Efficient energy transfer from Er$^{3+}$ to Ho$^{3+}$ and Dy$^{3+}$ in ZBLAN glass

JUNFENG WANG, XIUSHAN ZHU, MASOUD MOLLAAEE, JIE ZONG, and N. PEYHAMBARIAN

College of Optical Science, University of Arizona, 1630 E. University Blvd., Tucson, Arizona 85721, USA

*xxzhu@email.arizona.edu

Abstract: Spectroscopic properties of erbium (Er$^{3+}$-), holmium (Ho$^{3+}$-, dysprosium (Dy$^{3+}$)-doped and Er$^{3+}$/Ho$^{3+}$, Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN (ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF) glasses were studied. The experimental results show that efficient energy transfer from Er$^{3+}$ to Ho$^{3+}$ and Dy$^{3+}$ occurs in the Er$^{3+}$/Ho$^{3+}$ and Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN glasses, respectively. This valuable discovery enables us to design and develop high power Ho$^{3+}$-doped and Dy$^{3+}$-doped ZBLAN fiber lasers in the 3 $\mu$m wavelength region that can be pumped with readily available high-efficiency, high-power diode laser pumps at 980 nm.

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1. Introduction

Lasers in the mid-infrared (mid-IR) spectral region are of great interest for a wide range of scientific and technological applications including spectroscopy, medical surgery, free space communication, remote sensing, and material processing [1–5]. Compared to other laser platforms, optical fiber lasers have many well-known advantages such as excellent beam quality, high power scalability, outstanding heat dissipation capability, simplicity and compactness. ZBLAN (ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF) fibers have been widely used as the host media for rare-earth ions for mid-IR fiber lasers and the nonlinear media for high-efficiency ultra-broad band supercontinuum generation due to their low intrinsic loss, wide transparency window, and small phonon energy [6]. Rare-earth (Er$^{3+}$, Ho$^{3+}$, and Dy$^{3+}$) doped ZBLAN fiber lasers operating in the 3 $\mu$m wavelength region have attracted considerable interest because their emissions cover the fundamental rovibrational absorption lines of molecules containing C-H, N-H, and O-H chemical bonds, and they can be used for a lot of practical applications, such as medical diagnosis and surgery, remote sensing for gas and vapor, and material processing [7–10].

