

2023

## An investigation of 3.5 $\mu\text{m}$ emission in Er<sup>3+</sup>-doped fluorozirconate glasses under 638 nm laser excitation

Haiyan Zhao

*Shenzhen University, Shenzhen, China*

Ke Tian

*Harbin Engineering University, Harbin, China*

Xin Wang

*Shenzhen University, Shenzhen, China*

*See next page for additional authors*

Follow this and additional works at: <https://arrow.tudublin.ie/prcart>



Part of the [Electrical and Electronics Commons](#)

### Recommended Citation

Zhao, Haiyan; Tian, Ke; Wang, Xin; Liu, Dejun; Wang, Shunbin; Farrell, Gerald; and Wang, Pengfei, "An investigation of 3.5  $\mu\text{m}$  emission in Er<sup>3+</sup>-doped fluorozirconate glasses under 638 nm laser excitation" (2023). *Articles*. 46.

<https://arrow.tudublin.ie/prcart/46>

This Article is brought to you for free and open access by the Photonics Research Centre at ARROW@TU Dublin. It has been accepted for inclusion in Articles by an authorized administrator of ARROW@TU Dublin. For more information, please contact [arrow.admin@tudublin.ie](mailto:arrow.admin@tudublin.ie), [aisling.coyne@tudublin.ie](mailto:aisling.coyne@tudublin.ie), [vera.kilshaw@tudublin.ie](mailto:vera.kilshaw@tudublin.ie).



This work is licensed under a [Creative Commons Attribution-Share Alike 4.0 International License](#).

Funder: National Key Scientific Instrument and Equipment Development Projects of China (61727816); Shenzhen Fundamental Research Program (JCYJ20190808140805488, JCYJ20190808173401660, JCYJ20190808173619062); Basic and Applied Basic Research Foundation of Guangdong Province (2019A15110320); National Natural Science Foundation of China (11874332, 62105217).

---

**Authors**

Haiyan Zhao, Ke Tian, Xin Wang, Dejun Liu, Shunbin Wang, Gerald Farrell, and Pengfei Wang

# An investigation of 3.5 $\mu\text{m}$ emission in $\text{Er}^{3+}$ -doped fluoro-zirconate glasses under 638 nm laser excitation

Haiyan Zhao,<sup>a</sup> Ke Tian,<sup>b</sup> Xin Wang,<sup>a</sup> Dejun Liu,<sup>a</sup> Shunbin Wang,<sup>b</sup> Gerald Farrell,<sup>c</sup> and Pengfei Wang<sup>a,b,\*</sup>

<sup>a</sup>Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

<sup>b</sup>Key Lab of In-Fiber Integrated Optics of Ministry of Education of China, Harbin Engineering University, Harbin 150001, China

<sup>c</sup>Photonics Research Center, Technological University Dublin, Grangegorman Campus, Dublin 7, Ireland

---

## Abstract

Intense 3.5  $\mu\text{m}$  mid-infrared emission has been achieved in  $\text{Er}^{3+}$ -doped ZBYA glasses, which is ascribed to the  $\text{Er}^{3+}$ :  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{9/2}$  transition. Based on the absorption spectrum of  $\text{Er}^{3+}$  ions, a 638 nm laser was utilized to directly pump the upper level ( $\text{Er}^{3+}$ :  ${}^4\text{F}_{9/2}$ ) to achieve 3.5  $\mu\text{m}$  emission with enhanced quantum efficiency. Spectroscopic parameters were predicted by Judd-Ofelt theory. The maximum emission cross-section of the  $\text{Er}^{3+}$ -doped ZBYA glass was estimated to be  $5.5 \times 10^{-22} \text{ cm}^2$  at 3496 nm. Additionally, the fluorescence spectra and energy level lifetimes of ZBYA glass samples with different  $\text{Er}^{3+}$  ions doping concentrations were also measured. The theoretical and experimental results confirm the potential of  $\text{Er}^{3+}$ -doped ZBYA glasses for use in the development of 3.5  $\mu\text{m}$  mid-infrared fiber lasers.

