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# The studies on the upconversion mechanism of ZBLAN: $Er^{3+}$, $Yb^{3+}$

Zhao Suling*, Hou Yanbing, Sun Li, Xu Xurong

*Institute of Optoelectronic Technology, Northern Jiaotong University, Beijing 100044, People's Republic of China*

**Abstract**

ZBLAN glass is an interesting host for rare earth doped up-conversion materials due to a lot of advantages. In this paper, we studied the up-conversion mechanism of ZBLAN co-doped with $Er^{3+}$ and $Yb^{3+}$ ions. The energy transfer between $Yb^{3+}$ and $Er^{3+}$ was described.


*Keywords:* Up-conversion mechanism; ZBLAN glass; Excited state excitation

## 1. Introduction

Several recent demonstrations of up-conversion pumped solid-state lasers have renewed the interest in excitation mechanisms that result in emission at wavelengths shorter than that of the pump light. Efficient up-conversion is possible in rare earth doped materials with metastable, intermediate levels that can act as a storage reservoir for pump energy. Subsequent excitation of emission from higher lying states can occur by excited-state absorption of pump photons, or by energy transfer processes. Stimulated emission by up-conversion pumping was first reported by Johnson and Guggenheim [1] using infrared light from flash lamps to excite $Yb^{3+}$ ions in $BaY_2F_8$ doubly doped with $Yb^{3+}/Er^{3+}$ or $Yb^{3+}/Ho^{3+}$. Two successive energy transfer steps resulted in up-conversion excitation of red emission from $Er^{3+}$ and green emission from $Ho^{3+}$, respectively. The first cw up-conversion laser [2] was operated in 1986 using infrared dye-laser radiation to pump the 550 nm, $^4S_{3/2}\rightarrow{}^4I_{5/2}$ transition in $YAlO_3{:}Er^{3+}$.

The most efficient up-conversion materials are $Er^{3+}$ (or $Yb^{3+}$, $Er^{3+}$) doped fluoride materials. Both fluoride crystals [3,4] and fluoride glasses [5–7] have been extensively studied for up-conversion purposes. Fluoride glasses, particularly Zirconium tetrafluoride ($ZrF_4$)-based glasses, are one of the most adequate hosts. Although some studies on the optical properties of rare earth ions in the ZBLAN glass have concentrated on mechanism and the efficient of infrared-to-visible up-conversion [8], up to now, few works on excitation of excited state were reported.

Here we investigate the ZBLAN co-doped with $Er^{3+}$ and $Yb^{3+}$ through excitation of excited state.

## 2. Experiment

Our experiment sample is ZBLAN glass co-doped with $Er^{3+}$ and $Yb^{3+}$ ions, the concentrations of $Er^{3+}$ and $Yb^{3+}$ are 1 mol% and 3 mol%, respectively.

First, we measured the absorption spectra of ground state. Then measured the excitation spectra (include excitation of ground state and excited state). Fig. 1 shows the setup used in the excitation of excited state experiment. A diode laser was used to pump the ZBLAN: $Er^{3+}$, $Yb^{3+}$glass into the $^4I_{11/2}$ level. Through the lens, the laser focused on the glass and lined with the Xe lamp. The laser wavelength is 980 nm. All of the measurements were carried out under room temperature.

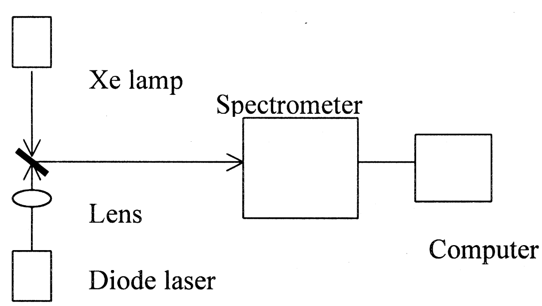


Fig. 1. Setup of experiment used to measure the excitation spectrum.

*Corresponding author.

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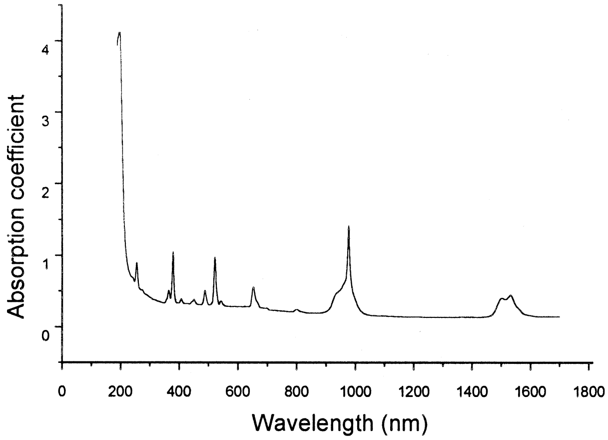


Fig. 2. Absorption spectra of sample.

## 3. Result and discussion

Fig. 2 illustrates typical absorption spectra of $Er^{3+}$ ions in our sample. The peaks of 1550 nm, 980 nm, 810 nm, 660 nm, 550 nm, 520 nm, 485 nm, 450 nm, 410 nm, 390 nm, and 370 nm are assigned to the transitions from the $^4I_{15/2}$ ground state to $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$ (and $^4F_{3/2}$), $^2H_{9/2}$, $^4G_{11/2}$, and $^4G_{9/2}$ states, respectively. We can observe that the absorption corresponds to the $Yb^{3+}$ optical transition $^2F_{7/2}$–$^2F_{5/2}$ is very strong, which this wavelength region is a favorable energy level for laser action near 980 nm.

A typical up-conversion spectrum of the glass sample presented in Fig. 3 are obtained under 980 nm excitation. The intense emission peaks of 520 nm, 550 nm, and 660 nm, correspond to the transitions from $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ states to the $^4I_{15/2}$ ground state, respectively, which is local at the simplified energy level diagram (Fig. 4). According to the analysis of reference [8], the green emission is due to a two-photon process and red emission is due to both two- and three-photon processes.

From the relation of up-conversion luminescence with the laser power, there are two main up-conversion paths for the red emission in $Er^{3+}/Yb^{3+}$-doped glass (Fig. 4). The first one, the excited state level $^4I_{11/2}$ is populated via energy transfer between $Er^{3+}$ and $Yb^{3+}$ ions, then goes to $^4I_{13/2}$ through a multi-phonon relaxation from where $^4F_{9/2}$ is populated by an excited state absorption. The another mechanism comprises the population of the $^4F_{7/2}$ level through absorbing two photons, and relaxes to $^4S_{3/2}$ level, then absorb a photon and transit to $^4G_{11/2}$ or $^2H_{9/2}$ level. From the level $^4G_{11/2}$ or $^2H_{9/2}$, the electrons descend to $^4F_{9/2}$ level by means of phonon cross relaxation between $Er^{3+}$ and $Yb^{3+}$ ions.

The excitation spectra of the monitor wavelength 661 nm and 550 nm are given in Fig. 5. The solid line (a) and the dash line are the ground state excitation spectra and the excited state excitation spectra of 660 nm emission, respectively. The solid line (b) and the dot line are the ground state excitation spectra and the excited state excitation spectra of 550 nm emission, respectively. In the excitation of excited state, other excitation peaks are found in addition to the peaks observed in the excitation of ground state. We can observe that two excitation spectra of excited state are well similar to each other. This means that

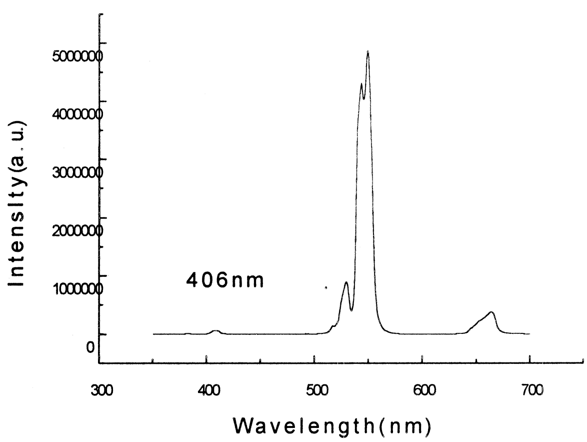


Fig. 3. Up-conversion spectra pumped by 980 nm.

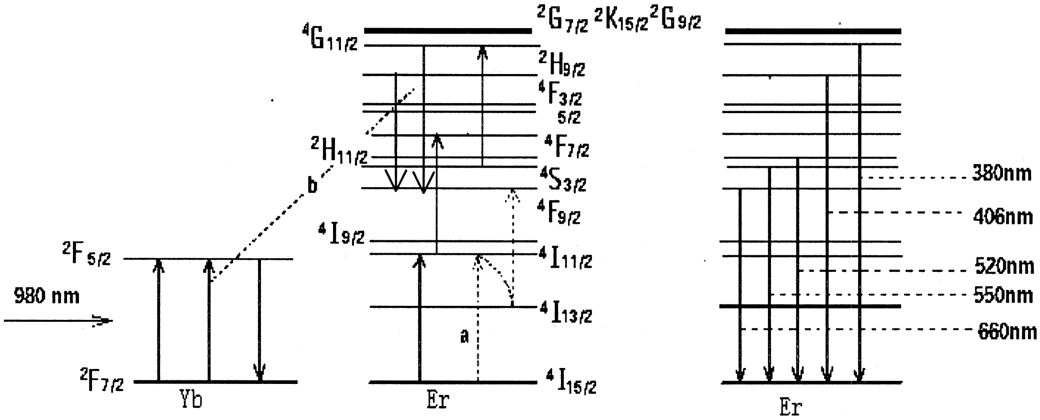


Fig. 4. Energy level diagram of sample pumped by 980 nm.