The first demonstration of rare-earth-doped ZBLAN fiber laser at 3 $\mu$m can be dated back to 1988 [6] and thereafter considerable investigations on Er$^{3+}$-doped ZBLAN fiber lasers have been completed due to the readily available diode lasers at the 790 nm and 980 nm absorption peaks of Er$^{3+}$ [11]. Several watt-level Er$^{3+}$-doped ZBLAN fiber lasers have been reported in late 1990s [11–13]. In 2007, Zhu and Jain reported the first 10-W-level 3 $\mu$m fiber laser, which was demonstrated with a 4-m 6 mol% Er$^{3+}$-doped double-clad ZBLAN fiber and a high power diode pump laser at 976 nm [14]. A slope efficiency of 21.3% was obtained by taking the advantage of energy transfer up-conversion process between Er$^{3+}$ and Er$^{3+}$ ions [14]. Since then, several 10-watt-level Er$^{3+}$-doped ZBLAN fiber lasers with higher output powers have been reported [15–16]. In 2015, a 30-W Er$^{3+}$-doped all-fiber laser operating at 2938 nm was demonstrated by using ZBLAN fiber Bragg gratings to form the all-fiber laser cavity and combining several high power laser diodes near 980 nm to provide a total pump power of 188 W [17]. The stokes limit has been exceeded in a 2.8 $\mu$m cascaded laser with 50% efficiency in 2017, which paves the way to 100-W-level mid-infrared fiber laser [18]. In 2018, a 2824 nm passive cooled Er$^{3+}$-doped fluoride fiber approaches an average output power of 41.6 W, which is the highest output average power achieved with the mid-infrared fiber laser [19].
Compared to Er\(^{3+}\)-doped ZBLAN fiber lasers, Ho\(^{3+}\)- and Dy\(^{3+}\)-doped ZBLAN fiber lasers can operate at a wavelength beyond 3 \(\mu\)m and even at 3.380 \(\mu\)m [20], where compact diode-pumped high power laser sources are in great demand for most of the applications mentioned above. However, high efficiency high power (10s-watt or even > 100 watts) diode lasers at the near-infrared (near-IR) absorption peaks of Ho\(^{3+}\) (885 nm and 1150 nm) and Dy\(^{3+}\) (1090 nm, 1300 nm, and 1700 nm) are still not available. So far, the maximum output power of a Ho\(^{3+}\)-doped ZBLAN fiber laser at 3 \(\mu\)m was 2.5 W, which was pumped with a 1100 nm Yb\(^{3+}\)-doped silica fiber laser [21]. The maximum output power of a Dy\(^{3+}\)-doped ZBLAN fiber laser pumped at near-IR was 180 mW [22]. Most recently, in-band pumping of the Dy\(^{3+}\)-doped ZBLAN fiber lasers with a Er\(^{3+}\)-doped ZBLAN fiber laser at 2.8 \(\mu\)m was proposed and an efficiency as high as 73\% was obtained [23]. A 10-W Dy\(^{3+}\)-doped ZBLAN fiber laser in all-fiber configuration was also demonstrated recently by in-band pumping with an Er\(^{3+}\)-doped all-fiber laser at 2.83 \(\mu\)m [24]. Optical transitions in synthesized samples such as Er\(^{3+}/Yb\(^{3+}\) and Er\(^{3+}/Nd\(^{3+}\) have already been studied [25,26]. All these demonstrations motivate us to design and fabricate Er\(^{3+}\) synthesized Ho\(^{3+}\)- and Dy\(^{3+}\)-doped ZBLAN fibers that can be used to develop compact all-fiber lasers above 3 \(\mu\)m directly pumped with readily available high power high efficiency diode lasers near 980 nm. In this paper, we present the spectroscopic studies of the Er\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), and their synthesized ZBLAN glasses and investigate the energy transfer processes between these ions. Our experimental results confirm that efficient energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) and Dy\(^{3+}\) can occur in Er\(^{3+}/Ho\(^{3+}\) and Er\(^{3+}/Dy\(^{3+}\) co-doped ZBLAN glasses. The energy transfer coefficients were also obtained by solving the rate equations and fitting the measured fluorescence.

2. Glass preparation and experimental setup

Rare-earth doped fluoride glasses with a composition of ZrF\(_4\)-BaF\(_2\)-LaF\(_3\)-AlF\(_3\)-NaF as the host network were fabricated by FiberLabs Inc. using the conventional melting-quenching technique. 2 mol\% Er\(^{3+}\)-doped, 1 mol\% Ho\(^{3+}\)-doped, 1 mol\% Dy\(^{3+}\)-doped, 2 mol\% Er\(^{3+}\)/1 mol\% Ho\(^{3+}\) co-doped, and 2 mol\% Er\(^{3+}\)/1 mol\% Dy\(^{3+}\) co-doped ZBLAN glasses were prepared. The singly doped ZBLAN glass samples with a thickness of about 1 cm were cut and polished for the transmission spectrum measurement. The singly doped and co-doped glass samples with a thickness of 1 mm were cut and their two large-area surfaces and one small-area surface were polished to optical quality for the fluorescence and lifetime measurements.

