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Elaboration and optimization of (Y,Er)$Al_3(BO_3)_4$ glassy planar waveguides through the sol–gel process

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In this work, a sol–gel route was used to prepare $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ glassy thin films by spin-coating technique looking for the preparation and optimization of planar waveguides for integrated optics. The films were deposited on silica and silicon substrates using stable sols synthesized by the sol–gel process. Deposits with thicknesses ranging between 520 and 720 nm were prepared by a multi-layer process involving heat treatments at different temperatures from glass transition to the film crystallization and using heating rates of 2 °C/min. The structural characterization of the layers was performed by using grazing incidence X-ray diffraction and Raman spectroscopy as a function of the heat treatment. Microstructural evolution in terms of annealing temperatures was followed by high resolution scanning electron microscopy and atomic force microscopy. Optical transmission spectra were used to determine the refractive index and the film thicknesses through the envelope method. The optical and guiding properties of the films were studied by *m*-line spectroscopy. The best films were monomode with 620 nm thickness and a refractive index around 1.664 at 980 nm wavelength. They showed good waveguiding properties with high light-coupling efficiency and low propagation loss at 632.8 and 1550 nm of about 0.88 dB/cm.

1. Introduction

In the last 10 years, a great attention has been done to the development of efficient and compact optical waveguide amplifiers and lasers in rare earth doped-glasses for integrated optical devices [1–3]. Among the rare-earth elements, Er^{3+} ion with 1540 nm photoluminescence emission is of particular interest for optical amplification in telecommunications. In order to make a compact amplifier, a few centimeters long, a high erbium concentration is required when compared with erbium doped fiber amplifiers involving typically several meters in length. However, due to the onset of concentration quenching at low doping levels in silica, the relatively low gain unit length which can be achieved has made such development difficult. Thus, there is a great interest to develop other amorphous host matrices with high solubility of rare-earth elements, especially erbium, for integrated systems [4].

On the other hand, borate materials are of interest due to their wide UV transparency and their non-linear properties associated to high optical damage thresholds [5,6]. Many of them, such as YBO_3, $LaBO_3$, $GdBO_3$, and Y_3BO_6 are also good host matrices for active luminescent rare earth ions [5,7,8].

The Yttrium aluminum borate matrix ($YAl_3(BO_3)_4$, YAB) is one of the potential host candidates. In the crystal form, it exhibits good properties for solid-state lasers: high physical and chemical stability, high thermal conductivity and good mechanical strength [9]. YAB can be also used for waveguiding. Indeed, its high refractive index ($n = 1.6$–1.7) compared to silica substrate ($n = 1.45$) allows to realize a large angle of light admittance and a high light confinement, thus increasing the pump absorption and amplification efficiencies [10].

Our purpose was to obtain homogeneous glassy thin films to develop waveguides without grain boundaries which lead to high optical losses in polycrystalline films. Erbium-doped YAB composition appears as a suitable host matrix for efficient integrated optical amplifiers due to its high rare-earth solubility, high glass transition temperature T_g, around 746 °C, and good thermal stability versus crystallization [11].

In a previous work, stable sols were successfully prepared by the sol–gel process [11]. The sol–gel technique is considered as a

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low cost deposition method which allows obtaining planar waveguides of high optical quality. Advantages of this method are the high control of chemical purity, low temperature of synthesis, easy incorporation of rare earth ions and the possibility to cover large substrates area by the spin-coating technique [12]. Likewise, the sol–gel process appears to be quite attractive for the preparation of multi-component systems as it's allows homogeneous reactions in solution of all the precursors at the molecular level. A new sol–gel route was developed by our group, in which $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ crystalline and amorphous powders and films were demonstrated to be synthesized with good optical quality [11,13]. The glass transition and crystallization temperatures of this matrix were found around 746 °C and 830 °C, respectively. In this previous work, only single-layer films were elaborated and the deposition conditions were optimized with regard to the sol chemistry. In the present work the elaboration and optimization of multi-layers thin films is presented. The waveguiding properties of these films were investigated, as well as the heat-treatment suitable to obtain amorphous and dense films without cracks and pores. This work was also devoted to optimize the structural, microstructural and optical properties of the thin films by using X-ray diffraction, scanning electron and atomic force microscopies and optical transmission characterizations. Moreover, the refractive index dispersion in the visible and near infrared regions was determined by the envelope method applied on the transmission spectra. Finally, *m*-line spectroscopy was used for determining the waveguiding properties such as refractive index, propagation modes and losses.

