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Sol-Gel Route to Inorganic Fluoride Nanomaterials with Optical Properties

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10.1 Introduction

A sol-gel method, which is the most significant wet process to prepare solids from liquids, can offer interesting and useful routes for synthesizing inorganic metal fluoride and oxyfluoride materials for applications in optics and photonics. Formerly, heavy-metal fluoride glasses were intensively studied for potential use in optical fibres. Now the method is extended to prepare a variety of metal fluorides such as alkaline earth and rare-earth fluorides and oxyfluorides in the form of nanoparticles, thin films and nanocomposites. They can be utilized as antireflective coatings, luminescent materials, VUV materials, IR materials, etc. This chapter describes fundamentals and possible applications of optically useful inorganic fluoride nanomaterials through the sol-gel method.
10.2 Principles of a Sol-Gel Method

10.2.1 Metal Oxide Materials

A sol-gel method is well-known as a technology for synthesizing metal oxide materials, including glasses, ceramics and nanomaterials, starting from chemical solutions [1–3]. Silica (SiO$_2$) gels and glasses are some of the most successful examples of sol-gel-derived materials. They can be obtained in the form of dense or porous bulk monolith, fibres and thin films. Many other crystalline oxide materials can also be produced by a sol-gel method by controlling solution chemistry and heat-treatment procedures. Recently, organic-inorganic hybrid materials have attracted much attention as a new class of functional materials that can enhance characteristics of each component.

In a typical synthesis, raw materials are first dissolved in a certain kind of solvents. Then the resultant solutions are dried at moderate temperatures and finally converted into solids at higher temperatures. During a sol-gel processing using metal alkoxides, chemical reactions such as hydrolysis and condensation proceed to form sols and gels. For example, in the sol-gel process of tetramethylorthosilicate (TMOS), the hydrolysis reaction generally occurs as follows

$$\text{Si}((\text{OCH}_3)_4 + n\text{H}_2\text{O} \rightarrow \text{Si}((\text{OCH}_3)_{4-n}\text{(OH)}_n + n\text{CH}_3\text{OH})$$

The formation of metal complexes is also an important step when metal salts (chlorides, nitrates, sulfates, acetates, etc.) are used as raw materials. Instead of the formation of sols, chemically stable metal complexes are formed in solutions. The sol-gel processing of zinc oxide (ZnO) is a good example [4]. Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) was dissolved in 2-methoxyethanol, and monoethanolamine (NH$_2$CH$_2$CH$_2$OH) was added to the solution. Aminoethanols such as monoethanolamine and diethanolamine act as bidentate ligands to Zn$^{2+}$, making the solution stable against any precipitates. Both oxygen and nitrogen in NR$_2$CH$_2$CH$_2$OH (R=H or CH$_2$CH$_2$OH) can make bonds with Zn$^{2+}$. When the precursor was heated at around 300°C, the decomposition began by having ‘(−N,−O)−Zn’ and ‘(−COO)−Zn’ bonds in the complex broken. The decomposition is followed by the nucleation and crystal growth of ZnO. This kind of a sol-gel reaction is of prime importance for designing chemical reactions in fluorine-containing sol-gel routes based on pyrolysis of organofluorine species.

10.2.2 Metal Fluoride Materials

Low refractive indices and low phonon energies of metal fluoride compounds are suitable for their use in optical devices. High-purity products of metal fluorides have been produced using ‘dry’ processing to avoid oxygen or other contamination. Because a sol-gel method is a typical ‘wet’ process, attention should be paid to influences of solution chemistry on the purity of final products.

Adoption of a sol-gel method to optical fluoride materials started with inorganic fluoride glasses. At first, the sol-gel processing appeared rather challenging because fluoride gels were not known and little was known about the chemical reaction between fluorinating
reagents and organometallics [5]. Strongly motivated by the thought that the sol-gel processing could utilize cheaper starting materials of high quality and offer a substantial energy savings in processing, it was intensively studied in the 1990s for the fabrication of heavy-metal fluoride glasses. Melling and Thomson first studied a ZrF$_4$–BaF$_2$–LaF$_3$–AlF$_3$ (ZBLA) glass system with zirconium propoxide (Zr(OC$_3$H$_7$)$_4$), barium ethoxide (Ba(OC$_5$H$_5$)$_2$), lanthanum propoxide (La(OC$_3$H$_7$)$_3$) and aluminum isobutoxide (Al(OCH(CH$_3$)C$_2$H$_5$)$_3$) as starting materials [6]. The metal alkoxides were dissolved in tetrachlorotetrafluoropropane (Freon 214) and added dropwise to a mixture of Freon 214 and bromine trifluoride (BrF$_3$) in an aluminum container to obtain amorphous solid products. Since then, a multiple-step process incorporating the sol-gel synthesis and reactive atmosphere processing has been devised to prepare ZBLA glasses [7]. A porous, monolithic, atomically homogeneous zirconium barium lanthanum aluminum hydrous oxide gel was prepared first starting from pertinent metal alkoxides and hydroxides. The resultant oxide gel was then treated in a reactive atmosphere of hydrofluoric acid (HF) and transformed into fluoride glasses. Later works have attempted to improve the processes as well as optical properties of the fluoride glasses.

Another promising approach to sol-gel-derived fluoride materials is based on the use of trifluoroacetic acid. The author’s group has succeeded in the sol-gel preparation of fluoride and oxyfluoride coating films [8,9], oxyfluoride glass-ceramics [10, 11] and oxide/fluoride nanocomposite thin films [12, 13]. It had been difficult to prepare directly oxyfluoride glass-ceramics by the sol-gel method because of the absence of appropriate fluorine sources. When fluoride ions (F$^-$) are added to the silicon alkoxide systems, they work as the most effective catalyst in accelerating the gelation process. The F$^-$ ions attack alkoxides by nucleophilic substitution, which leads to the formation of five-coordinated silicon [1]. New sol-gel technologies are therefore expected to be developed in the fabrication of many kinds of optically functional fluoride-based materials. Some examples will be presented in the following sections.

