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# Optics Letters

## Intense mid-infrared emission at 3.9 $\mu\text{m}$ in $\text{Ho}^{3+}$ -doped ZBYA glasses for potential use as a fiber laser

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**Intense mid-infrared emission at 3.9  $\mu\text{m}$  in  $\text{Ho}^{3+}$ -doped ZBYA glasses with direct upper laser level ( $\text{Ho}^{3+} : {}^5\text{I}_5$ ) pumping at a wavelength of 888 nm is reported for the first time, to the best of our knowledge. Spectroscopic parameters were determined using the Judd–Ofelt theory and the measured absorption spectrum. The maximum emission cross section of the  $\text{Ho}^{3+}$ -doped ZBYA glass is estimated to be  $2.7 \times 10^{-21} \text{ cm}^2$  at 3906 nm. Additionally, fluorescence spectra and lifetimes of ZBYA glasses with different  $\text{Ho}^{3+}$  ion doping concentrations were measured. The results provide theoretical and experimental basis for better selection of rare-earth-doped matrix glasses to achieve a fluorescence output centered on a wavelength of 3.9  $\mu\text{m}$ .** © 2020 Optical Society of America

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Mid-infrared lasers have found many important application areas with strong potential for use in military, atmospheric communications, biomedical, and other fields due to the compatibility of their output wavelength with these applications and good beam quality [1,2]. Rare-earth-doped mid-infrared fiber lasers have received particular recent attention [3,4]. Generally, due to the characteristic energy level spacing of rare-earth ions such as  $\text{Er}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Ho}^{3+}$  ions, mid-infrared band lasing in the range from 2.7  $\mu\text{m}$  to 3.9  $\mu\text{m}$  has been achieved in ZBLAN glass fiber [5–7]. Among these rare-earth ions, the transition of  $\text{Ho}^{3+} : {}^5\text{I}_5 \rightarrow {}^5\text{I}_6$  has proved to be an efficient means for obtaining 3.9  $\mu\text{m}$  laser emission [8]. Fluoride glass fibers also have the advantage of being capable of generating 3.9  $\mu\text{m}$  lasers because of their low phonon energy [9]. As early as 1995, Jutta Schneider [7] reported 3.9  $\mu\text{m}$  emission wavelength in a  $\text{Ho}^{3+}$ -doped fluoride fiber laser, which was pumped using 640 and 890 nm lasers. In recent years,  $\text{Ho}^{3+}$ -doped matrix glass with an emission at 3.9  $\mu\text{m}$  has been extensively investigated. Gomes *et al.*

(2016) reported the fundamental spectroscopic properties of fluoroindate glass for prospective application as a gain medium for fiber laser emission at 3.9  $\mu\text{m}$  using a pump laser at 889 nm [10]. 3.9  $\mu\text{m}$  fiber laser emission was generated in  $\text{Ho}^{3+}$ -doped fluoroindate fiber by pumping using an 888 nm multimode laser diode, whose maximum output power reached 200 mW [11]. However, fluoroindate glass fiber still has disadvantages including unstable composition and poor thermal stability [12].

Over the past few decades, the optical properties of ZBYA ( $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$ ) fluoride glass have been investigated and characterized [13,14]. The results show that ZBYA glass as an ion-doped matrix material is very suitable for use in the near-infrared and mid-infrared region producing a fluorescence output at these wavelengths. ZBYA glass is a fluoride glass material that exhibits ultrahigh transmittance (>90%) over an ultrawide transmission range (500 nm to 6  $\mu\text{m}$ ) with low phonon energy [15]. The phonon energy of ZBYA glass ( $\sim 580 \text{ cm}^{-1}$ ) is slightly higher than that of fluoroindate glass ( $\sim 510 \text{ cm}^{-1}$ ) [16]. Compared to fluoroindate glass and ZBALN glass, ZBYA glass shows better stability [13]. There are currently reports of ZBYA lasers that exist in microsphere devices only. In 2019, some of the authors of this current article also reported C-band laser operation in an  $\text{Er}^{3+}$ -doped ZBYA glass microsphere resonator [17]. They also subsequently demonstrated a triple-wavelength laser in a  $\text{Ho}^{3+}/\text{Tm}^{3+}$ -codoped ZBYA glass microsphere at 1.5  $\mu\text{m}$ , 1.8  $\mu\text{m}$ , and 2.1  $\mu\text{m}$  [18]. Consequently, ZBYA glasses may be considered as a promising candidate for use in mid-infrared laser devices.

