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Chemical processing for inorganic fluoride and oxyfluoride materials having optical functions

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ABSTRACT

Chemical processing such as a sol–gel method can offer interesting and useful routes for designing and synthesizing inorganic metal fluoride and oxyfluoride materials for applications in optics and photonics. In our series of studies during the last decade, a variety of fluoride materials including alkaline earth fluorides (MgF_2, CaF_2, SrF_2 and BaF_2), rare-earth fluorides (LaF_3, NdF_3, GdF_3, etc.), rare-earth oxyfluorides (LaOF, EuOF, GdOF, $Sm_4O_3F_6$, $Er_4O_3F_6$, etc.) and complex fluorides ($SrAlF_5$, $BaMgF_4$, $BaLiF_3$, $LiGdF_4$, etc.) have been prepared, using trifluoroacetic acid as a fluorine source, in the form of nanoparticles, thin films and oxide/fluoride nanocomposites. They can be utilized as anti-reflective coatings, luminescent materials, VUV materials, IR materials, and so forth. This article summarizes fundamentals and possible applications of optically useful inorganic fluoride and oxyfluoride materials, with emphasis on porous single-layer anti-reflective coatings and visible photoluminescence of doped Eu^{3+} or Eu^{2+} ions. Furthermore, our recent results on $LaF_3:Ce^{3+}$ and $LaOF:Ce^{3+}$ are originally reported here.

1. Introduction

Inorganic solid materials including fluorine as a fundamental component have various important functions for applications in the field of electronics, optoelectronics, photonics, etc. Alkaline earth and rare-earth fluorides and oxyfluorides have been intensively studied because of their unique physical properties reflecting chemical bonding between metal cations and fluoride ions.

Practical and viable approaches are currently being developed for preparing such materials economically and safely based on chemical processes [1,2]. In our series of studies, sol–gel chemistry has been utilized to prepare alkaline earth and rare-earth fluorides and oxyfluorides, aiming at designing and developing novel optically active materials. Generally, high-purity products of metal fluorides have been produced using a "dry" processing to avoid oxygen or other contaminations. On the other hand, 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. Our approach to sol–gel-derived fluoride materials is based on the use of trifluoroacetic acid (TFA; CF_3COOH). We have succeeded so far in the sol–gel preparation of, for example, fluoride and oxyfluoride coating films [3–7], oxyfluoride glass-ceramics [8,9] and oxide/fluoride nanocomposite thin films [10–15]. In this article, some important results are reviewed and additionally our recent development of $LaF_3:Ce^{3+}$ and $LaOF:Ce^{3+}$ materials is reported.

2. Chemical processing using TFA

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. The boiling point of TFA (72.4 °C) is lower than that of acetic acid (118 °C). Since the C–F bonding is relatively strong, TFA is not a reactive fluorine species under moderate conditions. At elevated temperatures, TFA decomposes into chemical species such as $(CF_3CO)_2O$, CF_3COF, COF_2, etc. [16]. Interestingly, metal salts of TFA, namely metal trifluoroacetates, can be decomposed into metal fluorides or oxyfluorides at higher temperatures of typically 300 °C [17]. For example, a general reaction scheme for lanthanide trifluoroacetates proceeds as follows:

$$Ln(CF_3COO)_3 \rightarrow LnF_3 + (CF_3CO)_2O + CO_2 + CO \qquad (1)$$

When we try to use this phenomenon in the sol–gel processing, it is necessary to control precisely the decomposition reaction to fabricate metal fluoride materials having specific morphologies and shapes for viable applications.

The sol–gel processing is a versatile method for depositing coatings on a variety of substrates in an economical manner. In order to fabricate metal fluoride coatings, solutions are first prepared from pertinent metal salts, TFA and organic solvents. A

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small amount of water is often added to enhance the solubility of salts. The solutions are then coated on substrates by dipping or spinning, dried at lower temperatures and heated at higher temperatures. This coating/heating procedure is repeated several times to control the film thickness. Metal fluoride and oxyfluoride powders can be obtained by heating dried trifluoroacetate gels [18–20].