### 10.3 Fluorinating Reagents and Method of Fluorination

In a conventional glass technology, fluoride glasses are produced by batching and melting of starting metal fluoride materials. Fluorine is therefore included in raw materials. In this case, the purity of raw materials must be 99.99% or higher [14]. Contaminations related to oxygen species as well as transition metals should be minimized for the use in high-quality optical components. Glass batches are melted in a platinum crucible under nitrogen. A reactive atmosphere of gaseous inorganic fluorides such as NF$_3$ and SF$_6$ is also employed to remove traces of oxygen.

In the sol-gel processing of fluoride glasses, the fluorination treatment is a more important process to obtain chemically and optically pure materials. Therefore, fluorinating reagents such as BrF$_3$, HF, NF$_3$ and SF$_3$ are used for direct fluorination of oxide precursors. It should be noted that BrF$_3$ is a toxic material and an extremely reactive fluorinating reagent with the potential to cause fire.

Konishi et al. [15] prepared amorphous 60ZrO$_2$–30BaO–10LnO$_{1.5}$ gels (Ln = La, Ce, Pr, Nd or Eu) and fluorinated them by NF$_3$. In the fluorination process, the reaction rates were found to be substantially different with the Ln species, becoming slower in the order of La, Ce,
Pr, Nd and Eu. Saad and Poulain [5] carried out fluorination of a wet oxide gel containing Zr, Ba, La, Al and Na using anhydrous HF as a fluorinating reagent. Figure 10.1 shows a typical experimental setup for fluorination. The reaction time was approximately 1 h for a 10 g batch at 200 °C. In this process, fluorination is implemented on an oxide gel, which still contains a significant amount of water and alcohol. At 200 °C, the chemical equilibrium

\[
\text{oxide} + \text{HF} \rightarrow \text{fluoride} + \text{H}_2\text{O}
\]

can be largely shifted to the right side, especially for basic oxides.

Metal fluoride nanomaterials can also be prepared by fluorination of oxide gels. The reaction of magnesium and aluminum alkoxides with HF in nonaqueous solvents led to the formation of amorphous or crystalline nanosized MgF\(_2\) and AlF\(_3\), respectively, with high specific surface areas [16, 17].

Figure 10.1  Diagram of the fluorination set-up made from fluorinated polymers (Teflon) and sintered alumina. Reproduced from reference 5 by permission of Elsevier

Trifluoroacetic acid (TFA; CF\(_3\)COOH) has been widely used as a nonaqueous solvent for both inorganic and organic compounds [18]. TFA is characterized as a strong acid with a larger electrolytic dissociation constant of 5.9 × 10\(^{-1}\) due to an electron-attracting trifluoromethyl (CF\(_3\)) group. Its boiling point is 72.4 °C, which is lower than that of acetic acid (118 °C). In terms of the fluorinating reagents, TFA is not a reactive fluorine species at moderate temperatures because of the relatively strong C-F bond. Interestingly, however, certain kinds of metal trifluoroacetates decompose into metal fluorides at elevated temperatures [19, 20]. A general reaction scheme for lanthanide trifluoroacetates proceeds as follows:

\[
\text{Ln(CF}_3\text{COO)}_3 \rightarrow \text{LnF}_3 + (\text{CF}_3\text{CO})_2\text{O} + \text{CO}_2 + \text{CO}
\]

Using this chemical phenomenon, heavy-metal fluoride glasses were prepared using trifluoroacetates of zirconium, barium, lanthanum, aluminum and sodium [21]. Figure 10.2 shows thermal gravimetric analysis of the ZBLAN powder in this process. A drastic decrease in weight (47.4%) was observed in the range of 220–300 °C, which was attributed to the decomposition from the trifluoroacetate to the solid ZBLAN fluoride.
Trifluoroacetic acid is miscible with other solvents such as ether, acetone, methanol, isopropanol, n-buthanol, benzene, xylene, water, so it can be included in the sol-gel processing to prepare homogeneous precursor solutions. In general, sol-gel precursor solutions are prepared by dissolving metal alkoxides or acetates in organic solvents mixed with TFA. When the solubility of metal compounds is low, the addition of water is helpful to dissolve them completely. In the solutions, the coordination between TFA ions (CF$_3$COO$^-$) and metal ions is made because CF$_3$COO$^-$ acts as a very weak base. Existing anions such as CH$_3$COO$^-$ and C$_2$H$_5$O$^-$ are stronger bases and hence associate with hydrogen ions. Other metal salts such as nitrates, chlorides and sulfates should not be used for the processing because the anions (NO$_3^-$, Cl$^-$ and SO$_4^{2-}$) could disturb the coordination between TFA and metal ions.

The precursor solutions or dried gels containing metal trifluoroacetate complexes are subject to heat treatments at temperatures higher than 300 °C, which is a typical decomposition temperature to form metal fluorides. Exact decomposition temperatures depend on the kind of metal elements involved [19, 22]. At much higher temperatures, metal oxyfluoride or metal oxide materials are also obtained. However, not all the metal elements form fluoride compounds in this process. At least, metal elements with electronegativity less than 1.5 can form metal fluorides through the decomposition in the air. Alkali, alkaline earth and rare-earth fluorides are therefore successfully obtained. Heat treatment atmospheres sometimes influence the decomposition behaviour of trifluoroacetate precursors [20].

