

MOCVD of CeF₃ films on Si(100) substrates: synthesis, characterization and luminescence spectroscopy

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CeF₃ thin films have been deposited on Si(100) substrates by metal–organic chemical vapor deposition (MOCVD). The Ce(hfa)₃-diglyme [Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, diglyme = (CH₃O(CH₂CH₂O)₂CH₃)] precursor has been adopted as a single source for both Ce and F components. This adduct has proved to be a good and reliable precursor, suitable for evaporation from the liquid phase due to its rather low melting point (75 °C).

The structural, compositional, morphological and spectroscopic properties of the films have been investigated by X-ray diffraction (XRD), wavelength dispersion X-ray analysis (WDX), scanning electron microscopy (SEM) and luminescence spectroscopy.

Introduction

Inorganic scintillators play an important role as radiation detectors in many fields of fundamental and applied research.^{1,2} Most physical experiments and medical diagnostic modalities are carried out in high-rate conditions in order to obtain high sensitivity, therefore there is a special demand for high-quality scintillators which couple both of the basic requirements of fast responses and high light yields. Recently, lanthanide-doped scintillators based on 5d→4f electronic transitions have attracted attention and today they represent the largest and most promising research field.³ Generally, these transitions occur in accessible spectral regions and for Ce³⁺, Pr³⁺ and Nd³⁺ have relatively high efficiencies.⁴ However, Ce³⁺-based scintillators appear to be the most efficient and the related emission spectra have better matches with the light sensor sensitivity curves.

Up to now, the luminescence of Ce³⁺ has been traditionally studied in bulk materials, such as CeF₃ crystals^{5,6} and Ce³⁺-doped glasses.^{7,8} Fluoride materials have good optical characteristics in terms of transparency, due to both low energy phonons and high ionicity. In addition they have a broad band gap,⁹ usually more than 10 eV.

In this context, CeF₃ crystals are among the heaviest and faster scintillators suitable for various high-energy physics experiments and represent a valid alternative to the presently adopted CsI crystals.¹⁰ CeF₃ crystals, owing to their high density, are as strong as CsI in terms of the stopping power for high-energy gamma rays. In addition, they have several advantages over CsI crystals, such as a 50% greater light output, which is only slightly dependent upon the temperature. It is important to note that the large temperature dependence of CsI is always troublesome in applications. The scintillation decay time of CeF₃ has no very slow components, unlike CsI crystals (1 μs) and BaF₂ (10 μs). This is important for both good timing, and preventing shifts of the signal baseline due to overlap of slow components in high-rate experiments. This feature becomes of greater relevance in handling low intensity signals. The CeF₃ crystal is not hygroscopic; this fact represents

a main drawback for the application of NaCl, CsI, and BaF₂. The mechanical properties of CeF₃ closely match those of metals thus preventing problems due to the differential thermal expansion found in calorimetric assemblies adopting CsI and metal. Finally, CeF₃ is expected to be cheaper than CsI once crystal growth methods are well established and optimized.

Many attempts have been carried out to grow large CeF₃ crystals.^{11–14} Despite these efforts, large and transparent crystals are not easily obtained.¹⁵

In this general context, the fabrication of CeF₃ thin solid films through a versatile technique characterized by a great throwing power could be a useful solution to the severe difficulties found with the growth processes of large crystals.

In a recent paper,¹⁶ Dujardin *et al.* have reported the fabrication by molecular beam epitaxy (MBE) and the optical spectroscopy of CeF₃ and LuF₃:Ce³⁺ thin films. To our knowledge, the fabrication of CeF₃ thin films using different synthetic techniques has not yet been reported in the literature.

It is well known that metal–organic chemical vapor deposition (MOCVD) is a promising technique for industrial applications due to large deposition areas, conformal step coverage, lower deposition temperatures, and adaptability to large scale processing. For these reasons, we found it interesting to investigate the possibility of the fabrication of CeF₃ films employing this flexible technique.

In this, paper we report on the growth of CeF₃ films on Si(100) substrates by MOCVD using a single source, namely the metal–organic Ce(hfa)₃-diglyme [Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, diglyme = (CH₃O(CH₂CH₂O)₂CH₃)] precursor. The structural properties, surface morphology and chemical composition have been investigated and the luminescence of thin films has been studied by emission and excitation spectroscopy.