To fabricate oxide/fluoride nanocomposite materials, trifluoroacetate solutions are mixed with solutions of other compositions. For example, a silicon alkoxide (typically tetramethylorthosilicate and tetraethylorthosilicate) solution is mixed with trifluoroacetate solutions in preparing SiO_2-based oxyfluoride glass-ceramics and nanocomposite powders [8,9,21]. Additional factors are concerned such as compositions, pH values and types of catalysts for the formation of SiO_2.

3. Alkaline earth fluoride thin films

Alkaline earth fluorides are highly transparent even in the UV region and therefore one of the most important materials as main optical components for UV, deep-ultraviolet (DUV) and vacuum-ultraviolet (VUV) applications. Anti-reflective (AR) coatings for these components are also composed of the UV optical materials. Porous MgF_2 and CaF_2 films having lower refractive indices are used as a single-layer AR coating, based on the following conditions:

$$n_1^2 = n_0 n_2 \tag{2}$$

$$n_1 d = \frac{\lambda}{4} \tag{3}$$

where n_0, n_1 and n_2 are the refractive index of air, the coating and the component, respectively, d is the thickness of the coating and λ is the wavelength of light. The $n_1 d$ value then represents the optical thickness. It is necessary to obtain the films with n_1 values less than 1.22 for the SiO_2 glass ($n_2 = 1.51$) at 248 nm (a wavelength of a KrF laser). Since the smallest refractive index is 1.40 (at 248 nm) of MgF_2 among the non-deliquescent, practical inorganic materials, porous films are required to prepare the single-layer AR coatings. Porous coatings are also effective to enhance the laser damage thresholds. We reported that the refractive index of sol–gel-derived porous MgF_2 thin films could be controlled by the heat treatment conditions [22]. Fig. 1 shows the variation of the refractive index with wavelength in the MgF_2 films prepared by drying the spin-coated trifluoroacetate solutions at 80 °C for 10 min and then heating at 300, 400 or 500 °C for 10 min in air. The index value decreases with increasing the heating temperature. 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,

$$1 - p = \frac{(n^2+2)(n_\mathrm{m}^2-1)}{(n^2-1)(n_\mathrm{m}^2+2)} \tag{4}$$

where p is the porosity and n and n_m are the theoretical and the measured refractive indices, respectively. In this case, the porosity of the films is probably changed by the generation of gaseous phases during the heat treatment of the coating films. Controllable parameters are merely drying and heating temperatures and hence the control of the refractive index is not easy.

Another attempt was made in the fabrication of porous CaF_2 AR coatings by the sol–gel method [23]. We investigated the effects of organic additives on the deposition and optical properties of the films. Amino alcohols (2-aminoethanol, 2-dimethylaminoethanol and triethanolamine) and alcohols with larger molecular weights (ethyleneglycol, 2-methoxyethanol, cyclohexanol and 2-(2-*n*-butoxyethoxy)ethanol) were examined as the organic additives. It was found that cyclohexanol was the most effective one to control the surface morphology and the optical properties of the films. The optical thickness ($n_1 d$) of the CaF_2 films can be controlled by changing the amount of cyclohexanol in the coating solutions. Moreover, it is possible to reduce light scattering and increase transmittance in the UV region as shown in Fig. 2.

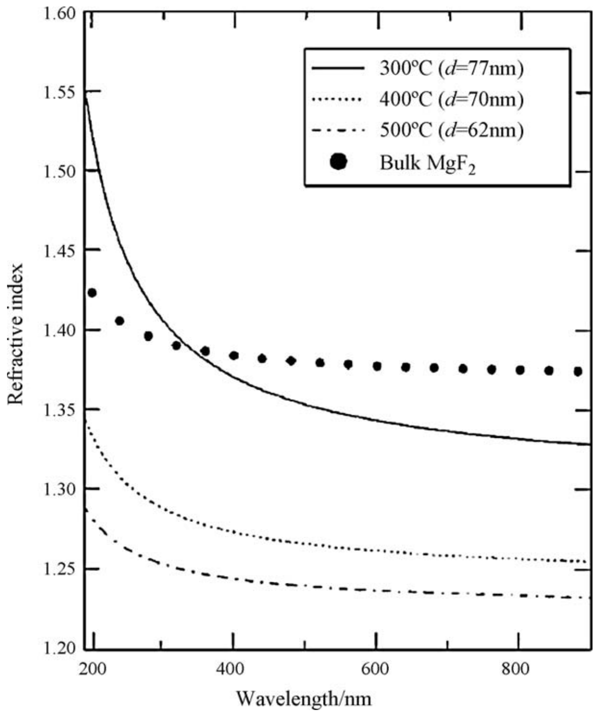

Fig. 1. Variation of the refractive index of the MgF_2 thin films obtained by drying at 80 °C and then heating at 300, 400 or 500 °C for 10 min.Reproduced from Ref. [22] by permission of Springer.

