1. Introduction

Nanomaterials chemistry has become an extremely important area of research over the past 20 years. Although many different nanomaterials have already found industrial applications, we are still just at the beginning of a new scientific and industrial revolution driven by the advances in nanomaterials science.

Over the past decades, many new synthesis techniques have been developed that give access to the fascinating world of nanomaterials with different chemical and physical properties. Sol-gel synthesis is certainly one of the most powerful synthesis routes in terms of the wide variety of synthesis approaches and technical applications. For a long time, the aqueous (hydrolytic) sol–gel synthesis route in particular, mainly forced by the development of silica, was and still is in the focus of thousands of chemists and materials scientists worldwide.

However, motivated by new developments, like atomic layer deposition, ALD, and others, non-aqueous sol–gel synthesis approaches have been developed recently, thus extending the synthesis access toward nanoscopic new materials. These new non-aqueous sol–gel approaches allow either the synthesis of novel materials, or in many cases give access to applications that are not possible via hydrolytic sol–gel routes. Thus, it is the intention of this review to provide an overview of a non-aqueous sol gel approach that gives for the first time direct access to novel nanoscaled metal fluorides.

Directly derived from the classical aqueous sol–gel synthesis is the non-aqueous thermally induced formation of nanoscopic metal oxides, the basics and applications of which are reflected in more detail in ref. 1. Another non-aqueous synthesis approach that lays in the focus of this review is the so-called fluorolytic sol–gel synthesis that yields nanoscopic metal fluorides in a similar variety and extent as the hydrolytic sol–gel route yields nanoscopic metal oxides. Thus, over the past few years a rapidly growing interest in nano metal fluorides has emerged from their attractive perspectives in applications such as catalysis, optics, photonics, optical amplifiers, optoceramics, composite materials, biosensing, and biolabelling. This increasing interest in new nano fluoride based materials is clearly evidenced by the number of publications published in the past two decades. Checking the Thomson Reuters Web of Knowledge for the key words “nano” in combination with “fluoride” will retrieve just 13 publications and 96 citations for the period 1990 until 2000. Until 2005, 96 publications appeared and 1353 citations, but until 2013 as many as 750 publications and 7219 citations can be
found! Moreover, the first book emphasizing synthesis and applications of new nano metal fluorides appeared just recently in 2010.2

This situation has resulted in new synthesis routes toward nano metal fluorides being developed recently. Most of them will be briefly mentioned in this review but special focus will be laid on the fluorolytic sol–gel approach.

2. The synthesis of nanoscaled metal fluorides

Many different synthesis approaches have been developed over the past years, such as thermolysis of precursors, flame pyrolysis, reversed micelle and microemulsion precipitation, solvothermal synthesis, precipitation from non-aqueous solutions, and mechanochemical synthesis. Most of these methods were recently reviewed by Fedorov et al.3 In fact, there are two different sol–gel based synthesis approaches, one representing a rather indirect (TFA sol–gel route) and the other a direct (fluorolytic sol–gel route) sol–gel process. Since the TFA sol–gel synthesis does not directly result in the formation of metal fluorides but of metal trifluoroacetate gels that might be further processed into metal fluorides after thermal degradation, this route will be reflected here just briefly, whereas the fluorolytic sol–gel synthesis resulting in direct metal fluoride formation will be discussed in more detail.

2.1. The trifluoroacetate (TFA) sol–gel synthesis

Probably the first synthesis method to obtain nanoscopic metal fluorides is the sol–gel derived trifluoroacetate (TFA) route, which has been established for the preparation of high specific surface area metal fluoride catalysts, fluoride glasses and thin metal oxide fluoride films of defined thickness and refractive index.

It has been found that even though fluorine is strongly bound in the CF3-group, certain metal trifluoroacetates can be thermally decomposed to form the corresponding metal fluorides. First studies investigated the preparation of lanthanide fluorides4 heavy-metal ZBLAN fluoride glasses5 by thermal decomposition of zirconium, barium, lanthanum, aluminium and sodium trifluoroacetates at temperatures between 220 and 300 °C. Later, that principle was extended to other metals, especially alkaline earth6 and rare-earth metal fluorides.6d,7 In addition, complex metal fluorides are accessible by the TFA route.8 Recently, several metal fluoride catalysts (MgF2, BaF2, CaF2, ZnF2, LaF3 and CeF3) with high specific surface areas between 20 and 125 m² g⁻¹ have been synthesized by thermal decomposition of metal trifluoroacetates.9

The chemical principle of the TFA route mainly developed by Fujihara et al.10 consists of the reaction of a metal alkoxide or acetate with trifluoroacetic acid in an organic, mainly alcoholic, solvent (cf. eqn (1)).

\[
\text{M(OR)}_n + n\text{CF}_3\text{COOH} \rightarrow \text{M(OOCFCF}_3)_n + n\text{ROH} \quad (1)
\]

Due to the electron-withdrawing CF3-group, TFA is strongly acidic and substitutes the acetate or alkoxide group from the coordination of the metals. As a result, a metal trifluoroacetate sol may form, which can be further processed, e.g. for coating10 or powder materials. Crystalline metal fluorides are formed by thermal decomposition of the trifluoroacetate sols and gels during calcination at temperatures up to 400 °C. At higher temperatures, oxide fluorides and oxides can also be formed as additional phases.6a In the gas phase, various fluorine species, such as \( \text{CF}_2\text{O} \), \( \text{CF}_3\text{O} \), \( \text{CF}_2\text{OF} \), \( \text{CO}_2 \), and \( \text{CO}_3 \), that act as fluorinating agents have been found by MS and IR spectroscopy.6e,11 Recently, Mosiadz et al. reported the evidence of difluoromethylene diradicals \( \text{(:CF}_2\text{)} \) as intermediate species of the decomposition of TFA.7 The general reaction scheme for lanthanide trifluoroacetates is given in eqn (2):

\[
\text{Ln(OOCFCF}_3)_3 \rightarrow \text{LnF}_3 + (\text{CF}_3\text{CO})_2\text{CO} + \text{CO}_2 + \text{CO} \quad (2)
\]

This overall route is shown in Scheme 1 starting from metal alkoxides or acetates, which are reacted with trifluoroacetic acid in solution to form a metal trifluoroacetate precursor sol, which can be used for the preparation of thin film coatings or xerogels. The final step is the thermal decomposition of the fluoroorganic compound to give the corresponding metal fluoride. Thus, substrates to be coated are limited to those materials that are stable under the given reaction conditions.

Fig. 1 exemplarily illustrates the procedure for sol–gel deposition of a porous MgF2 film on silicon substrates by the TFA route.6d The Mg(\text{CF}_3\text{COO})_2×\text{(CH}_3\text{COO})_2 precursor solution that is used for thin film coating is prepared by dissolving Mg-(\text{CH}_3\text{COO})_2×4\text{H}_2\text{O} in an ethanol–water mixture and adding 2 equivalents of trifluoroacetic acid. Depending on the concentration, viscosity, temperature, humidity and drawing velocity, a thin film of defined thickness is deposited on the substrate by dip-coating. During drying and initial heating, solvent and excess acetic and trifluoroacetic acid evaporate and exchange processes take place, yielding mixed magnesium hydroxo acetate trifluoroacetates. At temperatures above 230 °C, magnesium (oxide/hydroxide) fluorides are formed and the decomposition products of TFA are released. Crystallization of the film is observed at temperatures around 300 °C, resulting in a porous thin film. The final phase composition and morphology of the film is largely determined by the applied atmosphere (humidity, gas phase composition) and heat-rate of the calcination step.

