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Invited Article

Sol-gel route to highly transparent $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ thin films for active optical components operating at 2 μm

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ABSTRACT

We present a generic sol-gel route to the preparation of optically active nanocrystalline holmium-yttrium titanate $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ thin films, which exhibit a strong luminescence at 2 μm. The films were prepared by the sol-gel process and thermally treated in a rapid thermal annealing furnace. The nanocrystal size and optical properties were tailored by the processing temperature. The final film thickness was around 500 nm. X-ray diffraction analysis and Raman spectroscopy confirmed the high purity of the crystal phase of $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$. The activation energy of crystal growth was 35.7 kJ mol^{-1}. The films had excellent structural and surface homogeneity causing their high transparency close to the theoretical limit of 93.39%. Refractive index of the film heat-treated at 1000 °C was around 1.98. The films exhibited strong emission at 2 μm with a luminescence lifetime around 4.6 ms. Their properties together with processing feasibility make them promising materials for photonic applications.

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1. Introduction

Lanthanide-doped yttrium titanates, which crystallize in the face-centered cubic pyrochlore structure with the general formula $(Re_xY_{1-x})_2Ti_2O_7$ (RE = rare earth element) [1], have been in the scope of recent material research. The pyrochlore structures exhibit a set of excellent properties, such as thermal stability [2,3] and durability [4,5], etc. The presence of Y^{3+} ions in the pyrochlore matrix prevents the spin-coupling between RE ions [6,7] and brings about a strong photoluminescence [8,9]. These properties together with low phonon energy [10,11] and a high refractive index [12] make them promising materials for photonic applications such as bulk phosphors [8,9,11,13], planar optical components [14], and active optical fibers. Introducing of Ho^{3+} ions into the pyrochlore matrix shifts the working wavelength to 2 μm [9,15]. This spectral region is preferred for a manufacturing of novel, high-power active optical devices, such as optical amplifiers and fiber lasers, because it is considered “eye-safe” spectral region [13,16].

In this contribution we present a generic sol-gel route to highly transparent nanocrystalline holmium-yttrium titanate $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ thin films with tailored structural and optical properties. We investigate the effect of processing parameters on the nanocrystalline structure and optical properties of prepared thin films. We determine their structural, optical, and luminescence properties of prepared films. These results can be used for preparation of thin films with tailored properties. The prepared films are suitable active materials for high-power planar optical amplifiers operating around 2 μm.

2. Experimental

2.1. Materials and sample preparation

The starting sol was prepared by the condensation of titanium (IV) butoxide with inorganic salts of yttrium and holmium. Typically, a total of 3 g of titanium (IV) butoxide (Fluka, purum) was dissolved in 150 ml of anhydrous ethanol (Sigma-Aldrich, spectral grade). A total of 0.195 g of $Ho(NO_3)_3 \cdot 5H_2O$ (Alfa Aesar, 99,9%) and a total of 3.2 g of $Y(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99,9%) were dispersed in the solution. The formed dispersion was heated at 70 °C until a transparent sol was formed. It was refluxed at 85 °C for 3 h and then

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allowed to cool. Finally, the sol was concentrated under reduced pressure (30 mbar) at 65 °C to achieve a viscosity which allowed the deposition. This sol was dip-coated on a planar silica glass substrate (TGP, USA) at a withdrawal speed of 200 mm min^{-1}. Each of the dip-coated layer was densified in a rapid thermal annealing furnace AccuThermo AW410 (Allwin21 corporation) at 600 °C for 60 s under an oxygen flow of 5 l min^{-1} and heating rate of 10 $^{\circ}\mathrm{C}\cdot\mathrm{s}^{-1}$. Up to 15 layers were subsequently deposited to achieve the required thickness. Finally, the densified multilayered films were thermally treated at a heating rate of 10 $^{\circ}\mathrm{C}\cdot\mathrm{s}^{-1}$ to final temperatures ranging from 800 °C to 1100 °C under an oxygen flow of 5 l min^{-1}.

2.2. Characterization of the samples

X-ray diffraction analyses (XRD) of the prepared films were recorded with a Bruker D8 Discover diffractometer with Bragg-Brentano geometry using Cu-K_{α} radiation ($\alpha = 1.54056$ Å). The operating voltage was 40 kV, current 40 mA, and integration time 200 ms. The mean nanocrystal size, D, was calculated using Scherrer's equation [17]:

$$D = \frac{\kappa \cdot \lambda}{\beta \cdot \cos\theta}, \tag{1}$$

where κ is the structural factor equal to 0.89, λ is the X-ray wavelength equal to 0.154056 nm and β is the correlated FWHM value corresponding to the (222)-plane peak of holmium-titanium oxide (JCPDS N° 23-0283) at the diffraction angle 2θ equal to 30.8°.

Scanning electron microscope (SEM) images were taken with a TESCAN Lyra 3 XMU FEG/SEM device. The surface morphology of the films was analyzed by atomic force microscopy (AFM) analysis in the contact mode using Dimension 3100 AFM (Digital Instruments/Veeco, Woodbury, NY) operated in air. We used commercial Si_3N_4 cantilevers (DI) with an elastic modulus of 0.56 N m^{-1}. The thickness and surface profiles of the samples were measured with the optical profilometer NewView 7300 (Zygo).

