Sol-gel synthesis of Yb-doped NaLu(WO₄)₂ films

Xiumei Han and Carlos Zaldo*

Instituto de Ciencia de Materiales de Madrid. Consejo Superior de Investigaciones Científicas. c/ Sor Juana Inés de la Cruz 3, 28049 Madrid. Spain.

Abstract

Dense and (001)-textured thin films with composition NaLu₁₋ₓYbx(WO₄)₂ (x=0.01-0.5) have been prepared by multiple spin-coating deposition of sol-gel synthesized solutions, followed by a sintering thermal annealing. Films with thickness above 1 μm are transparent and have photoluminescence properties similar to those of isostructural single crystals. The role of Yb composition, film thickness and purity of the raw Yb₂O₃ used on the Yb³⁺ fluorescence efficiency are discussed in relation to the application of the films as diode laser pumped solid-state laser media.

© 2010 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Thin films, trivalent ytterbium, photoluminescence, sol-gel, spin-coating

1. Introduction

Nowadays very powerful (>100 W) semiconductor diode laser (DL) modules emitting around 800 nm or 980 nm are available in the market at affordable prices. These lasers are very efficient in terms of electrical to optical power transformation and therefore they have substituted to discharge lamps as optical pumping systems. [1,2] Typically the output of the DL is collected by an optical fiber and remotely delivered after some beam conditioning. To profit from such pump sources Tm³⁺ or Yb³⁺ lasants are preferred because of their high optical absorption cross sections at the above mentioned wavelengths. [3,4] Moreover, the laser operating schemes of these ions minimize the heat deposited in the optical amplification medium, therefore, temperature enhancement of the laser medium associated to the scaling of the laser power are partially avoided. Nevertheless, at certain operation power level Tm and Yb solid-state lasers require cooling.

Thin disks lasers [5] use a particularly successful design to remove heat from the laser active media. In such design the optically active laser medium is a disk, typically 5-10% Yb doped YAG, with thickness in the range 100-
350 μm. The disk is soldered onto a water cooled metallic holder and pumped through a multipass parabolic optical cavity. In practice, successful high power demonstration of these lasers is limited to YAG crystal due to its large mechanical stiffness and thermal conductivity (κ= 11 W/m·K). However, other materials are desired for specific laser applications.

Ytterbium–doped double tungstate single crystals with formula NaX(WO4)2 (X=Y, La, Gd or Lu) have attracted significant attention as solid state lasers. Around 1 W of laser light (at λ = 1036 nm) was obtained in cw regime [6] and sub-100 fs laser pulses were obtained by passive mode locking. [6,7,8] The favorable ultrafast laser properties of these tetragonal double tungstates are related to the large Yb3+ optical bandwidth induced by the Na and X occupancy of the same lattice sites, however an efficient cooling is required for high power applications since the thermal conductivity of these crystals is rather low (κ ≈ 1.5 W/m·K).

The control of crystal heating with the purpose of improving the laser power output was achieved in a 10.7 at%Yb-doped NaGd(WO4)2 disk with 100 μm of thickness attached to a water cooled copper heat sink. In this way 16 W of laser light at λ = 1027.5 nm were obtained, but such free standing disks were prone to mechanical damage. [9]

In this work we present the preparation of Yb-doped NaLu(WO4)2 films supported on substrates with good mechanical and thermal conductivity and we characterize the spectroscopic properties of the films obtained.

2. Synthesis procedure and film preparation

NaLu1-xYbx(WO4)2 (x=0.01, 0.1, 0.2, 0.5) was prepared by the sol-gel modified Pechini method [10]. The precursor chemicals used were Na2CO3 (99.5%), Lu2O3 (99.99%), Yb2O3 (99.9%; 99.99%; 99.998% and 99.9999%), (NH4)10W12O41.7H2O, HNO3 (60%), citric acid and ethylene glycol (ET). The required amounts of Yb2O3 and Lu2O3 raw materials were dissolved in diluted HNO3 and a suitable volume of deionized water under vigorous stirring and heating at 95 °C. When the solution was clear, Na2CO3, ammonium tungsten, citric acid complexing agent (CA) and ET were added to the solution. The molar ratio of chelated metal cations to the CA was 1:4 and the molar ratio of CA to ET was 1:10. The above mixture was stirred for 2 h more at 80 °C to get a stable solution precursor. Finally some ammonia was added to adjust the pH value around 4-5 with stirring for 10 hours at 80 °C. The viscosity of the solution obtained was 280 cp. Figure 1a shows the XRD pattern of the powder obtained calcination of the solution at 800 °C.

