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Synthesis and properties of Lu_2O_3 sol–gel films

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Abstract

Lutetium oxide films have been prepared by the sol–gel method and the dip-coating technique. Transparent and crack free coatings are obtained. Differential Thermal Analysis and Infrared spectroscopy were conducted on the dried sol–gel solution in order to determine the structure dependence of the material with temperature. The film microstructure was studied by Raman microscopy and X-ray diffraction. The crystallization of the lutetium oxide phase occurs at 600°C. Opto-geometrical parameters were determined depending on the annealing temperature. After heat treatment at 1000°C, very dense lutetium oxide films are obtained exhibiting a refractive index around 1.8 at 543.5 nm and a thickness of 410 nm.

Keywords: Thin films; Chemical synthesis; X-ray diffraction; Optical properties; Thermal analysis

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1. Introduction

In recent years, there has been a growth of interest in gadolinium phosphors preparation as host lattice constituent activated by rare earth (Gd_2SiO_5:Ce, Gd_2O_5S:Tb), mainly for their interesting scintillation properties in high resolution X-ray imagery [1,2]. These materials allow to use the green and blue emitting films inside of the detection system. Nowadays the use of CCD cameras is increasing with films in which sensibility is much better for red radiation.

Such application requires dense materials able to absorb high-energy photons. On the one hand europium activated dense materials as gadolinium and lutetium are very attractive because europium presents red emissions. On the other hand, high light diffusion is present into the grain size of the commonly used powders, which reduces spatial resolution. The film configuration appears to be an interesting alternative to reduce diffusion phenomena and to improve scintillation properties. Phosphors films are shown to be a very promising materials for high resolution display devices with low loss diffusion [3].

Sol–gel method is an excellent option to prepare high densified and high purity layers. Europium doped gadolinium oxide thin films with scintillation properties have been recently and successfully prepared by sol–gel process [4]. Nevertheless, lutetium oxide is known to be a denser material than gadolinium oxide. As a consequence doped Lu_2O_3 would then present a better luminescence efficiency than doped gadolinium oxide for scintillation properties. Sol–gel lutetium oxide films are thus prepared for the first time and their structural and opto-geometrical properties are studied and presented.

2. Experimental procedures

The lutetium oxide solution was prepared using as precursor lutetium(III)-2,4-pentanedionate, $Lu(CH_3COCHCO–CH_3)_3$.

The powder was dissolved in anhydrous isopropanol under strong agitation and controlled atmosphere in order to prevent hydrolysis of the precursor. The solution is then hydrolyzed in order to prepare a 0.23 M precursor sol. A yellow sol was obtained which was clear and stable for deposition stage.

The solution was filtered using a 0.2 μm Millipore filter and was immediately deposited on high polished silica substrates (Herasil from Heraeus®). Prior to their use, the substrates were carefully cleaned using a special procedure [5]. The solution was dip-coated with a constant withdrawal speed at ambient atmosphere in a glow box to avoid dust contamination.

At least 45 successive coatings are required to provide crack-free films presenting two optical transverse electric and transverse magnetic modes at 543.5 nm. This special

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feature is necessary to determine precisely both refractive index and thickness using m-lines measurements [6].

The coated films were dried at 100°C and annealed at 400°C between each coating in order to remove organic solvents. The layers were then successively heat-treated for 1 h at temperatures ranging from 400 to 1000°C. This procedure allows to obtain homogeneous and good optical quality films.

3. Results and discussion

3.1. Thermal behavior of the lutetium dried gel

The precursor solution was dried at 120°C for 24 h. A pale-yellow gel was obtained.

Differential Thermal Analysis (DTA) and Thermo Gravimetry (TG) measurements were conducted on the gel powder using a Netzsch-STA 409C apparatus. The DTA and TGA thermograms shown in Fig. 1 were recorded at a scan rate of 5°C min^{-1} under a flux of air.

The thermal behavior shows one endothermic peak A (110°C), which is assigned to the evaporation of residual water–isopropanol on the surfaces of the micropores. Two exothermic peaks are observed: the large exothermic peak B (400°C) corresponds to the decomposition of lutetium acetylacetonate and the broad second peak C (around 650°C) can be attributed to the beginning of lutetium oxide crystallization into the cubic phase. This was confirmed by XRD analysis presented in Section 3.3. About 40% of the weight loss, during the decomposition reaction are also observed in the TG thermogram (see discontinuous curve).

3.2. Dried gel IR absorption bands

Fourier Transform Infra-Red (FTIR) absorption spectra in the range 4000–360 cm^{-1} were recorded for the lutetium dried gel powder. This powder was heat-treated at different temperatures ranging from 400 to 1000°C. The typical spectra are shown in Fig. 2. Spectrum 'a' corresponds to the coating dried solution and is characterized by the bands corresponding to the coordination of the lutetium acetylacetonate compound [7].

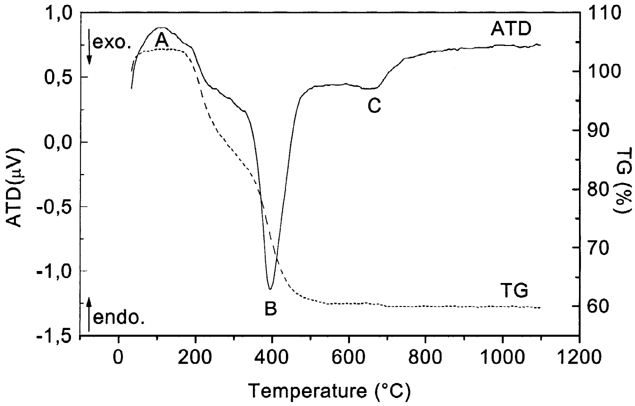

Fig. 1. DTA and TG thermograms of dried lutetium gel powder (heating rate: 5°C min^{-1}).

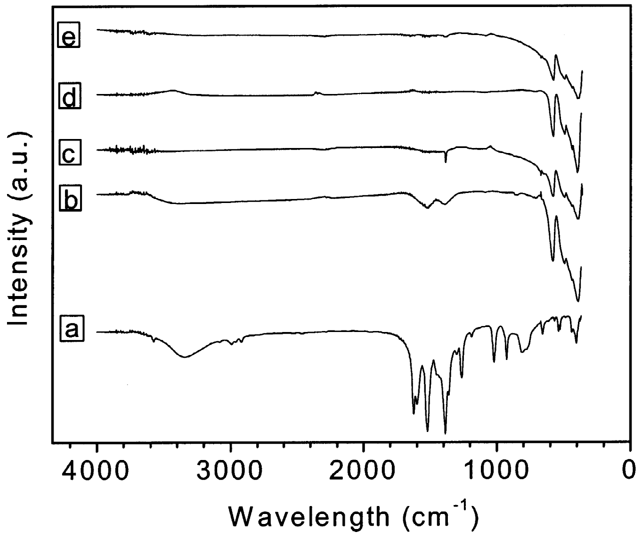

Fig. 2. IR spectra of the lutetium gel powder heat-treated for 1 h at 120 (a), 400 (b), 600 (c), 1000°C (d), and $\mathrm{Lu_2O_3}$ commercial powder (e).

This spectrum presents bands in the region 1605–1560 cm^{-1} and 1550–1500 cm^{-1} due to the $\mathrm{C}\,\overline{\cdots}\,\mathrm{O}$ and $\mathrm{C}\,\overline{\cdots}\,\mathrm{C}$ stretching vibrations. A second strong band is observed near 1380 cm^{-1} due to $\mathrm{CH_3}$ stretching vibration. The bands due to $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretching vibrations for these complexes are found at about 1540 and 1290 cm^{-1}. The acetylacetonate compound has two additional bands at 690–490 cm^{-1} and may also absorb near 430 cm^{-1} and at 400 cm^{-1}.

The gel powder heat-treated at 400°C (spectrum 'b') presents two bands at 1520 cm^{-1} due to $\mathrm{C}\,\overline{\cdots}\,\mathrm{O}$ and $\mathrm{C}\,\overline{\cdots}\,\mathrm{C}$ and 1380 cm^{-1} due to $\mathrm{CH_3}$ stretching vibration, which indicates that the acetylacetonate decomposition continues up to 450°C as is confirmed by the DTA thermogram (peak B). The powder heat-treated at 600°C (spectrum 'c') and 1000°C (spectrum 'd') present bands at 575, 490, and 437 cm^{-1}. These bands appear in the commercial powder spectrum (spectrum 'e') and are attributed to the crystallized lutetium oxide absorption bands [8].

3.3. X-ray diffraction results

The structure of the lutetium oxide layers are investigated using X-ray diffraction. XRD patterns, presented in Fig. 3, were obtained on 600 (a) and 1000°C (b) heat-treated lutetium oxide films.

The crystallization of the layer appears at 600°C. The complete series of Bragg reflections observed on the 600 and 1000°C heat-treated layers correspond to the cubic

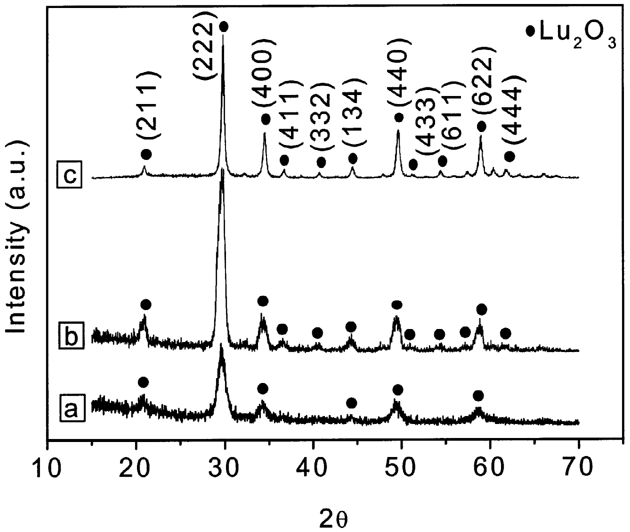

Fig. 3. XRD patterns of the lutetium film heat-treated for 1 h at 600 (a) and 1000°C (b). XRD pattern of lutetium oxide gel powder heat-treated at 1000°C (c).

Lu_2O_3 phase. The lutetium oxide cubic phase is already formed at 600°C and the band intensities increase with temperature up to 1000°C.

The lutetium gel powder heat-treated at 1000°C (Fig. 3(c)) and crystallized in the cubic phase (see IR analysis) confirms these results. Non a special oriented structure was observed neither using X-ray nor microscopy analyses, but the size of the crystallites present in the lutetium oxide film heat-treated at 700°C varies from 5 to 10 nm.

3.4. Raman spectroscopy measurements

Raman analyses were conducted on the lutetium oxide film and also on the cubic commercial powder. The micro Raman spectra were carried out using a micro Raman apparatus (Dilor XY).

The Raman spectrum of cubic Lu_2O_3 is presented for the first time (Fig. 4(b)) and is characterized by the main band at 390 cm^{-1}. This band was clearly confirmed by anti-stokes observations. The micro Raman spectrum of the film (Fig. 4(a)), is largely perturbed by the silica substrate contribution but the main band at 390 cm^{-1} (see arrow) is clearly identified, indicating that the film crystallizes in the cubic phase.

3.5. Opto-geometrical results

The thickness and refractive index of lutetium oxide films were measured using m-lines spectroscopy conducted at 543.5 nm [6]. The study was conducted on the 45 multimode layers annealed at different temperatures. These results are presented in Fig. 5.

The thickness of the 45 layers decreases from 570±1 nm (400°C) to 410±1 nm (1000°C). Approximately 70% of the thickness decreases before 600°C heat treatment indicating that the major part of the densification of the layer simultaneously occurs with the solvents and lutetium acetylacetonate decomposition. The densification of the layer continues during the lutetium oxide crystallization. The refractive index increases from 1.700±0.001 (400°C) to 1.790±0.001 (1000°C).

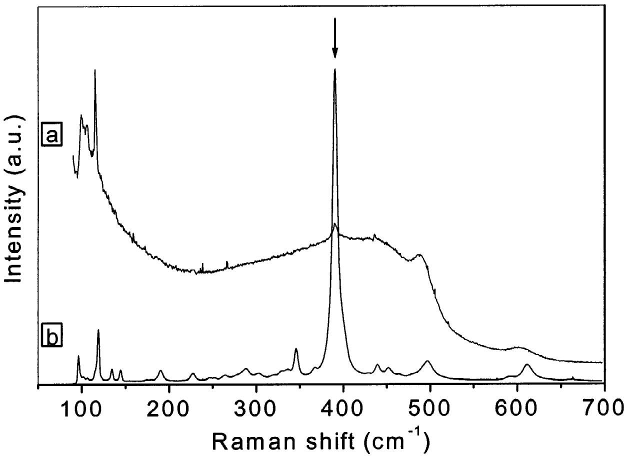

Fig. 4. Raman spectroscopy spectra of Lu_2O_3 film heat-treated at 1000°C (a) and commercial powder (b).

4. Conclusion

Crystallized, dense and crack-free Lu_2O_3 films have been successfully elaborated by sol–gel process. Lutetium acetylacetonate precursor allows to obtain a stable and transparent solution used to coat homogeneous and good quality layers. The lutetium oxide infrared absorption bands appear at 600°C, which is in agreement with XRD patterns. The crystallization corresponds to cubic phase which remains stable up to 1000°C. The increase of size particles allows to continuously increase the refractive index up to 1.790±0.001 after a 1000°C annealing treatment. The Lu_2O_3 layers are currently studied with Eu^{3+}

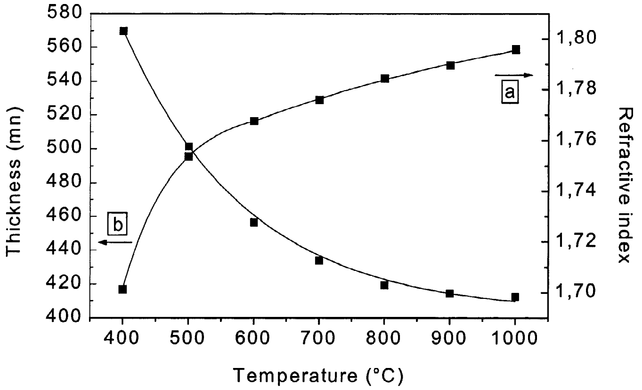

Fig. 5. Evolution of refractive index at 543.5 nm (a) and thickness (b) of Lu_2O_3 films under different annealing temperatures.

doping for scintillating applications. These results will be published later.

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