UV-VIS and NIR transmission spectra were recorded with a Lambda EZ 210 (Perkin-Elmer) and Ocean Optics NIR2000 spectrometer, respectively. Raman spectra were recorded using an Invia Raman spectrometer Renishaw. A laser operating at 785 nm was used as the excitation source. Raman signals were collected for the Raman shift from 150 to 1300 cm^{-1}.

Spectral ellipsometry measurements were made with a spectral ellipsometer Sentech 850SE. Data on all samples were acquired in reflection mode over a spectral range of 300–2200 nm in air at room temperature. The refractive index and the coefficient of optical losses were calculated using the built-in Spectra Ray software. The ellipsometric model employed a single Cauchy's layer on a silica glass substrate (Palik) of infinite thickness. Parameters n and k of the Cauchy's layer were calculated from the equations:

$$n(\lambda) = n_0 + \frac{n_1}{\lambda^2} + \frac{n_2}{\lambda^4}, \tag{2}$$

$$k(\lambda) = k_0 + \frac{k_1}{\lambda^2} + \frac{k_2}{\lambda^4}, \tag{3}$$

where n is the refractive index, k is the coefficient of optical losses, λ is the wavelength, and n_0, n_1, n_2, k_0, k_1, k_2 are the fitted parameters. This model considered the surface roughness on the level of 5 nm.

Photoluminescence spectra were recorded using a spectrophotometer Fluorolog 3 (Horiba, Jobin-Yvon) equipped with a 100-mW laser diode operating at 450 nm (Sony) as the excitation source and an extended InGaAs detector (Electro-Optical Systems Inc.) cooled by liquid nitrogen. Excitation spectra were collected in a range from 200 to 800 nm with a step of 1 nm and slit of 8 nm under emission at 1910 nm. The emission spectra were measured at 450-nm excitation for the emission range from 1000 to 2200 nm. The integration time was 0.1 s. Average of 10 recorded spectra are presented in the figures. Fluorescence decay curves were recorded using a LeCroy 300 MHz digital oscilloscope.

3. Results and discussion

3.1. Structure and morphology of the films

Fig. 1 shows the XRD spectra recorded for the films heat-treated from 800 to 1100 °C. The film heat-treated at 800 °C provided a set of broad peaks which corresponded to the diffraction pattern of the silica glass substrate. An absence of other diffraction peaks indicated that the film was still amorphous. A set of narrow peaks appeared in the XRD spectra of the films heat-treated over 900 °C. These peaks, which became more intensive and more pronounced with increasing heat-treating temperatures, were assigned to the pyrochlore structure of pure $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ [9]. No traces of side-formed phases, such as Ho_2O_3, or TiO_2, were detected.

Fig. 2a shows the thermal evolution of the mean nanocrystal size calculated from Scherrer's equation and film's thickness. The calculated mean nanocrystal size increased with increasing heat-treating temperature and ranged from 25 nm to 58 nm. The film's thickness regularly decreased with heat-treating temperature from 560 to 455 nm for temperatures increasing from 800 °C to 1100 °C.

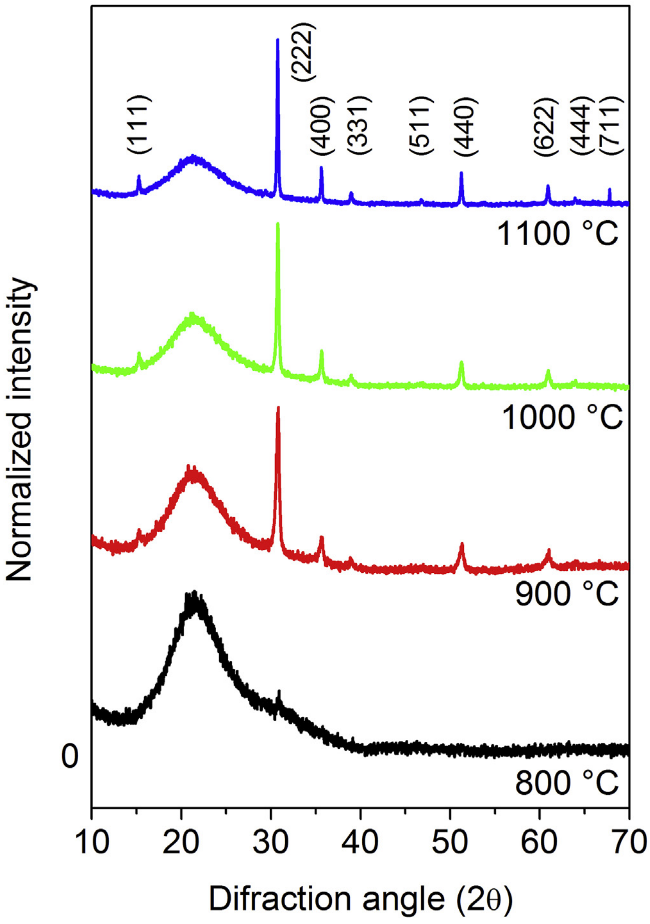

Fig. 1. XRD patterns of thermally processed thin films with denoted (hkl) indices.

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