Available online at www.sciencedirect.com
ScienceDirect
Optical Materials 29 (2007) 728–731
OPTICAL Materials
www.elsevier.com/locate/optmat

Growth and spectral properties of Yb^{3+}-doped $NaY(MoO_4)_2$ crystal

Xiuzhi Li [a,b], Zhoubin Lin [a], Lizhen Zhang [a], Guofu Wang [a,*]

[a] *Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Crystal Material Research Center, P.O. Box 143, Fuzhou, Fujian 350002, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

Received 21 June 2005; accepted 18 November 2005
Available online 7 February 2006

Abstract

Yb^{3+}-doped $NaY(MoO_4)_2$ with dimension of $\varnothing 22 \times 35\ mm^2$ has been grown by Czochralski method. Absorption and emission spectra of the crystal were investigated. The absorption band at 976 nm has a FWHM of 41 nm for π-polarization and 56 nm for σ-polarization, and the absorption cross-section σ_{ab} is $3.32 \times 10^{-20}\ cm^2$ for π-polarization and $2.49 \times 10^{-20}\ cm^2$ for σ-polarization at 976 nm. The emission cross-sections σ_{em} are estimated from the fluorescence spectrum using the Füchtbauer–Ladenburg formula, which is $2.32 \times 10^{-20}\ cm^2$ at 1016 nm for π-polarization and $2.02 \times 10^{-20}\ cm^2$ at 1015 nm for σ-polarization room temperature. The fluorescence lifetime τ_f is 535 μs and the radiative lifetime τ_r is 276 μs. The laser parameters β_{min}, I_{sat} and I_{min} have been calculated.

PACS: 42.70.Hj; 78.20.−e

Keywords: A1. Optical microscopy; A2. Czochralski method; A2. Growth from melt; B2. Molybdate; B2. Solid-state laser materials

1. Introduction

With the development of InGaAs diode lasers, much attention has been focused on Yb^{3+}-doped laser materials. The energy structure of ytterbium has only two manifolds, i.e. the ground state $^2F_{7/2}$ and the excited state $^2F_{5/2}$. The trivalent ytterbium has an advantage in comparison with other rare-earth ions, such as Nd^{3+}. There is no luminescence concentration quenching, no upconversion and excited-state absorption. The ytterbium-doped lasers have a longer emission lifetime than that of Nd^{3+}-doped materials, which enhance storage capacity and reduce quantum defect between absorption and emission.

Molybdate and tungstate crystals with general formula $M'Re(M''O_4)_2$ ($M' = Li, Na, K$; $M'' = W, Mo$) have been reported to be good host material for solid-state lasers [1,2]. Most of these crystals have a tetragonal symmetry with the structure of the scheelite $CaWO_4$ [3]. The $NaLa(MoO_4)_2$ crystal has been reported as laser host material [4]. The optical properties and laser performance of $NaLa(MoO_4)_2$ crystal doped with Nd^{3+} ions have been investigated [5–8]. Most of the molybdates melt almost congruently and can be grown from the melt by Czochralski method, for example $LiGd(MoO_4)_2$ [9], $NaBi(MoO_4)_2$ [10]. The crystal $NaY(MoO_4)_2$ belongs to the tetragonal symmetry with space group $I_{41/a}$: $a = b = 5.1989$ Å, $c = 11.3299$ Å [11]. Although the emission and growth of Nd^{3+}:$NaY(MoO_4)_2$ were reported [12], no attention was paid to Yb^{3+}-doped $NaY(MoO_4)_2$ crystal. This paper reports the growth and spectroscopic properties of Yb^{3+}:$NaY(MoO_4)_2$ crystal.

2. Crystal growth

Yb^{3+}:$NaY(MoO_4)_2$ crystals were grown by the Czochralski method. The raw materials of Yb^{3+}:$NaY(MoO_4)_2$ were synthesized by means of solid-state reaction. The

* Corresponding author. Tel./fax: +86 591 83714636.
E-mail address: wgf@ms.fjirsm.ac.cn (G. Wang).

0925-3467/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2005.11.028

chemicals used were Na_2CO_3 (99.95%), MoO_3 (99.95%), Y_2O_3 (99.99%) and Yb_2O_3 (99.99%). The chemical reaction is as follows:

$$0.5Na_2CO_3 + 0.5(1-x)Y_2O_3 + 0.5xYb_2O_3 + 2MoO_3 = NaY_{1-x}Yb_x(MoO_4)_2 + 0.5CO_2\uparrow$$

The stoichiometric amount of Na_2CO_3, Y_2O_3, Yb_2O_3 and MoO_3 were weighted accurately in addition to 2 wt.% excess MoO_3. The excess MoO_3 is to compensate the loss of MoO_3 volatilization in process of solid-state reaction and crystal growth. After grinding and extruding to form pieces, the samples were placed in the crucible and held at 650 °C for 24 h. The process was repeated once again and held at 850 °C for 24 h to assure adequate solid-state reaction.

