Journal of Luminescence 196 (2018) 36–39

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Intense red upconversion emission and energy transfer in $Yb^{3+}/Ho^{3+}/Er^{3+}:CaYAlO_4$

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ARTICLE INFO

Keywords:
Up-conversion
$CaYAlO_4$ crystal
Energy transfer

ABSTRACT

In this paper, we report on the intense red up-conversion emission in $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystal. The fluorescence spectra in three different doped crystals (Er^{3+}: CYA, Ho^{3+}/Er^{3+}: CYA and $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA) have been measured and compared in a full emission range (visible, near-infrared and mid-infrared). The energy transfer and up-conversion emission mechanisms were discussed. Results show with the doping of Yb^{3+} ion, the intensity of red emission in $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystal become much stronger, about 10 times, than that of Ho^{3+}/Er^{3+}: CYA, and 30 times than that of Er^{3+}: CYA. The energy transfer efficiency of Yb^{3+} to Ho^{3+}, Er^{3+} ion was calculated to be 0.727 which indicates that Yb^{3+} ion transfers a majority of its energy to Ho^{3+}, Er^{3+} ion and finally results in the strong red up-conversion emission in $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystal.

1. Introduction

Upconversion materials have attracted considerable attention for many years, for their widely applications in the fields of biosensing, bioimaging, solid-state multicolor display and lasing [1–3]. $CaYAlO_4$ (CYA) is a promising upconversion emission laser crystal. It crystallizes in the perovskite phase with tetragonal K_2NiF_4 structure, belonging to space group I4/mmm. The lattice parameters are a = 3.6451 and c = 11.8743 Å. The density is 4.64 g/cm^3 and the thermal conductivities are 3.7 W/m/K along a-axis and 3.3 W/m/K along c-axis respectively [4]. Besides the advantages of good mechanical strength and high thermal conductivity, as an aluminate, CYA crystal also has good chemical stability. The low phonon energy and multiphonon transition rates decrease the possibility of non-radiative decay and thus help to generate visible laser oscillations. Furthermore, some literature have reported the intense upconversion emission in this host [5,6]. All that indicate CYA could be an attractive upconversion medium.

Trivalent-lanthanide ions are always doped in hosts for their excellent characters such as abundant energy levels for various wavelength emissions, long excited state lifetime beneficial for converting low-energy photons into high-energy photons. Er^{3+} is usually used as one upconversion ion since it can emit green and red fluorescence according to the transitions ($^2H_{11/2}$, $^4S_{3/2}$)→ $^4I_{15/2}$ and $^4F_{9/2}$→ $^4I_{15/2}$ respectively. Upconversion emission involving Er^{3+} ion have been reported in many literatures [7–10]. In our previous work, we noticed when Ho^{3+} ion is co-doped in Er^{3+}:CYA crystal, the red emission became much stronger than that in Er^{3+}:CYA crystal while the green emission decrease obviously on the contrary [11]. So in this work, we discuss the energy transfer mechanisms between Er^{3+} and Ho^{3+} ion in CYA host. Furthermore, to enhance the strength of upconversion, Yb^{3+} ion was added since it has large absorption cross section around 974 nm and thus can act as a sensitizer. The fluorescence strength in three different doped crystals (Er^{3+}: CYA, Ho^{3+}/Er^{3+}: CYA and $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA) have been measured and compared in a full emission range (visible, near-infrared and mid-infrared). The energy transfer and up-conversion emission mechanisms were discussed and proposed.

2. Experimental

Three crystals 30 at% Er^{3+}: CYA, 0.5 at% Ho^{3+}, 30 at% Er^{3+}: CYA and 30 at% Yb^{3+}, 0.5 at% Ho^{3+}, 30 at% Er^{3+}: CYA single crystals were grown by the Czochralski technique. The polycrystalline materials for single crystal growth were prepared by the classical solid-state reaction. The chemicals were Al_2O_3, $CaCO_3$ (A.R. grade) and Y_2O_3, Yb_2O_3, Ho_2O_3, Er_2O_3 (4 N purity). The crystal growth was carried out with N_2 atmosphere protection in a NCIREO DGL-400 furnace, and a Ir crucible of 50 mm diameter by 30 mm high was used. Seeds were cut and oriented in [100] direction. The typical pull rate was 1–2 mm per hour and the rotation rate was 10–20 rpm. Samples with dimensions of 6.0 × 6.0 × 1.0 mm^3 were cut from the as-grown crystals and polished for further spectroscopy measurement. The absorption spectra were measured by Perkin-Elmer UV-VIS-NIR Spectrometer (Lambda-900) from 300 to 2300 nm. The fluorescence spectra and the relevant lifetime decay curves were recorded by Edinburgh Instruments FLS920 and