Although this was in fact the first sol–gel synthesis route leading to the formation of nanoscopic metal fluorides, several drawbacks are connected with this route. Thus, (i) not all metals form stable metal fluoroacetates, (ii) not all metal fluoroacetates decompose into metal fluorides but may also form more stable metal oxides, and (iii) even the formation of the respective metal oxide fluorides or mixtures of fluorides and oxides cannot be ruled out. Since this route demands a thermal post-treatment in any case, the suitable substrates for thin film coating are limited. Furthermore, eqn (2) is an over-
simplification of the reaction, and the formation of highly corrosive hydrogen fluoride and other harmful decomposition products therefore has to be taken into account.

2.2. The fluorolytic sol–gel synthesis

In the classical sol–gel synthesis, a metal alkoxide dissolved in an organic solvent, e.g. alcohol, is reacted with water thus transforming the metal alkoxide group (M–OR) by hydrolysis into a metal hydroxide group (cf. eqn (3)).

$$\text{M(OR)}_n + \text{nH}_2\text{O} \rightarrow \text{M(OH)}_n + \text{nROH} \quad (3)$$

In a second consecutive reaction step, M–OH groups formed this way may undergo condensation reactions either with a further M–OH group forming water (eqn (4)) or with an unconverted M–OR group thus elaborating alcohol (eqn (5)).

$$\text{M–OH} + \text{HO–M} \rightarrow \text{M–O–M} + \text{H}_2\text{O} \quad (4)$$

$$\text{M–OH} + \text{RO–M} \rightarrow \text{M–O–M} + \text{ROH} \quad (5)$$

Although these reactions are evidently more complex than implied by these simple reactions, the general reaction path is correctly represented. Depending on the metal alkoxides used, the hydrolysis and the condensation reactions very often are incomplete, hence, a thermal post-treatment is necessary in order to convert remaining M–OR groups into M–O–M bridges to obtain the desired metal oxide.

Since the initial reaction step represents a hydrolysis of the metal alkoxide bond, it may be defined as hydrolytic sol–gel synthesis in order to show the similarity but also the distinct difference to the fluorolytic sol–gel synthesis that will be reflected in more detail here. As a matter of fact, both the hydrolytic as well as the non-hydrolytic sol–gel syntheses result in the formation of M–X–M (X: O or F) bridges that – when properly performed – result in the formation of nanoscopic particles.

Formally, the fluorolytic sol–gel synthesis involves similar reaction steps as described above for the hydrolytic sol–gel
In recent years, much work has been done on adapting the fluoro-lytic sol–gel chemistry to other metals. In the attempt to get deeper insights regarding the mechanism of the fluoro-lytic sol–gel synthesis, most efforts have been made in the cases of AlF3 and MgF2 formation. Hence, the following sub-chapters will focus on different mechanistic aspects derived from these two metal fluoride systems.

2.2.1. Mechanistic aspects of the fluoro-lytic sol–gel synthesis

NMR investigation of the formation of AlF3 from Al(OiPr)3 and HF. Most metal fluorides obtained by fluoro-lytic sol–gel synthesis are either totally X-ray amorphous or at least highly distorted, hence, diffraction methods are often inappropriate to follow the reaction path. Although other methods, such as FT-IR, Raman or TEM, give valuable data for the final products, for a detailed insight into the mechanism of the fluoro-lytic sol–gel process, NMR spectroscopy has been found to be the method of choice. Both liquid and solid state NMR investigations allow direct observations of local structures and their changes, even if the matrices suffer from a lack of lattice periodicity. For the fluoro-lytic sol–gel process both liquid and solid state NMR experiments were performed including 1H, 13C, 27Al and 19F as sensitive spin probes. The use of 1D and 2D NMR experiments allows local structures in liquids and solids to be addressed and directly compared. Thus, compositional and structural changes with progressive fluorination degrees were followed and finally a possible reaction pathway for this process could be derived. Due to the good experimental accessibility of the mentioned spin probes, a detailed mechanistic study was conducted for the formation of nanoscopic AlF3. These investigations were further complemented by DFT calculations.

Since for these investigations aluminium isopropoxide in isopropanol was used as the precursor, the assignment of molecular structures existing in solid Al(OiPr)3 and its solution in iPrOH is mandatory. In agreement with XRD findings, 27Al MAS NMR measurements of solid Al(OiPr)3 gave an unambiguous indication of the existence of two distinguishable aluminium sites in the matrix. A simulation of the NMR spectra resulted in typical chemical shift values for AlO4 (δi = 61.5 ppm) and AlO6 (δi = 1.7 ppm) units. Thus, the kind and the intensity ratio of AlO4 : AlO6 being 3 : 1 confirm the tetra-meric molecular structure (see also Fig. 2, 1) existing in the tetragonal crystal structure.

Cross-polarization (1H–13C CP) MAS NMR spectra allow distinction not only between CHO and CH3 groups but also between terminal (Al–O) and bridging (Al–O–Al) isopropoxide units. Based on this and considering suggestions made by Abraham, terminal (63 ppm) and bridging (66 ppm) CHO groups were found to be located in the low-field part of the
spectrum; terminal CH₃ groups can be found in the range between 28–30 ppm and bridging CH₃ groups dominate the high-field part of the ¹H–¹³C CP MAS NMR spectrum.¹⁹

Because isopropanol was used as the standard solvent for the fluorolytic sol–gel synthesis,¹²–¹⁴ Al(OiPr)₃ isopropanolic solutions were carefully investigated. Whereas in etheric solutions only tetrameric aluminium isopropoxide species exist (AlO₆ (2.5 ppm, 26.7%), AlO₄ (61.8 ppm, 73.3%), ₁ in Fig. 2), the situation in isopropanolic solution is much more complex. Respective NMR investigations¹³,¹⁹ doubtlessly indicate not only the presence of AlO₆ and AlO₄ but additionally a fivefold coordinate aluminium species AlO₅ at 32 ppm, thus supporting the existence of trimeric Al(OiPr)₃ species (3 in Fig. 2).

Cyclic trimeric species (2 in Fig. 2) with possible distorted AlO₄ polyhedral also exist, supported by a strong low-field shifted resonance observed at 85 ppm.¹³,¹⁹ Moreover, there are indications for different trimeric species (4 and 4') involving central sixfold oxygen-coordinate aluminium, the latter being formed by the interaction of trimeric species 3 (Fig. 2) with a solvent molecule, as shown in Fig. 3.