Experimental

CeF₃ films were prepared in a reduced pressure, horizontal cold-wall MOCVD reactor from the Ce(hfa)₃-diglyme precursor. The metal–organic precursor used in this study was

synthesized as described elsewhere.¹⁷ Si(100) substrates were heated at 450 °C during the deposition process.

In this study, the precursor sublimation temperature was kept constant at 120 °C. Argon (100 sccm) and oxygen (100 sccm) flows were used as carrier and reaction gases, respectively. The mass flows were controlled with 1160 MKS flowmeters using an MKS 147 electronic control unit. Depositions were carried out for 90 min. The total pressure in the reactor was 3 Torr. The growth rate was 1 μm h⁻¹.

The atomic composition of the films was analyzed by wavelength dispersive X-ray analysis (WDX) using an Oxford Instruments WDX-3PC analyzer. The surface morphology was examined using a LEO Iridium 1450 scanning electron microscope (SEM). θ -2 θ X-Ray diffraction (XRD) patterns were recorded on a Bruker-AXS D5005 θ - θ X-ray diffractometer, using Cu K α radiation operating at 40 kV and 30 mA.

Room temperature emission and excitation spectra in the visible and UV regions were measured using a JASCO FP-777 spectrofluorimeter, with bandwidths of 1.5 nm for both excitation and emission.

Results and discussion

Thin films of CeF₃ were deposited on Si(100) substrates by MOCVD from the Ce(hfa)₃·diglyme precursor. The cerium adduct used in the present study proved to be a good precursor for the deposition of cerium-containing films since its low melting point (75 °C) allows it to be used in the liquid phase. This represents an important issue for MOCVD applications, where liquid source precursors appear to be the most desirable, due to the greater stability of the vapor pressure and to the absence of any effect of crystallite size on the evaporation rate and, hence, on the film growth rate. Note that the crystallite size may be responsible for changes of evaporation rate in different experiments and, even more importantly, for variations during the same experiment.¹⁸

In addition, Ce(hfa)₃·diglyme represents a single source precursor for the deposition of CeF₃ films. This approach toward the desired fluoride phase is certainly related to the fluorinated β -diketonate ligands. The adoption of the present single precursor is an important issue in the perspective of an easy and fast growth process. In fact, the 'first generation' Ce(tmhd)₄ (Htmhd = 2,2,6,6-tetramethyl-3,5-heptanedione) precursor certainly requires the use of additional fluorine sources, similar to that previously reported for the synthesis of LnF₃ from the Ln(tmhd)₃·H₂O precursors.¹⁹ On the other hand, severe drawbacks are associated with any possible use of the simpler 'Ce(hfa)₄', since its nature is strictly related to the synthetic route used for the preparation, and, even more importantly, it has a quite low vapor pressure and decomposes upon heating.²⁰ In addition, the Ce(hfa)₃·diglyme precursor allows the formation of high quality CeO₂ films on different substrates,^{17,21,22} when a water saturated oxygen flow is used as the reaction gas during the deposition process.

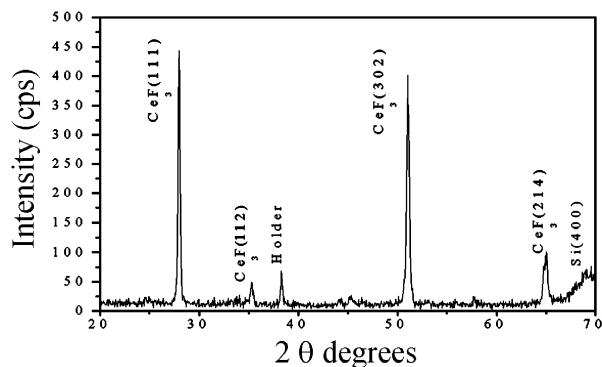


Fig. 1 XRD pattern of an MOCVD grown CeF₃ film on a Si(100) substrate using the Ce(hfa)₃·diglyme adduct.

