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Spectroscopic analyses of Tm^{3+}/Yb^{3+}: $BaGd_2(MoO_4)_4$ crystal for mid-infrared applications

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ABSTRACT

A Tm^{3+}/Yb^{3+} co-doped $BaGd_2(MoO_4)_4$ crystal was successfully grown and analyzed. The use of Tm^{3+} codoping for enhancement of the transition of Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ ~ 2 μm emissions was investigated. Compared with Tm^{3+} singly-doped $BaGd_2(MoO_4)_4$ crystal, the Tm^{3+}/Yb^{3+} codoped $BaGd_2(MoO_4)_4$ crystal possessed a longer fluorescence lifetime (2.467 ms), higher fluorescence emission cross section (1.174×10^{-20} cm^2) corresponding to the stimulated emission of Tm^{3+} :$^3F_4 \rightarrow {}^3H_6$ transition. The ~2 μm emission characteristics and energy transfer were investigated in detail. The energy transition efficiency from Tm^{3+}:$^3H_4$ level to Yb^{3+}:$^2F_{5/2}$ level, and from Yb^{3+}:$^2F_{5/2}$ level to Tm^{3+}:$^3H_5$ level were calculated to be 0.52 and 0.75, respectively. It indicates that Yb^{3+} can act as an effective bridge between $^3H_4$ level and $^3F_4$ level of Tm^{3+} to obtain efficient 1.9 μm emission under being pumped by a conventional 782 nm LD. Therefore, Tm^{3+}/Yb^{3+} co-doped BGM crystal is a promising candidate for mid-infrared applications.

1. Introduction

Nowadays, 2 μm laser have been widely used in laser remote sensing applications especially for coherent Doppler lidar wind detection. The nature of high absorption in liquid water makes the Tm^{3+} doped laser sources attractive in medical applications because of very short penetration lengths on human tissues, Moreover, one popular military application for Tm^{3+} doped laser sources is to use them as pump sources for longer wavelength mid-infrared generation via nonlinear frequency conversion, such as optical parametric oscillator (OPO) [1–5]. Among various rare earth (RE) ions, it is well know that Tm^{3+} is a natural candidate for 2 μm lasers owing to the $^3F_4 \rightarrow {}^3H_6$ transition [6,7]. Energy from the high-power AlGaAs laser diodes (LD) around 800 nm source excites the Tm^{3+} ions to its $^3H_4$ level and then decay radiatively to $^3F_4$ level, finally the emission spectral intervals are around 1.8–2.0 μm on the $^3F_4 \rightarrow {}^3H_6$ transition [8]. However, due to exist decay radiatively, energy transfer efficiency and the population of $^3F_4$ level of Tm^{3+} will be at a relative lower level. Then result in a relative low feeding to $^3F_4$ level upon high-power AlGaAs laser diodes (LD) excitation. In order to conquer the problem, Tm^{3+} doped crystal by Yb^{3+} are recognized as efficient systems for obtaining efficient ~2 μm emission. Yb^{3+} ions, has large absorption and emission cross section, relatively long lifetime, simple energy level scheme [9,10]. Which can transfer its energy to Tm^{3+} via a non-resonant energy transfer processes assisted by one or more phonons [11]. Fast diffusion among the Yb^{3+} ions can enhance the efficiency of the non-resonant energy transfer from Yb^{3+} to Tm^{3+} by $^2F_{5/2} + {}^3H_6 \rightarrow {}^2F_{7/2} + {}^3H_5$ [12]. Therefore, As the energy level scheme illustrated in Fig. 1 shows, under the excitation of 782 nm laser pump, the Tm^{3+} ion is excited to the excited state ($^3H_4$) and transfer the excitation energy to Yb^{3+}:$^2F_{5/2}$. then opposite direction transfer energy to Tm^{3+}:$^3H_5$ level via a non-resonant energy transfer process for obtaining efficient ~2 μm emission.

