CO_2 laser assisted processing of $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ coatings for infrared photonics

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Abstract. We demonstrated CO_2 laser assisted processing of highly transparent $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ nanocrystalline coatings. The amorphous coating of the thickness of 577 nm was prepared by subsequent spin-coating of a colloidal solution followed by densification at 700°C in a radiation furnace. The densified coating was irradiated by a laser beam of a power density of 20 mW/mm^2 for 60 s to induce the crystallization process. The nanocrystals formation caused the densification of the coatings reducing the thickness to 490 nm and increased the refractive index to 2.088. The coating exhibited strong luminescence at 2.1 and 2.95 μm corresponding to $^5I_7 \rightarrow {}^5I_8$ and $^5I_6 \rightarrow {}^5I_7$ electronic transitions, respectively. The corresponding time-resolved luminesce records showed the single-exponential decay course reaching the values of 8.4 ms and 0.221 ms for the emissions recorded at 2.1 and 2.95 μm, respectively. The demonstrated process can be used to prepare a luminescent coating with tailored properties. CO_2 laser assisted processing can be used in a manner of direct laser writing for the preparation of integrated optical waveguides and amplifiers as a powerful alternative to conventional thermal processing.

1 Introduction

Rare earth-doped yttrium titanium oxides crystallizing in the pyrochlore crystal lattice have attracted huge attention of material research for their phenomenal properties. They show excellent thermal and chemical stability. Low-phonon pyrochlore lattice supports the radiative energy transfers allowing their application as high-power lasers and amplifiers operating around 2 μm [1].

However, their high crystallization temperatures [2] limit the preparation of nanocrystalline coatings on common substrates and their application in the field of integrated optical devices including the amplifiers. A CO_2 laser assisted process can solve this challenge.

We present a CO_2 laser assisted approach to highly transparent nanocrystalline $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ coatings. We studied the luminescence properties of the coatings. The demonstrated method and the coatings can be used to prepare active optical components operating at wavelengths around 2.0 and 2.9 μm.

2 Experimental

Steady-state luminescence spectra of $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ nanocrystalline coating recorded under 450nm excitation. The starting sol was prepared according to demonstrated method [3] and spin-coated on silica glass substrates (Technical glass products, USA) at rotation speed of 2000 RPM. The coating was densified in AccuThermo AW410 radiation furnace (Allwin21 corporation) at 700 °C for 120 s under an oxygen flow of 5 l·min^{-1} and a heating rate of 10 °C·s^{-1}. Five layers were subsequently applied and finally irradiated by a continuous CO_2 laser SYNRAD 48–1 (Coherent) for 60 s. A laser beam was expanded to a 5mm circular spot, a power density of the laser beam was of about 20 mW/mm^2. UV-VIS transmission spectra were recorded with Lambda EZ 210spectrometer (Perkin-Elmer). The luminescence spectra were excited by a laser diode (Osram) emitting at 450 nm. The steady-state emission was recorded on Nicolet 5700 FTIR spectrometer. The time-resolved luminescence was collected using a bandpass optical filter centered at 2.1 μm or 2.950 μm (Edmund Optics) and the liquid nitrogen-cooled InAs detector P7163 (Hamamatsu). The coating thickness was measured on optical profiler NewView 9000 (Zygo).

3 Results and discussion

The CO_2 laser treatment is an alternative to a conventional thermal treatment that have a major effect on the crystallinity of the film and related optical properties [2]. The coatings' transmission spectra are shown in Fig. 1. The formation of nanocrystals caused a slight shift of the interference pattern toward shorter wavelengths. The interference maxima reached a value of 93.2%, which is in good agreement to the value of 93.39% evaluated for pure silica substrate [4]. The local interference minima fall down from a value of 82.2% to a value of 74.9%. According to the Swanepoel's approximation [5], the interference minima correspond to the refractive index of the coating. The formation of nanocrystals increased the refractive index from the value of 1.856 recorded for amorphous coating at 632 nm to the value of 2.088 for

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nanocrystalline coating. The formation of nanocrystals was accompanied by a thickening of the coating and a decrease in its thickness from 577 nm to 490 nm.