*Keywords:* Mid-infrared; ZBYA glass;  $\text{Er}^{3+}$ -doped; quantum efficiency

---

## 1. Introduction

Mid-infrared (MIR) laser sources in the wavelength range around 3-5  $\mu\text{m}$  play an essential role in applications areas such as gas spectroscopy, atmospheric communications, biomedical and material processing fields [1-3]. In the past few decades, fiber lasers based on  $\text{Er}^{3+}$  ions as activators

8 have attracted intensive study as MIR sources [4-6].  
9 Lasing in  $\text{Er}^{3+}$ -doped ZBLAN fiber has been widely  
10 investigated, generating MIR emission at  $\lambda \sim 2.8 \mu\text{m}$   
11 through the  $\text{Er}^{3+}$ :  ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$  transition using a 980 nm  
12 laser as a pump source [7]. Up to now, the highest  
13 power achieved for an MIR fiber laser is 70 W at  $\lambda \sim 2.8$   
14  $\mu\text{m}$  [8]. In more recent years, laser emission at  $\lambda \sim 3.5$   
15  $\mu\text{m}$ , corresponding to the transition  $\text{Er}^{3+}$ :  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ ,  
16 has attracted a lot of interest, given that such lasers can

---

\*Corresponding author: pengfei.wang@tudublin.ie

1 be used for in variety of application areas such as 51  
2 polymer processing and molecular spectroscopy [9, 52  
3 10]. Early in 1992, H. Többen *et al.* demonstrated 3.5 53  
4  $\mu\text{m}$  laser emission from an  $\text{Er}^{3+}$ -doped ZBLAN fiber 54  
5 at room temperature pumped by a dicyanomethylene 55  
6 (DCM) dye laser at 655 nm [11]. In such a laser,  $\text{Er}^{3+}$  56  
7 ions will be excited directly to the  $\text{Er}^{3+}: {}^4\text{F}_{9/2}$  level by 57  
8 absorbing 655 nm energy and will then relax to a lower 58  
9 level resulting in 3.5  $\mu\text{m}$  emission. However, the 59  
10 disadvantages of pumping at 655 nm were that the  
11 threshold power was high at 996 mW and the slope  
12 efficiency was poor at 2.8% due to relatively high 60  
13 multiphonon rate. In 2016, Ori Henderson-Sapir *et al.*  
14 reported a dual-wavelength pumping (DWP) scheme 61  
15 to implement a  $\text{Er}^{3+}$  ion 3.5  $\mu\text{m}$  laser [12]. By utilizing 62  
16 both 985 nm and 1973 nm wavelengths as pump 63  
17 sources, particles in the ground state were excited to 64  
18 the upper energy level for 3.5  $\mu\text{m}$  emission. In 2022, 65  
19 Maxime Lemieux-Tanguay *et al.* proposed a DWP all- 66  
20 fiber continuous-wave (CW) laser operating at 3.55 67  
21  $\mu\text{m}$  using Er: ZBLAN fiber which reached an output 68  
22 power of 14.9 W. This laser involved splicing 69  
23 silica fiber to the ZBLAN fiber and using two fiber 70  
24 Bragg gratings (FBGs) as laser reflectors [13]. In the 71  
25 same year, Qin Zhipeng *et al.* investigated a 658 nm 72  
26 diode-pumped CW and mode-locked fiber laser at 3.5 73  
27  $\mu\text{m}$ . Using a 7.0 mol.% Er: ZBLAN gain fiber, a CW 74  
28 output power of 203 mW was experimentally obtained 75  
29 at 3462 nm [14]. While DWP schemes can deliver 76  
30 lasers with high output power, single wavelength 77  
31 pumping schemes are more desirable since they not 78  
32 only simplify the pump source but also reduce the 79  
33 complexity of coupling. This in turn can lead to cost 80  
34 reductions which will promote the application of 3.5 81  
35  $\mu\text{m}$  MIR fiber lasers in a wide range of applications. 82  
36 Er: ZBLAN fiber as gain medium has yielded 83  
37 promising results, but two major drawbacks exist: a 84  
38 low glass transition temperature ( $T_g$ ) and poor 85  
39 chemical durability. Overall then progress in the MIR 86  
40 fiber laser area is restricted by the lack of high- 87  
41 performance gain medium. 88  
42  $\text{ZrF}_4\text{-BaF}_2\text{-YF}_3\text{-AlF}_3$  (ZBYA) fluorozirconate glass 89  
43 is considered to be a promising gain medium for MIR 90  
44 lasing emission. It has known merits that include a low 91  
45 phonon energy ( $571\text{ cm}^{-1}$ ), a higher chemical stability 92  
46 and glass transition temperature than ZBLAN glass, a 93  
47 higher damage threshold tolerance and a more stable 94  
48 composition than fluorindate glass [15, 16]. 95  
49 Recently, our group reported a 2.9  $\mu\text{m}$  MIR laser from  
50 an in-house fabricated  $\text{Ho}^{3+}/\text{Pr}^{3+}$  co-doped ZBYA

