluoride Materials from Solvay Fluor and their Industrial Applications 205

Placido Garcia Juan, Hans-Walter Swidersky, Thomas Schwarze and Johannes Eicher

7.1	Introduction	205
7.2	Hydrogen Fluoride	205
7.2.1	Anhydrous Hydrogen Fluoride, AHF	206
7.2.2	Hydrofluoric Acid	206
7.3	Elemental Fluorine, F_2	207
7.3.1	Fluorination of Plastic Fuel Tanks	207
7.3.2	Finishing of Plastic Surfaces	207
7.3.3	F_2 Mixtures as CVD-chamber Cleaning Gas	208
7.4	Iodine Pentafluoride, IF_5	208
7.5	Sulfur Hexafluoride, SF_6	209
7.5.1	SF_6 as Insulating Gas for Electrical Equipment	209
7.5.2	SF_6 Applications in Metallurgy	209
7.6	Ammonium Bifluoride, NH_4HF_2	210
7.7	Potassium Fluorometalates, KZnF_3 and K_2SiF_6	210
7.8	Cryolite and Related Hexafluoroaluminates, Na_3AlF_6 , Li_3AlF_6 , K_3AlF_6	211
7.9	Potassium Fluoroborate, KBF_4	212
7.10	Fluoboric Acid, HBF_4	212
7.11	Barium Fluoride, BaF_2	213
7.12	Synthetic Calcium Fluoride, CaF_2	213
7.13	Sodium Fluoride, NaF	213
7.14	Sodium Bifluoride, NaHF_2	213
7.15	Potassium Bifluoride, KHF_2	214
7.16	Potassium Fluoroaluminate, KAlF_4	214
7.17	Fluoroaluminate Fluxes in Aluminium Brazing	214
7.17.1	Flux Composition	214
7.17.2	Flux and HF	216
7.17.3	Flux Particle Size	217

7.17.4	Flux Melting Range	219
7.17.5	Current Status of Aluminium Brazing Technology	220
7.17.6	Cleaning and Flux Application	221
7.17.7	Wet Flux Application	221
7.17.8	Dry/Electrostatic Flux Application	222
7.17.9	Post Braze Flux Residue	222
7.17.10	Filler Metal Alloys	222
7.17.11	Flux Precoated Brazing Sheet/Components	223
7.17.12	Clad-less Brazing	223
7.17.13	Furnace Conditions	224
7.18	Summary	224
	References	225
8	New Nanostructured Fluorocompounds as UV Absorbers	229
	<i>Alain Demourgues, Laetitia Sronek and Nicolas Penin</i>	
8.1	Introduction	229
8.2	Synthesis of Tetravalent Ce and Ti-based Oxyfluorides	231
8.2.1	Preparation of Ce-Ca-based Oxyfluorides	231
8.2.2	Preparation of Ti-based Oxyfluorides	232
8.3	Chemical Compositions and Structural Features of Ce and Ti-based Oxyfluorides	233
8.3.1	Elemental Analysis	233
8.3.2	Magnetic Measurements	233
8.3.3	About the Chemical Composition of $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x}$ and $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x-y/2}\text{F}_y$ Series	234
8.3.4	About the Structure and Local Environment of Fluorine in $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x-y/2}\text{F}_y$ Series	237
8.3.5	Composition and Structure of Ti-based Hydroxyfluoride	252
8.4	UV Shielding Properties of Divided Oxyfluorides	263
8.4.1	The Ce-Ca-based Oxyfluorides Series and UV-shielding Properties	264
8.4.2	Ti Hydroxyfluoride and UV-shielding Properties	266
8.5	Conclusion	267
	Acknowledgement	269
	References	269
9	Oxyfluoride Transparent Glass Ceramics	273
	<i>Michel Mortier and Géraldine Dantelle</i>	
9.1	Introduction	273
9.2	Synthesis	274
9.2.1	Synthesis by Glass Devitrification	275
9.2.2	Transparency	277
9.3	Different Systems	279
9.3.1	Glass-Ceramics with CaF_2 as their Crystalline Phase	281
9.3.2	Glass-Ceramics with $\beta\text{-PbF}_2$ as their Crystalline Phase	281

9.3.3	Glass-Ceramics with $\text{CdF}_2/\text{PbF}_2$ as their Crystalline Phase	281
9.3.4	Glass-Ceramics with LaF_3 as their Crystalline Phase	282
9.4	Thermal Characterization	282
9.4.1	Kinetics of Phase-change/Devitrification	288
9.4.2	Thakur's Method	288
9.5	Morphology of the Separated Phases	289
9.6	Optical Properties of Glass-Ceramics	293
9.6.1	Influence of the Devitrification on the Spectroscopic Properties of Ln^{3+}	293
9.6.2	Effect of High Local Ln^{3+} Concentration in Crystallites	295
9.6.3	Comparison of the Optical Properties of Glass-Ceramics and Single-Crystals	297
9.6.4	Multi-doped Glass-Ceramics	299
9.7	Conclusion	301
	References	302
10	Sol-Gel Route to Inorganic Fluoride Nanomaterials with Optical Properties	307
	<i>Shinobu Fujihara</i>	
10.1	Introduction	307
10.2	Principles of a Sol-Gel Method	308
10.2.1	Metal Oxide Materials	308
10.2.2	Metal Fluoride Materials	308
10.3	Fluorinating Reagents and Method of Fluorination	309
10.4	Control of Shapes and Microstructures	313
10.5	Optical Properties	317
10.5.1	Low Refractive Index and Anti-Reflection Effect	317
10.5.2	Luminescence	322
10.6	Concluding Remarks	326
	References	326
11	Fluoride Glasses and Planar Optical Waveguides	331
	<i>Brigitte Boulard</i>	
11.1	Introduction	331
11.2	Rare Earth in Fluoride Glasses	332
11.2.1	Fundamentals	333
11.2.2	Applications: Laser and Optical Amplifiers	334
11.3	Fabrication of Waveguides: A Review	336
11.4	Performance of Active Waveguides	338
11.4.1	Optical Amplifier	340
11.4.2	Lasers	341
11.5	Fluoride Transparent Glass Ceramics: An Emerging Material	342
11.6	Conclusion	344
	References	344