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Luminescent properties and energy transfer processes of co-doped Yb–Er poly-crystalline YAG matrix

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Abstract

A poly-crystalline YAG matrix was obtained through the precipitation method; this matrix was single and co-doped with ytterbium and erbium ions, i.e., Yb:YAG, Er:YAG and Yb,Er:YAG. It is found that the measured luminescent properties are similar to those reported for a mono-crystal YAG matrix. In addition, by studying the energy transfer processes in co-doped samples, it is shown that at high erbium concentrations the red emission is enhanced through an up-conversion process that takes place from the $^4I_{13/2}$ to the $^4F_{9/2}$ state of erbium ions. This enhanced red emission becomes comparable in intensity to the observed green emission and occurs by pumping at 800 nm through a back energy transfer process.

Keywords: Spectroscopy; Yb^{+3}; Er^{+3}; Energy transfer

1. Introduction

Rare earth doped materials offer high potential applications for compact visible sources such as optical displays and memories, spectroscopy and medical optics. The importance of these materials is increasing since they can be excited with commercially available semiconductor diode lasers which have become cheaper. Most of the studied matrices correspond to glasses [1] and mono-crystal materials [2]; here we report a poly-crystal matrix which was made through the precipitation method. In contrast to the mono-crystals, the poly-crystalline matrix is easy to make and, as shown in this work, the luminescent properties for single doped with ytterbium and erbium and co-doped with ytterbium–erbium ions in a YAG matrix are similar to those observed in mono-crystals.

One use of the single-doped Er:YAG is to obtain laser emission around 1500 nm through the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition [1], however this system has a drawback, i.e., the erbium shows a low absorption cross section that limits the pump efficiency. This is solved by co-doping the system with ytterbium ions since these ions show a high absorption cross section and the absorption band is broader than the shown by erbium ions. Furthermore, for the co-doped system this band is even broader and non-radiative energy transfer processes occur that might benefit the luminescent properties of the material.

In this work, the luminescent properties of Yb:YAG, Er:YAG and Yb,Er:YAG with a YAG poly-crystalline matrix are reported. For each single-doped sample, the erbium and ytterbium concentration was 0.5 and 5.0 at%, respectively, while for the co-doped samples the ytterbium concentration was fixed at 6.5 at% and the erbium concentration was varied at the values 0.5,

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2.0, 5.0 and 10.0 at%. These samples were pumped at 940, 800 and 532 nm and the non-radiative energy transfer processes were studied. At low erbium concentration, the solution of the General Energy Transfer Master Equations [3] could predict the measured ytterbium decay curves, acting as an acceptor. However, at high erbium concentrations and pumping at 800 nm the decay curves for ytterbium showed a faster decay rate than the predicted by the solution to such equations. This is so because an additional up-conversion process takes place that enhances the red emission while the green emission remains unchanged.

2. Experimental

2.1. Sample preparation

The $Y_3Al_5O_{12}$ (YAG) samples were prepared by a precipitation process following the steps described elsewhere [4]. All the chemicals were analytical grade and were used as received. First, yttrium nitrate was dissolved in 100 ml of distilled water, mixed with 2 ml of acetic acid, and stirred 2 h at 50 °C. In a separate flask, aluminum nitrate was dissolved in distilled water and stirred for 1 h at room temperature. The rare earth ions were added to the aluminum solution in a salt form. Both solutions were mixed together and 2 ml of ethylene glycol were added. The final solution was further stirred at 70 °C, until foam was formed. The obtained foam was dried at 120 °C and grinded to obtain a powder. A heat treatment of 700 °C for 6 h was applied to the samples and then increased at a rate of 5 °C/min, until a temperature of 900 °C was reached. Finally the samples were kept at 1150 °C for 4 h.

2.2. Spectroscopic set-up

The absorption spectra of the powder samples were recorded by using a spectrophotometer (Perkin-Elmer Lambda 900) equipped with an integrating sphere. The luminescence spectra were measured with a R5660 PMT from Hamamatsu, coupled to a SpectraPro-5001 spectrograph from Acton Research. The signal from the PMT was processed by a SR830 lock-in amplifier from Standford Research and transferred to the computer for further analysis. The luminescence decays were measured with a 500 MHz bandwidth digital oscilloscope from LeCroy. To pump the samples at 532, 800 and 940 nm we used a MOPO system from Spectra Physics.

3. Results and discussion

3.1. The absorption and emission spectra

The absorption spectra of single and co-doped poly-crystalline samples, Yb:YAG, Er:YAG and Yb,Er: YAG, were measured. For the single-doped samples the recorded spectra were similar to the observed in the corresponding samples in a mono-crystal matrix. Fig. 1 presents the normalized absorption spectra for single-doped samples with Er(5.0) and Yb(5.0), respectively, as well as the spectrum for a co-doped sample with Er(5.0) and Yb(6.5). Here, the numbers enclosed in parenthesis denote ion concentrations in at%. From Fig. 1, in the case of single-doped samples, we clearly observe the transitions $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^2F_{7/2} \rightarrow {}^2F_{5/2}$ corresponding to erbium and ytterbium ions, respectively; and for the case of Yb–Er co-doped sample the absorption spectrum corresponds to the superposition of both transitions in the range 850–1050 nm, though below 850 nm the spectrum is rather characteristic of Erbium absorption band. Thus, the later sample can be excited at the broad band 880–1030 nm while the former samples keep their characteristic absorption bands as single-doped samples.

The single-doped erbium poly-crystal sample was pumped at 532 nm and, its emission spectrum was recorded and compared against a single-doped mono-crystal sample that we had at hand. Both samples showed identical peaks in the green (strong emission) and red (weak emission) regions around 560 and 670 nm, respectively. Similar emission bands were recorded when the co-doped poly-crystalline samples were pumped at 940 nm. This kind of emission spectra are shown in Fig. 2(a) and (b) for the case of co-doped samples with erbium concentrations at 0.5 and 10.0 at%, respectively, and with ytterbium concentration kept at 6.5 at% in each sample. From the corresponding absorption spectra it follows that at this pump wavelength (940 nm) the ytterbium ions are excited and the nature of the green and red bands shown in Fig. 2 comes from two processes: (i) the non-radiative energy transfer that takes

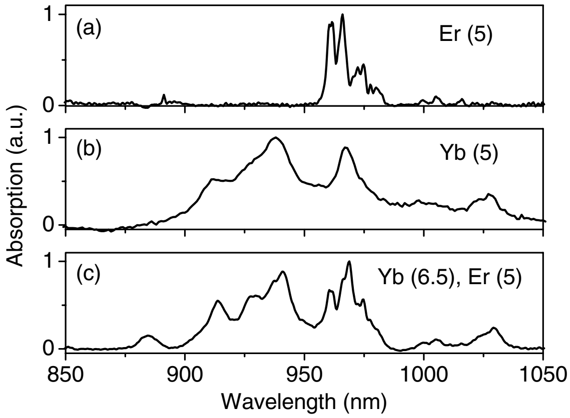

Fig. 1. Normalized absorption spectra of single and co-doped poly-crystalline YAG matrix doped with the following atomic concentrations: (a) 5.0% of Er, (b) 5.0% of Yb and, (c) 6.5% of Yb and 5% of Er. In the figure, the numbers enclosed in parenthesis denote dopant loadings in atomic concentrations.