In our experiment, the transmission spectra of the glass samples from 300-3300 nm were measured with a Cary 5000 spectrometer. The fluorescence emissions of the glass samples and the lifetimes of excited states of the Er\(^{3+}\), Ho\(^{3+}\), and Dy\(^{3+}\) were measured with conventional measurement techniques with the experimental setups depicted in Figs. 1(a) and 1(b), respectively. The pump light was launched onto the glass sample at a small region close to the edge of the polished small-area surface. The fluorescence emitting from the glass sample was collected by a black diamond aspheric lens (Thorlab C036TME-E) from the polished small-area surface at 90° to the direction of the pump light. For the fluorescence measurement, near-IR continuous-wave (CW) laser sources at their absorption peaks were used as the pumps to excite Er\(^{3+}\), Ho\(^{3+}\), and Dy\(^{3+}\). The CW fluorescence was modulated by a mechanical chopper and focused into a monochromator (Oriel Instruments, Model 77702) by a CaF\(_2\) plano-convex lens (Thorlab LA5370). To filter the scattered pump light and the fluorescence of no interest, long-pass filters with cut-on wavelengths of 2500 nm (Spectrogon LP-2500nm) and 1250 nm (Thorlab FEL1250) were used for the fluorescence measurement in the 3 \(\mu\)m and near-IR wavelength regions, respectively. The fluorescence intensity was measured with lock-in detection technique by using a lock-in amplifier (Princeton Applied Research, Model 5209) to detect the modulated signal received by the detector of the monochromator. A Labview software was used to control the monochromator and record the fluorescence spectrum.
For the lifetime measurement, a nanosecond pulse optical parametric oscillator (OPO) laser with a pulse duration of 10 ns at a repetition rate of 10 Hz (Continuum Surelite) was used as the pump source. The fluorescence emitting from the glass sample was collected and focused onto a detector (Thorlab PDA 20H) by two aspheric black diamond lenses (Thorlab C036TME-E). The fluorescence decay curve was recorded by an oscilloscope (Tektronics TDS 1012). A set of filters were used to obtain the fluorescence only corresponding to the transition of interest from a specific energy level. The lifetime of an energy level was achieved by fitting the fluorescence decay curve with an exponential decay function.

3. Experimental results and discussion

The partial energy-level diagrams of Er$^{3+}$, Ho$^{3+}$, and Dy$^{3+}$, and the transitions related to the ground state absorptions and mid-IR emissions are shown in Fig. 2. Er$^{3+}$ ions in the ground state can be excited to the excited level $^4I_{11/2}$ ($^4I_{15/2} \rightarrow ^4I_{11/2}$) by absorbing near-IR light at 976 nm. The radiative transition from level $^1I_{11/2}$ to level $^1I_{13/2}$ generates the light in the 3 µm wavelength region and that from level $^4I_{13/2}$ to the ground level generates the light in the 1.5 µm wavelength region. Ho$^{3+}$ ions has a near-IR absorption band at 1150 nm and the ground state absorption ($^3I_8 \rightarrow ^5I_6$) at this wavelength can populate the upper laser level $^5I_6$ for the 3 µm emission ($^5I_6 \rightarrow ^5I_7$). The radiative transition from level $^5I_7$ to the ground level $^5I_6$ generates the light in the 2 µm wavelength region. Dy$^{3+}$ ions have three near-IR absorption bands at 1090 nm, 1300 nm, and 1700 nm. The 3 µm emission can be produced by the radiative transition from level $^6H_{11/2}$ to level $^6H_{15/2}$. The transmission spectra of 2 mol% Er$^{3+}$-doped, 1 mol% Ho$^{3+}$-doped, and 1 mol% Dy$^{3+}$-doped ZBLAN glass samples with thickness of about 1 cm were measured and are shown in Fig. 3. Because the absorption bands of Ho$^{3+}$ and Dy$^{3+}$ at 1150 nm and 1090 nm are close to the absorption band of Er$^{3+}$ at 976 nm and the energy levels $^5I_6$ and $^6F_{9/2}$ are lower than that of the exited level $^1I_{11/2}$ of Er$^{3+}$, energy transfer from level $^1I_{11/2}$ of Er$^{3+}$ to level $^5I_6$ of Ho$^{3+}$ (ET$_{3+}$-6) and level $^6F_{9/2}$ of Dy$^{3+}$ (ET$_{3+}$-9) as shown in Fig. 2 could happen when they are co-doped in a ZBLAN glass. It should be noted that, the excited state absorption of 980 nm pump light was not considered in the simulation model because the pump power intensity is very low and the effect of excited state absorption on the measurement results is negligible.

