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Cerium-doped $SrHfO_3$ sol-gel films

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ABSTRACT

$SrHfO_3$ presents high density, which makes it interesting for host lattice when it is doped with rare earths for luminescent materials. The optical and structural studies of Ce^{3+}-doped strontium hafnate films prepared by the sol-gel process are presented in this work. Crack-free films with waveguiding performances were obtained with heat-treatments between 400°C and 700°C. The total elimination of organic compounds occurs above 800°C as indicated by Fourier transform infrared spectroscopy. The optogeometric properties (refractive index and thickness) are investigated by m-lines spectroscopy. Films structure is analysed using X-ray diffraction and transmission electron microscopy. The films crystallise from amorphous phase to pure $SrHfO_3$ orthorhombic phase at 750°C. The HfO_2 monoclinic phase superposes to $SrHfO_3$ orthorhombic phase after heat treatment performed at 1000°C. Finally, the potentiality to prepare Ce^{3+} activated $SrHfO_3$ sol-gel films with scintillation properties is explored.

Keywords: $SrHfO_3$, sol-gel, thin films, planar waveguide, scintillating film.

1 INTRODUCTION

The alkaline earth hafnate is a perovskite type compound ($Sr^{2+}Hf^{4+}O^{2-}{}_3$). The high density of $SrHfO_3$ (density around 7.6 g/cm^3), makes this compound attractive for host lattice activated by rare earth for applications as scintillating materials. Indeed, the high density of a material and the high atomic number of its constituents are characteristics for scintillating applications [1]. Recently, cerium doped $SrHfO_3$ materials have received attention because they are promising candidates for scintillation applications [2]. Up to now, $SrHfO_3$ has been elaborated using different methods such as solid state reaction [3], anodic spark conversion [4] for the bulk material and pulsed laser deposition [5] for the films.

The scintillating films can be obtained via sol-gel route [6] which allows the use of a large number of substrates. Sol-gel process arises as an elaboration method for high quality oxide materials. Moreover, the incorporation of doping agents with a good homogeneity at the molecular scale is very easy. This process is also well adapted to the preparation of very good quality thin films used as planar waveguides [7]. In addition, we take advantage of waveguide performances of the elaborated films to study the optical properties of sol-gel cerium-doped $SrHfO_3$. On one hand, it is well known that the optical properties of layers (refractive index, optical loss, etc.) are strongly dependent on the microstructure of the material. Therefore, several criteria such as porosity, grain size and grain boundaries must be taken into account to improve the performance of the films. On the other hand, well identified crystalline phase is necessary to improve scintillation properties of the films. Our layers were structurally characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The refractive index and the thickness of the waveguiding sol-gel films were determined by m-lines spectroscopy (MLS).

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of Ce^{3+} -Doped $SrHfO_3$ Sol-Gel Films

The starting solution was prepared using a stoichiometric mixture (Sr/Hf=1) of hafnium tetra-ethoxide ($Hf(OC_2H_5)_4$), (99.9%-Gelest) and strontium ethoxide, ($Sr(OC_2H_5)_2$). Cerium nitrate pentahydrated ($Ce(NO_3)_3$, $5H_2O$), (99.9%-Aldrich) is added as dopant in order to obtain a 1%mol concentration. The used

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solvent is 2-methoxyethanol and the sol elaboration is achieved in a nitrogen atmosphere (5% RH). The obtained sol was stable for more than four months. Further details on the preparation of the precursor solution are described by M. Villanueva-Ibáñez *et al.* [8].

The films were prepared from filtered solution using a 0.2 μm filter and deposited onto silica (Herasil® from Heraeus) substrates by the dip-coating technique (withdrawal speed of 30 mm/min) with a humidity controlled atmosphere (5%). After each coating, the layers were dried at 100°C and heat-treated at 400°C under oxygen flow to densify the layer and to remove the main part of organic compounds. Further details about sol-gel film deposition are described by Urlacher *et al.* [7]. Then, the films were annealed for 15 min. at temperatures ranging from 400°C up to 1000°C before analyses. Six successive coatings were required in order to get two propagating modes of each polarization (one transverse electric mode: TE_0 and one transverse magnetic mode: TM_0) in the film. Twenty two stacked layers were necessary to support two TE and two TM modes, i.e. TE_0, TE_1, TM_0, TM_1, respectively. At least such a number of modes was necessary for an accurate determination of refractive index and thickness of the film, assuming a step index model [9]. Fifty coatings were required to obtain a thick film (900 nm) for X-ray emission spectra measurements.

