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## Optimisation of a sol–gel synthesis route for the preparation of $\text{MgF}_2$ particles for a large scale coating process

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A synthesis route for the preparation of optically transparent magnesium fluoride sols using magnesium acetate tetrahydrate as precursor is described. The obtained magnesium fluoride sols are stable for several months and can be applied for antireflective coatings on glass substrates. Reaction parameters in the course of sol synthesis are described in detail. Thus, properties of the precursor materials play a crucial role in the formation of the desired magnesium fluoride nanoparticles, this is drying the precursor has to be performed under defined mild conditions, re-solvation of the dried precursor has to be avoided and addition of water to the final sol-system has to be controlled strictly. Important properties of the magnesium fluoride sols like viscosity, particle size distribution, and structural information are presented as well.

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## 1 Introduction

In contrast to the commonly used CVD, PVD and ALD technologies, sol–gel processing is a considerably less expensive method to produce antireflective coatings on optical substrates.<sup>1,2</sup> Using different techniques functional coatings consisting of  $\text{SiO}_2$  were developed and up-scaled for the production of self-cleaning windows, lenses, long-life phosphor lamps *etc.* For an optimum performance of the antireflective  $\lambda/4$  films the porosity of the coated material is very important.<sup>2</sup> Beside  $\text{SiO}_2$  (refractive index = 1.5)  $\text{MgF}_2$  is an attractive material due to its excellent optical properties (refractive index = 1.38).<sup>15</sup> In order to create a suitably low refractive index of 1.23 for the entire AR-layer, the porosity can be limited and hence, an enhanced thermal stability and better hardness is expected.<sup>3</sup>  $\text{MgF}_2$  can be synthesised by the so called trifluoroacetic acid method developed by Fujihara *et al.* and Joosten *et al.*<sup>4–7</sup> The disadvantage of this method is that even after treatment at 973 K impurities ( $\text{OH}$  and  $\text{COO}^-$ ) were experimentally proven in the  $\text{MgF}_2$  solids<sup>5</sup> and a lot of toxic gaseous products ( $\text{CF}_3\text{COF}$ ,  $\text{COF}_2$  and  $\text{HF}$ ) were formed.

Hence, a large scale coating process is strongly limited. Similar to the trifluoroacetic acid method Bass *et al.*<sup>8</sup> describe a thermally activated chemical solution deposition as easy method to tune the refractive index. The resulting materials demonstrate a range of tuneable compositions with varying refractive indices (1.08–1.2). These data are very surprising because  $\text{MgF}_2$  and  $\text{MgO}_i(\text{OH})_j$  are formed during the synthesis but  $\text{MgO}$  is known for his high refractive index (1.73). Furthermore, the authors don't give any information about the mechanical properties of such extreme highly porous materials. A very simple method to synthesise  $\text{MgF}_2$  nanoparticles is given by Nandiyanto *et al.*<sup>9</sup> They used a liquid-phase method in aqueous solution starting from  $\text{MgCl}_2$  and  $\text{NH}_4\text{F}$ . Control of the particle size was accomplished only by changing the composition of the reactants. Nanocrystalline  $\text{MgF}_2$  particles in suspensions can easily be synthesised by a polyol-mediated approach.<sup>10</sup> Unfortunately, such suspensions are not suitable for the coating of optical glasses, because the minimum viscosity of a 5 wt%  $\text{MgF}_2$  suspension in water is in a region of  $\sim 100$  mPa s. Several patents reflect the great interest on antireflective coatings consisting of  $\text{MgF}_2$ .<sup>11,12</sup> There are reports on the synthesis of  $\text{MgF}_2$  particles with an amorphous silicon oxide-based binder for the preparation of optical thin films on suitable substrates.<sup>11</sup> Recently, a patent was published about the chemical solution process to deposit porous coatings containing magnesium fluoride and/or oxidefluoride together with a surfactant porogen.<sup>12</sup> A comprehensive discussion of different strategies to obtain antireflective properties is given in.<sup>2,13</sup> The processing of the formation of the antireflective

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films is described such as porous  $\lambda/4$  layers, multilayer interference-type films and index-gradient like materials. Using trifluoroacetic acid as fluorination agent,  $\text{MgF}_2$  and quaternary Mg–F–Si–O sol–gel particles were prepared for coatings on large area glass substrates and solar collectors.<sup>14,15</sup> The optical properties of these coatings are very impressive but here, as mentioned above, a large scale industrial process is strongly limited.