The XRD pattern of a CeF₃ film deposited at 450 °C on Si(100) substrate is shown in Fig. 1. There is evidence of polycrystalline CeF₃ formation since peaks at $2\theta = 27.9, 35.2, 51.0,$ and 64.9° can be attributed to (111), (112), (302), and (214) reflections, respectively.²³ The remaining peak at $2\theta = 69.1^\circ$ is attributed to the (400) reflection of the Si substrate. The observed intensities are different from those reported for a polycrystalline powder, thus suggesting that some texturing occurs upon growth. In particular, the pattern presently observed is indicative of a slightly preferentially oriented film along the [302] direction, since the intensity of the (302) peak in a random polycrystalline CeF₃ powder is about 30% of the intensity of the (111) reflection, while in the present spectrum the intensity of the (302) reflection is similar to that of the (111) reflection.

The atomic ratio and chemical contamination of the cerium trifluoride films were determined by wavelength dispersion X-ray (WDX) analyses. Quantitative WDX data point to the correct 1 : 3 Ce : F ratio, with C contamination less than 0.1% in all films present.

The structure of thin polycrystalline films is better described in terms of grain size and grain shape. The size parameters can be deduced from the line broadening (full width at half maximum, FWHM) of the θ -2 θ reflections. This is related to the size (D) of the domains, which represent coherent volumes for the diffraction. On the other hand, the shape features may be investigated using scanning electron microscopy.

The grain size is related to the line broadening β , through the simple Scherrer relation $\beta = 0.9\lambda/D\cos\theta$. The FWHM of every reflection of CeF₃ films was used to determine the grain size, while the instrumental broadening was evaluated from the (200) reflection of a standard YSZ (100) oriented single crystal. The crystallite size of the CeF₃ films was averaged over all the FWHM reflections and the value thus obtained is 59 ± 3 nm.

The size distribution and grain shape of CeF₃ films was analyzed by SEM. The SEM image [Fig. 2(a)] of the cerium fluoride film shows a homogeneous surface with constant

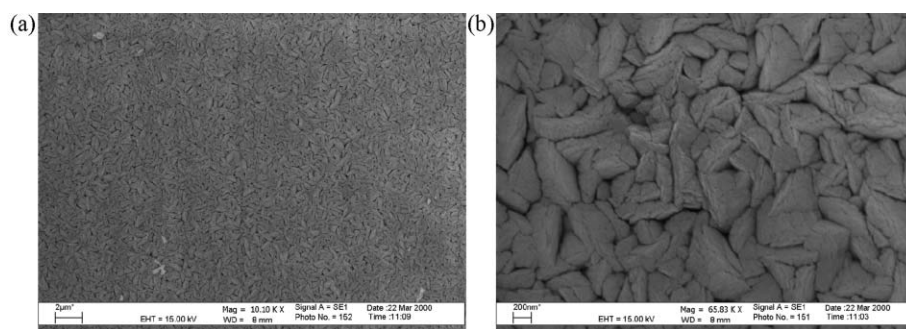


Fig. 2 (a) SEM image of a CeF₃ film surface, grown by MOCVD on a Si(100) substrate; (b) SEM image at high magnification of a CeF₃ film surface, grown by MOCVD on a Si(100) substrate.

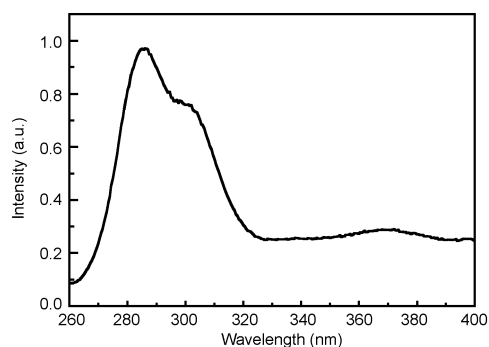


Fig. 3 Room temperature emission spectrum of a CeF_3 film surface grown by MOCVD on a Si(100) substrate, measured with excitation wavelength $\lambda_{\text{exc}} = 250$ nm.

particle size distribution. Each grain is *ca.* 500 nm and consists of aggregation of smaller particles [Fig. 2(b)].