Structural changes of isopropanolic Al(OiPr)₃ solutions that result from HF addition were followed by ²⁷Al and ¹⁹F NMR spectroscopy as a function of the molar Al : F ratio (see Fig. 4). The ²⁷Al NMR spectra reveal a decrease of AlO₆ species (central Al of ₁ in Fig. 2), as seen by the decrease of the narrow signal at 2.5 ppm and also a decreasing proportion of the sum over all fourfold coordinated Al species was found. Contrary to that, fivefold coordinated aluminium species AlO₅ (signals at about 35 ppm) increased.¹⁶a

All ¹⁹F spectra are characterized by a group of three sharp signals (chemical shifts of −161 ppm, −163 ppm, −165 ppm) with different intensities. The two additional signals in (a) at δiso = −147 ppm and δiso = −156 ppm are, according to ref. 17, characteristic of fluorine bound to aluminium centres in a mixed oxygen-fluorine coordination, e.g. AlF₃(OiPr)₃₋ₓ, with 1 < x < 4.¹³a,¹⁷,²⁰ the line broadening (Fig. 4, ¹⁹F,d) observed with increasing fluorine content for the peak at about −160 ppm is a result of ¹⁹F–¹⁹F homonuclear dipolar couplings ending up

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Fig. 2 Possible structural units of Al(OiPr)₃ in solution (Reproduced from ref. 16a with permission of the American Chemical Society).

Fig. 3 Possible equilibria between different trimeric Al(OiPr)₃ species in isopropanolic solution.

Fig. 4 ²⁷Al NMR and ¹⁹F NMR spectra of different sols and wet gels recorded at B₀ = 9.4 T. Increasing fluorine content from a–d with molar ratios Al/F: (a) 4 : 1, (b) 2 : 1, (c) 1 : 1, (d) 1 : 2 (Reproduced from ref. 16a with permission of the American Chemical Society).
in one broad peak in the static $^{19}$F NMR spectrum for the gel with molar ratio Al : F as 1 : 3. However, these isotropic chemical shifts give no proof of the coordination number of the involved aluminium atoms.

The $^{27}$Al MAS NMR spectra recorded at different magnetic fields of up to 21.1 T and $^{27}$Al 3QMAS experimental data derived at $B_0 = 14.1$ T enabled the simulation of the $^{27}$Al MAS NMR spectra, and thus, in addition to 6-fold coordinated species, the presence of 4- and 5-fold coordinated $\text{AlF}_x(\text{O}i\text{Pr})_{\text{CN}-x}$ (coordination number, CN, of 4 or 5) was unambiguously established for the first time for this system. A comparison of the chemical shifts observed for fluorine and aluminium isopropoxide fluorides with different F contents allows for a simple correlation for the appropriate species and hints of F-species connected to 4-fold and 5-fold coordinated Al species were corroborated. Moreover, $\text{AlF}_x\text{O}_{4-x}$ and $\text{AlF}_x\text{O}_{5-x}$ units present in the solids could be assigned based on a comprehensive $^{27}$Al and $^{19}$F chemical shift trend analysis that included known chemical shifts of solids containing pure $\text{AlO}_4$, $\text{AlO}_3$, $\text{AlF}_4$, and $\text{AlF}_3$ species. Interestingly, the plot of the sums of the intensities of each Al species group (Al species with CN 4, 5, and 6) versus the increasing degree of fluorination gave three almost linear correlations. A similar plot for the F species was obtained by plotting the intensities of each species against the initial molar F/Al ratio. These correlations obtained are an extremely useful tool for the interpretation of $^{27}$Al and $^{19}$F MAS NMR spectra of related Al/F/O systems. Based on the chemical shift trend analysis data, from $^{27}$Al and $^{19}$F MAS NMR spectra taken for sols of varying Al to F ratios the intermediately formed $\text{AlF}_x(\text{OR})_{\text{CN}-x}$ species can be unambiguously derived, as is shown in Fig. 5.

The most pronounced changes in the spectral features of $^{19}$F and $^{27}$Al NMR investigation can be observed at low fluorine contents up to a molar ratio of Al to F of one (Fig. 5). Whereas the spectral features of the initial $\text{Al(O}i\text{Pr})_3$ are still present in the $^{27}$Al MAS NMR spectra of samples with low fluorine content, a rising signal at 38 ppm is detected, which is provoked by a tetrahedrally coordinated aluminium site in the proximity to fluorine, as evidenced by $^{19}$F → $^{27}$Al CP MAS NMR experiments. Their $^{19}$F MAS NMR spectra (Fig. 5) are dominated by very sharp signals (FWHM less than 1 kHz), which indicate ordered (“crystal-like”) local structures. Most of the species in these solids are more or less isolated, no proximity of the certain F-sites to each other can be stated by $^{19}$F → $^{19}$F spin exchange experiments. The existence of defined fourfold and fivefold coordinated $\text{AlF}_x(\text{OiPr})_{\text{CN}-x}$ species as intermediate structures in aluminium isopropoxide fluorides was unambiguously shown utilizing for the first time ultra high-field MAS NMR at magnetic fields $B_0$ up to 21.1 T.

By further increasing the fluorine content (Al : F ratios equal to 1 : 2 and 1 : 3), an increasingly stabilized network is
formed. The amount and spread of four- and five-fold coordinated Al-species decreases, finally resulting in sixfold AlF₆(OiPr)₆₋ₓ species (x = 4 and 5), as deduced from the chemical shift correlation.¹³,²⁰,²³

A comparison of the development of the intensities of single species with rising fluorination degrees with the general development of the contributions of the appropriate ¹⁹F MAS NMR spectra allows a simple correlation of Al and corresponding F-species. Besides, a variety of possibly terminal fluorine-sites are evident for the highly disordered and amorphous aluminium isopropoxide fluorides in the up-field part of the spectra.²³ In conclusion, these NMR investigations clearly evidence the stepwise fluorination of the aluminium isopropoxide with increasing HF supply during the fluorolytic sol–gel synthesis whereby the four- and five-fold coordinated Al-sites of the starting isopropoxide become completely converted into sixfold coordinated Al-sites.

In line with the conclusions drawn from ²⁷Al and ¹⁹F MAS NMR investigations are insights gained from ¹H and ¹³C NMR spectra. As a rule, these ¹H and ¹³C NMR spectra of sols and gels showed two main effects with increasing fluorine supply: the portion of bridging isopropoxide groups decreases while the portion of terminal isopropoxide groups increases with higher fluorine supply.²⁰,²³

Obviously, the fluorination starts by protonation of bridging isopropoxide groups with the consequence of a line broadening of the corresponding signals, while the intensities of signals of terminal groups first remain constant. This first step is also supported by DFT calculations.²⁰,²⁴

A subsequent step of the fluorination may involve an attack of fluorine ions or HF, which can coordinate to central Al atoms of 1 and substitute the protonated isopropoxide group. During this process, central ALO₆ polyhedra are more and more distorted, accompanied by a decay of the signal intensity of the central Al atom in 1. Moreover, a species with a slightly downfield shifted signal for mainly sixfold oxygen-coordinated Al atoms, as represented in Fig. 5 by the possible intermediate b, occurs. Another consequence is the rising occurrence of five-fold Al species (Fig. 5, b and c), which results from the former fourfold ALO₅ species of 1. These first steps are also close to possible structures of intermediates as simulated with DFT calculations independently.

