Preparation of $Y_3Al_5O_{12}:Eu^{3+}$ waveguide films by sol-gel method

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ABSTRACT

$Y_3Al_5O_{12}:Eu^{3+}$ (5 mol% Eu^{3+}) optical thick films were obtained by sol-gel process and dip-coating technique. The synthesis was accomplished using $Al(OC_4H_9)_3$, $YCl_3 \cdot 6H_2O$, isopropanol and $Eu(NO_3)_3 \cdot 5H_2O$. The chelating agent was ($CH_3COCH_2COCH_3$, acacH). After the deposition stage, the YAG:Eu^{3+} films were dried and annealed for 1 h at 700, 900 and 1100 °C. Multilayers were deposited to obtain multimode waveguides. X-Ray diffraction analysis confirmed that $Y_3Al_5O_{12}:Eu^{3+}$ films presented characteristic YAG structure. Microscopic observations (HRTEM) of the films heat-treated at 1100 °C revealed that the YAG:Eu^{3+} films were constituted of particles with diameters of about 25 nm. The optogeometrical characteristics as thickness (*t*) and refractive index (*n*) were performed using the M-Lines Spectroscopy (MLS) using a He-Ne laser (632.8 nm). These results showed that the thickness and refractive index of the $Y_3Al_5O_{12}:Eu^{3+}$ film after a heat treatment at 1100 °C were 1.3 µm 1.6385 ± 0.001 respectively.

Keywords: sol-gel, waveguides, europium, m-lines, yttrium aluminium garnet.

1 INTRODUCTION

Planar and channel waveguides are used nowadays to build integrated photonic devices to be applied in optical communication as high-speed switches (operating at THz) as well as amplifiers and laser emitters in compact systems [1-4].Compounds in the system Y_2O_3-Al_2O_3 are promising materials for optical, electronic, advanced waveguide applications due to their chemical stability. Specifically, the cubic structure of yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) is characterized by their important applications as solid-state laser material widely used for fiber-optic telecommunication systems [5,6]. The specific optical properties are highly sensitive to the changes in ion dopants, host stoichiometry and processing conditions. This compound has been produced by conventional routes as the solid state reaction requiring high processing temperatures (above 1600 °C) [7], but when the reactants were heated below this temperature, it could not be obtained as a single phase coexisting with other phases [8]. The sol-gel route is an excellent option to produce high quality pure metal oxides, due to the absence of grinding and pressing steps, and lower processing temperatures to be used for derived ceramics [9]. The main objective of this work is to study the optogeometrical properties as a function of annealing treatment using M-lines spectroscopy. XRD and HRTEM were used to confirm the structural properties. SEM and AFM observation were done in order to analyze the quality of the films.

2 EXPERIMENTAL SECTION

2.1 Experimental procedure

Europium doped YAG films were prepared using the sol-gel process and dip-coating technique. A transparent sol was prepared mixing $Al(OC_4H_9)_3$ (Sigma-Aldrich, 99.9%) and acetilacetone, acac(H) (Aldrich 99%) in isopropyl alcohol (Fermont, 99.9%) in a molar ratio 1:0.5:60 respectively, sol *A*. Yttrium chloride (Alfa Aesar, 99.9%) was dissolved in isopropyl, sol *B*. Both sols were mixed under vigorous magnetic stirring at room temperature, the pH was 6. Finally, $Eu(NO_3)_3 \cdot 5H_2O$ (1 % mol/Al) was dissolved in isopropyl alcohol and the whole solution was stirred at room temperature for 1 h. The europium doped YAG precursor solution filtered through 0.22 µm was dip-coated on silica substrates. In order to obtain multimode waveguides 32 layers were deposited. The europium doped YAG films were heat treated between each coating at 100 °C and 300 °C for 10 min. The layers were heat treated at different temperatures ranging from 300 °C to 1100 °C. At this stage, crack free and transparent europium doped YAG thick films multilayers were obtained.

