Journal of Luminescence 144 (2013) 117–121

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

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

Spectroscopic investigations of Ho^{3+}/Er^{3+}:$CaYAlO_4$ and Eu^{3+}/Er^{3+}:$CaYAlO_4$ crystals for 2.7 μm emission

Shaozhen Lv [a,b,c,*], Zhaojie Zhu [a], Yan Wang [a], Zhenyu You [a], Jianfu Li [a], Chaoyang Tu [a]

[a] Key Laboratory of Optoelectronic Materials Chemistry and Physics of CAS, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 35002, PR China
[b] Graduate University of the Chinese Academy of Science, Beijing 100049, PR China
[c] Zhicheng College, Fuzhou University, Fujian 350007, PR China

ARTICLE INFO

Article history:
Received 31 December 2012
Received in revised form
9 June 2013
Accepted 27 June 2013
Available online 6 July 2013

Keywords:
Mid-infrared emission
$CaYAlO_4$ crystal
Spectra characteristics

ABSTRACT

Ho^{3+}/Er^{3+}:$CaYAlO_4$ and Eu^{3+}/Er^{3+}:$CaYAlO_4$ co-doped crystals were grown by Czochralski method. A detailed spectra analysis such as absorption spectra, up-conversion fluorescence, near-infrared and mid-infrared fluorescence spectra as well as luminescence decay curves was measured in order to optimize the deactivator for mid-infrared (2.7 μm) emission in Er^{3+}: $CaYAlO_4$ crystal. The influence of different deactivators on the spectra characteristics was studied. The energy transfer mechanisms, the related energy transfer coefficients and the stimulated emission cross-section were determined. Results show Ho^{3+} ion is the more appropriate deactivator than Eu^{3+} ion with which self-termination bottleneck effect was effectively suppressed. All imply that Ho^{3+} co-doping is beneficial for achieving 2.7 μm emission in Er^{3+}:$CaYAlO_4$ crystal.

1. Introduction

Mid-infrared lasers (~3 μm) have attracted considerable attention for many years, particularly for their great potentialities in surgery, military and remote chemical sensing application [1–3]. Pure fluid water shows strong absorption at 2.95 μm. But the absorption peak buleshifts toward around 2.7 μm when temperature and press are increased [4]. So, the laser around 2.7 μm is preferred in microsurgery, biological tissue ablation for small thermal damage and high accuracy. Herein, crystals as candidates for potential 2.7 μm laser were investigated.

$CaYAlO_4$ (CYA) crystallizes in the perovskite phase with tetragonal K_2NiF_4 structure. It belongs to space group I4/mmm with lattice parameters $a=3.6451$ 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 [5]. Besides the advantages of good mechanical strength and high thermal conductivity, as an aluminate, CYA crystal also has good chemical stability. What is more important, CYA crystal has low phonon energy 322 cm^{-1}[6] and relatively weak multiphonon transition rates which were reported close to that found in YAP [7]. It can help to generate 2.7 μm laser oscillations. So, CYA crystal is a promising mid-infrared emission laser crystal.

The lanthanide element Er^{3+} ion can be used for 2.7 μm mid-infrared emission, which corresponds to the transition from $^4I_{11/2}$ to $^4I_{13/2}$ level. However, in most cases, the lifetime of lower level $^4I_{13/2}$ is longer than that of upper level $^4I_{11/2}$, which usually results in the difficulty to maintain the required population inversion, and thus cause 2.7 μm lasing transition to "self-terminate". Thus, effective method should be studied to suppress the self-termination bottleneck. Some literature reported that introducing deactivator can effectively depopulated $^4I_{13/2}$ level [8–14]. Nd^{3+} and Pr^{3+} ions are widely studied as deactivators, but Ho^{3+} and Eu^{3+} are rarely investigated. So in this work, Ho^{3+} and Eu^{3+} were introduced in the Er^{3+}: CYA crystal. The influence of different deactivators on the spectra characteristics of Er^{3+}: CYA crystals are investigated. To analyze the energy transfer between Er^{3+} ion and deactivators, the energy transfer mechanisms are discussed and the energy transfer coefficients are determined.

2. Experimental

30 at% Er^{3+} single-doped and 0.5at% RE^{3+}/30at% Er^{3+} (RE^{3+}= Ho^{3+}, Eu^{3+}) co-doped CYA crystals were successfully grown by Czochralski method. The polycrystalline materials for single crystal growth were prepared by the classical solid-state reaction. The initial chemicals were Al_2O_3, $CaCO_3$ (A.R. grade) and Y_2O_3, RE_2O_3 (RE^{3+}=Ho^{3+}, Eu^{3+}), Er_2O_3 (4 N purity). The crystal growth was

* Corresponding author at: Key Laboratory of Optoelectronic Materials Chemistry and Physics of CAS, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 35002, PR China. Tel.: +8615396061844.
E-mail address: tcy@fjirsm.ac.cn (C. Tu).

0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.06.044

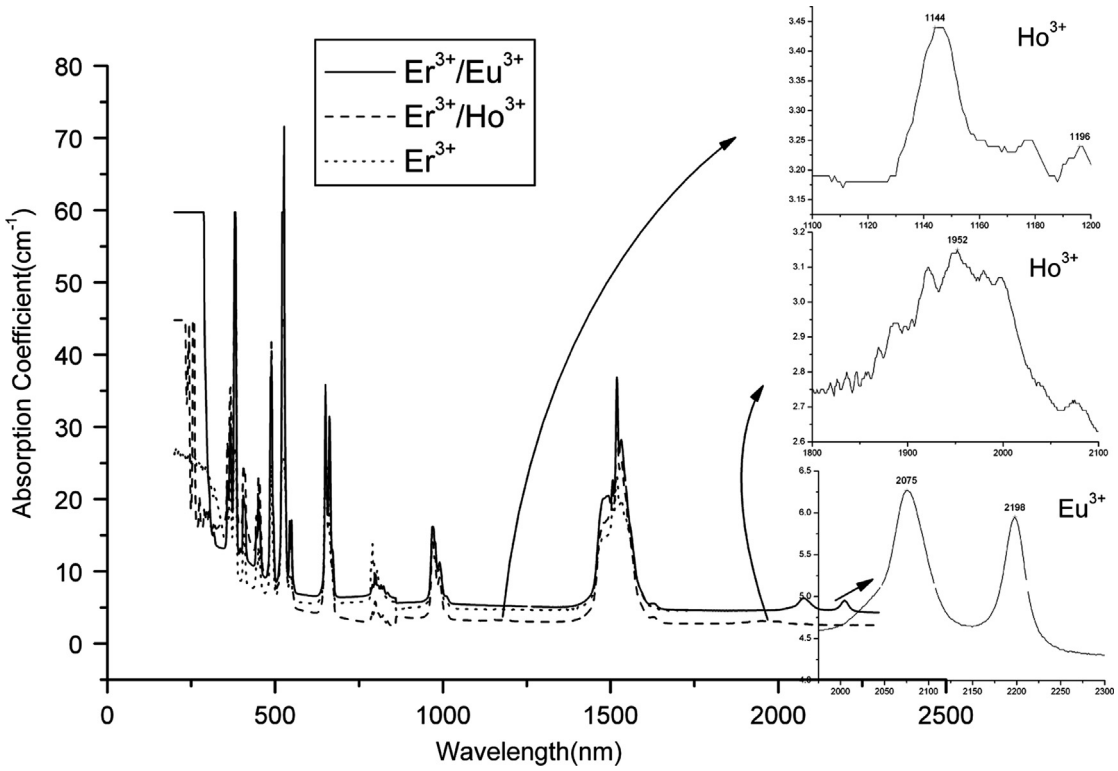

Fig. 1. The absorption spectra of Ho^{3+}/Er^{3+}, Eu^{3+}/Er^{3+} and Er^{3+} doped CYA crystals.

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 [1 0 0] direction. The typical pull rate was 1~2 mm per hour and the rotation rate was 10~20 rpm.

Three samples with dimensions of $5.0 \times 5.0 \times 1.0\ mm^3$ were cut from the three as-grown crystals respectively and polished for spectroscopic analysis. The absorption spectra was measured by Perkin-Elmer UV–vis–NIR Spectrometer (Lambda-900) from 300 nm to 2300 nm. The fluorescence spectra and the relevant lifetime decay curves were recorded by Edinburgh Instruments FLS920 and FSP920 spectrophotometer. The excitation source is OPO laser with excitation pulse length 5 ns. All experiments were measured at the room-temperature.

3. Results

3.1. Absorption spectra

The absorption coefficients of Er^{3+}: CYA, Ho^{3+}/Er^{3+}: CYA and Eu^{3+}/Er^{3+}: CYA crystals are presented in Fig. 1. The absorption spectra of Er^{3+}: CYA crystal consists of mainly nine bands centered at around 378 nm, 408 nm, 450 nm, 488 nm, 520 nm, 651 nm, 795 nm, 974 nm and 1520 nm, which are associated with the transition from the ground level $^4I_{15/2}$ to the upper levels $^4G_{11/2}$, $^2G_{9/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$+$^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ respectively. Owing to the much lower concentration of deactivators compared with Er^{3+} ion, the intensity of deactivators absorption bands are much weaker than that of Er^{3+} ion. In the Eu^{3+}/Er^{3+}: CYA crystal absorption spectrum, the weak absorption bands centered at 2075 nm and 2198 nm are corresponding to the transition Eu^{3+}: $^7F_0 \rightarrow {}^7F_4$ and $^7F_0 \rightarrow {}^7F_4$ respectively. In the Ho^{3+}/Er^{3+}: CYA crystal absorption spectrum, the absorption bands centered at 1144 nm and 1952 nm are corresponding to the transition Ho^{3+}:$^5I_8 \rightarrow {}^5I_6$ and $^5I_8 \rightarrow {}^5I_7$ respectively. These values obtained from absorption spectra are very close to the calculated energy level given by literature [15].

It is also noted from Fig. 1 that the absorption coefficient of the peak centered at 974 nm is much larger than that at 795 nm, so Ho^{3+}/Er^{3+}: CYA and Eu^{3+}/Er^{3+}: CYA crystals are more suitable for InGaAs pumping. Besides, the full width at half-maximum (FWHM) of the absorption peak at 974 nm is around 29 nm, which is probably due to the divalent Ca and trivalent Er cations statistically share the same crystallographic site[16,17]. The relative broad absorption bandwidth around the pump wavelength is very convenient because it allows one to avoid thermo-electronic cooling of the laser diodes. Thus this kind of crystals is a potential candidate of LD pumped laser material.

3.2. Fluorescence and energy transfer mechanism

Upon excitation of 974 nm, the up-conversion spectra, near-infrared emission spectra and mid-infrared emission spectra of Er^{3+}: CYA, Ho^{3+}/Er^{3+}: CYA and Eu^{3+}/Er^{3+}: CYA crystals within the range of 500–700 nm, 1400–1700 nm and 2500–3000 nm were measured and presented in Figs. 2–4. The same experimental conditions were maintained for the three samples in order to get comparable results.

In the up-conversion spectra, two intense fluorescence bands centered at 549 nm and 670 nm were observed. They are corresponding to transitions from Er^{3+}: ($^2H_{11/2}$, $^4S_{3/2}$)$\rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ respectively. When Ho^{3+} ions were introduced, the red up-conversion emission contains another source Ho^{3+}: $^5F_5 \rightarrow {}^5I_8$ transition. It is noted that the intensity of peak centered at 549 nm is stronger than that of 670 nm in Er^{3+}: CYA, but in Ho^{3+}/Er^{3+}: CYA crystals the intensity of peak at 670 nm become much stronger than that at 549 nm.

The near-infrared emission band centered at 1560 nm is corresponding to Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. The emission intensity in Ho^{3+}/Er^{3+}: CYA and Eu^{3+}/Er^{3+}: CYA crystals all decreased as