4. Eu^{3+}-doped materials

Red luminescence of trivalent europium (Eu^{3+}) ions due to intra-configurational f–f transitions is of technological importance because it has been widely applied to phosphors for displays, lighting and imaging devices [24]. Emission wavelengths of Eu^{3+} are determined primarily by its local environment in host crystals. Rare-earth oxyfluorides such as LaOF have been identified as one of the important host materials for Eu^{3+} ions. Luminescent LaOF:Eu^{3+} films are easily prepared by the sol–gel method using TFA [6]. In a typical synthesis, $La(CH_3COO)_3{\cdot}0.5H_2O$ and $Eu(CH_3COO)_3{\cdot}4H_2O$ were dissolved in isopropanol to which TFA and water were added. The resultant solution was stirred at room temperature and was spin-coated on silica glass substrates. Then the substrates were immediately placed in a furnace kept at a heat treatment temperature beforehand, and were heated at 500–700 °C for 10 min in air followed by quenching. While the film is composed of LaF_3 and LaOF by heating at 500 °C, single LaOF phase is obtained by heating at 600 and 700 °C. This fact means that the phase-selective deposition is possible simply by controlling the heating temperature.

In photoluminescence, the excitation of Eu^{3+} ions is achieved by the irradiation with UV light. A comparison between LaF_3:Eu^{3+} and LaOF:Eu^{3+} makes it easy to understand the excitation mechanism. The absorption of UV light results in inter-configurational, allowed charge-transfer excitations, $4f^6 \rightarrow 4f^7L^{-1}$ (L is ligand), in the Eu^{3+} ion. Fig. 3 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

