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Journal of Crystal Growth 289 (2006) 676–680

JOURNAL OF CRYSTAL GROWTH

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Cooperative and charge transfer luminescence in Yb^{3+}-doped yttrium aluminum perovskite ($YAlO_3$)

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Received 6 July 2005; received in revised form 22 November 2005; accepted 24 November 2005

Communicated by G. Muller

Abstract

$YAlO_3$ (YAP) crystals with different Yb^{3+} concentration have been grown by Czochralski method and cooperative fluorescence of Yb^{3+} ions in YAP crystal was studied under 940-nm infrared (IR) LD excitation at room temperature. The Yb concentration dependence of absorption intensity of IR and charge transfer bands exhibit different features. The green emission band in the region of 480–520 nm was assigned to the cooperative deexcitation of two Yb^{3+} ions. The remaining upconverted emission bands containing various sharp peaks associated with impurity ions were observed and discussed. Charge transfer luminescence of heavily doped 20 at% Yb:YAP is strongly temperature dependent and no concentration quenching of the charge transfer luminescence was found through the investigation of different Yb levels samples.

PACS: 78.55.−m; 42.70.Hj; 29.20.Lq

Keywords: A2. Czochralski method; B1. Perovskites; B1. Yttrium compounds

1. Introduction

In recent years, Yb^{3+}-doped crystals have attracted a great deal of attention with the rapid development of diode-pumped solid-state laser (DPSSL). Recent advances in a high-performance InGaAs laser diode with a wavelength between 900 and 1100 have stimulated interest in developing LD pumped Yb^{3+}-doped lasers [1,2]. Yb:YAP has demonstrated many attractive characteristics, such as longer lifetimes, higher polarized cross-sections, lower thermal load and high laser energy capacity. It is a very promising laser crystal in laser-diode-pumped solid-state configurations. Because of the simple electronic structure of Yb^{3+} ion, which consists of only two levels, such unfavorable processes like excited state absorption, upconversion or cross-relaxation are absent in Yb^{3+} lasers. Recently, charge transfer luminescence of Yb^{3+}-doped $YAlO_3$(YAP) becomes noticed as well due to its potential application for solar neutrino detection [3].

Cooperative luminescence is a special type of upconversion luminescence in which two interacting ions in the excited state return to the ground state simultaneously, emitting one photon of the sum of the energies of the single ion transitions. Cooperative luminescence from pairs of Yb^{3+} ions has been shown in bulk crystals, optical glasses, fiber and planar waveguides [4–12]. Although cooperative luminescence in Yb^{3+}-doped crystals is a deleterious factor affecting IR laser operation, it is still to be an effective way to produce visible (VIS) and ultraviolet (UV) emission.

In the present work, we investigated cooperative luminescence in Yb^{3+}-doped YAP. In addition, charge

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doi:10.1016/j.jcrysgro.2005.11.112

transfer luminescence of the heavily doped 20 at% Yb:YAP crystal excited by synchrotron was also studied.

2. Experiments

$Yb_xY_{1-x}AP$ crystals for $x = 0.05$, 0.1, 0.15 and 0.2 were grown by Czochralski method. The starting materials Y_2O_3 (5 N), Al_2O_3 (5 N) and Yb_2O_3 (5 N) were weighed according to a specific molar ratio. The chemical reaction formulas are as follows:

$$Al_2O_3 + (1-x)Y_2O_3 + xYb_2O_3 = 2Y_{1-x}Yb_xAlO_3.$$

After the compounds were ground and thoroughly mixed, they were pressed into the form of blocks. These pieces were sintered at 1350 °C for 24 h in air and then loaded into an iridium crucible for crystal growth. Seed crystal with ⟨1 0 1⟩ orientation was used. The growth atmosphere was highly pure nitrogen gas.

Samples of 1-mm thickness were cut from the as-grown Yb:YAP crystals perpendicularly to the growth axis and polished on both sides. The absorption spectra were recorded by means of a V-570 UV/VIS/NIR spectrophotometer. The light sources were a deuterium lamp (190–350 nm) and a halogen lamp (340–1200 nm), and the spectral resolution was 1 nm. The IR fluorescence spectra were acquired by a TRIAX 550 spectrophotometer (spectral resolution was 1 nm) with an InGaAs laser diode as the pump source (excitation wavelength 940 nm). Upconversion emission spectra were measured using ZOLIX SBP300 spectrofluorometer (spectral resolution was 0.5 nm). The pump power was 700 mW. All above measurements were taken at room temperature. The charge transfer luminescence spectra were recorded at the VUV Spectroscopy Station in National Synchrotron Radiation Laboratory, Hefei, China. The resolution of the primary monochromator (1 m Seya) and the secondary monochromator is 0.3 and 3 nm, respectively. The measuring temperature of the sample was varied from 20 to 300 K. The excitation wavelength was 230 nm and excitation spectra were corrected using sodium salicylate.