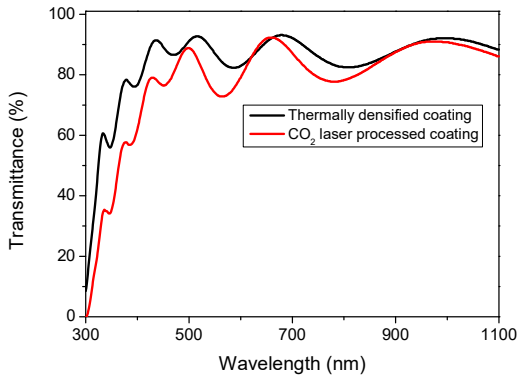

Fig. 1. Optical transmission spectra of the thermally densified coatings and coatings after CO_2 laser irradiation.

Steady-state luminescence spectrum were recorded under 450 nm excitation is shown in Fig. 2. Although the amorphous coating provided no detectable emission, the nanocrystalline coating showed two major emission bands located around 2 and 2.9 μm, corresponding to $^5I_7 \rightarrow ^5I_8$ and $^5I_6 \rightarrow ^5I_7$ electronic transitions, respectively. The emission bands exhibited fine Stark splitting that is characteristic for Ho^{3+} ions incorporated inside a regular crystal lattice [6]. The intensity recorded at 2.9 μm reached only 15% of the maximum value recorded at

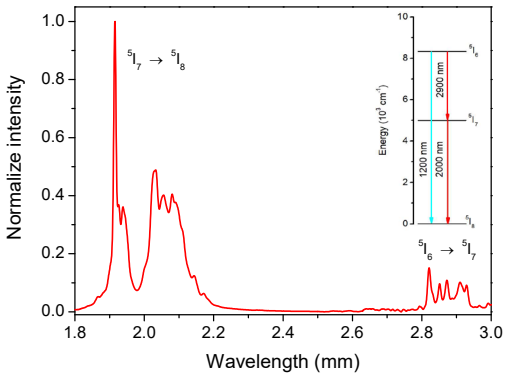

Fig. 2. Steady-state luminescence spectra of the coating recorded at 450nm excitation.

1.92 μm.

Fig. 3 shows the time-resolved luminescence records at 450 nm excitation. The time decay curves exhibited a single-exponential shape and the fitted parameters are summarized in Table 1. The radiation lifetime of the electronic transition $^5I_7 \rightarrow ^5I_8$ at 2.1 μm reached the value of 8.44 ms. Such a value is fully comparable with the value of 8.5 ms reported for Ho-doped YAG single crystals [7]. Comparing with YAG materials, low phonon energy of $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ enables the activation of the electronic transition $^5I_6 \rightarrow ^5I_7$ at 2.95 μm. Although, this emission band was observed in the steady-state spectrum, the corresponding lifetime is quite short, reaching the value of 0.221 ms only.

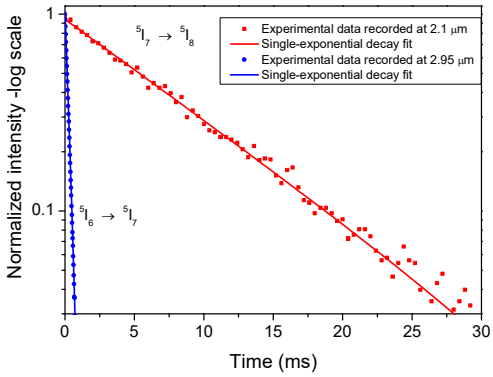

Fig. 3. Normalized decay curves recorded at 2.1and 2.95 μm for excitation at 450 nm.

Table 1. Values of the single-exponential decay fits of time-resolved luminescence recorded at 2.1 and 2.95 μm.

Emission (μm)	A	t (ms)	Y_0	R^2
2.1	0.967	8.44	0.032	0.9985
2.95	1.043	0.221	-0.011	0.9998

4 Conclusions

We used CO_2 laser beam to prepare highly transparent $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$ nanocrystalline coatings. The coatings exhibited strong luminescence at 2.1 and 2.95 μm corresponding to $^5I_7 \rightarrow ^5I_8$ and $^5I_6 \rightarrow ^5I_7$ electronic transitions, respectively. The corresponding time-resolved luminesce records showed the single-exponential decay course reaching the values of 8.4 and 0.221 ms respectively. The demonstrated process can be used to prepare luminescent coatings with tailored properties. CO_2 laser assisted processing can be used in a manner of direct laser writing for the preparation of integrated optical waveguides and amplifiers.

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