In this article, the luminescence spectra at near- and mid-infrared bands and energy level decay properties of different  $\text{Ho}^{3+}$  ion doping concentrations in ZBYA glasses are investigated, when subjected to direct upper laser level pumping at a wavelength of 888 nm. Spectroscopic measurements were carried out, and spectroscopic parameters were analyzed using

Judd–Ofelt theory. An intense emission located at 3.9  $\mu\text{m}$  in  $\text{Ho}^{3+}$ -doped ZBYA glasses was experimentally observed.

The chemicals used in this investigation were all high-purity raw materials. Powders were fully mixed according to the molar ratio of  $50\text{ZrF}_4\text{-}33\text{BaF}_2\text{-(}9-x\text{)YF}_3\text{-}7\text{AlF}_3\text{-}x\text{HoF}_3$  ( $x = 0.1, 0.2, 0.5, 1, 2, 3, 4, 5, 7, 9$ ), and ground in an agate mortar. The precursor materials were melted using a conventional melt quenching method in a dry and oxygen-free glove box environment at  $850^\circ\text{C}$  for 2 h. After the sample was completely molten, it was quickly transferred to a low-temperature furnace and annealed at  $320^\circ\text{C}$  for 3 h to remove residual stress and internal defects. It was naturally cooled to room temperature to obtain base glass samples. They were cut and polished for subsequent optical testing.

The experimental transmission spectra of the glass samples were measured using a Perkin-Elmer Lambda 900 UV spectrophotometer and an FT-IR spectrometer, which were used to record the spectral ranges  $\lambda \sim 200$  to  $\lambda \sim 3000$  nm and  $\lambda \sim 3300$  to 10,000 nm, respectively. An 888 nm diode laser, which was built by Changchun Institute of Optics and Fine Mechanics, with an output power of 2.5 W was used to excite the ZBYA glass samples in order to measure the fluorescence properties. The infrared fluorescence spectra were measured using a spectrometer (Zolix Omni- $\lambda$ 3015 monochromator) combined with a SCITEC Model 420 dual-phase lock-in amplifier. For the fluorescence decay lifetime measurements, the samples were excited using a Horizon OPO pulsed laser, whose wavelength was set as  $\lambda \sim 880$  nm, with pulses of 6  $\mu\text{s}$  duration and a repetition rate of 10 Hz. The test equipment consisted of a spectrometer (Synerjy 1000M) and a digital phosphor oscilloscope furnished by TEKTRONIX. All tests were performed at room temperature.

Figure 1 shows the energy transfer processes of  $\text{Ho}^{3+}$  ions pumped using an 888 nm laser. When the sample is pumped using the 888 nm laser, the  $\text{Ho}^{3+}$  ions residing in the  $^5\text{I}_8$  ground level state are excited to the  $^5\text{I}_5$  level by ground state absorption (GSA). Ions in the  $^5\text{I}_5$  level decay radiatively to  $^5\text{I}_6$  yielding a  $\lambda \sim 3.9 \mu\text{m}$  emission ( $^5\text{I}_5 \rightarrow ^5\text{I}_6$  transition). The depopulation of the  $\text{Ho}^{3+} : ^5\text{I}_6$  level can occur in a radiative manner via a  $\lambda \sim 2.9 \mu\text{m}$  ( $^5\text{I}_6 \rightarrow ^5\text{I}_7$  transition) and  $\lambda \sim 1150$  nm ( $^5\text{I}_6 \rightarrow ^5\text{I}_8$  transition) emission. Furthermore, ions in the  $^5\text{I}_5$  level transfer to the  $^5\text{F}_4$  level by excited state absorption (ESA) following an initial nonradiative decay to the  $^5\text{I}_6$  level, and drop to the ground state via a 535 nm emission. The upconversion is shown as a green color when the samples were pumped using the 888 nm laser diode source. In addition,  $\text{Ho}^{3+}$  ions demote from  $^5\text{I}_7$  to  $^5\text{I}_8$  resulting in  $\lambda \sim 2.0 \mu\text{m}$  emission. There are also energy transition processes involving cross-relaxation (CR):  $^5\text{I}_5 + ^5\text{I}_8 \rightarrow ^5\text{I}_7 + ^5\text{I}_7$  and energy transfer upconversion (ETU):  $^5\text{I}_7 + ^5\text{I}_7 \rightarrow ^5\text{I}_6 + ^5\text{I}_8$ ,  $^5\text{I}_6 + ^5\text{I}_6 \rightarrow ^5\text{F}_5 + ^5\text{I}_8$ .