2.2.2. Single crystal structures of aluminium alkoxide fluorides. Because the metal fluorides obtained via the fluorolytic sol–gel synthesis are either highly distorted or even completely X-ray amorphous, diffraction methods are usually less beneficial to gain further information. Especially in the case of AlF₃, it is extremely difficult to grow single crystals of intermediate species. This is mainly caused by the fact that a wide variety of oligomeric aluminium isopropoxide fluorides is present, as evidenced by mass spectrometric investigations, which prevent crystallisation.²⁵ However, several of such intermediates were successfully crystallized from the sols as a result of pyridine or DMSO coordination to these oligomers. Although these intermediates represent only an isolated view of the structural units in the sol and are far from being quantitative, the structures of these intermediates are in total agreement with the predictions from the NMR investigations. The structures presented in Fig. 6 are sorted according to their Al to F stoichiometry and clearly indicate that four- and five-fold Al-sites are consumed first in the course of fluorination, finally resulting in highly fluorinated materials. The latter cannot be proven by single crystal structures because crystallization is obviously no longer favoured above a critical degree of fluorination. As has been proven by MS-investigations,²⁵ many different partially fluorinated oligomeric/polymeric building blocks of different Al-numbers are present in such solutions. This is obviously the main reason why crystallization is sup-

Fig. 6 Structures of aluminium alkoxide fluorides obtained from sols of varying aluminium isopropoxide to HF ratios sorted according to their Al to F ratio within the structure. 1: Al₄(OiPr)₁₂; 2: Al₃F(OOiPr)₁₀·D (D = Py, DMSO), Al₁: F = 3 : 1; 3: Al₅F₄(µ₄-O)(OiPr)₈(HiPrO)₂, Al₁ : F = 1 : 1; 4: Al₉F₅(µ₅-O)(OiPr)₁₀, Al₁ : F = 1 : 1; 5: Al₃F₅(µ₄-O)(OiPr)₁₀·3Py, Al₁ : F = 1 : 1.43; 6: Al₁₀F₁₆(µ₄-O)₁₂(OiPr)₁₀·4Py, Al₁ : F = 1 : 1.6; 7: Al₁₀F₁₀(OiPr)₁₀·4Py, Al₁ : F = 1 : 1.67. Reproduced from ref. 26 with permission of the Royal Society of Chemistry.
pressed. Just by addition of electron donors such as pyridine, crystallization can be enforced and thus some of these clusters underwent crystallization, thus making single crystals available. Remarkably, DFT-calculations brought about the formation of terminal fluorine bound to tetrahedrally and pentahedrally coordinated Al-sites. Although these sites were also evidenced by MAS-NMR, just a few of these terminal F-sites were found in the single crystal structures of oligomers (cf. Fig. 6). This might be rationalized by the fact that the addition of pyridine as a stabilising donor molecule might have caused some kind of rearrangement inside the aluminium alkoxide fluoride oligomers.

2.2.3. The possible reaction mechanism. Considering all these experimental findings derived from comprehensive MAS NMR and single crystal structure determination, DFT calculations were performed to show a possible mechanism of the fluorolytic sol–gel synthesis of AlF₃. In order to reduce the degree of complexity, isopropoxide groups were replaced by methoxide, which can be expected to show similar reactivity and thus also being representative of the reaction of HF with Al(OiPr)₃. Although different reaction paths have been considered, only the most probable being in accordance with the experimental data will be presented here. Since the fluorolytic sol–gel synthesis is performed in anhydrous organic solvents (usually isopropanol), tetrameric Al₄(OiPr)ₑ₂ is most probably solvated. The HF forms oligomeric adducts of the type [F(HF)]⁻⋯[H⋯O(H)iPr]⁺ according to eqn (7), i.e., neither free fluoride ions nor protons are present. Similar types of HF-adducts have also been reported for the HF-dimethyl ether system.°

\[
(HF)_n \rightarrow H^+ + [F(HF)_{n-1}]^- + H^+ + HOiPr \rightarrow H \cdot \cdot O(H)iPr
\]

(7)

Thus, in the first reaction step a HF-complex is assumed to approach the tetrameric Al₄(OiPr)₁₂ units which might result in the coordination of fluoride ions via hydrogen bonds (Fig. 7a). Simultaneously, the proton attacks one of the four bridging O, which are next to F in the complex, followed by bond cleavage of both the O(bridging)–Al(central) and O(bridging)–Al(peripheral) bond. This is the first ring opening of the tetramer. As a consequence, the fluoride ion will be released from the hydrogen bonding and becomes covalently bound to an Al(peripheral). Therein the central Al-site is no longer 6-fold coordinated by O but in a 5-fold or pseudo 6-fold coordination involving the released ROH. The alcohol molecule which is set free remains in the vicinity of Al(central), although it is no longer covalently bound to but probably solvating the central Al (Fig. 7b).

In the next step, the isopropanol molecule is released from the complex and due to the high electrophilic character of the central aluminium, a fluoride ion is introduced resulting in a sixfold coordinated aluminium. The alcohol molecule moves towards that Al(peripheral), to which the first fluoride is bound, making it pseudo 5-fold coordinated without forming a new ring (Fig. 8).
The protonation might occur at different positions, either (i) at the terminal, (ii) bridging oxygen atoms of the pseudo 5-fold coordinated Al(peripheral) or (iii) at the bridging oxygen of the remaining two intact rings. The calculations of those three scenarios are illustrated in Fig. 9.

(i) A second alcohol molecule is set free and at the same time a new F-bridged ring is closed. Both alcohol molecules remain in the vicinity of Al(peripheral), which becomes pseudo 6-fold coordinated (A). This state might result in a stabilisation of the system, which is a tetramer with one F(bridging) and one F(terminal), and two alcohol molecules.

(ii) Formation of a trimer and a monomer each containing one fluorine (B) as intermediate species. Although those structures are not stable enough to be isolated, coordination of DMSO to the sixfold coordinated Al site has been found to increase the cluster stability. The computed structure of a DMSO-stabilized trimer (C) corresponds well to the compound that has been isolated and characterized by crystal structure analysis. That gives indirect support for the results of the calculations and assumptions of the reaction pathway. However, the reaction should not come to a stop at this point, which is potentially in agreement with the experiment.

(iii) As a consequence of the protonation of a bridging oxygen, isopropanol is formed and another O(bridging)–Al(peripheral) bond is cleaved. Then two new rings, each with an F(bridging), are closed one after the other. The system consisting of a tetramer with two F(bridging) in two different rings and of two alcohol molecules may become stabilised (D).

Based on the experimental findings and computational results, Scheme 3 summarises in a simplified manner the possible reaction pathway of the fluorolytic sol–gel synthesis starting with the tetrameric Al(OiPr)₃ and ending up in a cross-linked aluminium fluoride gel.

