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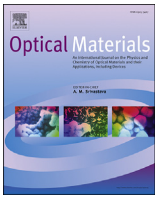

Luminescence properties of Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystals for 2.7 μm mid-infrared laser

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ABSTRACT

The enhanced 2.7 μm mid-infrared emission from the Er^{3+}:$^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition with Nd^{3+} ions as the sensitizer was achieved in the $Na_5Lu_9F_{32}$ single crystal which was successfully grown by a Bridgman method. The transmission spectrum was tested and almost no absorption of 2.7 μm band was observed. It was indicated that the content of OH- ion was very low in the crystal and it was beneficial to the 2.7 μm mid-infrared laser output. Intense 2.7 μm emissions were achieved with Nd^{3+} ions sensitizing Er^{3+} ions under the 800 nm LD pumping and the energy transfer processes between Er^{3+} and Nd^{3+} ions were analyzed. Meanwhile, the greatly decreased near infrared emission at 1.5 μm and green up-conversion emission were obtained. Additionally, the optimized concentration ratio of Er^{3+} to Nd^{3+} for efficient 2.7 μm emission was investigated in this work and the maximum emission cross section at 2.7 μm was calculated. The decay curve of 1.5 μm emission could be well fitted by Inokuti-Hirayama expression, which was strongly indicated the dipole-dipole energy transfer from Er^{3+} to Nd^{3+} ions. The results showed that Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystal had potential applications in 2.7 μm mid-infrared laser.

1. Introduction

Since 2.7 μm mid-infrared laser output was first observed in CaF_2 single crystal doped with Er^{3+} ions [1], many research work about Er^{3+} doped inorganic materials for this purpose were implemented because of the increasing demand of potential applications in ranging, remote sensing, military counter-measures, environment monitoring, medical treatment, light detection and many other fields [2–4]. It is well known that Er^{3+} can emit fluorescence at 2.7 μm due to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition. However, the laser transition could be self-terminating because the fluorescence lifetime of upper level $^4I_{11/2}$ is considerably shorter than that of the lower level $^4I_{13/2}$, which would make the 2.7 μm emission cannot be achieved easily [5,6]. Moreover, the lower absorption coefficient in the range of 700 nm–1200 nm for Er^{3+} is not beneficial to the laser output. Introducing Nd^{3+} as sensitizer for Er^{3+} can effectively solve these problems on account of the efficient energy transfer between the Er^{3+} and Nd^{3+} ions and consequently result in the enhancement of 2.7 μm emission [7].

The choice of matrix materials is also important for improving spectral performance. Generally, the fluorescence efficiency of rare earth ions enhances with the decrease of phonon energy of the matrix material, and the fluoride has the lower phonon energy which makes it a kind of suitable solid laser material. In addition, the fluoride also has great physical-chemical properties and wide optical transmittance in the infrared band which is favorable to obtain highly efficient infrared laser operation [8].

Recently, the research about rare earth ions doped $LiYF_4$ single crystal and the spectral characteristics of 2.7 μm mid-infrared band have been carried out in our laboratory. Such performance between Er^{3+} and Nd^{3+} in $LiYF_4$ single crystal has been analyzed [9]. However, it is found that there is an obvious absorption band at 2.7 μm in the transmission spectrum of $LiYF_4$ crystal, which has bad influence in the performance of 2.7 μm laser output. In contrast to it, the $Na_5Lu_9F_{32}$ crystal has favorable transmittance without absorption band at 2.7 μm, which can be regarded as good host material for achieving the 2.7 μm mid-infrared emission. Furthermore, the bulk $Na_5Lu_9F_{32}$ single crystal possesses the less scattering and higher transmission compared with its powder.

In this paper, the growth difficulties of singly-doped, and Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystals have been overcome. The

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Er^{3+} and Nd^{3+} ions can be easily substituted with Lu^{3+} lanthanide crystal sites in the single crystal due to the equal valence and similar ionic radius to reach a high concentration. In these samples, all concentrations of Er^{3+} are held constant, while those of Nd^{3+} are changed. The luminescence properties and energy transfer process between Er^{3+} and Nd^{3+} in samples are analyzed and studied.

2. Experimental

The Er^{3+} singly doped and Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystals were grown by a Bridgman technique. The high purified of commercially available NaF, LuF_3, ErF_3, and NdF_3 powders were used to be preparation of the materials. The molar composition of the mixed ingredients was $40NaF\text{-}(59\text{-}\chi)LuF_3\text{-}1ErF_3\text{-}\chi NdF_3$ ($\chi = 0$, 0.5, 1, 1.5, 2, 3). The obtained samples were expressed respectively as NFEN0, NFEN1, NFEN2, NFEN3, NFEN4, and NFEN5. The initial powders were mixed and ground sufficiently for 1 h in a porcelain mortal. A seed of pure $Na_5Lu_9F_{32}$ single crystal with the ⟨001⟩ direction was placed at the bottom of the Pt crucible. The temperature gradient across the solid-liquid interface was 70–80 °C/cm and the seeding temperature was about 850–870 °C. The growth process was carried out by lowering the crucible at a rate of 0.06 mm/h. The $Na_5Lu_9F_{32}$ single crystals were obtained after the crucible was uncovered. The detailed process is reported elsewhere [10]. Fig. 1 (a) shows the high-quality as-grown single crystal and the polished slice of crystal with 2.0 mm thickness.