2.2 Apparatus

The structure and crystallinity of the films were determined by an automated powder diffractometer (D8 Advance Bruker) and using a CuKα monochromatized radiation at 40 kV, 20 mA over the 2θ range 25-90º (0.1º/s) by X-ray powder diffraction and by High Resolution Transmission Electron Microscopy (HRTEM) measurements were performed using a JEOL Microscope operating at 200 kV. In order to determine the quality of the films, SEM and AFM analysis was carried out (Jeol 3200, 20 kV) and Nanoscope IV apparatus (Digital Instruments) in tapping mode on a europium doped YAG sample at 1150°C. The AFM analyses were carried out in air and at room temperature. The scan rate was about 1 Hz. For each sample, at least four areas were imaged in height and phase mode. The RMS roughness of the surface is calculated (with flattening corrections) on the z-scale as a standard deviation from AFM measurements and the pore size is measured by means of a cross-section (built-in software). Finally, the optogeometrical characteristics, such as thickness and refractive index, were investigated by m-lines spectroscopy (MLS). A 60 º LASF35 prism was used for coupling the light of He-Ne laser with a λ= 632.8 nm and 12 mW. Spectral transmittance of the films has been measured by UV-Vis-NIR Spectrophotometer (Perkin-Elmer, Lambda 9) in the spectral range from 400 nm to 1100 nm. These results have also been used to calculate the thickness of the coatings using the Swanepoel method [10].

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3 RESULTS AND DISCUSSIONS

3.1 Structural studies

Figure 1 shows the XRD patterns of europium doped $Y_3Al_5O_{12}$ films deposited on quartz substrate thermally treated at 700°, 900° and 1100 °C. In this Figure it can be notice the presence of a bragg reflexion appearing at 31.6° probably associated with the formation of monoclinic Al_2O_3 corresponding to the theoretical interreticular distances of the ($\bar{4}$ 0 1) plane. It is also notice that as temperature increases up to 1100 °C, the X-ray diffraction pattern of the as-deposited layers displays the crystallization of the YAG:Eu^{3+} corresponding to typical diffraction peaks of cubic phase (JCPDS 33-40). The crystallite sizes D (nm) in films were deduced and estimated by the Debye-Scherer equation [11] from the width of the (4 2 0) diffraction peak line for film heat-treated at 1100 °C. The crystallite size of the europium doped $Y_3Al_5O_{12}$ was 35 nm in agreement with Wu *et al.* [12] observed in YAG layers elaborated by sol-gel process and heat treated at 1000°C.

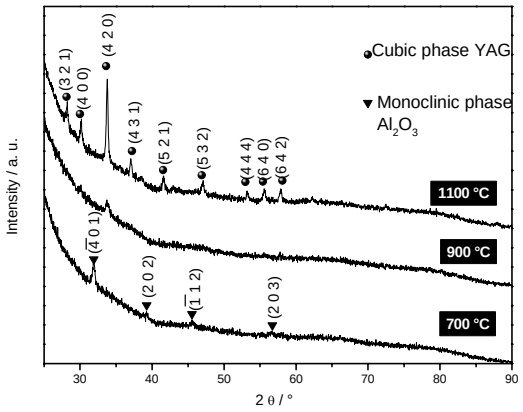

Figure 1. XRD patterns of $Y_3Al_5O_{12}:Eu^{3+}$ films heat treated at different temperatures.

3.2 Morphological studies

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Figure 2 depicts AFM micrograph of the surface of $Y_3Al_5O_{12}:Eu^{3+}$ waveguides films annealed at 1150 °C for 1 hour with 32 layers. The surfaces appear to be uniform, smooth and free from cracks. It can be observed that the $Y_3Al_5O_{12}:Eu^{3+}$ films consist of small crystalline particles of about 30-40 nm in average diameter. So it is reasonable to say the substituted Eu^{3+} ions can act as a grain growth inhibitor in YAG films.

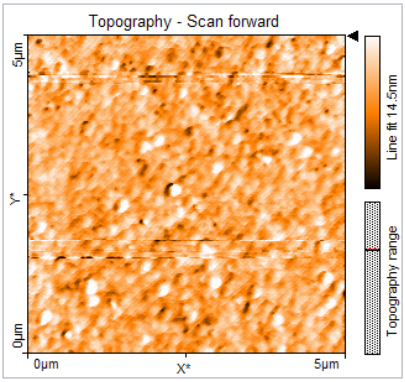

Figure 2. Top-view of AFM topography micrographs of $Y_3Al_5O_{12}:Eu^{3+}$ heat treated at 1100 °C.

This conclusion is consistent with the XRD result. The root-mean-square roughness (RMS) estimated from the AFM measurement for the surface of $Y_3Al_5O_{12}:Eu^{3+}$ film is 10 nm. This interesting observation could indicate that a good control of sintering temperature allows a good homogeneity in the morphology and composition of the $Y_3Al_5O_{12}:Eu^{3+}$ compound to prepare thin films.