Alkaline earth and rare-earth fluoroalkoxides ([M(OR)$_n$)$_m$], where M = metal elements and OR = fluoroalkoxo groups; R = CH$_2$CF$_3$, CH(CF$_3$)$_2$, C(CF$_3$)$_2$CH$_2$(OCH$_2$CH$_2$)$_2$OMe, C(CF$_3$)$_2$CH$_2$OCH$_2$CH$_2$N(CH$_2$CH$_2$OMe)$_2$, etc.) were examined as precursors for metal fluorides both in the sol-gel process and in the chemical vapour deposition [23, 24]. The fluoroalkoxides were prepared by the reaction of polyether-substituted fluoroalcohols with metal source reagents of Sr(OC$_3$H$_7$)$_2$ or BaH$_2$. It was possible to obtain pure metal fluoride powders by hydrolysis or pyrolysis of the precursors. According to the thermal analysis,
the rapid loss of weight started at 200 °C, and the residual weight reached a steady value at approximately 300 °C to form metal fluorides.

Fluorosilicic acid (H$_2$SiF$_6$) can possibly be a fluorine source in the sol-gel processing. Glass-ceramics in a SiO$_2$–Al$_2$O$_3$–CaO–CaF$_2$ system were prepared from tetraethyloorthosilicate (TEOS), Al(NO$_3$)$_3$·9H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, H$_2$SiF$_6$, ethanol and water [25]. An attempt was made to obtain pure and homogeneous glass-ceramics with controlled microstructure for application to dental and orthopaedic cements. Tetraethyloorthosilicate was first hydrolysed in ethanol at room temperature. The previously dissolved aluminum and calcium salts were then added dropwise to the TEOS solution. H$_2$SiF$_6$ was added further to the reaction solution. The fully mixed solution was then heated under reflux with continuous stirring until gelation occurred.

The preparation of silicon oxyfluoride materials with high fluorine contents was attempted by direct hydrolysis of fluoroalkoxysilane precursors [26]. Silicon oxyfluoride gels of nominal composition SiO($x$)F$_x$ were prepared by hydrolyzing triethoxyfluorosilane (Si(C$_2$H$_5$O)$_3$F). Transparent monolithic gels (Figure 10.3) were

\[ \text{Figure 10.3 Silicon oxyfluoride gel prepared under Ar atmosphere. Reproduced from reference 26 by permission of Springer} \]
obtained under careful control of hydrolysis and condensation reactions. Maintenance of the Si-F bond during gelling, heating and aging was likely to be achieved by treating the gels under an argon atmosphere.

One of the most useful materials containing fluorine is fluorine-doped tin dioxide (FTO). This is utilized as transparent conductive films in a variety of optoelectronic devices. Various types of fluorinated tin complexes were developed to fabricate FTO films and nanopowders by the sol-gel method [27–31]. The precursors including Sn-F bonds (for example, see Figure 10.4) are highly useful in obtaining conductive FTO because the amount of fluorine could remain well above the effective doping level.

Figure 10.4 Structure in solution of the fluorinated SnF(OR)\textsubscript{2}(acac)\textsubscript{2} compounds, where R stands for Et = C\textsubscript{2}H\textsubscript{5}, iPr = CH(CH\textsubscript{3})\textsubscript{2} and tAm = C(\text{CH}\textsubscript{3})\textsubscript{2}C\textsubscript{2}H\textsubscript{5}. Reproduced from reference 31 by permission of Elsevier

10.4 Control of Shapes and Microstructures

Optical properties of materials greatly depend on their microscopic as well as macroscopic shapes, based on the interaction with light as shown in Figure 10.5. Transparency of materials is determined by absorption and scattering of incident light. Reflection at interface is also an important factor influencing optical performance. To make good use of the excellent optical properties of metal fluorides, their morphology and microstructure should be carefully controlled.

In the bulk form, heavy-metal fluoride glasses and CaF\textsubscript{2} single crystals are the most important fluoride materials as main optical components. Some other single crystals of complex fluorides such as LiYF\textsubscript{4} are also important as laser materials [32]. Recently, LuLiF\textsubscript{4}:Tm,Ho has received considerable attention, although LuLiF\textsubscript{4} has some difficulty with crystal growth. Jing et al. succeeded in growing high-quality LuLiF\textsubscript{4}:Tm,Ho crystals by the Czochralski method [33]. As such, bulk fluoride materials are fabricated generally by high-temperature processes.

In contrast, low-temperature processes have been successfully employed for creating fluorine-containing nanomaterials. BaMgF\textsubscript{4} and SrAlF\textsubscript{5} powders and thin films were first synthesized by the sol-gel method using TFA as the fluorine source [34]. Damien et al. and Lepoutre et al. synthesized LiGdF\textsubscript{4}:Eu\textsuperscript{3+} and LiYF\textsubscript{4}:Er\textsuperscript{3+} crystallized powders by the sol-gel method [35, 36]. They showed that the organic groups were removed after annealing treatments at 550 °C in F\textsubscript{2} atmosphere. Yi et al. prepared high-quality LiYF\textsubscript{4}, BaYF\textsubscript{5} and
NaLaF$_4$ nanocrystals by codecomposition of precursors in organic solvents [37]. Trifluoroacetic acid and the reaction temperature were found to be crucial for the formation of NaLaF$_4$ and LiYF$_4$ nanoparticles. LiYF$_4$, BaYF$_3$ and NaLaF$_4$ nanoparticles, codoped with Yb (20%) and Er (2%), showed bright upconversion fluorescence upon 980 nm NIR excitation. Eu-doped BaMgF$_4$ nanopowders, which were prepared by the trifluoroacetate-based sol-gel method, were successfully used as precursors for the production of a BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ blue-emitting phosphor at the low heating temperature of 1300 ºC. This achievement was due to the higher reactivity of the sol-gel-derived materials as well as the lower melting point of BaMgF$_4$ [38].