Figure 2(a) shows the transmission spectra of  $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3\text{-HoF}_3$  glasses in the 200–10,000 nm wavelength band. The glass samples show outstanding transmittance over 500–6000 nm (approximately 90%), and an infrared cutoff wavelength of approximately 9000 nm. Figure 1 clearly shows the absorption bands located at  $\lambda \sim 2.0 \mu\text{m}$ , 1.2  $\mu\text{m}$ , 890 nm, which correspond to the transitions from the  $^5\text{I}_8$  ground level to the upper levels  $^5\text{I}_7$ ,  $^5\text{I}_6$ ,  $^5\text{I}_5$ , respectively. With an increase in  $\text{Ho}^{3+}$  ion doping concentration, the absorption strength of the corresponding absorption peak becomes greater. From the attenuation spectrum, it can be seen that ZBYA glass

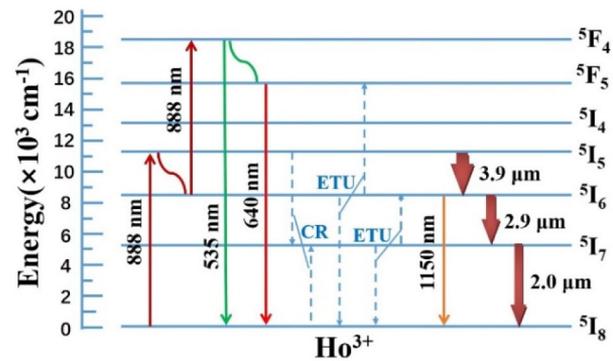


Fig. 1. Energy level diagram for  $\text{Ho}^{3+}$  ions in ZBYA glasses.

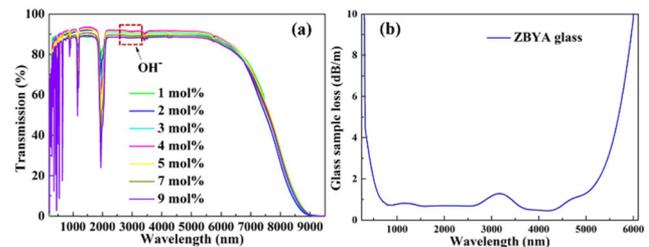


Fig. 2. (a) Transmittance spectra of different concentrations of  $\text{Ho}^{3+}$ -doped ZBYA glasses (thickness  $\sim 2$  mm) in the range  $\lambda \sim 200 - 10000$  nm; (b) attenuation spectrum of no-doped ZBYA glass (thickness  $\sim 18$  mm) in the range  $\lambda \sim 300 - 6000$  nm.

exhibits low loss in the 500–4500 nm band. There is evidence of a small  $\text{OH}^-$  absorption dip near  $\lambda \sim 3 \mu\text{m}$ . The  $\alpha_{\text{OH}^-}$  of the undoped ZBYA glass block was calculated as  $\sim 0.0098 \text{ cm}^{-1}$  from previous reported work [19]. The raw materials used and the weighing process were all conducted in the glove with water excluded, and the sample of molten glass was dehydrated in the glove box for 2 h. Compared with fluoroindate glass ( $\alpha_{\text{OH}^-} \sim 0.0032 \text{ cm}^{-1}$ ) [16], the  $\alpha_{\text{OH}^-}$  of the undoped ZBYA glass was therefore higher. For the current investigation, an 888 nm laser source was used to excite the  $\text{Ho}^{3+}$ -doped ZBYA glasses, which can directly excite the ions in the ground state to the upper energy level ( $^5\text{I}_5$ ), which ultimately results in the emission at 3.9  $\mu\text{m}$ , thereby improving the efficiency of the 3.9  $\mu\text{m}$  emission.

According to the absorption spectrum of 1 mol.%  $\text{Ho}^{3+}$ -doped ZBYA glass, the Judd–Ofelt intensity parameters ( $\Omega_t$ ) ( $t = 2, 4, 6$ ) [20] were calculated as  $3.89 \times 10^{-20} \text{ cm}^2$ ,  $2.52 \times 10^{-20} \text{ cm}^2$  and  $0.54 \times 10^{-20} \text{ cm}^2$ , respectively. Table 1 lists the intensity parameters  $\Omega_t$  ( $t = 2, 4, 6$ ) of  $\text{Ho}^{3+}$  ions in several typical glass substrates. Generally, the larger the  $\Omega_2$  value, the higher the covalency and the lower the symmetry around the rare-earth ion [21].

