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Optical spectroscopy of Yb/Er codoped $NaY(WO_4)_2$ crystal

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Abstract

Erbium and ytterbium codoped double tungstates $NaY(WO_4)_2$ crystals were prepared by using Czochralski (CZ) pulling method. The absorption spectra in the region 290–2000 nm have been recorded at room temperature. The Judd–Ofelt theory was applied to the measured values of absorption line strengths to evaluate the spontaneous emission probabilities and stimulated emission cross sections of Er^{3+} ions in $NaY(WO_4)_2$ crystals. Intensive green and red lights were measured when the sample were pumped by a 974 nm laser diode (LD), especially, the intensities of green upconversion luminescence are very strong. The mechanism of energy transfer from Yb^{3+} to Er^{3+} ions was analyzed. Energy transfer and nonradiative relaxation played an important role in the upconversion process. Photoexcited luminescence experiments are also fulfilled to help analyzing the transit processes of the energy levels.

Keywords: A. Optical materials; A. Inorganic compounds; B. Crystal growth; D. Luminescence; D. Optical properties

1. Introduction

Nowadays, peoples show great interests in compact laser operating in the infrared (~1.5 and 3 μm) for optical communications, medical and eye-safe light detecting and ranging (LIDAR) applications [1–3], and in the visible region (blue–green), for data storage, undersea communications, etc. Diode pumped solid-state lasers could provide compact and efficient devices with the advantage of easy coupling with fiber integrated optical systems. For diode pumped laser emission at mid infrared and visible regions (upconversion based lasers), Er^{3+} seems to be a natural candidate due to its 1.5 μm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) and 2.8 μm emissions ($^4I_{11/2} \rightarrow {}^4I_{13/2}$). Its green emission is at ~0.54 μm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and its absorption bands at ~0.8 and ~0.98 μm. Among several techniques that are currently used to obtain compact visible lasers, the upconversion lasing is one of the most promising techniques since it does not require a nonlinear media for second harmonic generation [4]. The overlapping of $^2F_{5/2}$ energy level of Yb^{3+} ions and $^4I_{11/2}$ energy level of Er^{3+} ions produce efficient resonant transfer between both ions. So it is possible to perform selective excitation of the Yb^{3+} ions and realize energy transfer between the two ions. Upconversion laser performance of Er^{3+} has been observed in some crystals and glass fibers [5–7].

The hosts play important roles in the upconversion luminescence. Er/Yb:$NaY(WO_4)_2$ crystal is a new kind of crystal demonstrating good optical performance. $NaY(WO_4)_2$ crystal (here denoted as NYW) is classified among the disorder crystalline host for lasing rare-earth ions [8]. The disorder structure presents the broadening of the optical features in the absorption and emission spectrum even at low temperature. This fact has some interesting results on the optical properties of the materials. The addition of proper RE oxides to the starting mixture allows obtaining crystals suitable for spectroscopic experiments. NYW has been demonstrated to be a promising host lattice for lasing ions: laser action has been reported for Nd^{3+} doped in the matrix [9]. In this letter, we report the absorption spectra of Yb/Er codoped NYW and whose analysis on the basis of the Judd–Ofelt theory. The three phenomenological J–O intensity parameters Ω_t ($t = 2, 4$ and 6) of Er^{3+} ions in NYW crystals are determined by performing a least square fit of calculated and observed absorption line intensities. These intensity parameters are then used to determine the spontaneous emission probabilities and branching ratios. We measured

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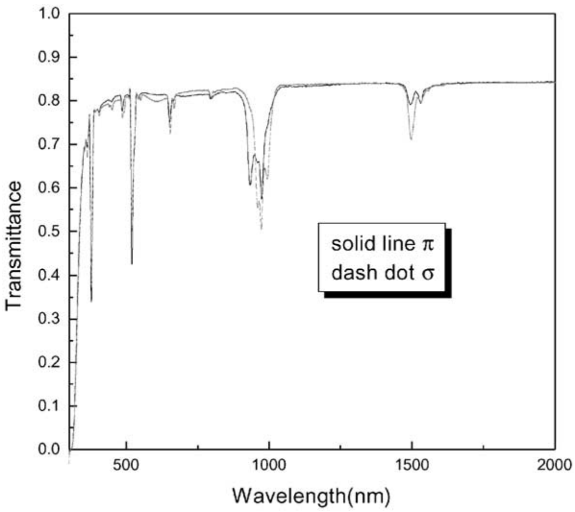

Fig. 1. Absorption spectra of Er/Yb codoped $NaY(WO_4)_2$ crystal at room temperature.

the upconversion luminescence of Er^{3+}/Yb^{3+} codoped $NaY(WO_4)_2$ crystal excited by 974 nm laser diode. The concentration of Er^{3+} and Yb^{3+} is about 0.5% and 2% respectively. The thickness of the sample is 3.5 mm and both sides are well polished.