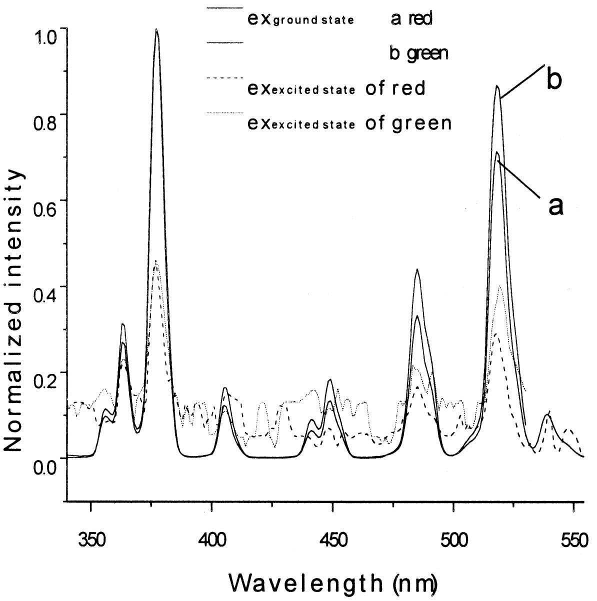


Fig. 5. Excitation spectra of sample.

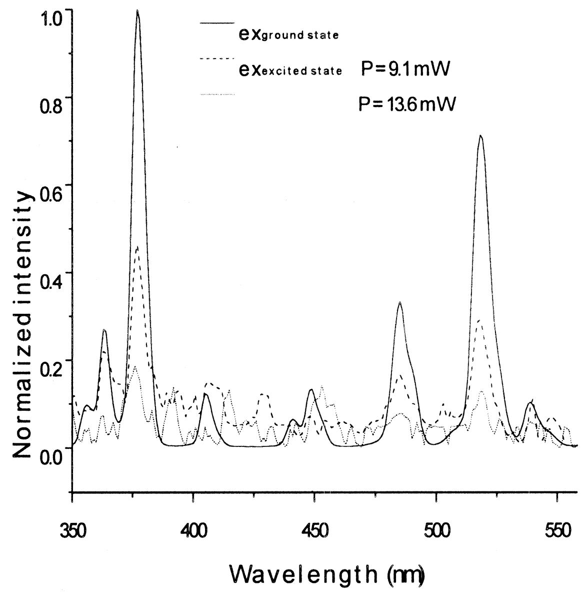


Fig. 6. Excitation spectra of red emission.

the sample can radiate visible light when co-pumped by 980 nm and those peaks recorded in excited state excitation spectra. The phenomenon will be useful for three-dimension display pumped by two lights at the same time.

Fig. 6 gives the details of the excitation spectra of 660 nm emission. The most evident changes due to the pumped by laser are observed between two kind spectra: more excited peaks are arisen; the excitation peaks of ground state become decreasing. The reason is that the most of ground state's electrons are pumped into the $^4I_{11/2}$ metastable state, then, a part of electrons relax to the $^4I_{13/2}$ level. The main peaks except the ground state excitation peaks local at 420 nm, 430 nm, 461 nm, and 547 nm, which are assigned to transitions from $^4I_{11/2}$ to $^2D_{7/2}$, $^2K_{13/2}$, $^2P_{7/2}$, and $^4G_{7/2}$, respectively. The peaks of 475 nm and 503 nm are assigned to transitions from $^4I_{13/2}$ to $^2K_{15/2}$ and $^4G_{11/2}$, respectively. The transition $^4I_{11/2}$ 64G7/2 means that $^2G_{7/2}$ can be populated through $^4I_{11/2}$ excited state absorption. Because of the small energy difference between $^4G_{7/2}$ and lower level $^4G_{11/2}$, the electrons of $^4G_{7/2}$ fast relax to $^4G_{11/2}$, and then can radiate red light. This result agrees with the up-conversion process described in diagram of energy level.

## 4. Conclusion

The absorption spectra have been measured at room temperature. Excited state excitation spectra under excitation of laser diode were measured. The monitor wavelengths are 550 nm and 660 nm. Some changes are observed when compared two kind excitation spectra. From excitation of excited state, we can know the up-conversion process of $Er^{3+}$ pumped by infrared light.

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