The synthesized materials of Yb^{3+}:$NaY(MoO_4)_2$ doped with 10 at.% Yb^{3+} ions were melt in a $\varnothing 50 \times 40\ mm^2$ platinum crucible. The crystal was grown by Czochralski method in a 2 kHz frequency furnace and at a pulling rate of 0.5–1 mm/h and a rotating rate of 10–30 r/min.

The transparent Yb^{3+}:$NaY(MoO_4)_2$ crystal with dimensions of $\varnothing 22 \times 35\ mm^2$ was obtained. The grown Yb^{3+}:$NaY(MoO_4)_2$ crystal is black, as shown in Fig. 1(a). This color is caused by color centers in the grown crystal. It is generally believed that the formation of color center was caused by the oxygen vacancies in deficiency oxygen atmosphere [13]. In order to remove the color center in crystal as far as possible, the grown Yb^{3+}:$NaY(MoO_4)_2$ was annealed in air at 700 °C for 20 h. The result of annealing shows the annealing can remove the most color center in crystal, as shown in Fig. 1(b).

The melting point of Yb^{3+}:$NaY(MoO_4)_2$ crystals measurement was performed by differential scanning calorimetry (DSC) analysis using a NETZSCH PC404 Simultaneous Thermal Analyzer. The result of DSC analysis indicates Yb^{3+}:$NaY(MoO_4)_2$ crystals melt congruently at about 1128 °C, as shown in Fig. 2. The hardness of Yb^{3+}:$NaY(MoO_4)_2$ crystal was determined using a 401MVA™ Vickers-microhardometer. The hardness of Yb^{3+}:$NaY(MoO_4)_2$ crystals is 314 VDH.

3. Spectral properties

The sample with dimension of $7 \times 7 \times 1.2\ mm^3$ was cut from the grown crystal and polished for the spectral measurement. The absorption spectrum of Yb^{3+}:$NaY(MoO_4)_2$ was measured using the Perkin–Elmer UV–VIS–NIR Spectrometer (Lambda-900). The fluorescence lifetime and fluorescence spectrum at room temperature were measured using an Edinburgh Instruments FLS920 spectrophotometer with a continuous Xe-flash lamp.

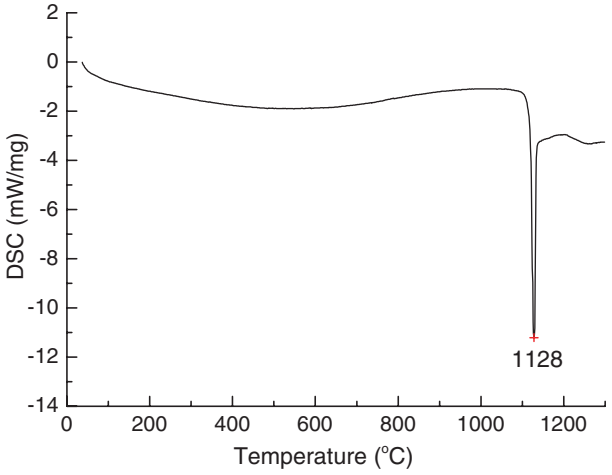

Fig. 2. DSC curve of Yb^{3+}:$NaY(MoO_4)_2$ crystal.

Fig. 3 shows the absorption spectrum of Yb^{3+}:$NaY(MoO_4)_2$ crystal. The absorption band observed in the 800–1100 nm is due to $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ion. The strong absorption occurs near 966, 976 and 994 nm for π-polarization and 935, 964 and 976 nm for σ-polarization, respectively. The absorption line at 976 nm has a full-width at half-maximum (FWHM) of 41 nm for π-polarization and 56 nm for σ-polarization, which is suitable for diode-laser pumping. The absorption cross-section σ_{ab} was determined using $\sigma_{ab} = \alpha/N_c$, α is absorption coefficient which is $12.78\ cm^{-1}$ for π-polarization and 9.58 nm for σ-polarization at 976 nm, N_c is the concentration of Yb^{3+} ions in Yb^{3+}:$NaY(MoO_4)_2$ crystal, which was determined to be 5.89 at.% by ionic coupled plasma (ICP) spectrometry, i.e. $3.84 \times 10^{20}\ cm^{-3}$. Then, the absorption cross-section σ_{ab} is $3.32 \times 10^{-20}\ cm^2$ for π-polarization and $2.49 \times 10^{-20}\ cm^2$ for σ-polarization at 976 nm, respectively.

Fig. 4 shows the fluorescence spectrum of Yb^{3+}:$NaY(MoO_4)_2$ crystal excited with 976 nm radiation. The

Fig. 1. Yb^{3+}:$NaY(MoO_4)_2$ crystals.