The host material for 2 μm lasers is expected to possess low phonon energy because which can decrease the non-radiative losses efficiently and thus increasing the quantum efficiency of $^3F_4 \rightarrow {}^3H_6$ transition. However, materials with low phonon energy will enhance the up-conversion luminescence, this characteristic have a negative contribution to the 2 μm emission [13–15]. Fortunately, we find a potential gain

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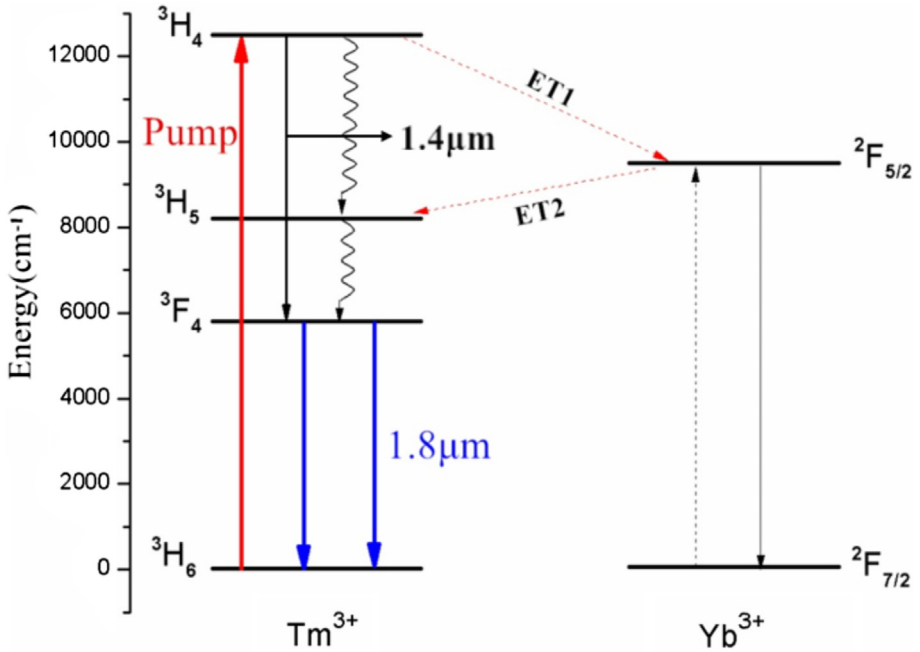

Fig. 1. Simplified energy level diagram of Tm^{3+} and Yb^{3+} co-doped system. ET1: energy transfer from Tm^{3+}:$^3H_4$ to Yb^{3+}:$^2F_{5/2}$ level; ET2: energy transfer from Yb^{3+}:$^2F_{5/2}$ to Tm^{3+}:$^3H_5$ level.

medium $BaGd_2(MoO_4)_4$ (BGM) crystal for efficient 2 μm laser operation. The maximum phonon energy of BGM crystal is only ~880 cm^{-1} [16], The energy gap between $^3F_4$ and $^3H_6$ multiplets are 5000 cm^{-1}, which is nearly match the energy gap to ensure 2 μm emission.

BGM crystal belongs to the monoclinic crystal system, unit cell with lattice parameters of a = 5.263 Å, b = 19.390 Å, c = 12.647 Å, It belongs to the space group C2/c and has a perfect (0 1 0) cleavage plane [17], offering two nonequivalent cationic sites for optically active Re^{3+} substitution. Consequently, BGM crystal is characterized by a high degree of structural disorder. Thus, the high degree of disorder of BGM crystal inevitably contributes to inhomogeneous broadening of the absorption and fluorescence spectra, bringing a large amount of advantages from the standpoint of applications as active media in LD-pumped solid-state lasers.

In this work, Tm^{3+}, Yb^{3+} co-doped BGM crystal was successfully grown by Czochralski method. Under the excitation of 782 nm LD, an enhance the ~2 μm fluorescence emission of Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ transition was obtained after the Yb^{3+} codoping in Tm^{3+} doped BGM crystal, the population of $^3F_4$ level of Tm^{3+} is increased by the effect of Tm^{3+}-Yb^{3+}-Tm^{3+} energy transfer. Yb^{3+} was demonstrated to greatly facilitate the Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ emission by efficient energy transfer (ET1) from Tm^{3+}:$^3H_4$ to Yb^{3+} :$^2F_{5/2}$ and efficient energy transfer (ET2) from Yb^{3+}:$^2F_{5/2}$ to Tm^{3+}:$^3H_5$. It indicated that Yb^{3+} can act as an effective bridge between $^3H_4$ level and $^3F_6$ level of Tm^{3+} to obtain efficient 2 μm emission.