2.2 Investigation Methods

Differential thermal analysis (DTA) were performed in powder sample and Fourier Transform Infrared Spectroscopy (FTIR 2000, Perkin-Elmer) was carried out between 4000 cm^{-1} and 370 cm^{-1} on the films annealed from 400°C up to 800°C in order to supplement the observations obtained by DTA. X-ray diffraction (XRD) measurements are achieved using a SIEMENS D500 X-ray diffractometer. The structure deduced from the XRD patterns is confirmed by transmission electron microscopy (TEM) using a TOPCON EM-002B operating at 200 kV equipped with energy dispersive spectroscopy (EDS) device to determine the Sr/Hf ratio into the film. Thickness and refractive index of the films are obtained by m-lines spectroscopy operating at λ=543.5 nm, this method was described by Ulrich and Torge in reference [9]. Optical losses are measured using the light beam of a 10 mW polarized He-Ne laser (λ=632.8nm) launched into the waveguide. The scattered light during the waveguided propagation of the laser beam is directly analyzed by a microcomputer-assisted video camera system [10]. For X-rays emission spectra measurements, an X-ray generator (XRD3000 INEL) is operated at 35 kV with a tungsten anode. The signal is detected using a monochromator Triax 320 with a CCD detector.

3 RESULTS AND DISCUSSION

In Figure 1 is presented the differential thermal analysis (DTA/TG) of a powder sample, in order to understand the evolution of the material with the heat-treatment. An important exothermic change starts at 90°C and presents a maximum at 800°C. The exothermic curve between 90°C and 700°C is attributed to the elimination of the organic compounds most volatile as attests the loss of corresponding mass and the analysis FTIR of powder (not presented here). The crystallization of the $SrHfO_3$ at 600°C occurs simultaneously. A significant loss of mass occurs between 700°C until 900°C and is probably due to the decomposition of the less volatile carbonaceous compounds.

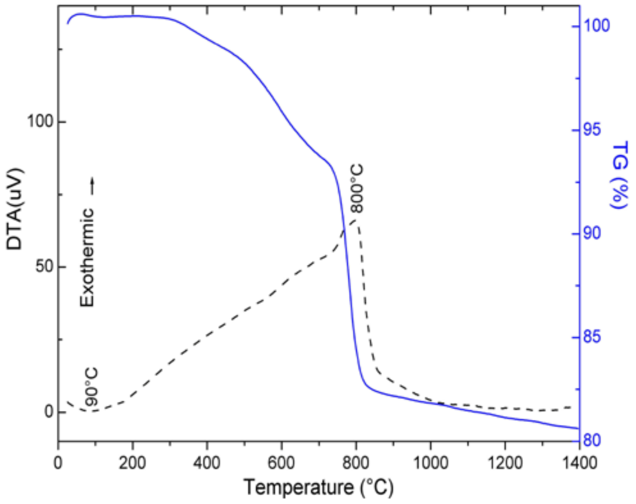

Figure 1: DTA/TG analysis for $SrHfO_3$:Ce 1%mol powder dried at 90°C.

The FTIR measurements are recorded to determine the thermal decomposition of the organic compounds in the films. In all spectra, presented in Figure 2, the bands located around 1040 cm^{-1} and 802 cm^{-1} are assigned to the silica substrate contribution. The spectrum of the film annealed at 400°C exhibits small peaks around 1400-1500 cm^{-1} which can be attributed to C–O, C=O stretching vibrations of organic residuals.

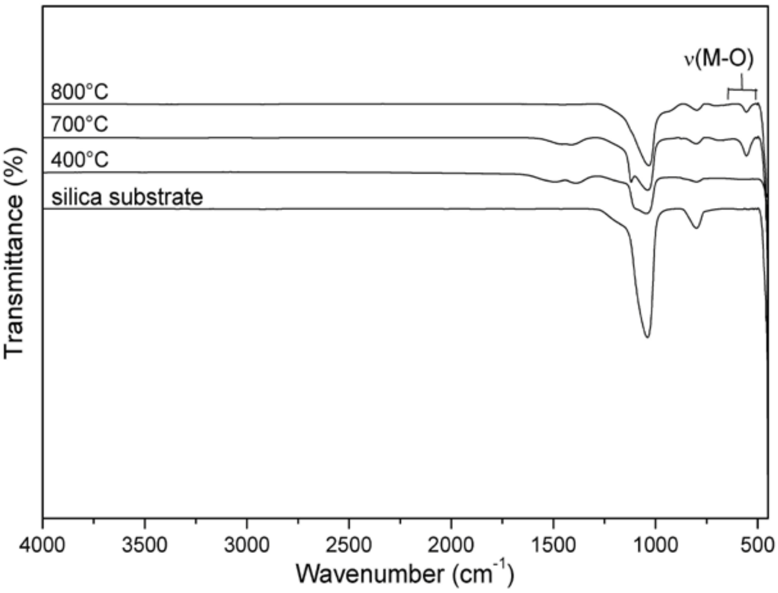

Figure 2: IR-spectra of the $SrHfO_3$:Ce^{3+} 1%mol (Sr/Hf=1) film deposited onto 1 mm thick silica substrate and heat-treated at different annealing temperatures.

The intensities of these bands decrease when the annealing temperature increases and they are completely eliminated after an annealing treatment at 800°C (see inset Figure 2). The band corresponding $SrHfO_3$ appears at 560 cm^{-1} [11] after a heat-treatment at 700°C.

The XRD pattern of the sample annealed at 1000°C is shown in Figure 3 and indicates that two phases are observed in the film. Some peaks (labeled using an open circle) are related to $SrHfO_3$ orthorhombic phase (JCPDS file No. 88-0014) and some others (labeled using a star) are due to HfO_2 monoclinic phase (JCPDS file No. 43-1017). In order to confirm XRD analysis, TEM observations are performed.

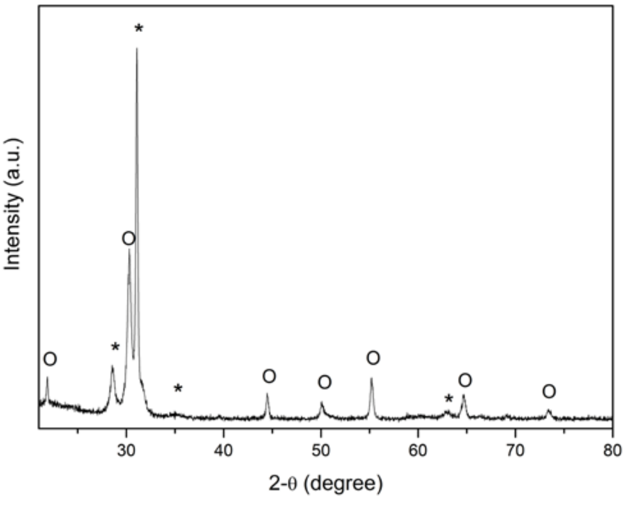

Figure 3: X-ray diffraction pattern of a Ce^{3+}-doped $SrHfO_3$ film heat-treated at 1000°C. The open circles and stars are assigned to $SrHfO_3$ orthorhombic phase and HfO_2 monoclinic phase, respectively.

For TEM studies, the films are peeled off from the substrate and put onto a microscope grid. In order to results obtained by DTA and FTIR, the sample has considerable amounts of organic compounds above 800°C, for this reason the TEM observations are conducted on samples heat-treated up to 750ºC. Figure 4a presents the TEM observations and the associated electron diffraction pattern of a 750°C heat-treated film. The film is partially crystallized and constituted by small crystallites exhibiting a diameter size around 10 nm. Their crystalline phase is determined to be orthorhombic $SrHfO_3$. Some of them are associated and organized into randomly oriented lamellae with a length around 140 nm. Amorphous phase is still present at this temperature as observed by high resolution transmission electron microscopy image (HR-TEM) (Figure 4b). When the annealing temperature increases to 1000°C, the lamellae structure has disappeared (see Figure 4c). The crystallized film appears as homogeneous and is constituted by small uniform crystallites with a grain size in the range between 20 and 30 nm (Figure 4c). The rings diameter of the associated electron diffraction pattern corresponds to the lattice spacing of $SrHfO_3$ orthorhombic phase (JCPDS 88-0014) and HfO_2 monoclinic phase (JCPDS file no. 43-1017). This observation confirms the XRD analysis for the films and previous results obtained for powders [11].

By using EDS, the film heat-treated at 1000°C presents a mean Sr/Hf ratio slightly lower than 1. Nevertheless, a ratio lower than expected (Sr/Hf = 0.7) is obtained in some areas of the film. For this the reason the HfO_2 monoclinic phase also detected in the final material.

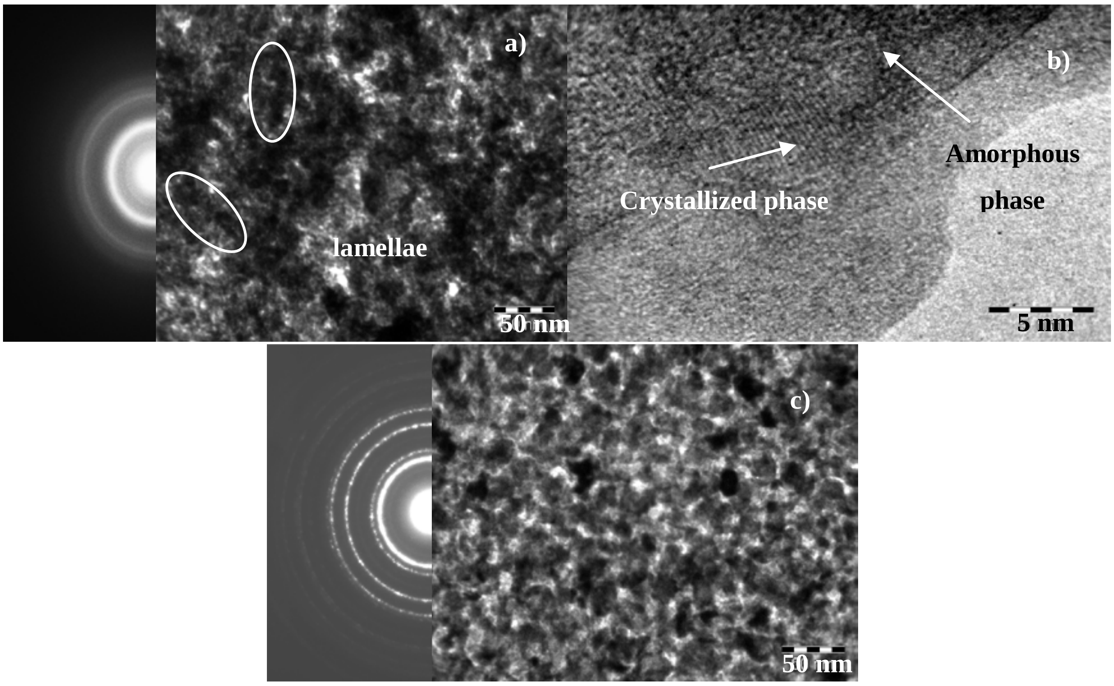

Figure 4: Transmission electron microscopy studies of 1%mol Ce^{3+}-doped $SrHfO_3$ films deposited onto silica: TEM image and diffraction pattern of a sample annealed at 750°C (a), HR- TEM observation of a layer heat-treated at 750°C (b), TEM image and diffraction pattern of a sample annealed at 1000°C (c).