2. Crystal growth

Single crystals of NYW are usually grown with CZ pulling method using a MCGS-3 RF single-crystal furnace.

The raw materials was prepared according to the following formula:

$$Na_2CO_3 + (1 - x - y)Y_2O_3 + xEr_2O_3 + yYb_2O_3 + 4WO_3 \rightarrow 2NaY_{1-x-y}Er_xYb_y(WO_4)_2 + CO_2\uparrow$$

In our experiment, the Er^{3+} and Yb^{3+} dopants concentrations are of 0.5% and 2% substituting for Y^{3+}. The depth of the Pt crucible was 30 mm, and the diameter is 55 mm. Crystal growth began on a ⟨101⟩ oriented seed. The rotation rate is 55–60 rpm and pulling rate 1.5 mm/h. The obtained sample shows pink color, and its size reaches up to $\varnothing 2 \times 4$ cm. No macro-defects were observed in the sample. The rare earth concentration in the sample was determined by atomic absorption spectrometry method. The distribution coefficient is close to unity. That is the rare earth concentration in the crystal is close to that in the formula. The quantities of Er^{3+} and Yb^{3+} ions in the sample are $3.27 \times 10^{19}/cm^3$ and $1.308 \times 10^{20}/cm^3$ respectively.

3. Optical measurements and results discussion

3.1. Absorption spectra and Judd–Ofelt analysis

The sample was cut along a-face and polished to optical grade. The polarized absorption spectra (π, $E \parallel c$-axis; σ, $E \perp c$-axis) at room temperature in 290–2000 nm of a 2.06 mm a-slice were measured on a Hitachi U-3500 spectrophotometer. The room temperature polarized absorption spectra of Er/Yb codoped $NaY(WO_4)_2$ crystal was shown in Fig. 1. The absorption bands of Yb^{3+} and Er^{3+} ions appear to be broader than expected for a crystalline material with ordered structure, due to the random distribution of the Na and rare earth ions in the dodecahedra sites of the scheelite structure. As a consequence of the band broadening, there is no point in attempting in an assignment of the Stark components of the individual states exploiting the selection rules for the polarized spectra. The observed absorption wavelength and the related assignments are listed in Table 1.

The data from these absorption spectra can be used to predict the radiative lifetime of the excited states, the branching ratios and the radiative transition probabilities of the fluorescence transitions, using the Judd–Ofelt (J–O) analysis method. For the polarized absorption spectra, the calculation was the whole consideration of the two polarized

Table 1
The calculated and measured oscillator strength, line strength and three J–O parameters of Er^{3+} in Er/Yb codoped $NaY(WO_4)_2$ crystal (the phenomenological parameters (10^{-20} cm^2), $\Omega_2 = 18.1$, $\Omega_4 = 2.59$, $\Omega_6 = 1.21$)

Energy level	Wavelength (nm)	Measured oscillator strength (10^{-6})	Calculated oscillator strength (10^{-6})	Measured line strength (10^{-20})	Calculated line strength (10^{-20})
$^4G_{9/2}$	365	4.7	4.01	1.38	1.18
$^4G_{11/2}$	379	60.8	59.6	18.5	18.1
$^2G_{9/2}$	406	1.03	0.99	0.33	0.32
$^4F_{3/2}$, $^4F_{5/2}$	442,450	1.15	1.50	0.42	0.54
$^4F_{7/2}$	487	3.10	2.90	1.22	1.14
$^2H_{11/2}$	520	32.3	33.5	13.5	14.1
$^4S_{3/2}$	543	0.88	0.61	0.385	0.27
$^4F_{9/2}$	653	3.49	3.68	1.84	1.94
$^4I_{9/2}$	800	0.68	0.71	0.44	0.46