3.3 Microstructural studies

SEM micrograph of the surface of $Y_3Al_5O_{12}:Eu^{3+}$ waveguiding films heat treated at 1100 °C is shown in

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Figure 3. It is seen that the surface of the film is uniform consist of fully grown and crack-free structures constituted by homogeneous networks. The microstructure was controlled by the calcination temperatures. These microstructure features would be greatly beneficial to obtain fully densified polycrystalline $Y_3Al_5O_{12}:Eu^{3+}$ specimen with high transparency. The morphology not reveals well formed grains, as was confirmed by AFM studies; moreover XRD of the powders gives a cubic feature probably due to the presence of some crystals which still remain in the cubic forms. The $Y_3Al_5O_{12}:Eu^{3+}$ waveguiding films could be heated without cracking by using alkoxide precursors.

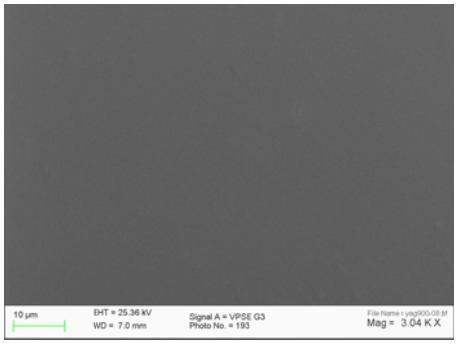
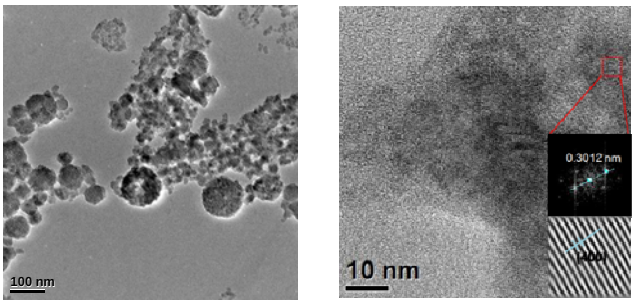


Figure 3. SEM image of $Y_3Al_5O_{12}:Eu^{3+}$ film calcined at 1100 °C.

In Figure 4 a,b we present TEM and HRTEM images of $Y_3Al_5O_{12}:Eu^{3+}$ layers heat treated at 1100 °C respectively. For these analyses, the as-deposited layers were peeled off from silica substrate.



(a) (b)

Figure 4. TEM micrograph of $Y_3Al_5O_{12}:Eu^{3+}$ (1 %mol) transparent ceramic (a) and high resolution lattice image of adjacent $Y_3Al_5O_{12}$ grains showing the morphology of grain boundary (b).

The TEM micrograph shown in Figure 4a presented typical microstructure morphology of $Y_3Al_5O_{12}$ ceramics, exhibiting that there was no secondary grain boundary phase existing at grain boundary. The high-resolution micrograph in Figure 4b revealed the lattice image, which further proves that no residual impurity was observed at grain boundary. This image also suggests that the crystallized particles exist within the amorphous part of film, in which crystallites around 30 nm were formed. The interreticular planes visible in $Y_3Al_5O_{12}:Eu^{3+}$ film has been indexed by means of Fourier transform of the images in order to determine interreticular distances. The measured distance 0.3012 nm is in perfect agreement with those expected for the cubic YAG, corresponding to the theoretical interreticular distances of the (4 0 0) plane.

3.4 Optogeometrical parameters

The optogeometrical parameters were determinate by means of m-lines spectroscopy using a He-Ne laser (λ=632.8 nm) [13]. According to the MLS requirement, at least 2 propagation modes are necessary to carry out the measurement, therefore a sufficient number of stacked layers have to be deposited in order to satisfy this requirement. Since the optogeometric parameters of the films strongly depend on the sols behavior, different numbers of layers are needed to be deposited for both systems in order to obtain a desired number of the propagation modes [14, 15]. In this work, 32 stacked layers are necessary to be coated to obtain 2TE and 2 TM modes (transverse electric and transverse magnetic, respectively). The optogeometrical parameters are presented in Figure 5.