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https://doi.org/10.1016/j.jlumin.2017.12.018
Received 28 August 2017; Received in revised form 2 November 2017; Accepted 11 December 2017
Available online 11 December 2017

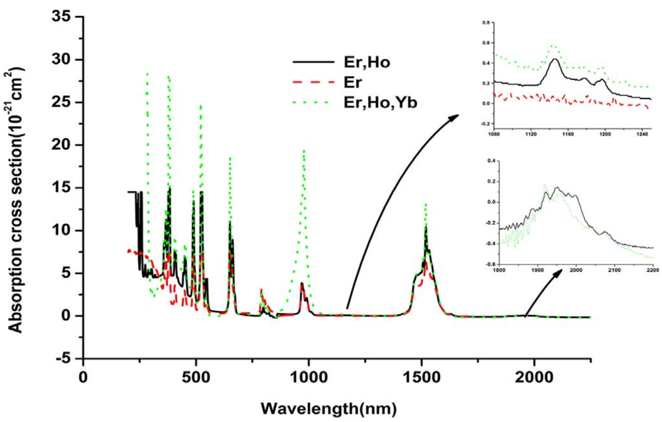

Fig. 1. The absorption spectra of $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA, Ho^{3+}/Er^{3+}: CYA and Er^{3+}: CYA crystals.

FSP920 spectrophotometer. All experiments were measured at room-temperature.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of Er^{3+}:CYA, Ho^{3+}/Er^{3+}:CYA and $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystals recorded at room-temperature are presented in Fig. 1. The absorption spectrum of each crystal consists of several main absorption bands which associates with the transitions of Er^{3+} ion from the $^4I_{15/2}$ ground state to the excited states $^4G_{11/2}$、 $^2G_{9/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}+^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ respectively. Since the concentration of Ho^{3+} ion is much lower than that of Er^{3+} ion, the intensity of Ho^{3+} absorption band is much weaker than that of Er^{3+} ion. Two relatively weak peaks centered at 1144 nm, 1952 nm associates with the transition from $^5I_8$ to $^5I_6$ and $^5I_7$ respectively. Particularly, it is noted that in Yb^{3+}/ Ho^{3+}/Er^{3+}: CYA crystal, the absorption peak centered at 978 nm become much stronger with absorption cross section up to 1.934×10^{-21} cm^2. Besides, the full widths at half-maximum (FWHM) of the absorption peak is about 28 nm. That means with the present of Yb^{3+} ion, the absorption coefficient at around 974 nm become much larger and thus Yb^{3+}, Ho^{3+}, Er^{3+}: CYA crystal is very suitable for commercial InGaAs LDs pumping.

3.2. Fluorescence spectra

The room temperature fluorescence spectra of the three crystals within the range of 500–700 nm, 1400–1700 nm and 2500–3000 nm have been recorded by using OPO laser excitation at 974 nm (Fig. 2). The same experimental conditions were maintained in order to get the comparable results.

The broad mid-IR emission bands centered at 2700 nm in Er^{3+}:CYA and Ho^{3+}/Er^{3+}:CYA crystals are corresponding to the transition Er^{3+}:$^4I_{11/2}\rightarrow^4I_{13/2}$. It is found that their emission shape and intensity are very similar and close. However, with the doping of Yb^{3+} ion, the emission shape totally change and the peak switches to 2865 nm which associates with the transition Ho^{3+}:$^5I_6\rightarrow^5I_7$.

The NIR emission bands centered at 1560 nm associate with the Er^{3+}:$^4I_{13/2}\rightarrow^4I_{15/2}$ transition. It is noted that, in Ho^{3+}, Er^{3+}:CYA crystal, the emission become weaker than that of Er^{3+}:CYA crystal,-which is due to effective energy transfer within Er^{3+} :$^4I_{13/2}\rightarrow Ho^{3+}$: $^5I_7$. When Yb^{3+} ion is added into the crystal, the fluorescence emission 1560 nm almost quench. Other two series emission bands were found in $Yb^{3+}/Ho^{3+}/Er^{3+}$:CYA crystal. Emission band at 1042 nm is assigned to Yb^{3+}:$^2F_{5/2}\rightarrow^2F_{7/2}$ transition, while emission band at 1198 nm is corresponding to the transition Ho^{3+}:$^5I_6\rightarrow^5I_8$. Comparing with the

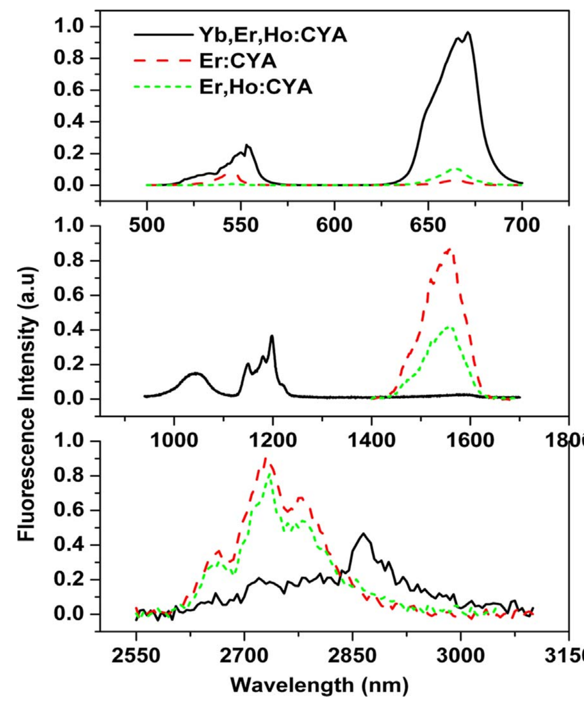

Fig. 2. Up-conversion, NIR, MIR emission spectra of Er^{3+}: CYA, Ho^{3+}/Er^{3+}: CYA and $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystals excited by 974 nm.

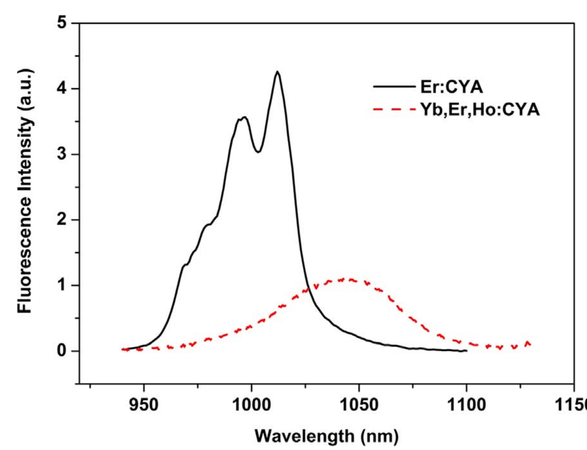

Fig. 3. Emission spectra of Er^{3+}: CYA, $Yb^{3+}/Ho^{3+}/Er^{3+}$: CYA crystals within 940–1130 nm range excited by 974 nm.

fluorescence emission of Er^{3+}:CYA crystal within 940–1130 nm range as it is shown in Fig. 3, It is noted that the emission band at 1012 nm which associates with the Er^{3+} $^4I_{11/2}\rightarrow^4I_{15/2}$ transition quench.

The up-conversion fluorescence spectra of 500–700 nm are also presented in Fig. 2. Green and red up-conversion emission bands centered at around 549 nm and 670 nm can be seen. It is interesting to find that the intensity of 549 nm emission band is weaker than that of 670 nm in Er^{3+}: CYA crystal while the intensity of peak at 549 nm become stronger than that of 670 nm in Ho^{3+}/Er^{3+}: CYA crystals. Besides, with the doped of Yb^{3+} ion, the intensity of red emission in triple doped crystal become much stronger, about 10 times, than that of Ho^{3+}/Er^{3+}: CYA, and 30times than that of Er^{3+}: CYA.

3.3. Energy transfer and up-conversion mechanism discussion

The mechanism of the up-conversion, NIR and mid-IR emissions in $Yb^{3+}/Ho^{3+}/Er^{3+}$:CYA crystal can be explained by the energy level diagram in Fig. 4. When the sample is excited by OPO laser at 974 nm,