Table 2 summarizes the data for the radiative parameters for transitions between various energy levels of  $\text{Ho}^{3+}$  ions including spontaneous radiation transition probabilities ( $A$ ), fluorescence branching ratio ( $\beta$ ), and the radiative lifetime ( $\tau_{\text{rad}}$ ) as used in the ZBYA glass sample. Compared with  $\text{Ho}^{3+}$ -doped fluoroindate glass, the spontaneous-emission probabilities for the  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_6$  transition in  $2.96 \text{ s}^{-1}$ , are higher than the corresponding values recorded in fluoroindate glass

**Table 1. Calculated Judd–Ofelt Intensity Parameters  $\Omega_t$  ( $t = 2, 4, 6$ ) of  $\text{Ho}^{3+}$  Ions in Several Typical Glass Substrates**

$\Omega_t$ ( $10^{-20} \text{ cm}^2$ )	$\Omega_2$	$\Omega_4$	$\Omega_6$
Fluoroindate [10]	1	2.8	1.9
ZBLAN [23]	2.30	2.30	1.71
Oxide-fluoride [24]	1.96	0.64	0.11
Tellurite [25]	6.9	2.8	1.4
ZBYA (this work)	3.89	2.52	0.54

**Table 2. Radiative Property Parameters for Transitions between Various Energy Levels of  $\text{Ho}^{3+}$  in ZBYA Glass**

Transition	Wavelength (nm)	$A$ ( $\text{s}^{-1}$ )	$\beta$ (%)	$\tau_{\text{rad}}$ (ms)
$^5\text{I}_5 \rightarrow ^5\text{I}_6$	3920	2.96	6.48	21.9
$\rightarrow ^5\text{I}_7$	1640	26	56.95	
$\rightarrow ^5\text{I}_8$	890	16.7	36.57	
$^5\text{I}_6 \rightarrow ^5\text{I}_7$	2860	6.26	9.3	14.8
$\rightarrow ^5\text{I}_8$	1190	61.1	90.7	
$^5\text{I}_7 \rightarrow ^5\text{I}_8$	2010	22.76	100	43.9

( $2 \text{ s}^{-1}$ ) [10]. In general, a higher value of spontaneous-emission probability ( $A$ ) provides greater potential for laser emission. Additionally, the radiative lifetime of the  $\text{Ho}^{3+} : ^5\text{I}_5, ^5\text{I}_6, ^5\text{I}_7$  energy levels in ZBYA glass were also calculated to be longer than in fluoroindate glass.

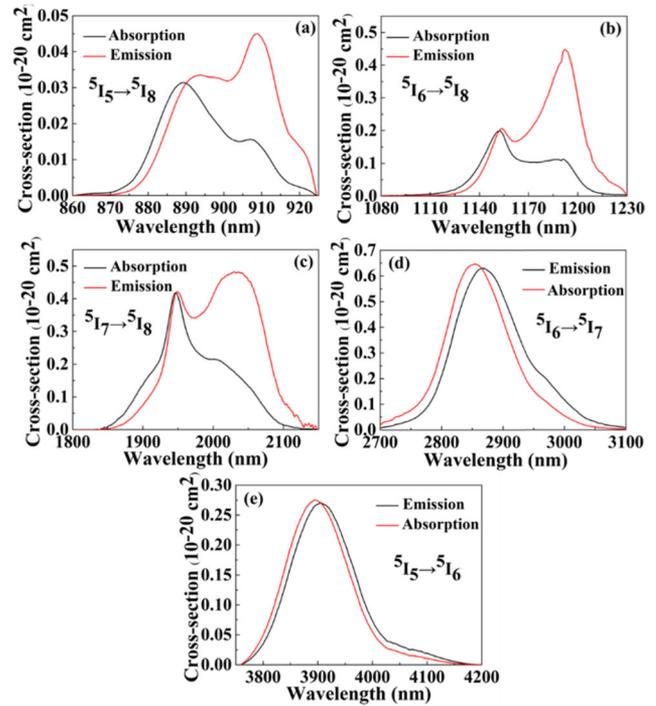
The absorption cross section  $\sigma_{\text{abs}}$  and the emission cross section  $\sigma_{\text{emi}}$  of  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_8$ ,  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_8$ , and  $\text{Ho}^{3+} : ^5\text{I}_7 \rightarrow ^5\text{I}_8$  transitions in ZBYA glass were calculated using the following formulas based on the McCumber theory [22], which is appropriate to the transition from the ground state to the excited state:

$$\sigma_{\text{abs}} = \frac{\ln[I_0(\lambda)/I(\lambda)]}{Nd} = \frac{2.303 \log[I_0(\lambda)/I(\lambda)]}{Nd} = \frac{2.303D(\lambda)}{Nd}, \quad (1)$$

$$\sigma_{\text{emi}} = \sigma_{\text{abs}}(\lambda) \exp[(\varepsilon - h\nu)/KT]. \quad (2)$$