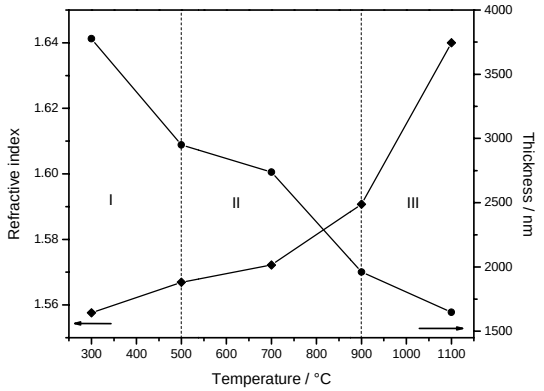


Figure. 5 Evolution of refractive index at 632.8 nm and thickness of $Y_3Al_5O_{12}:Eu^{3+}$ layers as a function of heat treatments.

The MLS measurements indicate that the refractive index (n) of the as-deposited layers heat-treated varies from 1.558 ± 0.001 at 300 °C to 1.640 ± 0.001 at 1100 °C. Their ass associated films thickness (t) are 3775 nm and 1647 nm for 300 and 1100 °C respectively. Generally, the sol–gel thin films accommodate the organic compounds which reduce the mean refractive index of the films and need to be heated at a certain high temperature to eliminate the organic residues. Fortunately, the YAG layers with 32 nm remains crack free after an 1100 °C heat treatment with a reduction of thickness related with evaporation of residual organic compounds. Figure 5 confirms that the refractive index decreases as the temperature increases which is associated

with crystallization of YAG layers into cubic phase. The improvement of refractive indices suggests three steps as is shown in Figure 5. **:** 300 °C - 500 °C, 500 °C – 900 °C and 900 °C -1100 °C. The first increasing step is due to the organic decomposition, the intermediate step is mainly attributed to the formation of monoclinic Al_2O_3, and, finally**,** the last step is due to crystallization of YAG:Eu^{3+} into cubic structure and also is due to densification process. Spectral dependencies of thickness were calculated from the optical transmission spectra of $Y_3Al_5O_{12}$:Eu^{3+} annealed waveguiding films using the Swanepoel method [16, 17], Figure 6.

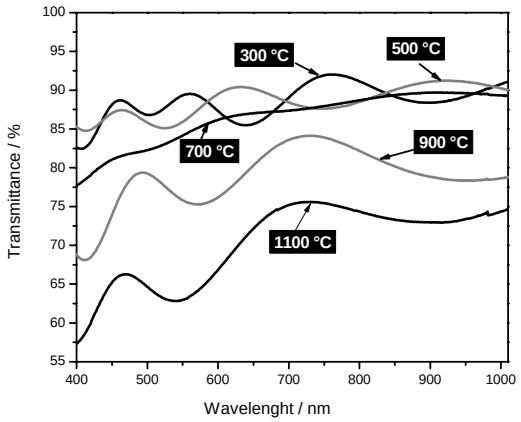


Figure 6. Optical transmission spectra of $Y_3Al_5O_{12}$:Eu^{3+} as a function of the heat treatment.

Table 1, summarizes the thickness of the $Y_3Al_5O_{12}$:Eu^{3+} waveguiding films prepared at different heat treatment. The film thickness for the $Y_3Al_5O_{12}$:Eu^{3+} annealed at 1100 °C was found to be about 1686 nm in agreement with that determined using m-lines spectroscopy.

Table 1. $Y_3Al_5O_{12}$:Eu^{3+} waveguiding films thickness determined by Swanepoel method.

YAG:Eu^{3+}	**Temperature / °C**				
	300	500	700	900	1100
Thickness / nm	3296	2230	2054	1890	1686

Conclusions

Europium-doped $Y_3Al_5O_{12}$ optical waveguide films were successfully obtained by sol-gel process and dip-coating technique. The crystalline structure was determined by XRD and HRTEM, both techniques evidenced the formation of cubic phase after heat treated at 1100 °C, the layers were constituted of crystallites with mean crystal size of 35 nm. SEM and AFM studies shown crack-free films composed by homogeneous networks. Optogeometrical properties shown that YAG:Eu^{3+} layers heat treated at 1100 °C presented a increase of refractive index (n) up to 1.640 ± 0.001 and a decrease of thickness (t), achieving 1647 nm associated with crystallization and densification process in agreement with Uv-Vis measurements. These layers present promising characteristics to be used in waveguiding applications.

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