Most of the above discussed  $\text{MgF}_2$  synthesis methods start from water containing educts ( $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{HF}_{(\text{aqueous})}$  etc.) or are performed in water containing solutions. It is known that water promotes the gelation in the sol–gel process and during the thermal treatment of the  $\text{MgF}_2$ -coatings additional oxide containing byproducts ( $\text{MgO}$  or  $\text{MgO}_x\text{F}_y$ ) might be formed. For that purpose a non-aqueous fluoro-lytic sol–gel method has been developed by our group for the preparation of transparent  $\text{MgF}_2$  sols.<sup>16,17</sup> Thereby the crucial point is the exclusion of water (water-free educts and anhydrous HF). This synthesis route leads to  $\text{MgF}_2$  particles with a particle size in the range of 5–10 nm and the coatings, prepared from these sols, are very homogeneous and exhibit a low refractive index  $\sim 1.32$ .<sup>18,19</sup> Unfortunately, the synthesis route starting from  $\text{Mg}(\text{OMe})_2$  is not recommended for a large scale industrial synthesis and coating process, because in the first step of the reaction between magnesium and methanol a lot of hydrogen is released and furthermore methanol is a toxic solvent. On the other hand, all attempts to start from commercially available magnesium ethoxide failed since this is insoluble in methanol or in ethanol and hence, no transparent sols are available due to the deposition of a protective  $\text{MgF}_2$ -layer onto the suspended solid  $\text{Mg}(\text{OEt})_2$  precursor particles. The alternative preparation method with  $\text{MgCl}_2$  as educt<sup>19</sup> is very easy to perform but suffers from the stoichiometric formation of HCl from  $\text{MgCl}_2$  as result of the reaction with HF. Since HCl is very corrosive, a practical application of such sols is not recommended.

In spite of these drawbacks we were interested in exploring a non-toxic, non-corrosive and low-cost precursor for a sol–gel synthesis of pure  $\text{MgF}_2$  particles, which can be used for a large scale antireflective coating process.

## 2 Experimental part

### 2.1 Sample preparation

**Route 1.** For the acetate synthesis route, the precursor  $\text{Mg}(\text{OAc})_2$  was obtained by drying the  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (Aldrich 99.8%) at 210 °C for 6 h in a vented furnace. The  $\text{MgF}_2$  sols were prepared by a stoichiometric reaction of the dried precursor  $\text{Mg}(\text{OAc})_2$  (56 g, 0.4 mol) suspended in 1 L ethanol (Roth 99.8%) with HF (anhydrous, Solvay Fluor GmbH, 15–20 molar in ethanol, Roth 99.8%) under vigorous stirring. To the resulting sol 10 mol% trifluoroacetic acid was added in order to suppress agglomeration of the reactive  $\text{MgF}_2$  particles formed.

**Route 2.** In an alternative synthesis route,  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was dried under mild conditions (100 °C, vacuum). After the

fluorination, 3 to 5 mol%  $\text{Al}(\text{O}^i\text{Pr})_3$  or TMOS and 1 mol% trifluoroacetic acid were added to the  $\text{MgF}_2$  sol.

### 2.2 Material characterisation

The kinematic viscosity of the sols was measured with a capillary viscometer (Schott AVS 400) at 25 °C. The capillary constant was 0.02908.

The X-ray powder diffractograms of all samples were recorded on a XRD 3003 TT diffractometer (Rich. Seifert & Co., Freiberg) using  $\text{Cu-K}\alpha$ -radiation ( $\lambda = 1.542 \text{ \AA}$ ).

The dried  $\text{Mg}(\text{OAc})_2$  was studied using Differential Thermal Analysis/Thermogravimetry (DTA-TG) measurements in a Netzsch STA 409C/CD thermobalance (heating rate  $10 \text{ K min}^{-1}$  under argon up to 700 °C).

The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the sols were carried out using a Bruker Avance II 300 spectrometer (Lamor frequencies 300.13 MHz for  $^1\text{H}$  and 282.4 MHz for  $^{19}\text{F}$ ). The  $^1\text{H}$  and  $^{19}\text{F}$  isotropic chemical shifts are given with respect to the  $\text{C}_6\text{D}_6$  and  $\text{CFCl}_3$  standards.

Dynamic light scattering experiments (DLS) were performed using a Zetasizer Nano ZS (Malvern Instruments, Worcester-shire, UK) in disposable PMMA cuvettes. The hydrodynamic diameters were calculated from the correlation functions using the Malvern Nanosizer Software.

## 3 Results and discussion

The classical non-aqueous fluoro-lytic sol–gel method developed in our group for the preparation of transparent  $\text{MgF}_2$  sols starts with the dissolution of metallic Mg in dry methanol under Schlenk conditions.<sup>18,20</sup> In a second step the resulting  $\text{Mg}(\text{OMe})_2$  is reacted with HF dissolved in MeOH to form a clear  $\text{MgF}_2$  sol (conc. 0.25–0.3 mol  $\text{L}^{-1}$ ). For a large scale application this synthesis procedure is inappropriate because of the formation of large quantities of hydrogen in the first synthesis step. Furthermore, methanol as solvent is toxic and should be avoided in an industrial process. Hence, an alternative preparation method based on a non-toxic solvent, such as EtOH, is strongly required. Commercially available alkoxides, such as  $\text{Mg}(\text{OMe})_2$  and  $\text{Mg}(\text{OEt})_2$  are insoluble in ethanol and other alcohols. It is therefore not possible to prepare transparent  $\text{MgF}_2$  sols in higher concentration *via* the reaction of these alkoxides with HF. We speculate, if the precursor is not dissolved the desired product  $\text{MgF}_2$  is formed preferentially at the surface of the solid alkoxide resulting in the formation of larger aggregates that cannot be broken off afterwards. Even limitation of the reaction due to the formation of a protective  $\text{MgF}_2$ -layer on solid  $\text{Mg}(\text{OR})_2$  particles has to be taken into account. Another source for complication is that the commercial alkoxides are partly hydrolysed by reaction with moist air, and hence, HF under these reaction conditions (nonprotic organic solvent) is not able to break off Mg–O–Mg moieties in the resulting  $\text{Mg}(\text{OR})_x(\text{OH})_y$  phases.

However,  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  is a commercially available, less expensive solid and should be suitable as starting material for



the sol–gel synthesis. The solubility of  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in EtOH is excellent and the reaction with HF to  $\text{MgF}_2$  is a very fast process. In order to obtain clear and transparent  $\text{MgF}_2$  sols starting from  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  as educt, some important synthesis parameters have to be respected and abided. In general these synthesis parameters are:

- Precise dehydration of the  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  precursor
- Resolution of  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  precursor in ethanol before fluorination
- Suppress water contamination of the sols

### 3.1 Dehydration of the $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ precursor

The water content in the magnesium acetate tetrahydrate precursor causes a relatively rapid gelation of the sols meaning long time stability of such  $\text{MgF}_2$ -sols is unacceptable. In Fig. 1 (left) a clear and transparent  $\text{MgF}_2$  sol is shown made from a pre-dried, nearly water free  $\text{Mg}(\text{OAc})_2$ . After addition of water (*ca.* 7 vol%) a rapid gelation within a few seconds was observed (Fig. 1 right). This is also known from the classical sol–gel reactions in oxidic systems such as  $\text{SiO}_2$ . Milea *et al.* observed an increasing gelation with raising water contents.<sup>21</sup> An interaction of the initially formed silica particles with water leads to the formation of a gel-network into which the solvent (alcohol) is embedded. In the course of the nonaqueous fluorination process used here and starting from dried  $\text{Mg}(\text{OAc})_2$  and anhydrous HF the formation of the desired product  $\text{MgF}_2$  is very fast and no hydrolysis process occurs during the synthesis. Nevertheless, by addition of water an increase of the viscosity resulting finally into gelation can be observed. Obviously, water (*e.g.* from the  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ) binds to the  $\text{MgF}_2$  particle surface by adsorption resulting in a very limited surface hydroxylation. These surface OH-groups might cause condensation reactions, and hence, an interaction (agglomeration) between the particles becomes possible finally leading to the formation of a particle network and gelation starts.

The viscosities of different  $\text{MgF}_2$  sols depending on their solution age and water content are given in Fig. 2. It clearly demonstrates a more pronounced viscosity increase in case of the precursor  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ . Because of the high viscosity, this sol is inappropriate for a dip-coating procedure on glass

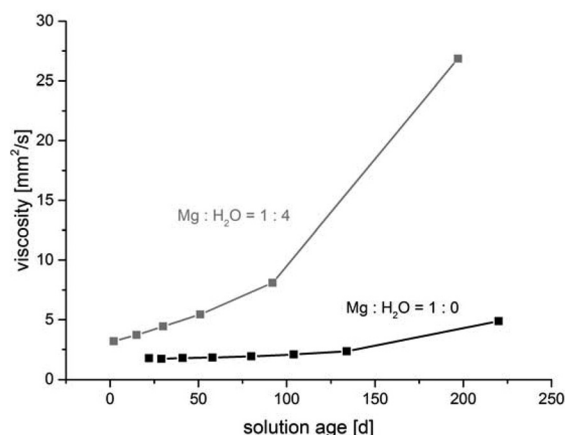


Fig. 2 Viscosities of the  $\text{MgF}_2$  sols depending on the solution age.

substrates over a longer period. Consequently, in order to suppress gelation tendency and to improve the long term stability of the resulting  $\text{MgF}_2$  sols water has to be kept out of the sol-system as completely as possible. Hence, the precursor  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was dehydrated before the reaction with HF. However, dehydration at 210 °C in air generates a product which is only partially soluble in EtOH and other alcohols. The XRD patterns of the dried  $\text{Mg}(\text{OAc})_2$  show reflections of a phase mixture consisting of  $\alpha\text{-Mg}(\text{OAc})_2$  (PDF 14-802) and a minor “unknown phase” (Fig. 3).

Unfortunately, it was not at all possible to process clear transparent  $\text{MgF}_2$  sols from these pre-dried acetate precursors. The same effect was observed when using commercially available  $\text{Mg}(\text{OAc})_2$  as starting material; under no circumstances clear  $\text{MgF}_2$  sols were obtained. We speculated that the unknown phase detected in the powder XRD might be the one that does not dissolve, and hence, remains unconverted thus being the origin for non-transparent, opaque sols. Therefore, much effort had been spent to synthesise and characterise this unknown phase. Finally, this unknown phase was identified as a basic magnesium acetate,  $\text{Mg}_5(\mu_3\text{-OH})_2(\text{OAc})_8 \cdot 1.19\text{H}_2\text{O}$ .<sup>22</sup> This compound (insoluble in water and alcohols) exhibits an

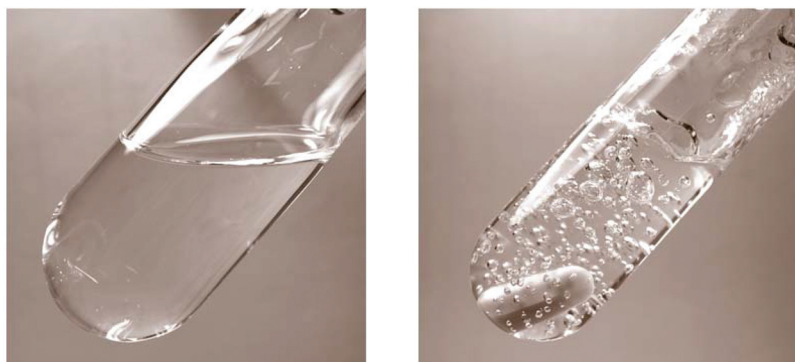


Fig. 1 Photographs of a  $\text{MgF}_2$  sol (left) and  $\text{MgF}_2$  gel with air bubbles (right).