The good optical quality of the films showed in Figure 5 allows to use them as waveguiding layers. At 400°C the amorphous films present waveguiding properties with a propagation length of 7 mm. An attenuation coefficient $\alpha = 4.0\pm0.5$ dB/cm is measured. The presence of lamellae and crystallites with grain size as great as several tens of nanometers explains the loss of waveguiding properties of the layer annealed at 750°C and 1000°C, respectively (see Figure 4).

Refractive index and thickness varied from 1.795±0.001 to 1.810±0.001 and from 430±3 nm to 375±3 nm after annealing treatment at 400°C and 700°C respectively. The increase of the refractive index and the decrease of the thickness are a consequence of the layer densification and the organic compounds removal. The film turns opalescent after heat treatment at 750°C due to the crystallization as mentioned above and its optical quality is not good enough to allow neither m-lines measurements nor attenuation coefficient determination.

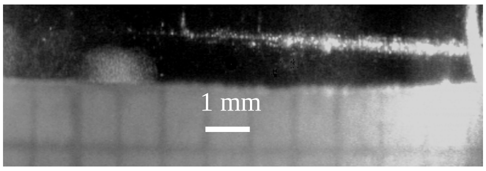

Figure 5: A laser beam propagation in a Ce^{3+}-doped $SrHfO_3$ (Sr/Hf=1) waveguide (TE_0 mode).

Room temperature emission spectrum under X-ray excitation from the Ce^{3+} 1% doped $SrHfO_3$ film heat-treated at 1000°C was recorded. The intensity of emission spectrum of this film is given on Figure 6.

The characteristic large emission spectrum of cerium 3+ with a maximum at 400 nm is conducted on the 1000°C heat-treated sample. As it were expected, the intensity of this emission is smaller to comparison with the reported for the powders [8].

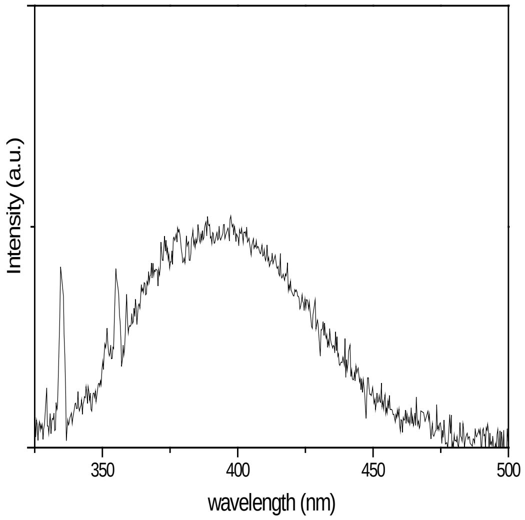

Figure 6:. Room temperature emission spectrum under X-rays excitation of $SrHfO_3$:Ce 1%mol sol-gel film with 900nm thickness and heat-treated at 1000°C.

Different parameters can be at the origin of this low intensity. The most important are probably a thickness too low and annealing at temperatures limited to 1000°C (what supports the majority presence of the ion Ce^{4+}). Just like in the case of the powders [8], it seems difficult to obtain films mainly crystallized in the orthorhombic phase $SrHfO_3$ pure. Indeed, in the case of the powders the presence of the HfO_2 monoclinic phase did not deteriorate the performances in scintillation since they had a well defined crystalline structure and they contained the Ce^{3+} ions.

4 CONCLUSIONS

Crack-free Ce^{3+}-doped strontium hafnate films are elaborated using the sol-gel process. Transparent and amorphous films heat-treated below 700°C present waveguiding properties. The structural analyses indicate that the crystallization of the film starts after an annealing treatment at 750°C and the appearance of lamellae structure explains the loss of waveguiding properties of such films. The structural analyses of the scintillating films indicate that depending on annealing temperature between 750°C and 1000°C one or two crystallized phases are observed.

The intensity of emission under excitation X of the thicker films, treated with 1000°C was observed but this intensity is far of being intense. Thickness too low and heat treatment at temperatures limited to 1000°C (this supports the majority presence of the ion Ce^{4+}) explain partly why the film has this intensity of emission under X-rays excitation. An important purpose derived from this study is to increase the film thickness because thick layers are necessary to provide efficient scintillators.

5 ACKNOWLEDGEMENT

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