2. Experimental section

The Tm^{3+} single doped, Yb^{3+} single doped and Tm^{3+}/Yb^{3+} co-doped BGM crystals were grown by the Czochralski method with an intermediate frequency induction heating system. Oxide powders of MoO_3(4N), Gd_2O_3(4N), Yb_2O_3(4N), Tm_2O_3(4N) and Ba_2CO_3(4N) were used as starting materials. The raw powders were mixed together and pressed into disks, followed by heating in air for 15 h at 900 °C. The bulks were loaded into an iridium crucible for crystal growth, and temperature was set to 1100 °C in air atmosphere. A pulling rate of 0.8–1.2 mm/h and rotation rate of 10–15 rpm were adopted during the growth. To prevent the crystal from cracking, it was cooled to room temperature very slowly with a rate of 15–25 °C/h and annealed at 900 °C in air atmosphere to reduce the color centers inside the crystal. The concentrations of Tm^{3+} ions and Yb^{3+} ions were detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. The single-doped crystal was measured to be 2.56 at.% (1.65×10^{20} ions/cm^3) of Tm^{3+}. The Yb^{3+} single-doped crystal was measured to be 10.8 at.% (6.90×10^{20} ions/cm^3). The co-doped crystal was measured to be 2.27 at.% (1.46×10^{20} ions/cm^3) of Tm^{3+}, and 8.8 at.% (5.61×10^{20} ions/cm^3) of Yb^{3+}, respectively. Three 5 mm thick crystals cut from the medium and polished for absorption spectra measurements, fluorescence spectrum and the fluorescence decay lifetime measurements. All the measurements were taken at room temperature.

3. Results and discussions

As shown in Fig. 2, the transmittance spectra of Tm^{3+} doped BGM crystal and Tm^{3+}/Yb^{3+} co-doped BGM crystal. The maximum transmittance of Tm^{3+} doped BGM crystal and Tm^{3+}/Yb^{3+} co-doped BGM crystal is 53% and 62%, respectively. The room temperature absorption spectra were measured by spectrophotometer (UV-3150, Shimadzu, Japan) in a range 400–2100 nm. Fig. 3 shows the absorption spectrum of the Tm^{3+} doped BGM and Tm^{3+}/Yb^{3+} co-doped BGM crystal. Six main absorption bands in spectral regions of 458–485, 668–727, 730–838, 1147–1288, 1661–1874 and 900–1046 nm were observed, which corresponded to the electronic transitions from ground $^3H_6$ level to $^1G_4$, $^3F_{2,3}$, $^3H_4$, $^3H_5$, $^3F_4$ levels and Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$, Respectively. The effective absorption cross-section of the transition $^3H_6 \rightarrow {}^3H_4$ is 1.126×10^{-20} cm^2 at 790 nm. The absorption cross-section is larger than that of some well-known Tm^{3+} doped laser crystals, such as $LiYF_4$ (0.5×10^{-20} cm^2 [18]), Sc_2SiO_5 (0.56×10^{-20} cm^2 [19]), YAG (0.63×10^{-20} cm^2 [20]), YAP (0.67×10^{-20} cm^2 [21]) and Lu_2SiO_5 (0.83×10^{-20} cm^2 [22]). The full width half maximum (FWHM) is 30 nm, broadband absorption is well-adapted for efficient diode-pumping, which implies that the Tm^{3+}/Yb^{3+} co-doped BGM crystal is very suitable for resonant pumping by a 782 nm AlGaAs laser diode.

According to the Judd–Ofelt theory [23,24], the intensity parameters $\Omega_{2,4,6}$ of Tm^{3+} (shown in Table 1) was calculated from the absorption spectrum, and shown in with other Tm^{3+} doped crystals for comparison. A lower root-mean-square RMS confirms a better