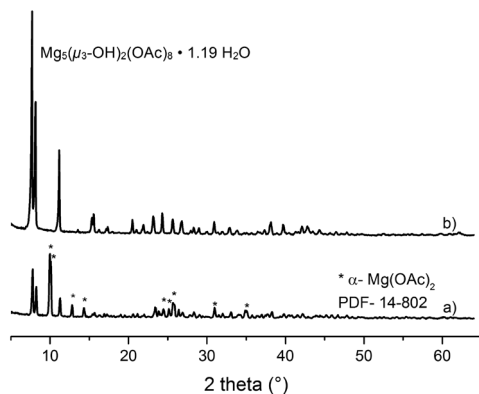


Fig. 3 X-ray diffraction patterns of dried  $\text{Mg}(\text{OAc})_2$  (a) and the basic magnesium acetate  $\text{Mg}_5(\mu_3\text{-OH})_2(\text{OAc})_8 \cdot 1.19\text{H}_2\text{O}$  (b).

open cage structure with channels along the  $a$ ,  $b$ , and  $c$  axes which probably is the reason for its insolubility in water and alcohols. Since this basic acetate phase is formed in the course of drying magnesium acetate tetrahydrate, a classical thermal dehydration process is not recommended for the fluorolytic sol-gel process when clear transparent  $\text{MgF}_2$  sols are desired. However, soluble  $\text{Mg}(\text{OAc})_2$  can be obtained by extracting the water under mild conditions (100 °C, vacuum). As can be seen from Fig. 4 the mass loss up to 300 °C is only 0.16%, that is the magnesium acetate is nearly water free. The formed product is X-ray amorphous, soluble in alcohols, and consequently, yields clear  $\text{MgF}_2$  sols after fluorination.

### 3.2 Resolution of $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ precursor in the ethanol

When dissolving the precursors  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Mg}(\text{OAc})_2$  in EtOH, already after 2 hours solvated magnesium acetates  $\text{Mg}(\text{OAc})_2(\text{H}_2\text{O})_3(\text{EtOH})$  or  $\text{Mg}_3(\text{OAc})_6(\text{EtOH})_2 \cdot 2\text{EtOH}$  are formed.<sup>23</sup> Unfortunately, these solvates are hardly soluble because of their oligomeric, one- or three dimensional struc-

tures and so the reaction with HF during the sol-gel synthesis process is limited. Therefore, for a successful synthesis of transparent  $\text{MgF}_2$  sols it is very important to reduce the time between dissolution of the precursor material,  $\text{Mg}(\text{OAc})_2$ , and the following reaction with HF according the fluorolytic sol-gel route in order to suppress undesired re-solvation processes.

### 3.3 Suppress water contamination of the sols

The reaction of pre-dried  $\text{Mg}(\text{OAc})_2$  with HF in ethanol leads to the formation of acetic acid which can consecutively react with ethanol forming the corresponding ethyl acetate and equimolar amounts of water (eqn (1) and (2)).



As this reaction progresses the water content in the system increases continuously and, as described above (point 3.1), causes gelation and/or agglomeration within a few days.  $^1\text{H-NMR}$  investigations demonstrate the time dependence of this undesired consecutive reaction (Fig. 5).

After one week the ratio of acetic acid to ethyl acetate is 97 : 3 but after four weeks it is already 84 : 16. The question arises, how much water can be tolerated before gelation occurs. Our investigations on sols obtained from water-free magnesium acetate as precursor showed that a water content above *ca.* 7 vol% leads to an immediate gelation (see chapter 3.1), above 5 vol% gelation starts after 2 days, above 2.5 vol% gelation occurs after 2 weeks and at *ca.* 0.5 vol% gelation needs about 3 months. Any water content below 0.1 vol% can be tolerated, meaning the sols are stable against gelation over several months (>3). In spite of these facts it is very amazing that sol-gel syntheses for the preparation of clear and low viscous  $\text{MgF}_2$  sols starting from the magnesium acetate tetrahydrate or syntheses in water containing solutions with aqueous HF are described in the literature.<sup>11,14,15,24</sup> Of course,

