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Sol-gel synthesis of Yb-doped $NaLu(WO_4)_2$ 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 $NaLu_{1-x}Yb_x(WO_4)_2$ (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 Yb_2O_3 used on the Yb^{3+} fluorescence efficiency are discussed in relation to the application of the films as diode laser pumped solid-state laser media.

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 Tm^{3+} or Yb^{3+} 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-

* Corresponding author. Tel.: +34-913349057; fax: +34- 913720623.
E-mail address: cezaldo@icmm.csic.es

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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 ($\kappa \approx$ 11 W/m×K). However, other materials are desired for specific laser applications.

Ytterbium–doped double tungstate single crystals with formula $NaX(WO_4)_2$ (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 Yb^{3+} 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 ($\kappa \approx$ 1.5 W/m×K).

The control of crystal heating with the purpose of improving the laser power output was achieved in a 10.7at%Yb-doped $NaGd(WO_4)_2$ 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 $NaLu(WO_4)_2$ 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

$NaLu_{1-x}Yb_x(WO_4)_2$ (x=0.01, 0.1, 0.2, 0.5) was prepared by the sol-gel modified Pechini method [10]. The precursor chemicals used were Na_2CO_3 (99.5%), Lu_2O_3 (99.99%), Yb_2O_3 (99.9%; 99.99%; 99.998% and 99.9999%), $(NH_4)_{10}W_{12}O_{41}.7H_2O$, HNO_3 (60%), citric acid and ethylene glycol (ET). The required amounts of Yb_2O_3 and Lu_2O_3 raw materials were dissolved in diluted HNO_3 and a suitable volume of deionized water under vigorous stirring and heating at 95 ºC. When the solution was clear, Na_2CO_3, 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 ºC 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 ºC. 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 ºC.

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 ºC 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 ºC. Finally, the samples were sintered at the same temperature for 5 h.

3. Results

The sol-gel deposition of $NaLu_{1-x}Yb_x(WO_4)_2$ 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.

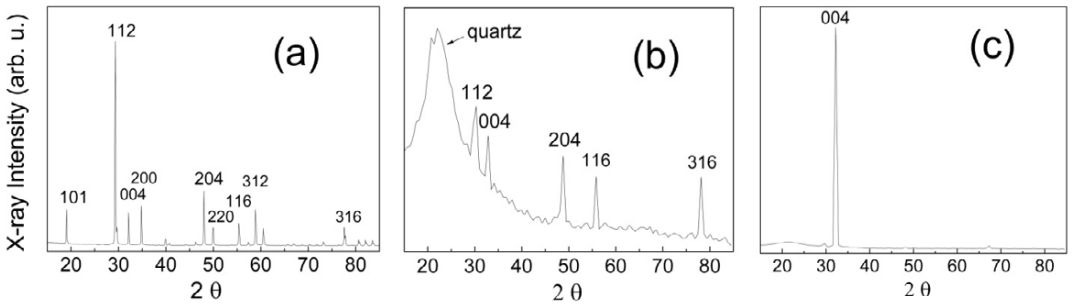

Figure 1. θ-2θ X-ray diffraction scans of $NaLu_{1-x}Yb_x(WO_4)_2$. (a) Sol-gel powder (x=0.5) annealed 24 h to 850 ºC. (b) Film (x= 0.2, 15 layers) on amorphous quartz. (c) Film (x= 0.5, 35 layers) on r-cut crystalline sapphire.

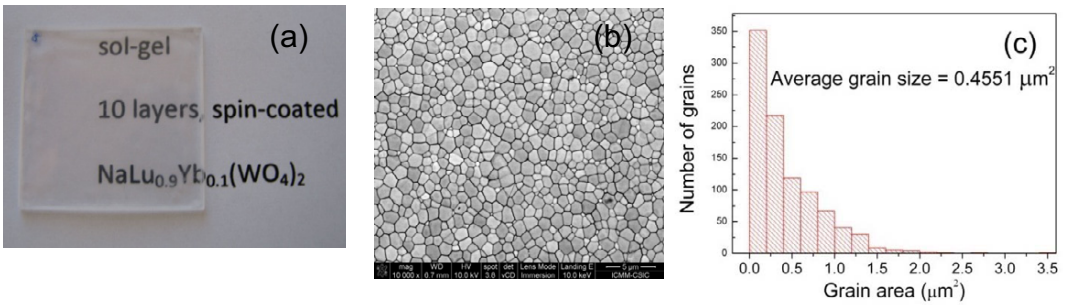

Figure 2. (a) $NaLu_{0.9}Yb_{0.1}(WO_4)_2$ film deposited by spin coating on amorphous quartz. (b) Scanning electron micrograph of the surface of a $NaLu_{0.5}Yb_{0.5}(WO_4)_2$ film with 35 layers deposited on amorphous quartz. (c) Histogram of the grain size of the above film.

The thermal onset of film crystallization is about 450 ºC, i.e. far below the compound temperature decomposition, 1134 ºC. However, annealing temperatures above 750 ºC produce the presence of either Yb_2O_3 or Yb-doped Lu_2O_3. This is due to the high volatility of Na and W. 600 ºC 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 λ= 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).

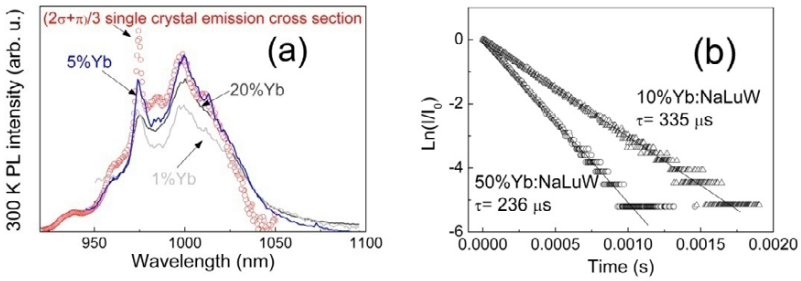

Figure 3. Room temperature spectroscopic properties of $NaLu_{1-x}Yb_x(WO_4)_2$ films deposited by spinning of sol-gel synthesized solutions. (a) Comparison of the emission spectra (lines) of films with x= 0.1, 0.2 and 0.5, with the single crystal cross section (points). (b) Fluorescence dynamics of Yb^{3+}.

The $^2F_{5/2}$ 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_2O_3 precursor oxide. The largest $^2F_{5/2}$ lifetime obtained in films with 10 at% of Yb using the highest Yb_2O_3 purity, τ= 335 μs, is close to the radiative lifetime obtained in single crystal, 368 μs [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 ºC. 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 ($x \leq 0.5$) and thickness up to ≈1 μm. 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

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References

1. T. Y. Fan and R. L. Byer 1988 *Diode laser-pumped solid state lasers* IEEE J. Quant. Electron. 24, 895-912.
2. E. Sorokin, I. T. Sorokina and E. Wintner 2001 *Diode-pumped ultra-short-pulse solid-state lasers* Appl. Phys. B 72, 3-14.
3. H. Kalaycioglu, A. Sennaroglu and A. Kurt 2005 *Influence of doping concentration on the power performance of diode-pumped continuous-wave Tm^{3+}:$YAlO_3$ lasers* IEEE J. Sel. Top. Quant. Electron. 11, 667-673.
4. G. Boulon 2008 *Why so deep research on Yb^{3+}-doped optical inorganic materials?* J. Alloys & Comp. 451, 1-11.
5. K. Petermann, D. Fagundes-Peters, J. Johannsen, M. Mond, V. Peters, J. J. Romero, S. Kutovoi, J. Speiser and A. Giesen 2005 *Highly Yb-doped oxides for thin disk lasers J. Cryst. Growth* 275, 135-140.
6. C. Cascales, M. D. Serrano, F. Esteban-Betegón, C. Zaldo, R. Peters, K. Petermann, G. Huber, L. Ackermann, D. Rytz, C. Dupré, M. Rico, J. Liu, U. Griebner and V. Petrov 2006 *Structural, spectroscopic, and tunable laser properties of Yb^{3+}-doped $NaGd(WO_4)_2$* Phys. Rev. B 74, 174114.
7. A. García-Cortés, J. M. Cano-Torres, M. D. Serrano, C. Cascales, C. Zaldo, S. Rivier, X. Mateos, U. Griebner and V. Petrov 2007 *Spectroscopy and lasing of Yb-doped $NaY(WO_4)_2$: Tunable and femtosecond mode-locked laser operation* IEEE J. Quant. Electron. 43, 758-764.
8. A. García-Cortés, J. M. Cano-Torres, X. Han, C. Cascales, C. Zaldo, X. Mateos, S. Rivier, U. Griebner, V. Petrov and F. J. Valle 2007 *Tunable continuous wave and femtosecond mode-locked Yb^{3+} laser operation in $NaLu(WO_4)_2$* J. Appl. Phys. 101, 063110.
9. R. Peters, C. Kränkel, K. Petermann and G. Huber 2008 *Power scaling potential of Yb:NGW in thin disk laser configuration* Appl. Phys. B 91, 25-28.
10. M. P. Pechini, US Patent 3.330.697 (1967).