In Eqs. (1) and (2),  $I_0(\lambda)$  and  $I(\lambda)$  represent the optical intensity before and after the light passes through the sample, respectively;  $D(\lambda)$  is the optical absorbance, which can be derived from absorption spectrum of the glass sample;  $N$  is the density of the rare-earth ions; the value used in this investigation was  $1.688 \times 10^{20} \text{ cm}^{-3}$ ; and  $d$  is the absorption path length of the light, which is the thickness of the glass ( $\sim 2 \text{ mm}$ ).  $h$ ,  $\nu$ ,  $K$ , and  $T$  represent the Planck constant, photon frequency, the Boltzmann constant, and room temperature, respectively.  $\varepsilon$  is the zero-line energy and represents the free energy required to excite an ion from a low energy level to a high energy level at temperature  $T$ . The value of  $KT$  used was  $0.026 \text{ eV}$ .

The cross section values of the transitions  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_6$  and  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_7$ , which transfer between excited states, were obtained using Fuchbauer–Ladenburger theory [23], for which the formula is expressed as follows:

**Fig. 3.** The absorption cross section  $\sigma_{\text{abs}}$  and the emission cross section  $\sigma_{\text{emi}}$  of the optical transition (a)  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_8$ , (b)  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_8$ , (c)  $\text{Ho}^{3+} : ^5\text{I}_7 \rightarrow ^5\text{I}_8$ , (d)  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_7$ , and (e)  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_6$ .

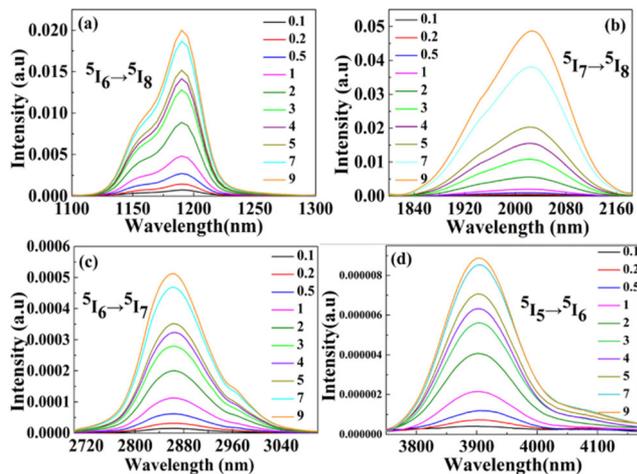
$$\sigma_{\text{emi}} = \frac{\lambda^4 A_{\text{rad}}}{8\pi cn^2} \times \frac{\lambda I(\lambda)}{\int \lambda I(\lambda) d\lambda}, \quad (3)$$

where  $n$  represents the refractive index of ZBYA glass, which is around 1.5;  $c$  is the speed of light in vacuum; and  $A_{\text{rad}}$  is the spontaneous transition probability.  $I(\lambda)$  represents the optical intensity of  $2.9 \mu\text{m}$  or  $3.9 \mu\text{m}$  emission, and it greatly affects the calculation results. The maximum emission cross section of  $2.7 \times 10^{-21} \text{ cm}^2$  occurs at  $3.9 \mu\text{m}$ , and this value is slightly lower than that of fluoroindate glass ( $3.3 \times 10^{-21} \text{ cm}^2$ ) [10].

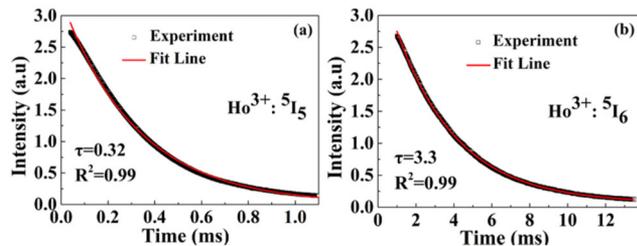
Figures 3(a)–3(e), respectively, present the measured absorption and emission cross section spectra for the optical transitions  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_8$ ,  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_8$ ,  $\text{Ho}^{3+} : ^5\text{I}_7 \rightarrow ^5\text{I}_8$ ,  $\text{Ho}^{3+} : ^5\text{I}_6 \rightarrow ^5\text{I}_7$ , and  $\text{Ho}^{3+} : ^5\text{I}_5 \rightarrow ^5\text{I}_6$  obtained using the above theoretical formulas.