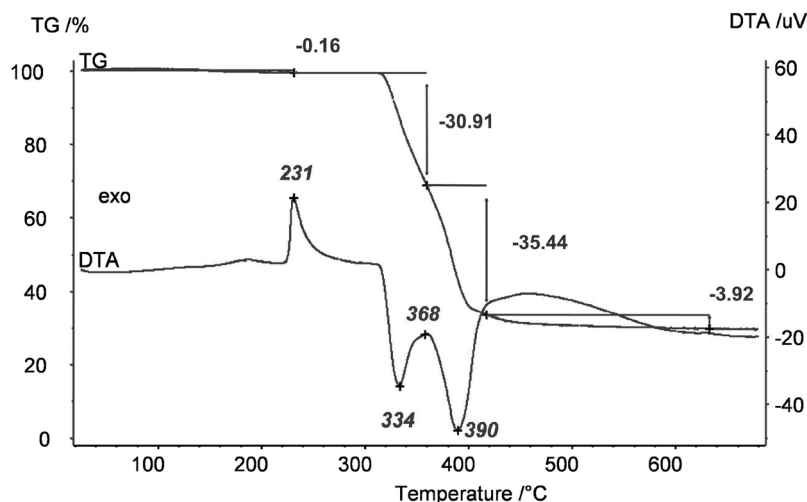


Fig. 4 Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of dried  $\text{Mg}(\text{OAc})_2$  (100 °C, vacuum).





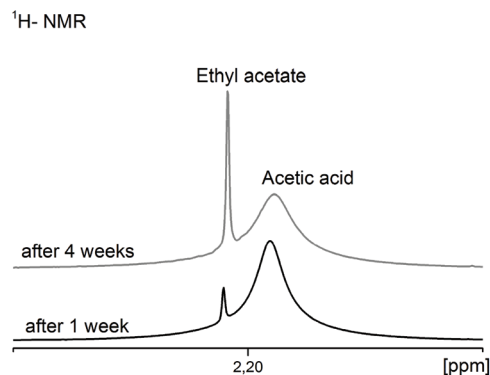


Fig. 5  $^1\text{H}$ -NMR spectra of the  $\text{CH}_3$ -groups of the resulting ethyl acetate in comparison to the acetic acid depending on the aging time of the  $\text{MgF}_2$  sols.

all these publications do not reflect details about viscosities of sols after a prolonged life time. However, our results prove that the  $\text{MgF}_2$  sols in alcoholic solvents tolerate only small contents of water  $\sim 0.1$ – $0.2$  vol%. Thus,  $\text{MgF}_2$  sols described in the above mentioned publications shouldn't be stable for a long time. At water concentrations above *ca.* 0.1 vol%, gelation is a matter of fact and it is impossible to coat any substrates with  $\text{MgF}_2$ . Consequently, any carboxylate based magnesium precursor will form the respective carboxylic acid in the reaction with HF, and thus, potentially creates the basis for water formation as a result of esterification.

To better understand the reaction progress, NMR-spectra of reaction mixtures with increasing HF to  $\text{Mg}(\text{OAc})_2$  ratios were taken (see Fig. 6). At very low fluorine to magnesium ratios ( $<0.5$  eq.)  $\text{Mg}(\text{OAc})_2$  reacts initially to partially fluorinated intermediates,  $\text{MgF}_x(\text{OAc})_{2-x}$ . These acetate fluorides are soluble in EtOH to be seen from several narrow signals between  $-170$  and  $-190$  ppm (*cf.* Fig. 6). At this stage no  $\text{MgF}_2$  can be detected. Unfortunately, so far it was not possible to

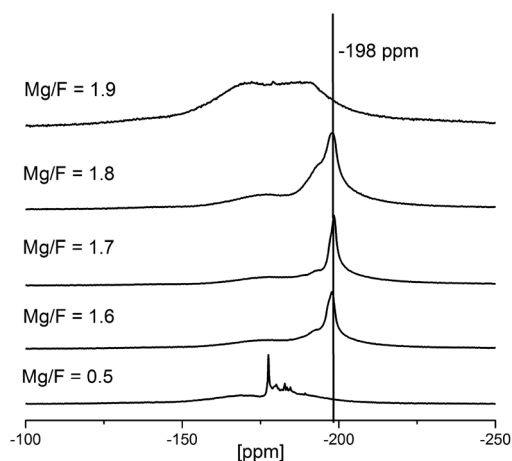


Fig. 6  $^{19}\text{F}$ -NMR spectra of  $\text{MgF}_2$  sols with HF to  $\text{Mg}(\text{OAc})_2$  ratios 0.5, 1.6, 1.7, 1.8, and 1.9.

grow crystals from these unknown species for the identification by single crystal X-ray analysis. The formation of such partially fluorinated intermediates is supported by the classical fluorolytic sol-gel reaction which starts with magnesium methoxide,  $\text{Mg}(\text{OMe})_2$ , as precursor. There, the intermediate formation of dicubane-like intermediates was evidenced by  $^{19}\text{F}$ -NMR spectroscopy of the sols and by powder XRD investigations of the dried xerogels as well as single crystal determination.<sup>20</sup> When the HF to  $\text{Mg}(\text{OAc})_2$  ratio is further increased (1.6 and 1.7) the  $^{19}\text{F}$ -NMR signal of  $\text{MgF}_2$  in rutile structure ( $-198$  ppm) becomes visible. The relatively high signal width ( $\sim 1$ – $2$  kHz) indicates the formation of  $\text{MgF}_2$  nanoparticles. During agglomeration and/or gelation of the  $\text{MgF}_2$  particles with HF/Mg ratios of 1.8 and higher the mobility of the fluorine species is suppressed (obviously strongly adsorbed at the NPs) and the signals in the  $^{19}\text{F}$ -NMR spectra become very broad and are almost invisible.