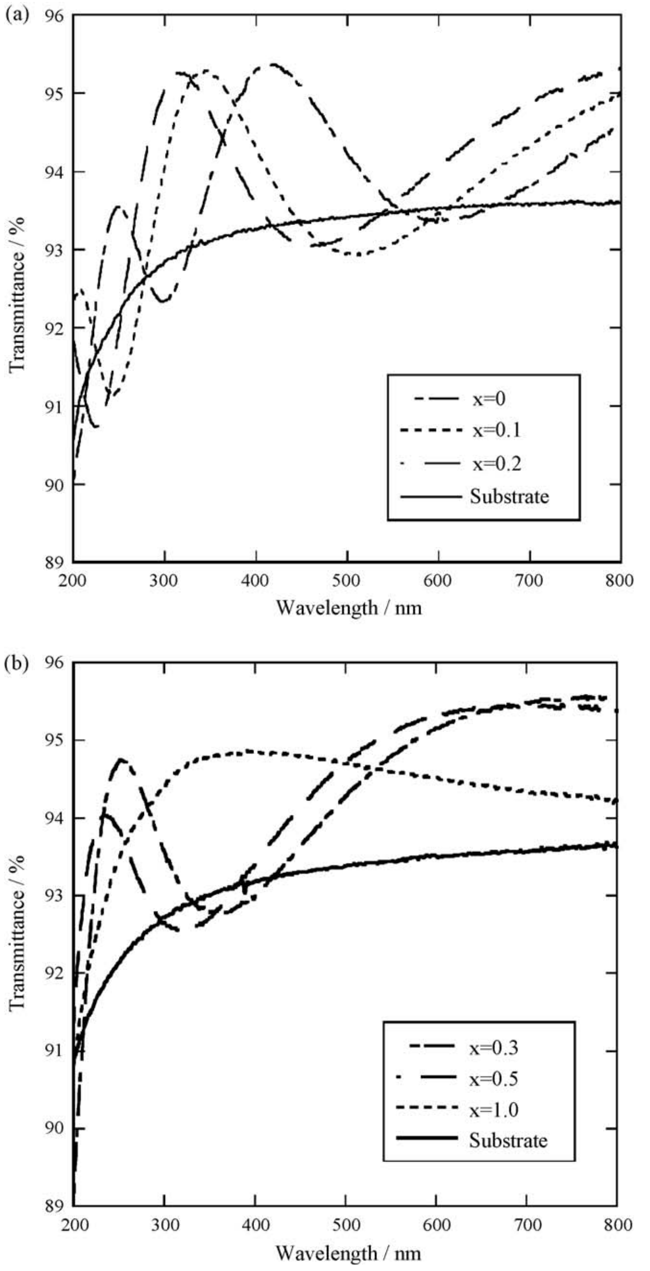

Fig. 2. (a) Optical transmission spectra of the silica glass substrate coated with the CaF_2 films obtained from the solutions containing cyclohexanol (a) with the amount of $x = 0$, 0.1 or 0.2 and (b) $x = 0.3$, 0.5 or 1.0. The x value was defined in the ratio "cyclohexanol:isopropanol = x:1."Reproduced from Ref. [23] by permission of Springer.

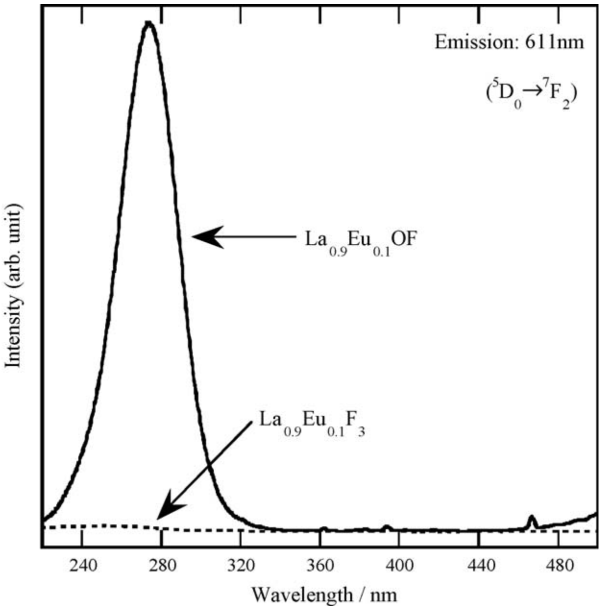

Fig. 3. Excitation spectra for the $^5D_0 \rightarrow {}^7F_2$ (611 nm) emission of Eu^{3+} in $La_{0.9}Eu_{0.1}F_3$ and $La_{0.9}Eu_{0.1}OF$ thin films.Reproduced from Ref. [11] of the author's own work.

sol–gel method using TFA [11]. While $La_{0.9}Eu_{0.1}OF$ exhibits a strong excitation band at 272 nm resulting from an O^{2-}–Eu^{3+} charge-transfer, no strong excitation band is observed for $La_{0.9}Eu_{0.1}F_3$ in the measured wavelength region. The F^-–Eu^{3+} charge-transfer band is located at much shorter wavelengths because 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 $La_{0.9}Eu_{0.1}OF$.

Multiphoton phosphors that employ novel wavelength conversion schemes (quantum cutting phenomenon) to provide efficient visible emissions have attracted much attention for potential use in lighting. The sol–gel synthesis was explored to obtain a $LiGdF_4$:Eu^{3+} phosphor which could have a quantum efficiency of 190% [25]. Actually, sol–gel-derived $LiGdF_4$:Eu^{3+} powders can show emission of two visible photons per absorbed VUV photon [26]. This mechanism is explained by a two-step energy transfer when exciting Gd^{3+} ions in their ^6G_J high energy level. The sol–gel process was also utilized for preparing SiO_2/$LiGdF_4$:Eu^{3+} nanocomposite powders [21]. Crystallization of the fluoride phase occurred after the heat treatment at 700 °C under inert atmosphere. Emission spectra as well as decay times of Eu^{3+} recorded from the nanocomposite samples were similar to those obtained from the single $LiGdF_4$:Eu^{3+} fluoride.