The structure of crystal was measured by using a XD-98X diffractometer (XD-3, Beijing) for X-ray diffraction (XRD). The absorption spectra were recorded with a Cary 5000 UV/VIS/NIR spectrophotometer. The FTIR transmission spectra were investigated with a TENSOR 27 NIR spectrometer (Bruker Germany). The emission spectra in the infrared region of 1000–3000 nm were recorded under the excitation of 800 nm laser diode (LD) by a Triax 320 type spectrometer. The up-conversion spectra were measured on a HITACHI F-4500 fluorescence spectrometer excited by 800 nm light. The fluorescence lifetimes were obtained with the FLSP920 fluorescence spectrophotometer. Meanwhile, the actual concentrations of Er^{3+} and Nd^{3+} ions in all the samples were measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). The measured concentrations of Er^{3+} and Nd^{3+} ions in all crystals were listed in Table 1. All the measured data were tested at room temperature.

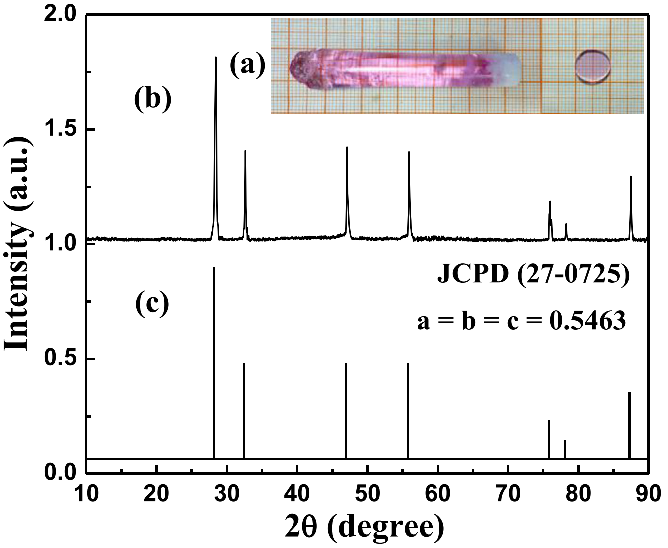

Fig. 1. (a) Photograph of Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystal. (b) XRD pattern of the $Na_5Lu_9F_{32}:Er^{3+}/Nd^{3+}$. (c) Standard line pattern of the $Na_5Lu_9F_{32}$ (27-0725).

3. Results and discussion

3.1. X-ray diffraction and infrared transmittance spectrum

Fig. 1 shows the comparison of the X-ray diffraction pattern between Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ crystal and the standard line pattern of $Na_5Lu_9F_{32}$ in the JCPD card (27-0725). It can be seen that all the diffraction peak positions are matched perfectly with those in standard $Na_5Lu_9F_{32}$, indicating that the co-doping with Er^{3+} and Nd^{3+} ions have scarcely any effect on the crystal structure. As seen from Table 1, the concentrations of Er^{3+} are around 0.99 mol% which are close to the designed values. However, the concentrations of Nd^{3+} have certain difference with the designed ones, which caused by segregation phenomenon of the Nd^{3+} ions in the $Na_5Lu_9F_{32}$ crystal [11]. Hence, the measured concentrations of Er^{3+} and Nd^{3+} ions are used in the context below.

The transmission spectra of $Na_5Lu_9F_{32}$ crystal and $LiYF_4$ crystal are shown in Fig. 2. It is found that there is an obvious absorption band at 2.7 μm in the transmission spectrum of $LiYF_4$ crystal, which has bad influence in the performance of 2.7 μm laser output. In contrast to $LiYF_4$ crystal, there is a better transmittance of $Na_5Lu_9F_{32}$ single crystal in 4000–7150 nm band, and the maximum transmittance is about 90%. There is almost no absorption band in the 2.7 μm band, which indicates that fewer content of OH- ions in the $Na_5Lu_9F_{32}$ single crystal. Therefore, $Na_5Lu_9F_{32}$ single crystal is expected to be a suitable mid-infrared laser material at 2.7 μm.

3.2. Absorption spectra and Judd-Ofelt parameters

Fig. 3 shows the absorption spectra of Er^{3+} singly doped and Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ single crystals in the wavelength region of 300–1700 nm. The main absorption bands, corresponding to the transitions of Er^{3+} and Nd^{3+} from their ground state to higher excited levels, are marked. Compared with the Er^{3+} singly doped $Na_5Lu_9F_{32}$ crystal, it can be found that the co-doped samples with the introduction of Nd^{3+} do not change the level positions. All the co-doped samples have similar features only their relative intensities which are concentration dependent. Apparently, an enhanced absorption band can be observed at 800 nm for Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ crystal, which indicates that Er^{3+}/Nd^{3+} co-doped sample can be excited by the 800 nm pumping energy more efficiently than Er^{3+} singly doped one. This benefits from both the contributions of the transitions $Er^{3+}:{}^4I_{15/2} \rightarrow {}^4I_{9/2}$ and $Nd^{3+}:{}^4I_{9/2} \rightarrow {}^4F_{5/2} + {}^2H_{9/2}$.

The radiative properties of rare-earth ions within a matrix can be determined by employing the Judd-Ofelt theory [12,13] based on the measured absorption spectra and chemical-physical properties. According to the absorption spectra data, the Judd-Ofelt parameters Ω_t (t = 2, 4, 6) of Er^{3+}/Nd^{3+} co-doped $Na_5Lu_9F_{32}$ samples can be calculated by a standard Judd-Ofelt calculating procedure.

The experimental oscillator strengths are obtained by using the following expression [14]:

$$f_{exp} = \frac{mc^2}{\pi e^2 N} \int \frac{2.303OD(\lambda)}{\lambda^2 d} d\lambda \qquad (1)$$

where m is the electron mass, e is the electron charge, $OD(\lambda)$ is the optical density, N is the number of the rare-earth ions per unit volume, c and d are the speed of light and the thickness of the crystal, respectively.

According to Judd-Ofelt theory, the calculated oscillator strength f_{cal} is expressed as the following: