Role of Er^{3+} concentration in spectroscopic and laser performance of CaYAlO$_4$ crystal

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ABSTRACT

Three heavily Er^{3+}-doped CaYAlO$_4$ single crystals were successfully grown by Czochralski method. The emission spectra and the fluorescence decay curves have been recorded at room temperature. A combination of experimental data, rate equation and Dexter theory are used to investigate the influence of Er^{3+} doping concentration on the spectra character and the inner cross relaxation of Er^{3+}:CaYAlO$_4$ crystal. Results show that the self terminate effect of the transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ can be suppressed by heavy Er^{3+}doping. But if the doping concentration goes too high, the much larger cross relaxation coefficient of $^4I_{11/2}$ level than that of $^4I_{13/2}$ level would results in the increase of up-conversion emission and the quench of near and mid infrared emission. The laser performance was also studied. The maximum output power of 225 mW at 2733 nm was acquired with an optical conversion efficiency of 14.9%.

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1. Introduction

The lanthanide element Er^{3+} ion is widely used as active ion in many hosts for a broad range of luminescent transition from 500 to 3000 nm. Some report indicates the Er^{3+} laser wavelengths are somehow depended upon the concentration [1,2]. Generally, lowly doped concentration benefits emission transition like $^4I_{13/2} \rightarrow {}^4I_{15/2}$ for its large emission cross section and high luminescent branching ratio. The 2.7 μm transition, however, usually has the "self-terminate" effect owing to the shorter upper level $^4I_{11/2}$ lifetime than the lower level $^4I_{13/2}$. But, when Er^{3+} ion is heavily doped, the cross-relaxation plays a dominant role and the fluorescence kinetics changes obviously. Thus, it is suggested that high Er^{3+} concentration can increase the population of $^4I_{11/2}$ and depopulate $^4I_{13/2}$ level and so benefits 2.7 μm emission [3–5].

CaYAlO$_4$ (CYA) crystal is iso-structural with K$_2$NiF$_4$. The advantages of good mechanical strength, chemical stability, high thermal conductivity and especial the weak multiphonon transition rates [6–8] make Er^{3+}:CYA crystal a promising mid-infrared emission laser crystal. Literatures have reported Er^{3+}:CYA for 1.5 μm emission [9,10]. While in this work, we studied on the heavily doped Er^{3+}:CYA. The influence of Er^{3+} doping concentration on the spectra characteristics and luminescence decay of Er^{3+}:CYA crystal has also been investigated. The inner fluorescence kinetics and energy cross relaxation were investigated by a combination of experimental data, rate equation and Dexter theory analysis. Laser experiments are also investigated. Two laser wavelengths 2728 nm and 2792 nm were obtained in c-cut and a-cut CYA crystal respectively. The largest laser output (225 mW) was achieved in a c-cut crystal with Toc of 2% for cavity length 15 mm. The slope efficiency and optical conversion efficiency are 30.2% and 14.9% respectively.

2. Experimental

Three Er^{3+}:CYA single crystals were successfully grown by Czochralski method. The polycrystalline materials for single crystal growth were prepared by the classical solid-state reaction. The chemicals were Al$_2$O$_3$, CaCO$_3$ (A.R. grade) and Y$_2$O$_3$, Er$_2$O$_3$ (4 N purity). The crystal growth was carried out with a N$_2$ atmosphere protection in a NCIREO DGL-400 furnace, and a Ir crucible of 50 mm diameter by 30 mm high was used. Seed was cut and oriented in [100] direction. The typical pull rate was 1–2 mm per hour and the rotation rate was 10–20 rpm. The concentrations of Er^{3+} ions were measured by the inductively coupled plasma-atomic emission spectrometry (ICP-AES). The measured ion concentrations and the calculated segregation coefficients are listed in Table 1. The fluorescence spectra and the relevant lifetime decay curves under excitation of 974 nm were recorded at room-temperature

Table 1
The ion concentration and segregation coefficient K in CYA crystal.

Crystals	Corresponding Er³⁺ concentrations (ions/cm³)	K of Er³⁺
A (30 at% Er³⁺:CYA)	2.878×10^{21}	0.757
B (50 at% Er³⁺:CYA)	4.285×10^{21}	0.676
C (70 at% Er³⁺:CYA)	5.181×10^{21}	0.584

by Edinburgh Instruments FLS920 and FSP920 spectrophotometer. An OPO laser is used as excitation source, and a liquid-N_2-cooled InSb is used as infrared detector. The fluorescence signal was recorded by a computer-controlled system. To suppress the radiation trapping in the samples, the CYA crystal samples were cut in thin films with low thickness less than 1 mm and the surfaces were ground to avoid the internal reflection.

3. Results and discuss

Fig. 1(a)–(c) shows the room temperature up-conversion spectra, near-infrared emission spectra and mid-infrared emission spectra of the three different doped crystals excited by 974 nm. The same experimental conditions were maintained for each emission spectrum in order to get comparable results. Two intense fluorescence bands centered at 549 nm and 670 nm were observed which are assigned to $(^2H_{11/2}, {}^4S_{3/2}) \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions respectively. The 1560 nm emission band corresponds to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition and the broad mid-IR emission band centered at 2730 nm associates with the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition. After excited by 974 nm into $^4I_{11/2}$ level, ions in $^4I_{11/2}$ level relax

to $^4I_{13/2}$ level and generate 2.7 μm emission. Then the Er³⁺ ions in $^4I_{13/2}$ level relax to ground state to generate 1.5 μm emission. Ions in $^4I_{11/2}$ level can be excited to the $^4F_{7/2}$ level by cross-relaxation process $(^4I_{11/2} \rightarrow {}^4I_{15/2}) + (^4I_{11/2} \rightarrow {}^4F_{7/2})$, then quickly relax to $(^2H_{11/2}, {}^4S_{3/2})$ level and generate 549 nm emission. Meantime, ions in $(^2H_{11/2}, {}^4S_{3/2})$ level relax to $^4F_{9/2}$ level and generate 670 nm luminescence. It is noted that with the increasing of doping concentration, the intensity of up-conversion emission increased, while the fluorescence intensities of near-infrared emission and mid-infrared emission both decreased.

For better understanding of fluorescence dynamics, the luminescence decay curves of the $^4I_{11/2}$ and $^4I_{13/2}$ levels in the three crystals excited by 974 nm were recorded and shown in Fig. 2. It is noted that the luminescence decay curves recorded at 1565 nm and 2725 nm both show multi-exponential nature for cross relaxation involved. The lifetimes were calculated using the formula in literature [5] and then listed in Table 2. The decay times of the Er³⁺:CaYAlO₄ with 30% doping were slightly different from our previous work [11] since different part of grown crystal was used here. As it is shown in Table 1, the segregation coefficient of 30 at% Er³⁺:CaYAlO₄ is 0.757, that means during the crystal grown procedure the melt concentration changes from time to time. It finally results in the different actual Er³⁺ doping concentration in the different part of the grown crystal.

It is noted from Table 2 that with the increase of the doping concentration from 0.5 at% to 100 at%, the luminescence lifetime of $^4I_{11/2}$ and $^4I_{13/2}$ levels both decreased. But the decrease extent of the lifetime of lower level $^4I_{13/2}$ is much larger than that of upper level $^4I_{11/2}$. In crystal A, the lifetime of $^4I_{11/2}$ level reduced to 1/1.6 while the lifetime of $^4I_{13/2}$ level reduced to 1/2.8 compared with
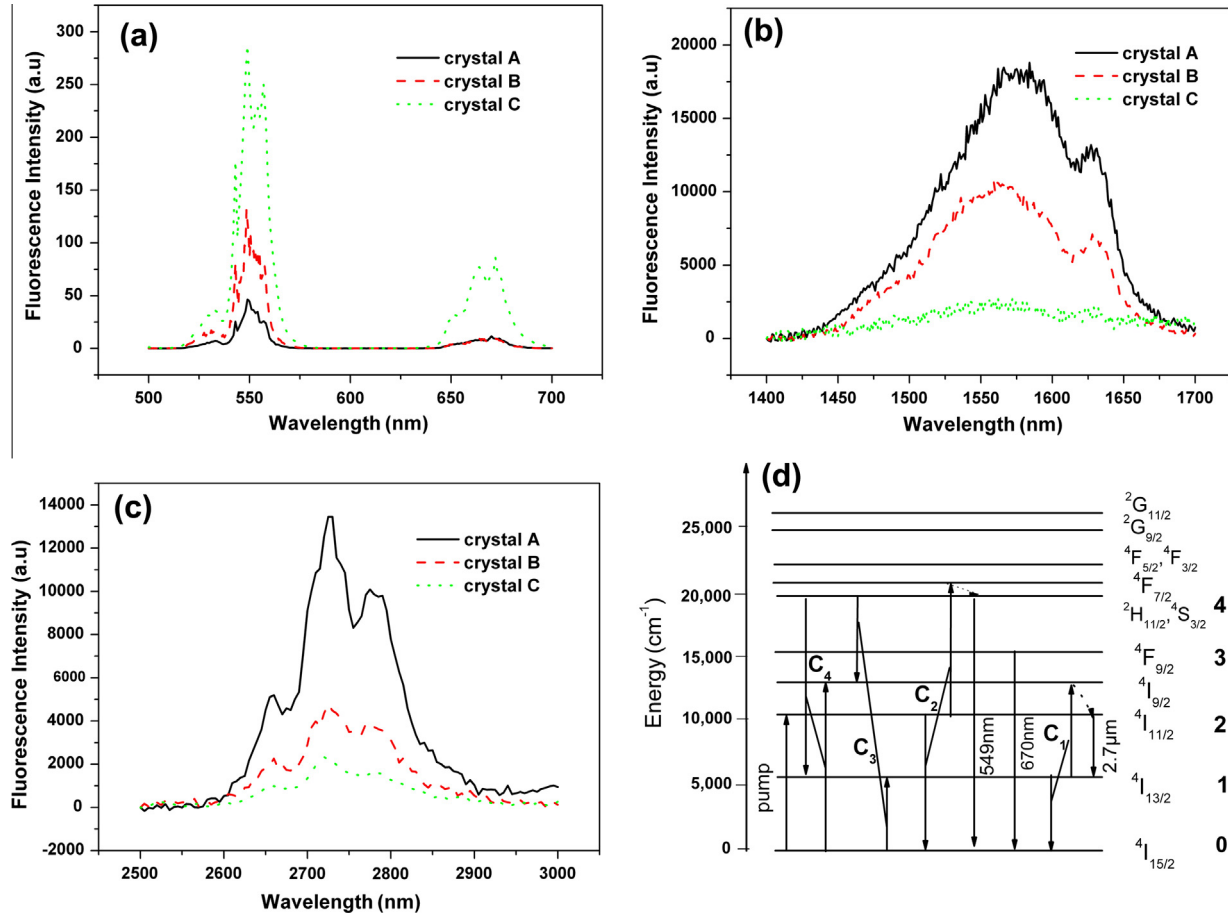
Fig. 1. (a) Up-conversion, (b) NIR, (c) MIR and (d) energy level diagram of Er³⁺:CYA.