The fluorescence spectra of singly Er$^{3+}$-, Ho$^{3+}$-, and Dy$^{3+}$-doped ZBLAN glass in the 3 µm wavelength region were measured and are shown in Fig. 4. Clearly, the Er$^{3+}$-doped ZBLAN has a fluorescence emission covering from 2500 nm to 3000 nm with a peak at 2740 nm. There are small dips on the fluorescence spectrum around 2740 nm that are due to the absorption of the water vapor in the measurement setup. The fluorescence of the Ho$^{3+}$-doped ZBLAN has a peak at 2850 nm and the long wavelength emission extends to 3100 nm. The Dy$^{3+}$-doped ZBLAN has a very broad fluorescence covering from 2600 nm to 3400 nm, which is of great interest for developing ultra-wide wavelength tunable laser source and ultrashort pulse laser source in the 3 µm wavelength region. For example, a wavelength-tunable Dy$^{3+}$-doped ZBLAN fiber laser with a tuning range of 2.8-3.4 µm was reported [20] and a mode-locked Dy$^{3+}$-doped fiber laser with a tuning range of 2.9-3.3 µm was demonstrated [27]. The lifetimes of level $^4I_{11/2}$, level $^1I_6$, and level $^6H_{13/2}$ of singly Er$^{3+}$-, Ho$^{3+}$-, and Dy$^{3+}$-doped ZBLAN glass in the 3 µm wavelength...
Fig. 2. Partial energy-level diagrams of Er$^{3+}$, Ho$^{3+}$, and Dy$^{3+}$ and the transitions and energy transfer processes related to the emissions in the mid-IR.

Fig. 3. Measured transmission spectra of (a) 0.75 cm-thick 1 mol% Ho$^{3+}$-doped, (b) 1.1 cm-thick 2 mol% Er$^{3+}$-doped, and (c) 1 cm-thick 1 mol% Dy$^{3+}$-doped ZBLAN glass samples.

region were measured to be 6.9 ms, 3.76 ms, and 0.512 ms, respectively, as shown in Fig. 5. Because the lifetimes of level $^5I_6$ and level $^6H_{13/2}$ are smaller than that of level $^4I_{11/2}$, efficient energy transfer from Er$^{3+}$ to Ho$^{3+}$ and Dy$^{3+}$ can occur in ZBLAN.

Fig. 4. Measured fluorescence spectra of the 2 mol% Er$^{3+}$-, 1 mol% Ho$^{3+}$-, and 1 mol% Dy$^{3+}$-doped ZBLAN glasses in the 3 μm wavelength region.

As mentioned above, a lot of investigations on Er$^{3+}$-doped ZBLAN fiber lasers have been conducted and several ten-watt-level fiber lasers at 2.8 μm have been demonstrated during the last decade due to the readily available high power pump diodes at 976 nm. Therefore, similar
progress on Ho\(^{3+}\) and Dy\(^{3+}\)-doped ZBLAN fiber lasers could be achieved if they can be pumped with high power high efficiency diode lasers. However, high power diode lasers at the absorption peaks of Ho\(^{3+}\) and Dy\(^{3+}\) are still not available. Therefore, using energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) and Dy\(^{3+}\) could be a promising solution to this problem.

The fluorescence spectra of the 2 mol% Er\(^{3+}\), 2 mol% Er\(^{3+}\)/1 mol% Dy\(^{3+}\), and 2 mol% Er\(^{3+}\)/1 mol% Ho\(^{3+}\) doped ZBLAN glass samples pumped with a 976 nm diode laser at a power level of 316 mW were measured at ranges of 1400-2200 nm and 2500-3500 nm and are shown in Fig. 6. Figures 6(a) and 6(b) show the fluorescence spectra of the singly Er\(^{3+}\)-doped ZBLAN glass with peaks at 1540 nm and 2740 nm, corresponding to the transitions of \(4\mathrm{I}_{13/2} \rightarrow 4\mathrm{I}_{15/2}\) and \(4\mathrm{I}_{11/2} \rightarrow 4\mathrm{I}_{13/2}\), respectively. The fluorescence spectra of the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN glass in the near-IR and the 3 \(\mu\)m wavelength regions are shown in Figs. 6(c) and 6(d), respectively. Besides the fluorescence of Er\(^{3+}\) at the 1.5 \(\mu\)m wavelength region, the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN glass has fluorescence emission with a peak at 1950 nm, corresponding to the transition from \(5\mathrm{I}_{7} \rightarrow 5\mathrm{I}_{8}\) of Ho\(^{3+}\). Moreover, the fluorescence of the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN glass in the 3 \(\mu\)m wavelength region exhibits the combined features of the fluorescence of singly Er\(^{3+}\)- and Ho\(^{3+}\)-doped ZBLAN samples. Because Ho\(^{3+}\) ions don’t have absorption at 976 nm, these results clearly prove that energy transfer from level \(4\mathrm{I}_{13/2}\) of Er\(^{3+}\) to level \(5\mathrm{I}_{6}\) of Ho\(^{3+}\) occurs in ZBLAN as illustrated by the ET\(_{3-2}\) process in Fig. 2. The fluorescence spectra of the Er\(^{3+}\)/Dy\(^{3+}\) co-doped ZBLAN glass in the 1.5 \(\mu\)m and 3 \(\mu\)m wavelength regions are shown in Figs. 6(e) and 6(f), respectively. The fluorescence spectrum of the Er\(^{3+}\)/Dy\(^{3+}\) co-doped ZBLAN at 3 \(\mu\)m is almost the same as that of the singly Dy\(^{3+}\)-doped ZBLAN, showing that very efficient energy transfer from level \(4\mathrm{I}_{11/2}\) of Er\(^{3+}\) to level \(6\mathrm{F}_{9/2}\) of Dy\(^{3+}\) occurs as illustrated by the ET\(_{3-2}\) process in Fig. 2. The fluorescence of the Er\(^{3+}\)/Dy\(^{3+}\) co-doped ZBLAN at 1.54 \(\mu\)m, however, is much smaller than that of the singly Er\(^{3+}\) doped ZBLAN, also indicating most energy is transferred from Er\(^{3+}\) to Dy\(^{3+}\).

The energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) and Dy\(^{3+}\) was also confirmed by measuring the 3 \(\mu\)m fluorescence decay from level \(4\mathrm{I}_{11/2}\) of Er\(^{3+}\) in the codoped glass samples using the lifetime measurement setup shown in Fig. 1(b). The glass samples were pumped with 10 ns second pulse laser at 976 nm. The decaying curves of the 3 \(\mu\)m fluorescence of Er\(^{3+}\)/Ho\(^{3+}\) and Er\(^{3+}\)/Dy\(^{3+}\) codoped ZBLAN samples were measured by using filters to remove the light below 2.5 \(\mu\)m and are shown in Figs. 7(a) and 7(b), respectively. The decay time of the 3 \(\mu\)m fluorescence of the 2 mol% Er\(^{3+}\)/1 mol% Ho\(^{3+}\) co-doped ZBLAN sample is 6.15 ms, which is smaller than that of the singly Er\(^{3+}\)-doped ZBLAN, indicating that the energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) occurs. The decay time of the 3 \(\mu\)m fluorescence of the 2 mol% Er\(^{3+}\)/1 mol% Dy\(^{3+}\) co-doped ZBLAN sample is only 0.84 ms, which is significantly reduced due to the efficient energy transfer from Er\(^{3+}\) to Dy\(^{3+}\). It is worth noting that the fluorescence decay times are consistent with the measured fluorescence spectra. In the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN, the energy transfer from Er\(^{3+}\) to Ho\(^{3+}\),
Fig. 6. Fluorescence spectra of the 2 mol% Er$^{3+}$-doped, 2 mol% Er$^{3+}$/1 mol% Ho$^{3+}$ co-doped, and 2 mol% Er$^{3+}$/1 mol% Dy$^{3+}$ co-doped ZBLAN glass samples measured at 1400-2200 nm and 2500-3500 nm when they were pumped at 976 nm.

is not significant, so the fluorescence decay time is close to the lifetime of level $^4I_{11/2}$ of Er$^{3+}$ and the fluorescence spectrum exhibits the combined features of the fluorescence of Er$^{3+}$ and Ho$^{3+}$. The energy transfer from Er$^{3+}$ to Dy$^{3+}$ is very efficient in the Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN, so the fluorescence decay time is close to the lifetime of level $^6H_{13/2}$ of Dy$^{3+}$ and the fluorescence spectrum is almost the same as that of the singly Dy$^{3+}$-doped ZBLAN.

Fig. 7. Measured 3 µm fluorescence decay curves and fitting curves of (a) 2 mol% Er$^{3+}$/1 mol% Ho$^{3+}$ co-doped and (b) 2 mol% Er$^{3+}$/1 mol% Dy$^{3+}$ co-doped ZBLAN glasses in the 3 µm wavelength region.

In addition to the energy transfer processes from level $^4I_{11/2}$ of Er$^{3+}$ to Ho$^{3+}$ and Dy$^{3+}$ (ET$^{3-6}$ and ET$^{3-9}$ processes shown in Fig. 2), the energy transfer processes from level $^4I_{13/2}$ of Er$^{3+}$ to level $^5I_7$ of Ho$^{3+}$ (ET$^{2-5}$ process shown in Fig. 2) and level $^6H_{11/2}$ of Dy$^{3+}$ (ET$^{2-8}$ process shown...
in Fig. 2) also occur in the co-doped ZBLANs and were confirmed by the measured fluorescence spectra and the reduced lifetime of level $^4I_{13/2}$ of Er$^{3+}$ when they were pumped at 1480 nm. The fluorescence of Er$^{3+}$/Ho$^{3+}$ co-doped ZBLAN sample pumped by a 1480 nm diode laser was measured and is shown in Fig. 8(a). Besides the fluorescence of Er$^{3+}$ at the 1.55 $µ$m wavelength region, the fluorescence of Ho$^{3+}$ with a peak at 1950 nm was also measured although Ho$^{3+}$ ions don’t have any absorption at 1480 nm, indicating that energy transfer from $^4I_{13/2}$ of Er$^{3+}$ to level $^5I_7$ of Ho$^{3+}$ occurs. Figure 8(b) shows the fluorescence of Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN sample pumped by a 1480 nm diode laser. Besides the fluorescence of Er$^{3+}$ at the 1.55 $µ$m wavelength region, the fluorescence of Dy$^{3+}$ with a peak at 2850 nm was also measured, confirming the energy transfer from level $^4I_{13/2}$ of Er$^{3+}$ to level $^9H_{11/2}$ of Dy$^{3+}$. The 1.55 $µ$m fluorescence decay curves of the three ZBLAN glass samples pumped at 1480 nm were also measured and are shown in Fig. 9. The lifetime of level $^4I_{13/2}$ of the Er$^{3+}$/Ho$^{3+}$ co-doped ZBLAN was calculated to be 3.18 ms and that of the Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN was calculated to 0.462 ms. Both lifetimes are much smaller than that of the singly Er$^{3+}$-doped ZBLAN (10.92 ms), again proving the efficient energy transfer from level $^4I_{13/2}$ of Er$^{3+}$ to level $^5I_7$ of Ho$^{3+}$ and level $^9H_{11/2}$ of Dy$^{3+}$, respectively.

**Fig. 8.** Measured fluorescence spectra of (a) Er$^{3+}$/Ho$^{3+}$ and (b) Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN samples pumped at 1480 nm.

**Fig. 9.** Measured 1.55 $µ$m fluorescence decay curves and fitting curves of (a) 2 mol% Er$^{3+}$-doped, (b) 2 mol% Er$^{3+}$/1 mol% Ho$^{3+}$ co-doped, and (c) 2 mol% Er$^{3+}$/1 mol% Dy$^{3+}$ co-doped ZBLAN glasses pumped at 1480 nm.

The backward energy transfer from Dy$^{3+}$ and Ho$^{3+}$ to Er$^{3+}$ was also investigated in our experiment. The fluorescence spectrum of the Er$^{3+}$/Ho$^{3+}$ co-doped ZBLAN sample pumped at 1150 nm was measured at 1400-2200 nm and is shown in Fig. 10(a). In addition to the 2 $µ$m emission from Ho$^{3+}$, a very weak fluorescence at 1.55 $µ$m from Er$^{3+}$ was measured and is shown
in Fig. 10(a), indicating that the backward energy transfer from Ho$^{3+}$ to Er$^{3+}$ occurs but the energy transfer probability is very low. The fluorescence spectrum of the Er$^{3+}$/Dy$^{3+}$ co-doped ZBLAN sample pumped at 1090 nm was measured at 1000-2000 nm and is shown in Fig. 10(b). The fluorescence at 1.55 $\mu$m from Er$^{3+}$ was not measured, indicating that the backward energy transfer from Dy$^{3+}$ to Er$^{3+}$ is negligible.