The room temperature luminescence spectrum of the CeF_3 film on a Si(100) substrate was measured with a $\lambda_{\text{exc}} = 250$ nm excitation wavelength (Fig. 3). The film shows a strong luminescence intensity. The strong emission in the 260–330 nm range is assigned to unresolved transitions originating from the lowest state belonging to the $5d^1$ configuration to the levels $^2F_{5/2}$ and $^2F_{7/2}$ of the $4f^1$ configuration. We note that the spectral profile is similar to that measured at 12 K by Dujardin *et al.* for CeF_3 films deposited by MBE on Si(111).¹⁶ The present spectrum is less well resolved, probably due to the higher temperature presently adopted. The weak feature at higher wavelength (*ca.* 370 nm) is assigned to the same transitions for Ce^{3+} ions in perturbed sites, in analogy with the assignment made for similar bands by Auffray *et al.*¹⁵ and Dujardin *et al.*¹⁶ Since the relative intensity of this band can be used as a criterion for the crystal quality, these data indicate that present MOCVD thin films are somewhat less perfect than those fabricated *via* MBE.¹⁶

The excitation spectrum of the thin films under investigation measured with an emission wavelength $\lambda_{\text{em}} = 250$ nm, is shown in Fig. 4. The spectrum, although less resolved, shows several features similar to those observed by Dujardin *et al.*¹⁶ The bands in the 200–260 nm region are assigned to allowed $5d^1 \leftarrow 4f^1$ interconfigurational transitions, split by the combined effect of the crystal field of C_2 symmetry and spin orbit coupling.

The observed small reduction in the quality of the luminescence spectra, compared with those obtained for MBE films, could reflect the polycrystalline nature of the MOCVD films presently grown, and therefore the presence of a limited concentration of surface defects in the crystallites. As a matter of fact, the MBE films are expected to have a better texturing, although their possible epitaxial nature has not been characterized. This is a well-known issue. In fact, MBE films of

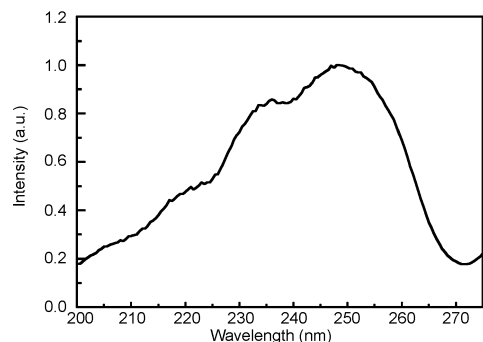


Fig. 4 Room temperature excitation spectrum of a CeF_3 film surface grown by MOCVD on a Si(100) substrate, measured with emission wavelength $\lambda_{\text{em}} = 286$ nm.

whatever materials are usually of higher quality than those prepared *via* MOCVD since they are obtained by a layer-by-layer growth mode.

Conclusions

The present study reports on the growth of CeF_3 thin films by MOCVD from the single source $\text{Ce}(\text{hfa})_3$ -diglyme precursor. To our knowledge, this represents the first report of MOCVD-grown CeF_3 films completed with a characterization of their luminescence properties. As already pointed out, the only reported study on the optical properties of CeF_3 thin films refers to materials obtained by MBE.¹⁶

The structural investigation points to the formation of an essentially random CeF_3 thin film, and SEM micrographs indicate that the deposited films are of good quality, with very homogeneous and smooth surfaces. Luminescence and excitation spectra are typical of CeF_3 single crystals and film samples, and consist of f–d allowed interconfigurational transitions.

The presence of the emission band near 370 nm, attributed to Ce^{3+} in perturbed sites, indicates that the present MOCVD films are somewhat less perfect than films obtained by MBE. Nevertheless, the simplicity and effectiveness of the MOCVD technique, in particular when a single liquid precursor is adopted, makes the method very promising and competitive for low-cost manufacturing of highly luminescent CeF_3 films.

Further work is in progress to grow oriented and/or epitaxial CeF_3 films by MOCVD and further focus on the impact of the structural properties of the films on their luminescence.

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