5. Eu^{2+}-doped materials

Excited divalent europium ions (Eu^{2+}) can show emissions in a wide wavelength range from UV to red due to an allowed 5d → 4f transition [24]. This is because energy levels of outer 5d electrons are largely affected by the crystal field strength. The Ba^{2+} ion has the similar ionic radii as well as the same configuration of outermost electrons (5 $s^2 5p^6$) to the Eu^{2+} ion. As a result, many of inorganic compounds having Ba^{2+} ions can be used as host crystals for Eu^{2+} ions. As described below, fluorides such as $BaMgF_4$ and $BaLiF_3$ are good examples.

$BaMgF_4$ thin films can be obtained by the sol–gel method from trifluoroacetate solutions containing Ba^{2+} and Mg^{2+} [18]. Heat treatments of the coated films should be carried out with care because the decomposition temperature of each metal trifluoroacetate is slightly different. Doping of Eu^{2+} ions in $BaMgF_4$ is achieved by adding Eu^{3+} ions to the trifluoroacetate solutions [27]. That is, heat treatments of the films at temperatures of approximately 650 °C in flowing nitrogen atmosphere promote the reduction of Eu^{3+} to Eu^{2+}. As shown in Fig. 4, the $BaMgF_4$:Eu^{2+} (15 mol%) film that was heated at 650 °C shows excitation and emission bands due to electronic transitions in the Eu^{2+} ions. The excitation at 290 nm gives a strong, structureless and broadband blue-violet emission with a peak approximately at 420 nm, evidencing the presence of optically active Eu^{2+} ions in the film. The intensity of the Eu^{2+} luminescence depends sensitively on the heating temperature, heating time and the europium concentration.

Perovskite-type $BaLiF_3$ can be synthesized in a similar way [28]. The reaction temperature of 600 °C necessary for producing a single-phase $BaLiF_3$ is lower than that for a conventional solid-

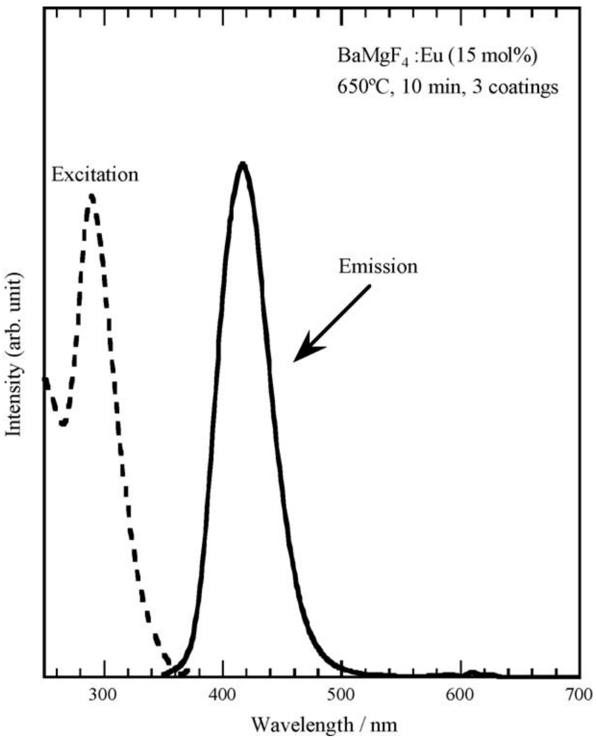

Fig. 4. Photoluminescence excitation and emission spectra of the $BaMgF_4$:Eu (15 mol.%) thin film that was heated at 650 °C. Excitation spectra were measured for the 420 nm emission. Emission spectra were recorded with 290 nm excitation.Reproduced from Ref. [27] by permission of Elsevier.

state reaction or a melting method. Eu^{2+}-doped $BaLiF_3$ shows a broad blue-violet emission at 408 nm with excitation at 254 nm. The concentration quenching of the blue emission occurs at 5 at.% of Eu^{2+} in $BaLiF_3$.

In both cases, the reduction from Eu^{3+} to Eu^{2+} seems to be much feasible in the fluoride lattices due to the stabilization effect of the Ba^{2+} site. This is one of the great advantages of the TFA-based sol–gel processing because the $Eu^{3+} \rightarrow Eu^{2+}$ reduction is generally achieved by firing materials at high temperatures in a reducing atmosphere such as H_2.