**Mechanistic aspects of the sol–gel synthesis of MgF₂**

Magnesium fluoride is the second most investigated fluoride system regarding mechanistic aspects. Although in detail different, the reaction resembles in many aspects the synthesis approach as described for AlF₃. Therefore, structural and topological aspects that were not followed for AlF₃ will be reflected for MgF₂ briefly. Different soluble precursors can be utilized for the sol–gel synthesis of magnesium fluorides. While the reaction is thermodynamically driven by the crystallization of MgF₂, the reaction pathway can be different from the structure and chemical nature of the precursor. The reaction of magnesium alkoxides with HF is well investigated by NMR, IR and X-ray diffraction methods. Magnesium methoxide, which forms cubic [Mg₄(OCH₃)₈(CH₃OH)₈]₉ units in solution (see Fig. 10), is fluorinated at room temperature to give nanocrystalline MgF₂ according to eqn (8).

\[
\text{Mg(OCH₃)}₃ + 2\text{HF} \rightarrow \text{MgF}_2 + 2\text{CH}_3\text{OH}
\]  

Fig. 9 (A) An F-bridged ring is closed and Al(peripheral) becomes (pseudo) 6-fold coordinated. (B) The tetramer has become cleaved forming a trimer and a monomer. (C) Calculated structure of the trimer of (B) stabilised by DMSO. (D) Tetramer containing two fluoride ions.
Similar to the sol–gel synthesis of AlF₃, the formation of MgF₂ proceeds via partially fluorinated species that can be isolated and characterized. The understoichiometric reaction of Mg(OCH₃)₂ with 0.1 to 0.4 equivalents of HF leads to partial fluorination and formation of an intermediate Mg₆F₂(OCH₃)₁₀(CH₃OH)₁₂ that has a dicubane structure. In the first step of the sol–gel reaction, methoxide groups are partially replaced by fluoride and the structure is transformed into the dicubane by addition of dimeric magnesium methoxide due to coordinatively unsaturated fluoride. Different crystalline modifications of this structure were identified by single crystal analysis and powder diffraction, indicating its stability and relevance in the sol–gel reaction of Mg(OCH₃)₃ with HF. ¹⁹F NMR spectroscopy of the sols and xerogels shows only one signal at −174 ppm, which is characteristic of fluorine in its [FMg₄] surrounding of the dicubane units.

While in contrast to the aluminium system no other intermediate species could be crystallized, XRD and ¹⁹F MAS NMR spectroscopy gave further insight into the mechanism of the fluorination and structural evolution from magnesium methoxide to MgF₂. Fig. 11a shows the X-ray powder diffraction patterns of MgF₂₋ₓ(OCH₃)ₓ xerogels with x = 0–2. At low HF/Mg ratios (up to 0.4), the diffraction patterns show rather well resolved reflections, which can be attributed to the magnesium methoxide fluoride dicubane structure in different modifications. When the fluoride content is increased, only three broad peaks are found, which reflect the formation of polymeric MgF₂₋ₓ(OCH₃)ₓ. In this structure, Mg is octahedrally coordinated by methoxide and fluoride to form a layered struc-
ture as in magnesium hydroxide. Further addition of HF leads to gradual transformation from the layered into the rutile structure of MgF$_2$ at an F/Mg-ratio of 2 : 1. These data are complemented by $^{19}$F MAS NMR investigations, which prove to be a valuable spin probe to deduce structural changes in the Mg/O/F system as well.$^{31}$ At low degrees of fluorination, the dicubane structure is also found as the main intermediate species, while there are no indications for other defined molecular intermediates. The $^{19}$F chemical shift is found to strongly depend on the local coordination environment of the fluorine atoms. During further fluorination, the $^{19}$F signal experiences a high-field shift from the dicubane at $-174$ ppm with an [FMg$_3$] environment up to $-185$ ppm when the number of oxygen atoms in the second order coordination sphere is decreased. This signal is further shifted to $-198$ ppm for the rutile structure of MgF$_2$, where fluorine is in a [FMg$_4$] coordination.$^{31}$

The reaction yields crystalline MgF$_2$, as seen from the XRD patterns in Fig. 11a and 12c. The reflections are very broad, indicating particles with a mean crystallite size of below 5 nm. TEM images of sol particles confirm an average size of the primary particles in the range of 3 to 5 nm (Fig. 12c). Investigations of particles size by dynamic light scattering (DLS) and small angle X-ray scattering (SAXS) give evidence for the formation of rather large agglomerates with a diameter of a few hundred nanometers. Thus, a direct application of the fresh sols for thin film coatings or for the preparation of inorganic–organic nanocomposite materials is not possible. During ageing, the agglomerates are breaking apart, resulting in transparent sols with particles in the lower nm-scale (Fig. 12b). At the same time, re-crystallization processes are observed by X-ray diffraction methods of these sols that are closely connected to the stabilization of the primary particles and deagglomeration. This process goes in line with re-arrangement of the MgF$_2$ crystallite structure that is observed when measuring the sol at different ageing times by X-ray diffraction (Fig. 11c). Similarly as for metal oxide nano particles, magnesium fluoride sols can be surface modified and thus the stability of small particles can be significantly improved. Due to the very small particle size and thus strong interparticle interactions, the adsorption of small organic acids, such as carboxylic and phosphonic acids, has been thoroughly investigated. Proteins, such as bovine serum albumin (BSA), which are frequently used for particle stabilization in biological media, are limited because of the high volume fraction compared to the MgF$_2$ particle. It has been found that already small amounts of trifluoroacetic acid or phenylphosphonic acid are beneficial to stabilizing magnesium fluoride particles, and prevent the sols from agglomeration and gelation. Thus, the surface properties of metal fluoride particles become addressable, which opens a new field of application and allows for the preparation of organic–inorganic composite materials.

It has been reported that the crystallization of MgF$_2$ in different sizes and morphologies can be directed by variation of the Mg/F ratio and concentration using alternative magnesium precursors like MgCl$_2$ and Mg(CH$_3$CO$_2$)$_2$, as well as NH$_4$F and NaF as the fluorine source.$^{32}$ Yet, those reactions are far from being applicable, because of low concentrations and non-stoichiometric reactions. Recently, we demonstrated the use of MgF$_2$ sols prepared from anhydrous magnesium chloride in dry ethanol and HF for anti-reflective coatings.$^{33}$ In contrast to the reaction of magnesium methoxide with HF, which proceeds via defined intermediate molecular cubane and dicubane structures, $^{19}$F NMR spectroscopy and XRD indicate the direct formation of nanocrystalline MgF$_2$ even at low Mg/F ratios. Yet, the crystallite size has been found to be in a similar range to that for the reaction of HF with Mg(OCH$_3$)$_2$ and the sols show a much lower tendency for agglomeration and gelation. Although chloride is not evidenced in the xerogels or thin film coatings after drying and further processing, and coatings show excellent anti-reflective and mechanical properties, the technical application is rather difficult due to the high corrosive content of HCl formed as the result of Cl against F exchange.
3. Potential applications of nanoscaled metal fluorides