Directly after the fluorination of the  $\text{Mg}(\text{OAc})_2$  the formed  $\text{MgF}_2$  sols are turbid because of the interaction and agglomeration of the very active  $\text{MgF}_2$  particles. After an aging time of several hours, sometimes days or even weeks (this depends on the concentration and the quantity of the sol) the sols clear up, thus getting totally transparent. Fig. 7 demonstrates the change in particle size distribution depending on the sol age determined by dynamic light scattering (DLS).

In some cases in the liquid NMR spectra of freshly synthesised  $\text{MgF}_2$  sols an additional small signal at  $-180$  ppm can be detected. There are several strong hints that this signal originates from immobilised HF that is adsorbed on the particles surface. Although just traces of this unconverted HF are bound *via* hydrogen bridges, probably this HF and/or the corresponding unconverted M-OAc-sites are the origin for agglomeration by bridging surfaces of the particles. If, during the aging process, the unconverted and bridging HF reacts with the remaining acetate sites, these bridges break off, and hence, the sol clears up.

Consequently the clearing up process of freshly prepared sols can be significantly accelerated just by addition of suitable dissolved alkoxides such as TEOS/TMOS (a) or  $\text{Al}(\text{O}^i\text{Pr})_3$  (b). In this way the formerly adsorbed HF can react, and thus, weak agglomerates break down. The same effect can be achieved by addition of an understoichiometric amount of HF to the  $\text{Mg}(\text{OAc})_2$  (c).

(a) In case of TMOS as reactant, in addition to the broad signal of the  $\text{MgF}_2$  nanoparticles at  $-198$  ppm several signals in the region between  $-140$  to  $-160$  ppm appear (Fig. 8). These very small signals originate from dissolved  $\text{SiF}_x(\text{OR})_y$  ( $\text{R} = \text{OMe}$ ) species formed by the reaction of TMOS with adsorbed/unreacted HF. The special impact of the alkoxides (*e.g.* TMOS) is still not fully understood, but evidently, the interaction between TMOS and the fluoride on the  $\text{MgF}_2$  particle surface leads to a deagglomeration of aggregates formerly formed. Within a few hours such sols clear up, being transparent, low viscous and stable over several months.

(b) Fig. 9 represents the size distribution of the hydrodynamic diameters of  $\text{MgF}_2$  nanoparticles after addition of



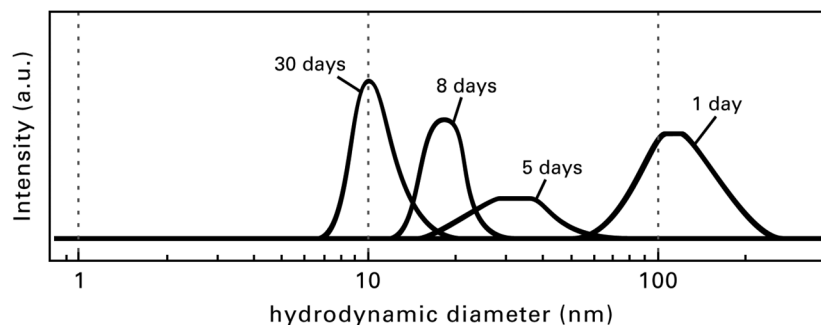


Fig. 7 Particle size distribution (DLS) depending on the sol age.

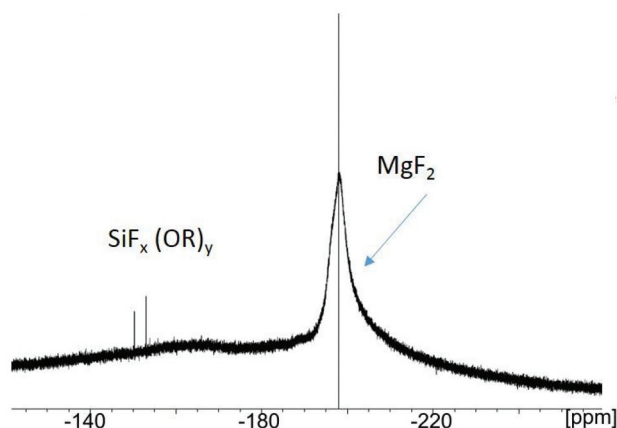


Fig. 8  $^{19}\text{F}$ -NMR spectra of a  $\text{MgF}_2$  sol stabilised with TMOS.

$\text{Al}(\text{O}^i\text{Pr})_3$  measured by dynamic light scattering (DLS). A distribution of two size classes with hydrodynamic diameters around 10 and 1000 nm was obtained (Fig. 9, left). It is known from Rayleigh's approximation that the intensity of the scattering of particles is proportional to their diameter with a coefficient of  $I = d^6$ . So, the intensity of larger particles seems to be higher than those of smaller particles. In reality it can be ascertained that the number of smaller particles with a hydrodynamic diameter of 10 nm is much larger than the number

of particles with 1000 nm. This effect is represented in Fig. 9 (right), size distribution depending on the volume of the particles. Here the majority of the particles with 10 nm is clearly demonstrated. Such a particle size distribution can be obtained after addition of the alkoxides  $\text{Al}(\text{O}^i\text{Pr})_3$  or TEOS/TMOS shortly after the fluorination.