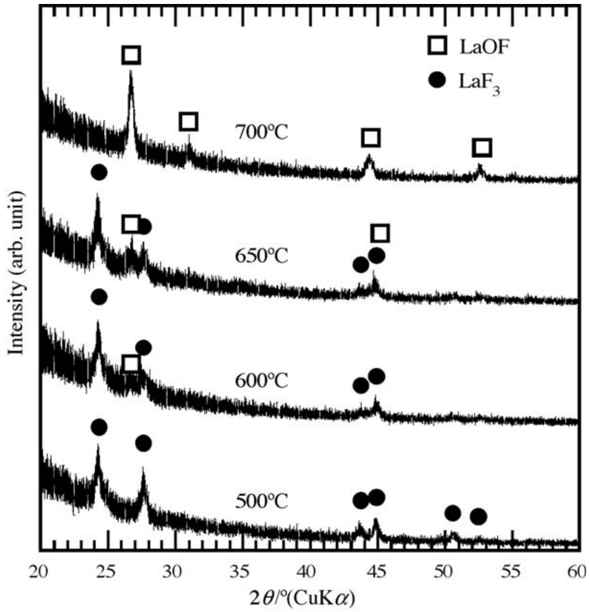

Fig. 5. XRD patterns of Ce-doped LaF_3 and LaOF thin films obtained by heating at different temperatures.

6. Ce^{3+}-doped materials

With regard to cerium, the TFA-based sol–gel method seems to place a significant restriction on synthetic conditions of fluorine-containing compounds. Actually, it is not cerium trifluoride (CeF_3) but cerium dioxide (CeO_2) that is formed through a typical TFA-based procedure, arising from the fact that cerium has a great tendency of undergoing oxidation from Ce^{3+} to Ce^{4+} [29]. We have recently found that CeF_3 and its solid solutions can be synthesized by controlling the solution composition and the heat treatment condition, which will be reported elsewhere. Because the technological importance of optically active Ce^{3+} ($4f^1$) ions is rapidly increasing to facilitate design of luminescent materials in UV and VUV regions [30], it is desirable to examine new routes to prepare fluoride materials containing Ce^{3+}.

The formation of LaF_3:Ce^{3+} and LaOF:Ce^{3+} thin films by the TFA method is described here as an original report. $La(CH_3COO)_3 \cdot 1.5H_2O$ and $Ce(CH_3COO)_3 \cdot H_2O$ were dissolved in a mixed water/isopropanol solvent to which TFA was added. The resultant solutions were spin-coated on quartz glass substrates and heat-treated at temperatures between 500 and 700 °C for 10 min in $4\%H_2/96\%N_2$ atmosphere, followed by quenching. The coating/heating procedure was repeated two additional times to increase the film thickness.

Fig. 5 shows XRD patterns of the heat-treated films with a cerium dopant level of 10 at.%. A single-phase LaF_3 film is obtained at 500 °C, while the film is composed of LaF_3 and LaOF by heating at 600 and 650 °C. Single LaOF phase was obtained by heating at 700 °C. No peak due to fluorite-type cubic CeO_2 is seen in any sample. We also confirmed that the diffraction angles changed monotonously with increasing the cerium dopant level from 0.1 to 1.0 and 10 at.% both in the LaF_3 and the LaOF phase. These facts suggest that Ce^{3+} replaces La^{3+} in the LaF_3 and the LaOF lattice. The presence of Ce^{3+} could also be observed in X-ray photoelectron spectroscopy. Although Ce^{3+} peaks were dominant in the samples heated at 650 °C or below, mixed Ce^{3+} and Ce^{4+} peaks appeared in the sample heated at 700 °C.

Optical transmission spectra of the films (10 at.% Ce) are shown in Fig. 6. All the films show high transparency in the wavelength