3.1. Particles and porous materials in heterogeneous catalysis

By removing the solvents from the sols obtained via the fluoro-lytic sol-gel route, dry powders of nano metal fluorides will be obtained. Depending on the chemical nature of the metal, varying amounts of organic residues may still be contained in the solid materials. These can be removed by a thermal post-treatment either in inert gas atmosphere or—as in case of AlF₃—in a fluorinating gas flow containing either hydrogen fluoride, or a suitable haloalane, e.g. CHClF₂ or CCl₃F₂.¹²,¹⁴b,³⁴ Metal fluorides obtained this way exhibit extremely high surface areas in the range of 200 to 300 m² g⁻¹ and even higher. Because of their high surface areas, these metal fluorides are usually defined as HS-MFₓ (HS = high surface). Due to the strong electron withdrawing effect of the fluorine environment, the high degree of structural distortion, and the large surface area, these metal fluorides exhibit extraordinarily high Lewis acidity. HS-AlF₃ has been found to be one of the strongest Lewis acids being comparable with SbF₅ and aluminium chloride fluoride (ACF).³⁴ CO-adsorption FT-IR-investigations revealed the strongest Lewis acid sites ever measured at solid surfaces.³⁵ Fig. 13 illustrates the shift of the IR-frequency of pyridine adsorbed onto HS-AlF₃, thus indicating extremely strong Lewis acid sites at the surface, which has never been observed at any solid Lewis acid before.

As a consequence, these new metal fluoride materials are exciting catalysts for Lewis acid catalyzed reactions and were proven to outperform even the best homogenous catalysts in some reactions.¹⁵d,³⁶ A comprehensive overview of the catalytic properties of this new class of catalysts and their wide applications in different fields of catalyzed reactions can be found in a recently published review ref. 26. Therefore, just a few highlighting examples shall be given here.

Dehydrohalogenation reactions of chlorofluorocarbons give convenient access to fluoro(chloro)olefins, which are very interesting synthones for fluropolymers. Solid Lewis acids are the choice for this kind of reaction but need temperatures between 500 and 600 °C in order to give high conversions. Since the C-Cl bond is weaker than the C-F bond, all classically known solid Lewis catalysts also catalyse dehydrochlorination reactions. Excitingly and uniquely, HS-AlF₃ was found to catalyse the dehydrofluorination reaction of 3-chloro-1,1,1,3-tetrafluorobutane (eqn (9)) with >99% conversion and 100% selectivity exclusively toward the dehydrofluorination product at as low as 200 °C.³⁶a

\[
\mathrm{CF}_3\text{-CH}_2\text{-CFCl-CH}_3 \rightarrow \mathrm{CF}_3\text{-CH=CCl-CH}_3 + \text{HF} \quad (9)
\]

Interestingly, with nanoscopic high surface area BaF₂ as the solid catalyst exclusively, the hydrodechlorination reaction (eqn (10)) was observed, giving ca. 98% conversion and 100% selectivity regarding the hydrodechlorination product.

\[
\mathrm{CF}_3\text{-CH}_2\text{-CFCl-CH}_3 \rightarrow \mathrm{CF}_3\text{-CH-CF-CH}_3 + \text{HCl} \quad (10)
\]

Mechanistically, the contrary catalytic behaviour was discussed based on the hard and soft acids and bases (HSAB) concept. This means that the very hard Lewis acid Al³⁺ preferentially interacts with the very hard fluorine atom (Scheme 4, left) of the CFC, whereas the weak acidic Ba²⁺-surface sites preferentially interact with the weak chlorine atoms of the CFC, as rationalized in Scheme 4, right.

Another exciting example of the superior catalytic power of nanoscaled metal fluorides is the catalytic cleavage of C-F bonds, which became possible for the first time without any precious metal and surprisingly under room temperature conditions. Thus, this became possible by creating silylium-like species at the surface of aluminium chloride fluoride (ACF) and HS-AlF₃, as was evidenced by ¹H MAS NMR spectroscopy, as shown in Fig. 14c.³⁶b

![Fig. 13 CO IR difference spectra on sol gel derived HS-AlF₃. \(\nu(\text{CO}) = 2150\) cm⁻¹ = physisorbed CO; \(\nu(\text{CO}) = 2175\) cm⁻¹ = medium strong Lewis acid sites; \(\nu(\text{CO}) = 2240\text{--}2220\) cm⁻¹ = very strong Lewis acid sites. Reproduced from ref. 26 with permission of the Royal Society of Chemistry.](Image 14x290 to 26x354)

![Scheme 4 Proposed catalytic mechanism for the dehydrogenation and dehydrochlorination of 3-chloro-1,1,1,3-tetrafluorobutane. Reproduced from ref. 26 with the permission of the Royal Society of Chemistry.](Image 54x118 to 281x331)
On treatment of CH$_3$F, CH$_2$F$_2$, and CHF$_3$ with these aluminium fluoride catalysts in C$_6$D$_6$ in the presence of Et$_3$SiH at room temperature at one atmosphere, vigorous reactions and the evolution of gaseous products were observed (Fig. 15). In all these cases, formation of fully hydrogenated methane was observed for the first time under heterogeneous conditions, at low temperature and in the absence of a precious metal catalyst.

Although classically prepared MgF$_2$ is a rather neutral compound, nanoscopic MgF$_2$ obtained via the fluorolytic sol–gel synthesis exhibits very interesting catalytic properties. Post fluorination of the dried xerogels at 120 °C with HF yields nearly X-ray amorphous magnesium fluoride (HS-MgF$_2$) with a specific surface area in the range of 200 to 300 m$^2$ g$^{-1}$. The acid–base properties of the sol–gel MgF$_2$ were determined by FT-IR spectroscopy and the adsorption of different probe molecules. While the adsorption of carbon monoxide shows medium to weak Lewis acid sites due to coordinatively unsaturated magnesium, we explored the basicity of surface fluorine medium to weak Lewis acid sites due to coordinatively unsaturated fluorine molecules. While the adsorption of carbon monoxide shows medium to weak Lewis acid sites due to coordinatively unsaturated magnesium, we explored the basicity of surface fluorine medium to weak Lewis acid sites due to coordinatively unsaturated fluorine molecules.

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The remaining OR-groups can be reacted with water in the second step, resulting in the formation of hydroxide fluorides (eqn (12)).

$$\text{M(OR)}_n + n - x \text{ HF} \rightarrow \text{M(OR)}_{n-x} + n - x \text{ ROH}$$

(11)

$$\text{M(OR)}_{n-x} + x\text{H}_2\text{O} \rightarrow \text{M(OH)}_{n-x} + x\text{ROH}$$

(12)

This way, metal hydroxide fluorides are accessible in which the metal site is coordinated by both anions, hydroxide and fluoride, thus presenting real hydroxide fluorides that are almost inaccessible via any other synthesis route. By varying the F to OH ratio, the whole series of M(OH)$_x$F$_{n-x}$ from M(OH)$_n$ to MF$_n$ can be synthesized. As a result, the Lewis to Bronsted acid site ratio of these materials can be tuned over a wide range resulting in optimized solid catalysts being of high interest for any kind of acid–base catalysed reactions.