(c) In the classical oxidic sol-gel chemistry, usually immediately after the hydrolysis and condensation process clear sols are formed under appropriate conditions. With time and as a result of *Ostwald* ripening the particles can grow to larger domains and the sols become turbid or gelation occurs. In contrast to that, in the course of the fluorolytic sol-gel synthesis the fresh sols usually are not clear but clear up after several hours or even several days and parallel the viscosity decreases. Finally, optically transparent, clear  $\text{MgF}_2$  sols are formed. Fig. 10 displays the  $^{19}\text{F}$ -NMR spectra of a fresh and a 3 days aged understoichiometric ( $\text{MgF}_{1.8}(\text{OAc})_{0.2}$ ) sol (HF/Mg-ratio 1.8). The very broad signal of the fresh sol indicates the presence of larger agglomerates which disaggregate after around 3 days (see the smaller  $^{19}\text{F}$ -NMR signal in Fig. 10).

Expectedly, sols formed from understoichiometric HF/ $\text{Mg}(\text{OAc})_2$  ratios clear up without addition of any additional alkoxide because no excessive unreacted HF is present at the  $\text{MgF}_2$  particle surface. Alternatively, the time of this clearing process can be reduced by a treatment of freshly prepared sols in an autoclave as discussed by Murata *et al.*<sup>24</sup> However, for a

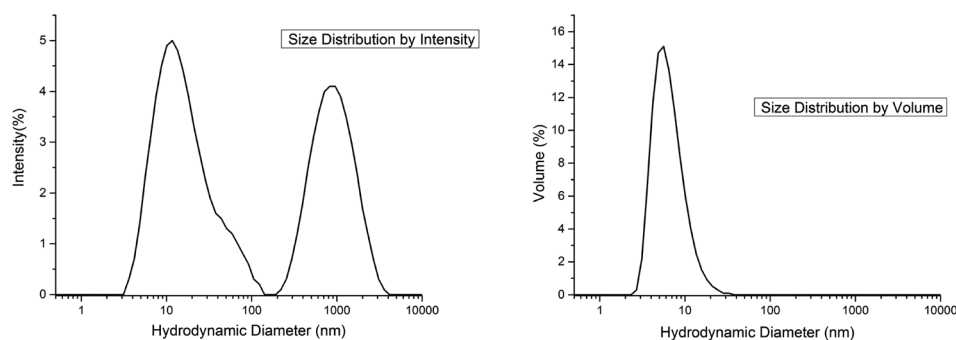


Fig. 9 Hydrodynamic diameters of particles in  $\text{MgF}_2$  sols; size distribution by intensity (left) and size distribution by volume (right).



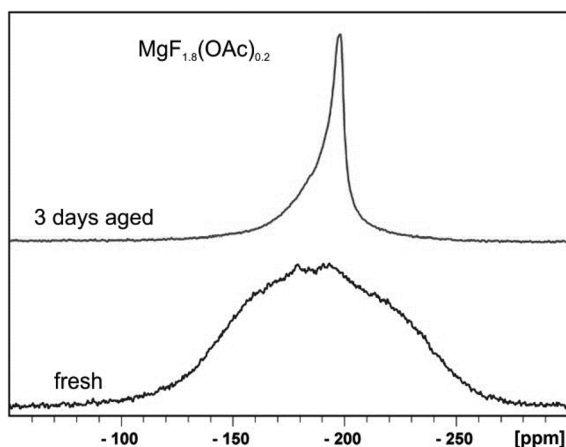


Fig. 10  $^{19}\text{F}$ -NMR spectra of a  $\text{MgF}_{1.8}(\text{OAc})_{0.2}$  sol fresh prepared and after an aging time of 3 days.

large scale preparation of  $\text{MgF}_2$  sols for antireflective coatings this procedure is inappropriate.

## 4 Conclusions

These comprehensive investigations of the fluorolytic sol gel-synthesis conditions for the preparation of  $\text{MgF}_2$  sols as anti-reflective coating material starting from magnesium acetate as precursor demonstrate that commercial magnesium acetate tetrahydrate is an appropriate starting material. However, several important pre-requisites with significant impact on the performance of the final sol should be addressed:

(i) The precursor must be dried under well controlled mild conditions (100 °C vacuum) in order to prevent the formation of a basic magnesium acetate that was just recently identified. To our experience, the industrial drying process does not prevent the formation of this unwanted phase, hence, commercially available dried magnesium acetate can not be used for the preparation of clear  $\text{MgF}_2$  sols. However, optimisation of the industrial drying process should overcome this present restriction.

(ii) The time between dissolving the precursor and reaction with HF should be as short as possible in order to prevent resolution, because solvated magnesium acetates are heavily soluble, and hence, do not completely react with HF.

(iii) The  $\text{MgF}_2$  sol system tolerates only a very small content of water (0.1–0.2 vol%) otherwise gelation occurs after a short time, resulting in sols that cannot be stored for a longer period, and hence, will not be suitable for practical applications.