The parameters of energy transfer processes ($k_{25}$, $k_{36}$, $k_{28}$, $k_{39}$) can be obtained by solving the rate equations for Er$^{3+}$/Dy$^{3+}$ and Er$^{3+}$/Ho$^{3+}$ co-doped ZBLAN samples to calculate the populations on the corresponding energy levels and fitting the measured fluorescence spectra. The rate equations for Er$^{3+}$/Ho$^{3+}$ co-doped ZBLAN pumped at 976 nm can be written as follows.

\[
\frac{dN_1}{dt} = -R_{13}N_1 - A_{31}N_3 - A_{32}N_3 - k_{36}N_3N_4 = 0 
\]

\[
\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 - k_{25}N_2N_4 = 0 
\]

\[
\frac{dN_3}{dt} = -R_{13}N_1 + A_{31}N_3 + A_{21}N_2 + k_{36}N_3N_4 + k_{25}N_2N_4 = 0 
\]

\[
N_1 + N_2 + N_3 - N_{Er} = 0 
\]

\[
\frac{dN_4}{dt} = k_{36}N_3N_4 - A_{64}N_6 - A_{65}N_6 = 0 
\]

\[
\frac{dN_5}{dt} = k_{25}N_2N_4 + A_{65}N_6 - A_{54}N_5 = 0 
\]

\[
\frac{dN_6}{dt} = -k_{25}N_2N_4 - k_{36}N_3N_4 + A_{64}N_6 + A_{54}N_5 = 0 
\]

\[
N_1 + N_2 + N_3 - N_{Ho} = 0 
\]

Where, $N_i$ is the population on the corresponding energy level of Er$^{3+}$ and Ho$^{3+}$ shown in Fig. 2; $R_{13}=(\sigma_{abs}P_p)/(h\nu A_{eff})$ is the pump rate, $\sigma_{abs}$ is the absorption cross-section of Er$^{3+}$, which is $2\times10^{-25}$ m$^2$ at 976 nm, $P_p$ is the laser pump power, $A_{eff}$ is the effective area of the pump spot, which is h is the plank constant, and $\nu$ is the frequency of the pump; $A_{ij}$ is the transition rate of the spontaneous emission from level i to level j and the values of $A_{ij}$ can be achieved according to their lifetimes and branch ratios; and $k_{ij}$ is the parameter for the energy transfer process from level i to level j between Er$^{3+}$ and Ho$^{3+}$. All the related parameters are given in Table 1.
Table 1. Transition rates and absorption cross-section of Er\(^{3+}\), Ho\(^{3+}\).

<table>
<thead>
<tr>
<th>Transition</th>
<th>A(s(^{-1}))</th>
<th>Absorption cross-section (\sigma_{\text{abs}}) (m(^2))</th>
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</thead>
<tbody>
<tr>
<td>(^{4}\text{I}<em>{11/2} \rightarrow ^{4}\text{I}</em>{15/2})</td>
<td>118.9</td>
<td>2\times10(^{-25}) (976 nm)</td>
</tr>
<tr>
<td>(^{4}\text{I}<em>{11/2} \rightarrow ^{4}\text{I}</em>{13/2})</td>
<td>26.05</td>
<td>3.6\times10(^{-25}) (1480 nm)</td>
</tr>
<tr>
<td>(^{4}\text{I}<em>{13/2} \rightarrow ^{4}\text{I}</em>{15/2})</td>
<td>91.5</td>
<td></td>
</tr>
<tr>
<td>(^{5}\text{I}<em>{6} \rightarrow ^{5}\text{I}</em>{7})</td>
<td>32.65</td>
<td></td>
</tr>
<tr>
<td>(^{5}\text{I}<em>{6} \rightarrow ^{5}\text{I}</em>{8})</td>
<td>233.24</td>
<td>1.73\times10(^{-25}) (1150 nm)</td>
</tr>
<tr>
<td>(^{5}\text{I}<em>{7} \rightarrow ^{5}\text{I}</em>{6})</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

Figure 11(a) shows the measured 3 µm fluorescence spectra of the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN pumped by the 976 nm diode laser at 120 mW and 316 mW and their fitting curves. The parameters \(k_{36}\) and \(k_{25}\) were calculated to be 5.46 \pm 0.78 \times 10\(^{-19}\) cm\(^3\)/s and 1.24 \pm 0.21 \times 10\(^{-18}\) cm\(^3\)/s, respectively, by fitting the fluorescence spectra of the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLANs with the fluorescence spectra of the singly Er\(^{3+}\)- and Ho\(^{3+}\)-doped ZBLANs. Clearly, the energy transfer rate from level \(^{4}\text{I}_{11/2}\) of Er\(^{3+}\) to level \(^{5}\text{I}_{6}\) of Ho\(^{3+}\) is smaller than that from level \(^{4}\text{I}_{13/2}\) of Er\(^{3+}\) to level \(^{5}\text{I}_{7}\) of Ho\(^{3+}\). It should be noted that, the parameter \(k_{25}\) can be also obtained by fitting the fluorescence spectrum of the Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN pumped at 1480 nm that is shown in Fig. 8(a).