A slightly modified synthesis approach is the application of still stoichiometric amounts of HF but in the presence of water. Thus, in the presence of water the fluorolytic of the methoxide stands in direct competition with the hydrolysis. As a consequence of different reaction kinetics, e.g. magnesium hydroxide fluoride, particles with an MgF$_2$-like structure were obtained when the sol–gel synthesis was performed with aqueous hydrofluoric acid and a F/Mg ratio of 2 : 1. The $^{19}$F MAS NMR spectra show a major signal at ~198 ppm corresponding to the rutile structure of MgF$_2$ and a broad shoulder in the lower field (~184 ppm), which evidences an oxygen-rich coordination sphere around [FMg$_x$] sites. FT-IR adsorption studies using CO and lutidine have identified Lewis acid sites of medium strength and Bronsted acidic MgOH sites. The latter can be explained by the electron withdrawing effect of the magnesium fluoride backbone on the hydroxyl group at.
the particle’s surface. Different MgF$_{2-x}$(OH)$_x$ phases with varying ratios of Lewis to Bronsted acidic surface sites can be obtained by variation of the HF concentration in water.$^{41}$

Due to their high surface areas in combination with adjustable acid–base properties, these new materials also have great potential as catalyst support materials, as has been reported in several recent publications.$^{39,41}$

### 3.2. Optical materials

This section discusses several applications of nano metal fluorides as optical materials as (i) host material for luminescent nanoparticles, (ii) transparent ceramics, and (iii) anti-reflective thin film coatings. Due to their high thermal, mechanical and chemical stability, and high transparency over a broad spectral range from the VUV to IR, metal fluorides find application in various fields of optics. Lanthanide metal doping of metal fluorides, especially complex yttrium fluoride or calcium fluoride, that act as host matrices has been intensively studied for the use in solid-state lasers. Alkaline earth metal fluoride ceramics with very high optical quality can be prepared by a hot-pressing technique, that show similar properties as single crystals.$^{42}$

The fluoroletic sol–gel method gives access to the preparation of doped metal fluoride nanoparticles with luminescent properties and the synthesis of transparent ceramics of complex metal fluorides of the elpasolite type.

In the past years, the wet-chemical synthesis of rare-earth-doped calcium fluoride by precipitation methods has been reported by several groups.$^{43}$ Feldmann et al. showed the stabilising effect of diethylene glycol on the formation of the nanoparticles that might be used in bio-analytical applications.$^{43c}$

The non-hydrolytic sol–gel method offers great advantages to the previously mentioned precipitation routes since it can be carried out at room temperature in large batches using standard glass vessels and usually no surfactants are required. Also great variability in the choice of precursors and solvents is given, having a direct influence on the product properties. Recently, Ritter et al. reported the sol–gel-synthesis of luminescent CaF$_2$ nanoparticle sols by the reaction of calcium lactate dissolved in methanol with anhydrous HF.$^{44}$ Doping of up to 10 mol% with Eu$^{3+}$ and Tb$^{3+}$ was achieved by addition of the lanthanide acetate before fluorination. The reaction yields fully transparent sole of crystalline CaF$_2$ particles with a size in the lower nm-range, as seen in Fig. 16. Incorporation of the lanthanide metal ions in the CaF$_2$ host structure can be followed both by EDX analysis and changing lattice parameters in XRD. Under illumination with 366 nm radiation, the sole appear in the characteristic colours (Fig. 16b) of $^5$D$_{0} \rightarrow ^7$F$_{j}$ and $^5$D$_{4} \rightarrow ^7$F$_{j}$ transitions for Eu$^{3+}$ and Tb$^{3+}$, respectively. Co-doping of CaF$_2$ with Eu and Tb exhibits a different emission spectrum than the physical mixture of the pure sole.$^{44}$

The sol–gel synthesis can be applied for the preparation of complex metal fluorides of the types MAIxF$_4$ (M = K, Cs), M$_2$AlF$_6$ (M = Li, Na, K) and Na$_2$AlF$_4$. Especially doping of fluorides in the elpasolite type A$_2$BAlF$_6$ (A and B = alkali metals) with three-valent metals (Cr, Yb, La, etc.) and their application in solid-state lasers has been investigated.$^{46}$ In contrast to the earth alkaline fluorides, as-prepared Rb$_2$NaAlF$_6$ can be transformed into highly transparent ceramics by simple pressing already at low temperatures. Beside those pure metal fluoride ceramics, nanoscopic metal fluorides, especially MgF$_2$, have recently been reported for their superior properties as sintering additive in corundum ceramic manufacturing.$^{47}$

Without interfering with the technological process but just by addition of ca. 0.1% of nanoscopic MgF$_2$ to the starting ceramic powder, optically transparent Al$_2$O$_3$-discs can be obtained with >70% optical transmittance. As can be seen from Fig. 17, the addition of nanoscopic MgF$_2$ resulted in highly transparent ceramic materials. Remarkably enough, the Martens hardness, which for corundum ceramic is usually in the region of 2100, increases significantly up to 3200, thus corresponding to values that are characteristic for silicon carbide and/or boron nitride ceramics.

Thin films of organic and inorganic materials find wide industrial applications, e.g. in decorative and anti-reflective coatings of glass.$^{48}$ Metal fluorides, especially AlF$_3$ and MgF$_2$, belong to the group of inorganic materials with the lowest refractive indices. Apart from the aforementioned TFA route, several methods for the deposition of thin magnesium fluoride films have been investigated in the past decades, such as physical vapour deposition (PVD),$^{49}$ chemical vapour depo-

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**Fig. 16** Picture of transparent Eu$^{3+}$ and Tb$^{3+}$-doped CaF$_2$ sole (left) and the same sole excited with 366 nm (right). From left to right: CaF$_2$:Tb10, mixture of 52% of CaF$_2$:Tb10 + 48% of CaF$_2$:Eu10, CaF$_2$:Tb5.2,Eu4.8 and CaF$_2$:Eu10; reproduced from ref. 44 with permission of The Royal Society of Chemistry.
sition (CVD), ion beam sputtering (IBS), and atomic layer deposition (ALD). Yet, the broad application is limited to small substrates, low deposition rate and due to the formation of highly toxic and corrosive HF and other fluorine species. The sol–gel method has proven to be a much more elegant route to the preparation of thin defined films with high homogeneity. Fig. 18 shows the refractive index of a film deposited on a silicon wafer by spin-coating of an MgF$_2$ sol determined by ellipsometry in comparison to crystalline reference. As an effect of porosity inside the films, the refractive index of a sol–gel prepared MgF$_2$ film on silicon wafers is significantly lower than that of bulk material. The AFM image (Fig. 18) of a film after coating three times confirms homogeneous surfaces with an average roughness of 1.7 ± 0.3 nm consisting of nanoparticles with a diameter between 10 nm and 20 nm. The great variability in the sol preparation and the fact that fluorine release during coating and post-treatment is effectively circumvented allow this approach for the coating of large substrates in the square meter-scales.

The anti-reflective behaviour of the coatings is clearly visualised in Fig. 19. While on the left side of the glass slide one can see the reflection of the image above, the right side is highly transparent.