The fluorescence emissions arising from the transitions  $^5\text{I}_6 \rightarrow ^5\text{I}_8$ ,  $^5\text{I}_7 \rightarrow ^5\text{I}_8$ ,  $^5\text{I}_6 \rightarrow ^5\text{I}_7$ ,  $^5\text{I}_5 \rightarrow ^5\text{I}_6$  are shown in Fig. 4, with peak wavelengths located at  $1190 \text{ nm}$ ,  $2100 \text{ nm}$ ,  $2.9 \mu\text{m}$ , and  $3.9 \mu\text{m}$  respectively. An increase of  $\text{Ho}^{3+}$  ion doping concentration clearly gives rise to an increase of the intensity of each emission. The highest doping concentration of  $\text{Ho}^{3+}$  was  $9 \text{ mol.}\%$  in this work, and no concentration quenching phenomenon was observed for these transitions up to that value.

Figure 5 shows the emission decay curves of the experimentally measured fluorescence decay lifetime of the  $\text{Ho}^{3+} : ^5\text{I}_5$  and  $^5\text{I}_6$  levels as a function of  $\text{Ho}^{3+}$  doping concentration. Emissions at  $890 \text{ nm}$  and  $1150 \text{ nm}$  were monitored under excitation from the pump source located at  $880 \text{ nm}$ . As the  $\text{Ho}^{3+}$  concentration increases, the lifetime values of the  $^5\text{I}_5$  and  $^5\text{I}_6$  levels remained approximately constant at  $0.32 \text{ ms}$  and  $3.3 \text{ ms}$ , respectively. Compared with fluoroindate glass, the lifetime



**Fig. 4.** Luminescence spectra of different doping concentration  $\text{Ho}^{3+}$ -doped ZBYA glass at (a)  $\lambda \sim 1190$  nm, (b)  $\lambda \sim 2010$  nm, (c)  $\lambda \sim 2.9$   $\mu\text{m}$ , and (d)  $\lambda \sim 3.9$   $\mu\text{m}$  wavelength and pumped at  $\lambda \sim 888$  nm.



**Fig. 5.** Emission decay curve measured at (a) 890 nm and (b) 1150 nm after laser excitation at 880 nm.

of the  $\text{Ho}^{3+} : ^5\text{I}_5$  level is slightly higher while the  $\text{Ho}^{3+} : ^5\text{I}_6$  level is slightly lower in ZBYA glass [16]. This is owing to the nonradiative relaxation caused by the inherent phonon energy of the glass and the energy transfer processes between the ions. It is evidence that transition process of  $^5\text{I}_5 \rightarrow ^5\text{I}_6$  is a self-terminated process, resulting in the fact that it is difficult to maintain particle number inversion and spontaneously generate lasing at 3.9  $\mu\text{m}$ . Hence, an 888 nm laser was adopted to directly excite the  $\text{Ho}^{3+}$  ions in from the ground state to the  $^5\text{I}_5$  level, and the ETU process ( $^5\text{I}_6 + ^5\text{I}_6 \rightarrow ^5\text{F}_5 + ^5\text{I}_8$ ) can effectively eliminate the lower energy level population, thereby enhancing the 3.9  $\mu\text{m}$  emission that further produces a high efficiency of the transition,  $^5\text{I}_5 \rightarrow ^5\text{I}_6$ . The 3.9  $\mu\text{m}$  emission can therefore be achieved in ZBYA glasses.

A comprehensive experimental investigation on the mid-infrared emission properties of  $\text{Ho}^{3+}$ -doped ZBYA glasses has been conducted. The maximum emission cross section for the resulting 3.9  $\mu\text{m}$  emission was calculated to be  $2.7 \times 10^{-21}$   $\text{cm}^2$ . It was experimentally demonstrated that the intensity of the 3.9  $\mu\text{m}$  emission enhances with the increase of  $\text{Ho}^{3+}$  ion doping concentration under excitation at 888 nm. The results demonstrate the potential viability of the use of this material as an effective 3.9  $\mu\text{m}$  mid-infrared laser.

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