The sol-gel processing is a versatile method for depositing coatings on a variety of substrates in an economical manner. Thin film is also a common shape of metal fluorides in optics. Fluoride coatings are useful because of their wide range of wavelengths giving high optical transparency. A well-known example is the use of MgF$_2$ in anti-reflective (AR) coatings. LaF$_3$ is an excellent host crystals for luminescent rare-earth ions. Since optical amplification is possible in such materials, an optical waveguide amplifier based on rare-earth thin films was proposed. Buchal et al. studied photoluminescence at 1.5 µm in Er$^{3+}$-doped YF$_3$, LuF$_3$ and LaF$_3$ thin films prepared by vacuum evaporation [39]. The sol-gel method using TFA was then investigated to prepare LaF$_3$ and YF$_3$ thin films [9, 40]. Eu$^{2+}$-doped BaMgF$_4$ and BaLiF$_3$ thin films, which were fabricated without using reducing atmosphere, could exhibit strong violet/blue luminescence upon irradiation with UV light [41, 42].

Nanocomposite is an ideal structure of metal fluoride nanocrystals for viable optical applications. The idea originates from designing oxyfluoride glass ceramics where nanometer-scale metal fluoride crystals are dispersed in glass matrices of high transparency. Wang and Ohwaki attempted to prepare transparent oxyfluoride glass ceramics based on
aluminosilicates, in which Pb$_x$Cd$_{1-x}$F$_2$ microcrystallites codoped with Yb$^{3+}$ and Er$^{3+}$ ions were precipitated, by a conventional melting method and observed enhanced optical properties [43]. Since then, various kinds of oxyfluoride glasses have been prepared by using a similar melt-quench processing because they could offer an economical alternative with substantial performance improvements over fluoride glasses [44–48]. However, it has not been possible to fabricate thin films for applications such as planar waveguides.

LaF$_3$ is an ideal host for luminescent rare-earth ions because it has extensive solid solutions with all rare-earth ions, a lower phonon energy ($350 \text{ cm}^{-1}$) than ZBLAN ($580 \text{ cm}^{-1}$) and adequate thermal and environmental stability [46]. The first attempt to prepare oxyfluoride glass-ceramics by the sol-gel method was therefore made with a simple SiO$_2$–LaF$_3$ composition [49]. Dry silica gels containing La$^{3+}$ and trifluoroacetate ions (CF$_3$COO$^-$) were prepared from TMOS, methanol, dimethylformamide (DMF), lanthanum acetate, trifluoroacetic acid, water and nitric acid. By heating the gels at temperatures above 300 °C, LaF$_3$ microcrystals with a size of 10–30 nm were formed in the silica matrix. Because of the good dispersion, LaF$_3$ did not show crystal growth at temperatures up to 800 °C. A large specimen of SiO$_2$–LaF$_3$ glass-ceramics was obtained by carefully controlling a composition of the precursor solution (Figure 10.6) [50]. Colorization, crack formation and fragmentation of gels during drying and heating are greatly dependent on the amount of TFA, which acts both as a fluorine source and an acid. It was possible to suppress fragmentation of the heated gels by using lanthanum trifluoroacetate gels as a precursor in preparing the solutions.

Figure 10.6 Appearance of the SiO$_2$–LaF$_3$ glass ceramics prepared by the sol-gel method. Reproduced from reference 50 by permission of Springer

Transparent oxyfluoride glass-ceramic thin films were prepared using the sol-gel method [10, 13]. SiO$_2$–LaF$_3$ and SiO$_2$–LaOF glass-ceramics were formed by heating at temperatures of 300–500 °C and 600–900 °C, respectively. Eu$^{3+}$ activators were successfully incorporated into oxyfluoride crystals, as evidenced by their characteristic luminescent properties. Films of a SiO$_2$–(Gd,Eu)F$_3$ nanocomposite structure, in which (Gd,Eu)F$_3$ nanocrystals were dispersed in a silica matrix, were also deposited on silica glass substrates at temperatures of 300–500 °C.
The above-mentioned pioneering works have been followed by many excellent works on luminescent glass-ceramics. Biswas et al. prepared transparent $0.1{\text{ErF}}_3 - 0.1{\text{YbF}}_3 - 5{\text{LaF}}_3 - 94.8\text{SiO}_2$ (mol %) glass-ceramics by the sol-gel method using TFA [51]. A bulk sample could be obtained by heating finally at 1000 °C. The rare-earth ions ($\text{Er}^{3+}$ and $\text{Yb}^{3+}$) were partitioned in the low phonon energy $\text{LaF}_3$ nanocrystals with average size of 10–20 nm embedded in silica glass, as seen as black spots in a TEM image (Figure 10.7). As a result, efficient visible upconversion emissions were observed under NIR excitation. Luo et al. studied a crystallization behaviour of $\beta$-$\text{PbF}_2$ in transparent glass-ceramics of $x\text{ErF}_3 - 10\text{PbF}_2 - 90\text{SiO}_2$ (mol %, $x = 0, 1, 2$) compositions by the sol-gel method using TFA [52]. They evaluated the apparent activation energy for the crystallization of $\beta$-$\text{PbF}_2$ phase to be about 162 kJ/mol and 167 kJ/mol for dried xerogels with $x = 0$ and 1, respectively. It was revealed that few $\text{Er}^{3+}$ ions contributed to or were incorporated into the $\beta$-$\text{PbF}_2$ lattice; rather they seemed to segregate at the surface of the crystallites and hindered the growth of $\beta$-$\text{PbF}_2$. This result is different from the successful incorporation of the rare-earth ions into the $\text{LaF}_3$ nanocrystals. Interestingly, the presence of $\text{Pb(NO}_3)_2$ was observed at around 200 °C in their work, which indicated that there existed a competition between $\text{NO}_3^-$ (added to the solution as the acid $\text{HNO}_3$ catalyst) and $\text{CF}_3\text{COO}^-$ to coordinate with the $\text{Pb}^{2+}$ ion.

Ribeiro et al. attempted to fabricate $\text{Eu}^{3+}$ and $\text{Tm}^{3+}$-doped $\text{SiO}_2$–$\text{LaF}_3$ glass-ceramics as waveguides [53]. Actually, thin films obtained by dip-coating on $\text{SiO}_2$ substrates and treated at 300, 500 and 800 °C displayed guided modes in the visible and infrared regions. $\text{YF}_3$–$\text{SiO}_2$ [54], $\text{Er}^{3+}$-doped $\text{BaF}_2$–$\text{SiO}_2$ [55], $\text{Er}^{3+}$-doped $\text{SrF}_2$–$\text{SiO}_2$ [56], $\text{Er}^{3+}$-doped...
CaF$_2$–SiO$_2$ [57], Eu$^{3+}$- or Er$^{3+}$-doped SiO$_2$–LaF$_3$ [58,59] and Ho$^{3+}$–Yb$^{3+}$ or Yb$^{3+}$–Tm$^{3+}$ co-doped SiO$_2$–LaF$_3$ [60,61] glass-ceramics have been prepared through a similar sol-gel processing so far.

The porosity of glass ceramics is an important factor for determining their optical properties. The precise control of the porosity can often enhance the interaction between light and materials. Here is an interesting attempt to increase photoluminescence intensity. SiO$_2$–BaMgF$_4$:Eu$^{2+}$ glass-ceramic thin films were prepared by the sol-gel method using TFA [12]. Eu$^{2+}$ was successfully doped in BaMgF$_4$ nanoparticles dispersed in a silica glass matrix. The addition of DMF to a starting solution greatly influenced microstructure of the glass-ceramic films. That is, the film without DMF was dense while that with DMF was porous as shown in Figure 10.8. DMF is commonly used as a drying control chemical additive in preparing monolithic silica glasses in the sol-gel process. In contrast, DMF can be a cause of pore formation in the thin-film fabrication process where the coated solutions are put into the furnace kept at the heat-treatment temperature beforehand. Vaporization and/or decomposition of DMF from the inside of the film led finally to the porous microstructure. The films could exhibit blue emission peaking at 420 nm arising from the Eu$^{2+}$ 5d $\rightarrow$ 4f transition by the UV excitation at 290 nm. This emission was effectively enhanced in the porous film as shown in Figure 10.9, which was caused by multiple scattering of the excitation light.

10.5 Optical Properties

10.5.1 Low Refractive Index and Anti-Reflection Effect

Alkaline earth fluorides having low refractive indices are useful, especially as coatings, in optics because of their high optical transparency in a wide range of wavelengths from IR to
UV. Metal fluoride coatings that are prepared by common techniques such as evaporation or sputtering are normally dense and have refractive indices close to that of bulk fluoride materials.

For a single-layer AR coating as shown in Figure 10.10, complete anti-reflection is attained when each optical parameter is under the following conditions:

\[ n_1^2 = n_0 n_2 \]
\[ n_1 d = \lambda / 4 \]

where \( n_0, n_1 \) and \( n_2 \) are the refractive index of the air, the coating and the component, respectively, \( d \) the thickness of the coating and \( \lambda \) the wavelength of incident light [62]. Because the smallest refractive index is 1.40 (at 248 nm) of MgF\(_2\) among the nondeliquescent, practical inorganic materials, porous films are required to prepare single-layer AR coatings. Generally, the refractive index of materials decreases as the porosity increases according to the extended Lorentz-Lorenz formula [1]:

\[ 1 - p = (n^2 + 2)(n_m^2 - 1) / \left\{ (n^2 - 1)(n_m^2 + 2) \right\} \]

**Figure 10.9** Photoluminescence spectra of the SiO\(_2\)-BaMgF\(_4\):Eu\(^{2+}\) films without and with the DMF addition. Reproduced from reference 12 by permission of the Chemical Society of Japan

**Figure 10.10** Schematic configuration of an AR coating
where $p$ is porosity and $n$ and $n_m$ are the theoretical and the measured refractive indices, respectively. Optical design of a single-layer AR coating is therefore closely related to materials processing.

Porous metal fluoride coatings are exclusively prepared by chemical solution deposition techniques including the sol-gel deposition method. The first work was done by Joosten et al. using a solution of magnesium trifluoroacetate or other fluorine-containing magnesium derivatives [63]. The solutions were deposited onto a fused silica substrate and then heated to 500–600°C. The resultant MgF$_2$ films had excellent optical performance with relatively lower refractive index of 1.21. Thomas adopted colloidal suspension methods using methanol solutions of metal acetates or alkoxides and HF [64]. MgF$_2$ and CaF$_2$ suspensions were prepared as follows,

$$
\text{Mg(CH}_3\text{COO)}_2 + 2\text{HF} \rightarrow \text{MgF}_2 + 2\text{CH}_3\text{COOH} \\
\text{Mg(CH}_3\text{O)}_2 + 2\text{HF} \rightarrow \text{MgF}_2 + 2\text{CH}_3\text{OH} \\
\text{Ca(CH}_3\text{COO)}_2 + 2\text{HF} \rightarrow \text{CaF}_2 + 2\text{CH}_3\text{COOH}
$$

For MgF$_2$, the reactions were carried out in anhydrous methanol in which all the reagents were soluble and the product insoluble. In contrast, some water was required as cosolvent with the methanol to obtain complete solubility in the reaction of CaF$_2$. Coatings were made on fused silica disks and polished calcium fluoride disks, which led to 45 % porous MgF$_2$ and 50 % porous CaF$_2$ films. Such porous coatings are also effective to enhance laser damage thresholds [65]. Larger colloidal particles (0.15 to 1 μm) of MgF$_2$ are obtained from aqueous solutions of NaF and MgCl$_2$ by aging at 80°C for 3 h [66].

Metal fluoride coatings can also be prepared through the trifluoroacetate-based sol-gel processing, as described above, using the dip- or spin-coating technique. In this case, their optical properties depend greatly on processing parameters. Figure 10.11 shows wavelength dependence of the refractive index of MgF$_2$ films prepared using spin coating [67]. The coated films were dried at 80°C before annealing at 300, 400 or 500°C, which appeared to be effective to suppress abrupt vaporization of the solvents. It is seen that the higher heating temperature results in the lower refractive index. The porosity of the films heated at 300, 400 and 500°C were calculated to be 8.6, 28.7 and 39.4 %, respectively, using the extended Lorentz-Lorenz formula. It should be noted that the film thickness is relatively difficult to control because an increase in the number of coating layers in the deposition procedure may lead to inhomogeneity of the films in a depth direction.

The heat-treatment temperature is not an only way to control optical properties, as mentioned above for the porous glass-ceramic thin films. The porosity and the optical thickness, $n_d$, of CaF$_2$ films were controlled by adding organic compounds to coating solutions [68]. Organic additives such as aminoalcohols, 2-methoxyethanol, ethyleneglycol and cyclohexanol greatly influenced the deposition temperature and optical properties of porous CaF$_2$ films because of the evaporation and/or decomposition of the additives during heating.

Rywak and Burlitch prepared a nanocrystalline MgF$_2$ sol, abrasion-resistant MgF$_2$ films from it and SiO$_2$–MgF$_2$ composites both in the bulk and in the thin-film form [69]. In the synthesis of the composites, MgF$_2$ sols were prepared from methanolic H$_2$O$_2$ and
Mg(OCH$_3$)$_2$ treated in HF and mixed with silicate sols prepared from the acid catalysed hydrolysis and condensation of TMOS. Thin films of nanocrystalline MgF$_2$ were prepared by spin-coating of the nanocrystalline MgF$_2$ sol onto Si(100). The film thickness could be built up by repeating the coating procedure, but films thicker than 100 nm generally showed haziness caused by ‘islands’ on the surface. In contrast, using this multiple coating process, thicker SiO$_2$–MgF$_2$ composite films (ca. 150 nm) could be prepared on Si(100). These films had surface roughness of approximately ±5 nm after being heated at 550 °C.

![Graph](image.png)

**Figure 10.11** Variation of the refractive index of the MgF$_2$ thin films heat-treated at 300, 400 and 500°C for 10 min. Reproduced from reference 67 by permission of Springer

Murata *et al.* used MgF$_2$ sols obtained from magnesium acetate and HF to prepare ultra-low refractive index MgF$_2$ thin films [70–72]. The sols were autoclaved in a Teflon cell at 100–180 °C and then coated on SiO$_2$ glass or CaF$_2$ crystal substrates by spin-coating. Subsequently, the coated films were heat treated at 150 °C. As shown in Figure 10.12, the MgF$_2$ films exhibit the AR effect over a very wide range of wavelengths in the VUV range. They also fabricated porous MgF$_2$–SiO$_2$ thin films consisting of MgF$_2$ particles connected by an amorphous SiO$_2$ binder [73]. The films had a low refractive index of 1.26, sufficient strength to withstand wiping by a cloth and a high environmental resistance. The films could be uniformly formed on curved substrates and at relatively low temperatures, such as
100 °C. Because the wet-processed fluoride coatings generally have lower mechanical strength than the dry-processed ones, the nanocomposite with SiO$_2$ may be the best way to produce AR coatings with improved performance.

Sermon and Badheka reported the preparation of MgF$_2$ xerogels with high surface area (821 m$^2$/g at 423 K), high pore volume (1.00 cm$^3$/g) and small particle size (5–7 nm) [74]. They could be readily applied to substrates by traditional methods to give high porosity xerogel coatings.

Recently, Krüger et al. reported the deposition of MgF$_2$ films of optical quality through an anhydrous low temperature sol-gel synthesis using MgF$_2$ sols [75, 76]. The MgF$_2$ precursor solution was prepared from a suspension of magnesium methoxide in methanol and a nonaqueous HF solution in methanol. The solution was then deposited onto Si substrates by spin coating. The refractive index of the resultant films was smaller than those of the bulk phase due to a lower density of the MgF$_2$ films as compared to the bulk material.

Quite an interesting approach has been made recently by Grosso et al. to prepare magnesium oxyfluoride-based ultralow-dielectric-constant optical thin films [77]. Precursor solutions were prepared simply by mixing magnesium acetate, water and TFA. Highly porous and resistant semicrystalline magnesium oxyfluoride thin films were obtained through liquid deposition followed by a flash and short thermal treatment. The TEM observation revealed that the film was composed of rigid and atypical porous inorganic networks made of coalesced hollow particles and vesicles. Lately, MgF$_2$-based optical thin films exhibiting refractive indices ranging from 1.08 to 1.2 were reported [78]. The generation of the porosity (Figure 10.13) responsible for the ultralow refractive indices of these materials was thought to be triggered by the thermal decomposition of metallic precursor ligands.

![Figure 10.12 Transmittance of CaF$_2$ substrate with antireflection coatings made from the autoclaved MgF$_2$ sol on both sides. Reproduced from reference 70 by permission of Springer](image-url)


10.5.2 Luminescence

Luminescence of rare-earth ions doped into inorganic solid materials has found numerous practical applications in phosphors and lasers [79]. Doped rare-earth ions can be excited by electromagnetic radiations, cathode rays, electric voltages or any other energy sources through intraconfigurational $f$–$f$ transitions of inner 4$f$ electrons, interconfigurational $f$–$d$ transitions, charge transfers between rare-earth ions and anions or host lattice absorptions. Luminescent behaviour of excited rare-earth ions is subject to crystal fields of host lattices and also to lattice imperfection. Furthermore, lattice phonon affects quantum efficiencies of emissions from excited rare-earth ions. It is interesting and important to design, synthesize and utilize host lattices containing fluorine for desired luminescence because fluoride crystals generally give lower phonon energies than oxide crystals.

Trivalent europium (Eu$^{3+}$) ions show red luminescence due to intraconfigurational $f$–$f$ transitions. A comparison between LaF$_3$ and LaOF makes it easy to understand effects of host crystal lattices on luminescence. In the excitation, as well as intraconfigurational $f$–$f$ excitations of inner 4$f^6$ electrons, interconfigurational charge-transfer excitations, $4f^6 \rightarrow 4f^5 L^{-1}$ (L is ligand), can take place in the Eu$^{3+}$ ion. The charge-transfer excitations are allowed, are usually positioned in the UV region and have much higher intensity than the $f$–$f$ excitations [79]. Figure 10.14 shows excitation spectra for a $^5D_0 \rightarrow ^7F_2$ (611 nm) emission of La$_{0.9}$Eu$_{0.1}$F$_3$ and La$_{0.9}$Eu$_{0.1}$OF thin films prepared by the sol-gel method using TFA [10,80]. La$_{0.9}$Eu$_{0.1}$OF exhibits a strong excitation band at 272 nm, resulting from an O$^{2-}$–Eu$^{3+}$ charge transfer [81]. On the other hand, the charge-transfer excitation is not
observed in La$_{0.9}$Eu$_{0.1}$F$_3$ in the measured wavelength regime. The position of the charge-transfer band generally shifts to higher energy for decreasing covalency in chemical bonds. It takes much more energy to remove an electron from an F$^-$ ion in La$_{0.9}$Eu$_{0.1}$F$_3$ than from the O$_2^-$ ion in La$_{0.9}$Eu$_{0.1}$OF.

Lanthanum oxyhalides including LaOF doped with luminescent rare-earth ions were studied as phosphors for potential applications in the earlier times [82]. Crystal structures and optical or luminescent properties of rare-earth oxyfluoride compounds were extensively investigated in the 1990s [81–87]. Usually, rare-earth doped oxyfluoride materials are synthesized by heat treatments of rare-earth fluorides in the air [88] or mixtures of rare-earth oxides and NH$_4$F/nitrogen atmosphere [89].

Eu$^{3+}$-doped YOF and LaOF hollow spheres were synthesized by a facile template route [90]. The templating carbonaceous spheres were prepared and dispersed in metal nitrate solutions. An NH$_4$F solution was then dropped in. The resultant suspension was aged and heated to 700 °C. Emissions from Eu$^{3+}$ were typical in rare-earth oxyfluoride structure. Du et al. prepared monodisperse doped lanthanide oxyfluoride (Tb$^{3+}$, Ce$^{3+}$, Eu$^{3+}$, Yb$^{3+}$ or Er$^{3+}$-doped LaOF and GdOF) nanocrystals by codecomposing lanthanide trifluoroacetate (Ln(CF$_3$COO)$_3$) precursors in oleic acid/oleylamine [91]. The nanocrystals showed controlled sizes (2–7 nm) and shapes (nanopolyhedra and elongated nanocrystals) and could form a large-area superlattice on copper grids via self-assembly. Luminescent behaviours of differently sized and shaped nanocrystals were revealed to be largely dependent upon their microstructures due to small size effects and surface-structure effects. Armelao et al. developed fluorinated β-dichetonate compounds La(hfa)$_3$-diglyme (Hhfa = 1,1,5,5,5-hexafluoro-2,4-pentanedione; diglyme = bis(2-metoxyethyl)ether) and employed them as

![Figure 10.14](image-url)  
**Figure 10.14** Excitation spectra for a $^5$D$_0 \rightarrow ^7$F$_2$ (611 nm) emission of Eu$^{3+}$ in La$_{0.9}$Eu$_{0.1}$F$_3$ and La$_{0.9}$Eu$_{0.1}$OF thin films. Reproduced from reference 10 by permission of the American Ceramic Society
single-source precursors in the sol-gel processing of lanthanum fluoride and oxyfluoride thin films [92]. As shown in Figure 10.15, LaF$_3$ and LaOF thin films prepared were highly transparent in the 200–2500 nm wavelength range and expected to be utilized in the realization of visible and infrared emitting materials and devices by doping with a variety of rare-earth ions.

![Figure 10.15](image)

**Figure 10.15** Transmittance spectra in the 200–2500 nm wavelength range for the lanthanum oxyfluoride films annealed for 1 h in air at different temperatures. Reproduced from reference 92 by permission of the American Chemical Society

These days, the development of multiphoton phosphors that employ novel conversion schemes to provide efficient visible emissions is highly required using, for example, quantum cutting phenomenon. Then the sol-gel synthesis was explored to obtain a LiGdF$_4$:Eu$^{3+}$ phosphor which could have a quantum efficiency of 190% [36]. The samples prepared in the system LiGd$_{1-x}$Eu$_x$F$_4$ showed the characteristic Eu$^{3+}$ emission upon UV irradiation in one of the absorbing level of Gd$^{3+}$ ($^6$I$_{7/2}$, $^6$P$_{5/2}$ or $^6$P$_{7/2}$) or upon blue light excitation in the $^5$D$_2$ manifold of the Eu$^{3+}$ ions. Lately, it has been demonstrated that sol-gel-derived LiGdF$_4$:Eu$^{3+}$ powders can show emission of two visible photons per absorbed VUV photon [93]. This mechanism is explained by a two-step energy transfer when exciting Gd$^{3+}$ ions in their $^6$G$_J$ high energy level.

Divalent europium (Eu$^{2+}$) ions can show $5d \rightarrow 4f$ emissions in a wide wavelength range because energy levels of outer $5d$ electrons are largely affected by the crystal field strength. Eu$^{2+}$-activated BaMgF$_4$ thin films were easily obtained by the sol-gel method from trifluoroacetate solutions containing Ba$^{2+}$, Mg$^{2+}$ and Eu$^{3+}$ [41]. Heat treatments of the films at temperatures of approximately 650°C in flowing nitrogen atmosphere led to the reduction of Eu$^{3+}$ to Eu$^{2+}$, which was accommodated in the BaMgF$_4$ structure. It is somewhat difficult to synthesize rare-earth-doped complex fluorides because the decomposition temperature of each metal trifluoroacetate is slightly different. Thus the intensity of the blue-violet luminescence of Eu$^{2+}$ depended sensitively on the heating temperature,
heating time and the europium concentration. The strongest emission was observed with the BaMgF₄:Eu²⁺ (15 mol %) film that was heated at 650 °C for 10 min.

Perovskite-type BaLiF₃:Eu²⁺ was synthesized in a similar way [42]. The trivalent Eu³⁺, which was used as the acetate for the starting material, was reduced to divalent Eu²⁺ in the pyrolysis process of BaLiF₃. Figure 10.16 shows photoluminescence spectra of the BaLiF₃:Eu (3 at %) film. The excitation wavelength used was 254 nm. A broad blue emission with a peak wavelength of 408 nm is due to the 4f⁶5d → 4f⁷ transition of excited Eu²⁺. The concentration quenching of the blue emission occurred at 5% of Eu²⁺ in BaLiF₃, indicating that Eu²⁺ was homogeneously dispersed in the BaLiF₃ host lattice. The Eu³⁺ → Eu²⁺ reduction is generally achieved by firing materials at high temperatures in a reducing atmosphere or air. When H₂ gas is used, a reduction easily proceeds as follows:

\[ 2\text{Eu}^{3+} + \text{H}_2 \rightarrow 2\text{Eu}^{2+} + 2\text{H}^+ \]

In contrast, the reduction in the air should be caused by chemical interactions between Eu³⁺ and constituents of host lattices. Peng et al. explained the reduction of Eu in Sr₄Al₁₄O₂₅ based on a charge compensation model where strontium vacancies played a key role [94]. The Eu reduction seems to be more feasible in fluoride lattices due to chemical interactions between Eu³⁺ and F⁻. When Eu³⁺ is doped in the BaLiF₃ lattice through a solid-state reaction between BaF₂, LiF and EuF₃, it is reduced to Eu²⁺ by a following reaction, which was actually achieved at 750 °C in the flowing nitrogen atmosphere [95],

\[ \text{Eu}^{3+} + \text{F}^- \rightarrow \text{Eu}^{2+} + \text{F} \]

Figure 10.16  Photoluminescence spectra of the BaLiF₃:Eu²⁺ (3 at%) film. The excitation wavelength used was 254 nm. Reproduced from reference 42 by permission of Elsevier
The decomposition reaction of the metal trifluoroacetates involves the generation of gaseous phases such as (CF$_3$CO)$_2$O, CF$_3$COF and COF$_2$ [19] in addition to the dehydration and the vaporization of the organic components. It seems that F$^-$ can be supplied from these organofluorine species because, in the presence of water, F$^-$ ions can be supplied by hydrolysis of CF$_3$COF and COF$_2$. Thus the Eu$^{3+} \rightarrow$ Eu$^{2+}$ reduction process is regarded as a solid–gas reaction in this case.

Eu-doped CaF$_2$ and MgF$_2$ films were synthesized by the sol-gel method using TFA [96]. It was found that the films of CaF$_2$ and MgF$_2$ doped with Eu resulted in luminescence of Eu$^{2+}$ and Eu$^{3+}$ ions, respectively. Eu$^{2+}$-activated CaF$_2$ and SrF$_2$ nanoparticles were also prepared by the sol-gel method assisted with a thermal-carbon reducing atmosphere (TCRA) treatment [97]. Photoluminescence with a peak at 425 and 416 nm due to Eu$^{2+}$ was observed for CaF$_2$ and SrF$_2$, respectively.

Li et al. reported systematic manipulation of the morphologies and architectures of β-NaYF$_4$ microcrystals using a simple and mild solution-growth method [98]. They investigated influences of fluoride sources (NaF and NH$_4$F) and pH values on the shapes of β-NaYF$_4$ microstructures developed during hydrothermal treatments. In addition, experimental results indicated that optical properties of β-NaYF$_4$:Tb$^{3+}$ phosphors with different microarchitectures were strongly dependent on their morphologies and sizes. Nano-sizing and microstructure engineering are now becoming key to the fabrication of novel luminescent materials both in oxides and non-oxides.

10.6 Concluding Remarks

This chapter reviewed recent advances in sol-gel technologies for the elaboration of novel, structure-controlled and high-performance metal fluoride nanomaterials in the form of nanocrystals, thin films, nanocomposites and oxyfluoride glass ceramics. Their excellent optical properties, which can surpass those of metal oxides, mean that metal fluorides are increasingly studied by chemists, physicists and materials scientists. The sol-gel method described in this chapter includes the direct fluorination of oxide precursor gels, the thermal decomposition of metal organofluorine materials and the building-up of metal fluoride crystals from F$^-$ ions and metal cations in the solutions. Although the functions mentioned in this chapter were limited to antireflective effects and luminescence, there is no doubt that these fluoride nanomaterials have a great potential for use in optics, photonics and optoelectronics. Energy and environmental materials are also emerging from fluoride nanomaterials, which can also be fabricated by the sol-gel method.

References