As the MgF$_2$ sols derived from the methoxide in methanol as solvent are not stable over longer time when exposed to air and tend to gelation, we recently reported about MgCl$_2$ as a precursor in ethanol as the solvent. Thereby, the handling of toxic methanol in larger amounts and the necessity for operation under inert conditions is circumvented. Compared to the methanolic sol–gel synthesis, the addition of HF to the solution of magnesium chloride directly leads to the formation of nanocrystalline MgF$_2$ with slightly increased crystallite and also particle size. Refluxing the sol leads to further crystallisation, which is directly visible in the SEM cross-section images of the film (Fig. 20). With a minimum reflectance of 0.2% at 600 nm, the films show excellent antireflective properties, which are due to the porosity being much better than for bulk MgF$_2$. The films exhibit superior mechanical
stability, as proven by the crockmeter test applying steel wool pads.

Even lower refractive indices down to 1.11 can be obtained by deliberately introducing pores into the films by templating methods. Although discussed in the context of optical applications, defined porosity also has a strong influence on the catalytic properties of materials in terms of mass-transport phenomena and product selectivity. We have shown that the nature of the template, mostly block copolymers or polymer structures, directly determines the later pore sizes and arrangement.55

3.3. Inorganic–organic nanocomposites

Composite materials made by combination of inorganic nano particles and organic polymers are of high interest for materials science. Various inorganic materials have been used for the enhancement of the properties of organic polymers in terms of thermal behavior, mechanical stability and additionally new functionality to the polymer material, such as electrical or thermal conductivity or improved flame retardancy. One aspect in the use of metal fluoride fillers is their beneficial properties for optical applications. Metal fluorides, and especially magnesium and aluminium fluoride, exhibit lower refractive indices than metal oxides and can be utilized for the adjustment of the optical properties of polymers. Since the scattering of light at the filler particles strongly relates to their diameter, particles smaller than 20 nm have to be introduced into the polymer matrix and be effectively stabilized against agglomeration. If processed properly, optical transparent composites with a defined refractive index can be obtained, such as shown in Fig. 21 of a representative composite sample with...
10 wt% MgF$_2$ in a PolyHEMA matrix.\textsuperscript{56} It has been shown by IR and NMR spectroscopy that trifluoroacetate strongly binds to the particle surface of magnesium\textsuperscript{56} and aluminium fluoride\textsuperscript{57} particles and thus leads to increased compatibility between the polymer matrix and the particles. Fig. 21 illustrates the trends of decreasing refractive indices of the resulting composite films depending on the amount and type of filler material. While the pure polymer has a refractive index of 1.498 at 589 nm wavelength, introduction of a metal fluoride filler strongly reduces the overall refractive index of the composite. The filler material does not contribute to absorption or light scattering in the visible spectral range, as determined by ellipsometry. Since aluminium fluoride has an even lower refractive index than magnesium fluoride, the effects of its incorporation are much more pronounced. Note that porosity, which essentially accounts for the very low refractive indices of thin films, cannot be considered in the case of composites. The resulting optical constants are described by the sum of the volume fractions of individual components.\textsuperscript{56}

Furthermore, the introduction of metal fluoride nanoparticles as filler material also has positive influence on the Martens hardness of the composites.\textsuperscript{56,58} For instance, introduction of 15 wt% MgF$_2$ nanoparticles stabilized by vinyl- or phenylphosphonic acid into a HDDMA polymer cause the Martens hardness (determined by microindentation) to be more than doubled from 107 to 222 N mm$^{-2}$ and also the storage modulus $G'$ raises from 2.2 to 2.8 Gpa.\textsuperscript{58}

4. Conclusion

Nanoscaled metal fluorides have gained enormous interest over the past decade due to their novel properties in several fields of application. Consequently, much effort has been made to develop new synthesis approaches towards nano fluoridel materials. Although several new synthesis routes have been developed, each of these suffers from at least one or even more drawbacks. The authors are convinced that the fluorolytic sol-gel synthesis—like the classical hydrolytic sol-gel synthesis of metal oxides—is the most powerful approach for nanoscaled metal fluorides. There are several advantages arising from this approach, which are (i) easy scale up even up to the ton-scale, (ii) resulting directly by a one-step process into monodispersed particle formation, and as a result of that, into formation of clear transparent sols, and (iii) possible processing of these sols according to already established technologies for classical metal oxide sols. The use of anhydrous hydrogen fluoride might be considered as a real drawback, however, each fluoride atom in any fluorine containing compound—no matter if inorganic or organic—originates at the very beginning of any synthesis procedure from HF that has to be used for its synthesis. That means the performance of hundreds of kilotones of HF is state of the art for chemists specializing in fluorine chemistry in both academia and industry.

Not only pure metal fluorides, some of them exhibiting extremely strong Lewis acidity, can be obtained by reacting the metal precursor with anhydrous hydrogen fluoride but also hydroxide fluorides are accessible exclusively \emph{via} this route, mainly based on two different approaches. The first one is based on using an under-stoichiometric amount of HF during the first synthesis step followed by the addition of the stoichiometrically remaining amount of water just to complete the reaction. This way, almost all nominal compositions of M(OH)$_{n-x}$F$_x$ are accessible. However, these hydroxide fluorides can be easily transformed into the corresponding metal oxide fluorides (MO$_{n-x/2}$F$_x$) just by post-thermal treatment. These metal hydroxide fluorides have big potential as tuneable bifunctional solid catalysts, since just by tuning the oxygen to fluoride stoichiometry inside these phases, the surface acid character can be altered from strongly Lewis acidic at high F-content towards weak Lewis but stronger Brønsted acidic or even basic depending on the metal M at high oxygen content. Mainly determined by the O to F ratio, these oxide fluoride phases store their amorphous character (depending on the metal M) up to temperatures of about 600 °C and exhibit surface areas up to 700 m$^2$ g$^{-1}$. It is noteworthy that some of these metal fluorides or oxide fluorides are thermally stable up to at least 1000 °C, meaning no notable hydrolysis or pyrolysis reactions take place.

On the other hand, having such hydroxide fluorides in hand, the whole repertoire of chemical modifications of these nano materials as known for metal oxides can be applied in order to modify their surface, thus making them compatible with metal oxide materials, organic polymer systems, metal surfaces and many other materials systems.

The introduction of a second or even a third metal into these new compounds allows for further functionalization, resulting in unlimited new compounds with high impact on applications in catalysis, optics, sensing, up- and downconversion, electrode materials, and many others.

With this review, the authors intended to shown that these new nanoscaled metal fluoride based materials and the large variety of metal hydroxide fluorides, MF$_x$(OH)$_{n-x}$, metal oxide fluorides, MO$_{n-x/2}$F$_x$, phases represent a new class of materials that became accessible recently for further exploration in many different fields of application.

Of course, limitations in application may arise from chemical resistivity (hydrolysis) depending on the metal used. However, since this fluorolytic sol gel synthesis can principally be applied for most of the metals, there are many options to select appropriate metal fluorides that fulfill both requirements, being temperature stable but also hydrolysis resistant.

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