Films were prepared by spin coating on amorphous quartz and r-cut sapphire substrates. The spinning rate of the substrates was 500 rpm for the first 6 s and 3000 rpm for the next 30 s. Several layers were deposited to obtain the film thickness desired. Each layer was dried at 120 °C during 10 min and crystallized at a higher temperature for 10 min more. The following crystallization temperatures were tested: 450, 550, 600, 650, 750 or 850 °C. Finally, the samples were sintered at the same temperature for 5 h.

3. Results

The sol-gel deposition of NaLu1-xYbx(WO4)2 films by the method described in section 2 produced crystalline material in all cases, however films on amorphous quartz produced polycrystalline films, see Figure 1b, while films deposited on crystalline sapphire produced c-textured films, see Figure 1c.
Figure 1. 0-2θ X-ray diffraction scans of NaLu$_{1-x}$Ybx(WO$_4$)$_2$. (a) Sol-gel powder (x=0.5) annealed 24 h to 850 °C. (b) Film (x=0.2, 15 layers) on amorphous quartz. (c) Film (x=0.5, 35 layers) on r-cut crystalline sapphire.

Figure 2. (a) NaLu$_{0.9}$Yb$_{0.1}$(WO$_4$)$_2$ film deposited by spin coating on amorphous quartz. (b) Scanning electron micrograph of the surface of a NaLu$_{0.5}$Yb$_{0.5}$(WO$_4$)$_2$ film with 35 layers deposited on amorphous quartz. (c) Histogram of the grain size of the above film.

The thermal onset of film crystallization is about 450 °C, i.e. far below the compound temperature decomposition, 1134 °C. However, annealing temperatures above 750 °C produce the presence of either Yb$_2$O$_3$ or Yb-doped Lu$_2$O$_3$. This is due to the high volatility of Na and W. 600 °C was found an optimum compromise between the crystallization rate and the control of film phase purity.

Figure 2a shows a NaLu$_{0.9}$Yb$_{0.1}$(WO$_4$)$_2$ film, which after deposition of 10 layers is transparent to the naked eye. Similar transparency degree was obtained in thicker films up to the maximum thickness prepared of 50 layers. Films formed under these conditions have the morphology shown in Figure 2b. Films are composed of a dense grain structure growing from the substrate by a columnar mechanism. The grain size distribution of the films was obtained by a digital analysis of the SEM micrographs, see Figure 2c. Most of the grains have cross sections below 1 μm$^2$. Moreover the SEM study of the film cross section allowed the evaluation of the film thickness. The deposition rate obtained was about 25 nm/layer.

The film fluorescence (excitation and emission) spectra and fluorescence lifetime have been characterized at room temperature. The optical excitation was provided by a tunable Quanta-Ray MOPO-HF system. Fluorescence was dispersed in a single grating Spex spectrometer (f=34 cm) and detected with a Hamamatsu InP/InGaAs cooled photomultiplier. Figure 3a shows a comparison of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ Yb$^{3+}$ emission excited at $\lambda = 940$ nm in the film and in single crystals. Similar peaks and band shapes are found in both cases (also in the excitation spectra not shown for brevity).
Figure 3. Room temperature spectroscopic properties of NaLu$_{1-x}$Yb$_x$(WO$_4$)$_2$ films deposited by spinning of sol-gel synthesized solutions. (a) Comparison of the emission spectra (lines) of films with $x=$ 0.1, 0.2 and 0.5, with the single crystal cross section (points). (b) Fluorescence dynamics of Yb$^{3+}$.

The $^2\Sigma_{5/2}$ Yb$^{3+}$ lifetime was measured on samples with only 5 layers to minimize re-absorption effects. The emission decays are single exponential curves, see Figure 3b. The lifetime decreases with increasing Yb concentration and with the reduced purity of the Yb$_2$O$_3$ precursor oxide. The largest $^2\Sigma_{5/2}$ lifetime obtained in films with 10 at% of Yb using the highest Yb$_2$O$_3$ purity, $\tau=335 \mu$s, is close to the radiative lifetime obtained in single crystal, 368 $\mu$s [7].

4. Conclusions

Single phase tetragonal NaLu$_{1-x}$Yb$_x$(WO$_4$)$_2$ films have been obtained by spin coating sol-gel synthesized precursor solutions and further annealing to 600 °C. This means a very significant reduction of the synthesis temperature in comparison to that required for the growth of single crystals. Multilayer deposition allowed the preparation of textured films with high Yb concentration ($x>0.5$) and thickness up to $\lambda=1 \mu$m. These films are highly transparent and show luminescence properties equivalent to those of isostructural single crystals. Therefore the films could be of use for thin disk or waveguide laser purposes.

5. Acknowledgments

Work supported by project MAT2008-06729-C02-01.

References