![Figure 11](image_url)

**Fig. 11.** Measured 3 µm fluorescence spectra and their fitting curves for (a) Er\(^{3+}\)/Ho\(^{3+}\) co-doped ZBLAN and (b) Er\(^{3+}\)/Dy\(^{3+}\) co-doped ZBLAN pumped with 120 mW and 316 mW 976 nm laser.

The rate equations for Er\(^{3+}\)/Dy\(^{3+}\) co-doped ZBLAN pumped at 976 nm can be written as follows.

\[
\frac{dN_1}{dt} = R_{13}N_1 - A_{31}N_3 - A_{32}N_3 - k_{39}N_3N_7 = 0 \tag{9}
\]

\[
\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 - k_{28}N_2N_7 = 0 \tag{10}
\]

\[
\frac{dN_3}{dt} = R_{13}N_1 + A_{31}N_3 + A_{21}N_2 + k_{39}N_3N_7 + k_{28}N_2N_7 = 0 \tag{11}
\]

\[
N_1 + N_2 + N_3 - N_{\text{Er}} = 0 \tag{12}
\]

\[
\frac{dN_7}{dt} = k_{39}N_3N_7 + k_{28}N_2N_7 - A_{87}N_8 = 0 \tag{13}
\]

\[
N_7 + N_8 - N_{\text{Dy}} = 0 \tag{14}
\]
The 3 μm fluorescence spectra of the Er\(^{3+}/\text{Dy}^{3+}\) co-doped ZBLAN pumped with the 976 nm diode laser at 120 mW and 316 mW and their fitting curves are shown in Fig. 11(b). After fitting the fluorescence spectra of the Er\(^{3+}/\text{Dy}^{3+}\) co-doped ZBLANs with the fluorescence spectra of the singly Er\(^{3+}\) and Dy\(^{3+}\)-doped ZBLANs, the parameters \(k_{38}\) and \(k_{39}\) were calculated to be \(2.18 \pm 0.06 \times 10^{-20} \text{cm}^3/\text{s}\) and \(2.89 \pm 0.03 \times 10^{-18} \text{cm}^3/\text{s}\), respectively. It is obvious that the energy transfer rates from Er\(^{3+}\) to Ho\(^{3+}\) are much smaller than that from Er\(^{3+}\) to Dy\(^{3+}\). This is consistent with the fluorescence and lifetime measurement results. The parameter \(k_{38}\) of 2.18 \(\pm\) 0.06 \(\times\) 10\(^{-20}\) cm\(^3\)/s was also obtained by fitting the fluorescence spectrum of the Er\(^{3+}/\text{Dy}^{3+}\) co-doped ZBLAN pumped at 1480 nm shown in Fig. 8(b).

4. Conclusion

Spectroscopic properties of Er\(^{3+}\), Ho\(^{3+}\), Dy\(^{3+}\), Er\(^{3+}/\text{Ho}^{3+}\), and Er\(^{3+}/\text{Dy}^{3+}\)-doped ZBLAN glasses were studied and energy transfer from Er\(^{3+}\) to Ho\(^{3+}\) and Dy\(^{3+}\) ions in ZBLAN were confirmed with the experimental results. The parameters for energy transfer processes from level \(4I_{13/2}\) of Er\(^{3+}\) to level \(3I_{17}\) of Ho\(^{3+}\) and level \(4I_{13/2}\) of Dy\(^{3+}\) were estimated to be \(5.46 \pm 0.78 \times 10^{-19}\) cm\(^3\)/s and \(2.89 \pm 0.03 \times 10^{-18}\) cm\(^3\)/s, respectively. This discovery opens a new path to design and develop high power diode-pumped Ho\(^{3+}\)- and Dy\(^{3+}\)-doped fiber lasers at 3 μm.

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Disclosures

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References