Finally, strict consideration of these reaction parameters enables the upscaling of the synthesis conditions for optimised  $\text{MgF}_2$  sols (cf. Fig. 11) which can be stored and handled for at least 3 to 4 months. Such sols are suitable for coating of glass substrates under industrial conditions. The optical performance is better and the mechanical properties are comparable to the classical  $\text{SiO}_2$  coatings as described in.<sup>25</sup>



Fig. 11  $\text{MgF}_2$  sol stabilised by  $\text{Al}(\text{O}^i\text{Pr})_3$  after 2 days of fluorination prepared in a 10 L reactor.

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## Notes and references

- 1 M. A. Aegerter, R. Almeida, A. Soutar, K. Tadanaga, H. Yang and T. Watanabe, *J. Sol-Gel Sci. Technol.*, 2008, **47**, 203.
- 2 P. Löbmann, *Antireflective Coatings and Optical Filters in Chemical Solution Deposition of Functional Oxide Thin Films*, ed. T. Schneller, R. Waser, M. Kosec and D. Payne, Springer, Wien, Heidelberg, New York, 2013, 707.
- 3 M. Pietrowski and M. Wojciechowska, *J. Fluorine Chem.*, 2007, **128**(3), 219.
- 4 S. Fujihara, M. Tada and T. Kimura, *Thin Solid Films*, 1997, **304**, 252.
- 5 S. Fujihara, S. Ono, Y. Kishiki, M. Tada and T. Kimura, *J. Fluorine Chem.*, 2000, **105**, 65.
- 6 S. Fujihara, H. Naito and T. Kimura, *Thin Solid Films*, 2001, **389**, 227.
- 7 P. H. Joosten, T. J. A. Pompa, H. J. P. Nabben, H. A. M. Van Hal and J. Haisma, *US* 4492721, 1983.
- 8 J. D. Bass, C. Boissere, L. Nicole, D. Grosso and C. Sanchez, *Chem. Mater.*, 2008, **20**, 5550.
- 9 A. B. D. Nandiyanto, F. Iskandar, T. Ogi and K. Okuyama, *Langmuir*, 2010, **26**(14), 12260.
- 10 F. Waltz, M. A. Swider, P. Hoyer, T. Hassel, M. Erne, K. Möhwald, M. Adlung, A. Feldhoff, C. Wickleder, F. W. Bach and P. Behrens, *J. Mater. Sci.*, 2012, **47**, 176.
- 11 I. Hitoshi and N. Shunsuke, *US* 20110122497A1, 2011; M. Bockmeyer and I. Henze, *WO* 2011116980A1, 2011.
- 12 S. Jewhurst and N. Kalyankar, *US* 20140147594A1, 2014.



- 13 W. Glaubitt and P. Löbmann, *J. Eur. Ceram. Soc.*, 2012, **32**(11), 2995.
- 14 H. K. Raut, S. S. Dinachali, K. K. Ansah-Antwi, V. A. Ganesh and S. Ramakrishna, *Nanotechnology*, 2013, **24**, 505201.
- 15 V. H. Le-Caer, E. De Chambrier, S. Mertin, M. Joly, M. Schaer, J. L. Scartezzini and A. Schüler, *Renewable Energy*, 2013, **53**, 27.
- 16 S. Rüdiger and E. Kemnitz, *Dalton Trans.*, 2008, 1117.
- 17 E. Kemnitz, U. Gross and St. Rüdiger, *EP* 1666411, 2006; E. Kemnitz, U. Gross and St. Rüdiger, *EP* 1732853, 2012.
- 18 H. Krüger, E. Kemnitz, A. Hertwig and U. Beck, *Thin Solid Films*, 2008, **516**, 4175.
- 19 J. Noack, K. Scheurell, E. Kemnitz, P. Garcia-Juan, H. Rau, M. Lacroix, J. Eicher, B. Lintner, T. Sontheimer, T. Hofmann, J. Hegmann, R. Jahn and P. Löbmann, *J. Mater. Chem.*, 2012, **22**, 18535.
- 20 J. Noack, F. Emmerling, H. Kirmse and E. Kemnitz, *J. Mater. Chem.*, 2011, **21**, 15015.
- 21 C. A. Milea, C. Bogatu and A. Duta, *Bulletin of the Transilvania, University of Brasov*, 2011, Series I, vol. 4 (53) No. 1, 59.
- 22 K. Scheurell, S. I. Troyanov and E. Kemnitz, *Z. Anorg. Allg. Chem.*, 2015, **641**(6), 1106.
- 23 K. Scheurell, R. König, S. I. Troyanov and E. Kemnitz, *Z. Anorg. Allg. Chem.*, 2012, **638**(9), 1265.
- 24 T. Murata, H. Ishizawa, I. Motoyama and A. Tanaka, *J. Sol-Gel Sci. Technol.*, 2004, **32**, 161.
- 25 K. Scheurell, E. Kemnitz, P. Garcia-Juan, J. Eicher, B. Lintner, J. Hegmann, R. Jahn, T. Hofmann and P. Löbmann, *J. Sol-Gel Sci. Technol.*, 2015, **76**, 82.