2. Experimental procedure

2.1. Sol synthesis and multi-layer depositions

Aluminum acetylacetonate ($Al(acac)_3$, Aldrich 99%), tri-i-propylborate ($B(OPr^i)_3$, Strem 98%), yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$, Aldrich 99.9%), and erbium nitrate pentahydrate ($Er(NO_3)_3{\cdot}5H_2O$, Aldrich 99.9%), were used as precursors to obtain the $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ solid solution phase by the sol–gel method. Ethyl alcohol (C_2H_5OH, Riedel-de Haen 99.8%), and propionic acid ($C_2H_5CO_2H$, PropAc, Merck 99%) were used as solvents. The preparation of the sols was performed in a dry glove box (N_2 atmosphere). The precursor dissolution was first carried out in ethyl alcohol (EtOH) and propionic acid (PropAc) at 80 °C during 2 h in airtight silica cells to avoid any evaporation. Pure water was added for the hydrolysis at 80 °C during 1 h. In all our experiments, the relative molar amounts of cation precursors, corresponding to the YAB composition, and of water were fixed at 0.9 Y:0.1 Er:3 Al:4 B:55 PropAc:95 EtOH:5 H_2O. For more details see Ref. [11]. The resulting sols were filtered at room temperature (26 °C) by using filters of 0.2 μm porosity. During these heat treatments, the solution was placed into a closed silica glass flask with polypropylene cover. Finally, by removing the cover, the solvent were partially evaporated, around 65 vol.%, at 80 °C during 70 min. These concentrated solutions were used to prepare thin films by spin-coating deposited on silica glass and (1 0 0) silicon substrates. Before coating deposition, these substrates were cleaned by detergent (Argos, biodegradable anionic surfactant), rinsed with deionized water and then immersed in a $HNO_3 + HCl$ (16 HNO_3 + 28 HCl + 56 H_2O molar proportions) solution during 5 min. The substrates were rinsed again with deionized water and ethyl alcohol and finally dried through air flow. A spin-coater (RC8 SussMicrotech™) equipment involving the gyrset technology allowed to improve the film uniformity. Rotation acceleration, rotation speed and spinning time were fixed at 500 rpm/s, 2250 rpm, and 5 s, respectively. After the deposition of each layer, the films were dried at 80 °C for 30 min. Then, a first annealing at 400 °C during 2 h was applied with a heating rate of 1 °C/min while a second one (2 h at 700 °C) was achieved at 2 °C/min. This procedure was repeated for each layer (7-layers), and the resulting films were finally annealed under oxygen between 740 and 850 °C during 2 h with a heating rate of 1 °C/min.

2.2. Microstructural and structural characterizations

Grazing incidence X-ray diffraction (GIXRD) measurements were performed with a home made diffractometer using a PSD (position-sensitive detector) from Inel. The Fe $K\alpha$ (λ = 1.936 Å) radiation (34 kV/25 mA) with 2 mm divergence and 0.6 mm reception slits and a graphite monochromator were the main set of experimental parameters. The incident angle of X-ray beam was fixed at $\theta_i = 0.5°$, the scan range (2θ) was fixed between 12 and 90° while the total collecting time of each GIXRD pattern was 7200 s.

Raman spectra were registered at room temperature using a micro-Raman Renishaw R2000 system. The samples were excited with a 632.8 nm He–Ne line and the Raman spectra collected between 1050 and 1800 cm^{-1} with a spectral resolution of approximately 1 cm^{-1}.

Surface quality and microstructure of the films were analyzed using a high resolution scanning electron microscope (HR-SEM) (FEG-VP Supra 35, Zeiss), while the surface morphology of the films was observed by an atomic force microscope (AFM – Digital instrument Nanoscope III) using the tapping mode to measure the surface root-medium-square (RMS) roughness and grain sizes.

2.3. Optical characterizations

Optical transmission spectra in the UV–Visible–NIR near regions (200–2000 nm) were recorded at room temperature using a Perkin–Elmer spectrophotometer (Lambda 9, 240 nm min^{-1}, resolution of 0.2 nm). Waveguiding properties were investigated by *m*-line spectroscopy [14] involving a symmetrical 60° prism (Schott SF 58 glass) with a refractive index $n_p = 1.8736$ at the 980 nm wavelength. Loss measurements were recorded on 15 mm long samples by a scanning optical fiber probe moving along the length of the propagating light streak in a Metricon® equipment (model 2010). The attenuation coefficient was obtained by fitting the data with an exponential decay function, assuming a homogeneous longitudinal distribution of the scattering centers and a constant loss parameter for these planar waveguides. The measurements were performed by excitation of the fundamental transverse electric mode of the planar waveguide at 632.8 nm and 1550 nm.

3. Results and discussion

3.1. Structural characterizations

The GIXRD patterns of $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ thin films deposited on silica substrates and annealed during 2 h at the final 780, 820, and 850 °C temperatures are presented in Fig. 1. One can observe that the films are amorphous below 820 °C while after an annealing at 820 °C, the resulting film is partially crystallized in the $Al_4B_2O_9$ compound (JCPDS No. 09-0158). At 850 °C, two crystalline phases, $Al_4B_2O_9$ (JCPDS Card No. 09-0158) and YBO_3 (JCPDS Card No. 88-0356) coexist with a remaining amorphous phase. These results are in agreement with our previous results for the crystallization of fine amorphous $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ powders prepared by the sol–gel process [11,13], and also, with those reported by Madarasz et al. [15]. They observed, for the YAB composition, the formation of $Al_4B_2O_9$ by solid state reaction at 800 °C. On the other hand,