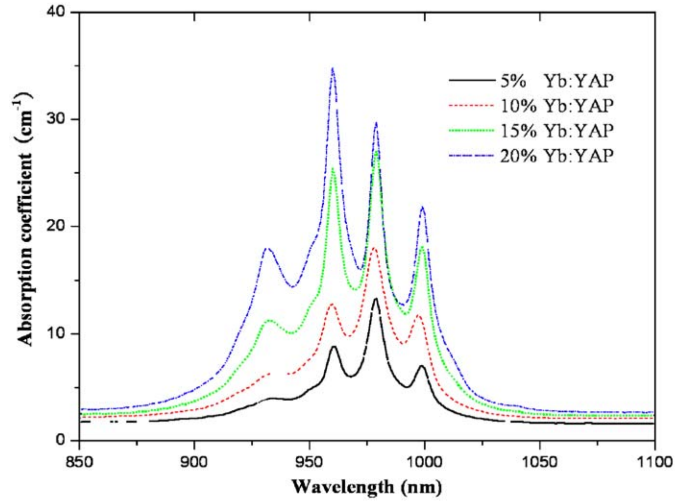

Fig. 1. IR absorption spectra of Yb:YAP crystals at room temperature.

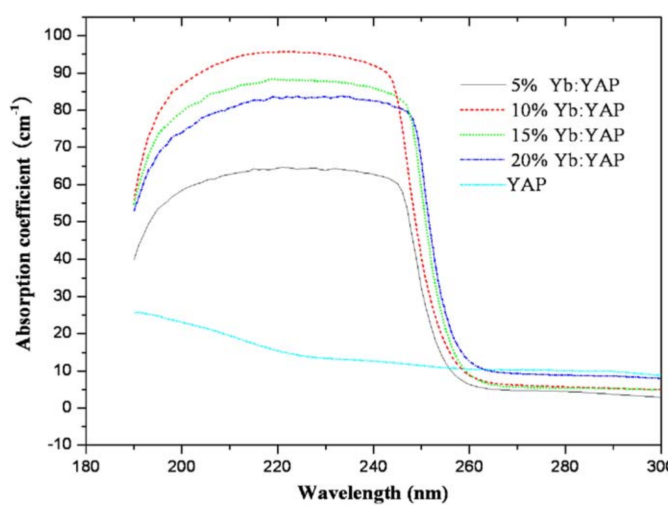

Fig. 2. Ultraviolet absorption spectrum of undoped YAP and Yb:YAP crystals at room temperature.

3. Results and discussion

Fig. 1 shows the absorption spectrum of 5, 10, 15 and 20 at% Yb:YAP crystals at room temperature. The four strong absorption bands located at 932, 960, 979 and 999 nm are attributed to the $^2F_{7/2} \rightarrow {^2F_{5/2}}$ Yb^{3+} transition. In the wavelength range from 850 to 1100 nm, each absorption peak of Yb:YAP crystals increased in intensity and the absorption coefficients at 960 and 979 nm increased from 8.79 to 34.75 cm^{-1} and 13.23 to 29.75 cm^{-1} with an increase in the concentration of Yb^{3+}.

Fig. 2 presents the absorption spectrum of undoped YAP and Yb:YAP crystals. The broad absorption band in the range of 190–260 nm, which is not observed in the spectra of the undoped sample, is assigned to the transitions from $^2F_{7/2}$ ground state of Yb^{3+} to the charge transfer state (CTS) [13]. The center position of the absorption band is in good agreement with the estimation of the lowest charge transfer band using Jorgensen's optical electro-negativity:

$$V_{CT} = 30000[\chi_{opt}(O^{2-}) - \chi_{opt}(Yb^{3+})]\ \text{cm}^{-1}$$

with $\chi_{opt}(O^{2-}) = 3.2$ and $\chi_{opt}(Yb^{3+}) = 1.68$. The charge transfer band is predicted to be at 218 nm. The charge transfer absorption edge in the region of 260–270 nm is observed and it shifts to longer wavelengths with the increase of the Yb^{3+} doping level. Previous study [14] has shown that the lattice parameter was reduced and density increases slightly with the increase of the Yb^{3+} concentration. Measurements show that the cell volume of the 5, 10, 15 and 20 at% Yb:YAP crystals is 203.396, 203.394, 203.167 and 203.091 Å^3, respectively. The reduced