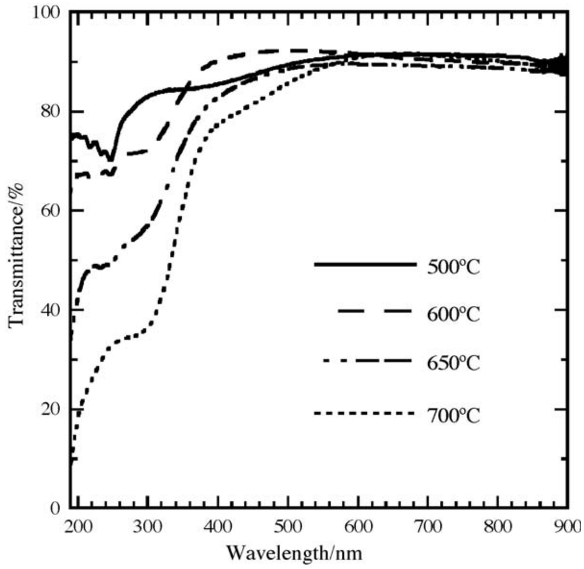

Fig. 6. Optical transmission spectra of Ce-doped LaF_3 and LaOF thin films obtained by heating at different temperatures.

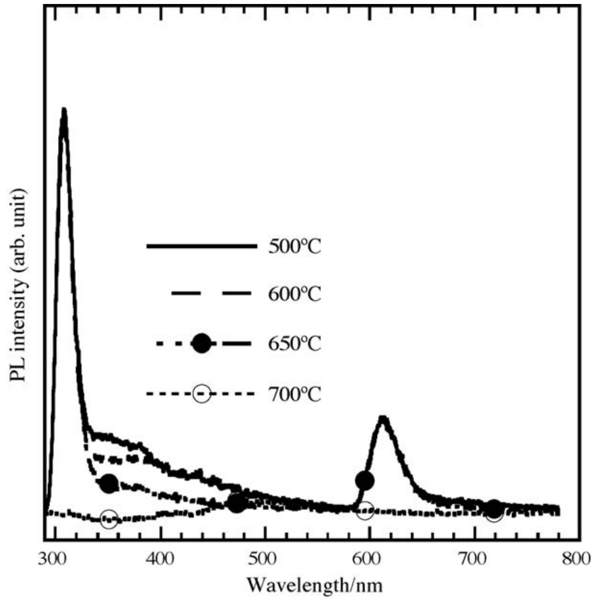

Fig. 7. Photoluminescence spectra of Ce-doped LaF_3 and LaOF thin films obtained by heating at different temperatures.

range between 550 and 900 nm. In the shorter wavelengths, however, clear difference is seen among the samples. Absorption bands centered at 250, 240 and 220 nm, which are observed in the sample heated at 500 °C, correspond to 4f → 5d electronic transition of Ce^{3+} in the LaF_3 lattice [31,32]. The intensity of UV absorption increases with increasing the heating temperature from 600 to 700 °C. A clear absorption band appears at 300 nm, resulting from the O^{2-}–Ce^{4+} charge-transfer, in the sample heated at 700 °C.

Photoluminescence spectra of the films (10 at.% Ce) are shown in Fig. 7. The excitation wavelength used was 254 nm which corresponded to one of the Ce^{3+} f–d absorption bands. Emission bands are observed at 308 and 613 nm in the samples heated at 500, 600 or 650 °C. The intensity of the emission are almost the same among these samples. In contrast, the sample heated at 700 °C shows no appreciable emission. The UV emission at 308 nm is attributed to the 5d → 4f transition of the excited Ce^{3+} ion. The origin of the red emission at 613 nm is not clearly understood at present.

As compared to the films heated in air [6], the hydrolyzation from LaF_3 to LaOF occurs at the higher temperatures under reducing atmosphere. This seems to be also effective to the suppression of the $Ce^{3+} \rightarrow Ce^{4+}$ oxidation in the LaF_3 phase. Thus the sol–gel processing is promising as the method for fabricating Ce^{3+}-containing fluoride materials.

7. Summary

This article reviewed our recent studies on the sol–gel technologies for fabricating the metal fluoride and oxyfluoride materials using trifluoroacetic acid as the fluorine source. The process is based on *in situ* fluorination of metal cations during the thermal decomposition of trifluoroacetates. We appreciate other chemical routes for fluoride materials such as the direct fluorination of oxide precursor gels, the thermal decomposition of metal organofluorine materials other than trifluoroacetates and the building-up of metal fluoride crystals from F^- ions and metal cations in the solutions, which will be reviewed in a coming book chapter [33]. Although the functions mentioned in this article were limited to the optical and photonic properties, there is no doubt that the chemical processing of fluorides has a great potential for preparing nanostructured materials used, for example, in energy and environmental applications based on electrochemistry.

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