glass fiber where the maximum unsaturated output  
power reached 2.16 W [17]. This indicates that ZBYA  
glass is a useful gain medium for a MIR laser. In this  
paper, we prepared  $\text{Er}^{3+}$ -doped ZBYA glasses using  
conventional melt-quenching method in a glove box.  
Under 638 nm laser diode (LD) excitation, intense 3.5  
 $\mu\text{m}$  emission was observed in Er: ZBYA glasses and  
the fluorescence properties for lasing have been  
studied.

## 2. Experiment

The  $\text{Er}^{3+}$ -doped ZBYA glasses were prepared  
through the conventional melt-quenching method in a  
glove box to avoid contamination by water. First,  
high-purity  $\text{ZrF}_4$  (99.99%),  $\text{BaF}_2$  (99.99%),  $\text{YF}_3$   
(99.99%),  $\text{AlF}_3$  (99.9%) and  $\text{ErF}_3$  (99.99%) were  
employed as raw materials. These powder samples  
were weighed and mixed evenly in the ratio: 50  $\text{ZrF}_4$  -  
33  $\text{BaF}_2$  - (10-x)  $\text{YF}_3$  - 7  $\text{AlF}_3$  - x  $\text{ErF}_3$  (x=0.1, 0.2, 0.5,  
1, 2, 3, 4, 5, 7, 9) (mol%). Batches of 15 g were  
thoroughly mixed and then melted in a covered  
platinum crucible at 850  $^\circ\text{C}$  for 2 h. After that, the melt  
was cast into a preheated brass plate (320  $^\circ\text{C}$ ) for 3 h  
to relieve stress. The bulk samples were cut into blocks  
and optically polished with a thickness of 2 mm for  
subsequent measurements.

The absorption spectrum of the glass sample was  
measured using a Perkin-Elmer Lambda 900 UV  
spectrophotometer over the wavelength range of 200-  
1800 nm. Under the excitation of an in-house  
fabricated 638 nm LD, fluorescence emission spectra  
were detected by a Zolix Omni- $\lambda$ 300i fluorescence  
spectrometer with an InGaAs detector or liquid  
nitrogen cooled InSb detector, which were used to  
measure the near and mid-infrared emission spectra,  
respectively. The emission spectra of Er: ZBYA  
glasses were measured when pumped by a 638 nm  
laser diode at 1.0 W with a beam waist of 2 mm.  
Fluorescence decay curves were detected and recorded  
using a fluorescence spectrometer (Techcomp  
FLS1000), with an optical parametric oscillator  
(Horizon II OPO) used as the pump source. The  
parametric oscillator wavelength was tuned to  $\lambda\sim$ 630  
nm, with a pulse width of 6  $\mu\text{s}$  and repetition rate was  
10 Hz. All measurements were performed at room  
temperature.

### 3. Results

The absorption spectrum of 1.0 mol% Er<sup>3+</sup>-doped ZBYA glass is shown in Fig. 1, the wavelength range is 200 nm-1800 nm with a test step size of 1 nm. The absorption peaks of 378 nm, 520 nm, 640 nm, 800 nm, 980 nm and 1530 nm correspond to the transitions from the ground state <sup>4</sup>I<sub>15/2</sub> to the excited state energy levels of <sup>4</sup>G<sub>11/2</sub>, <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>F<sub>9/2</sub>, <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>I<sub>11/2</sub>, and <sup>4</sup>I<sub>13/2</sub>, respectively, which have been marked in Fig. 1.

Since the high efficiency 3.5 μm fluorescence emission of Er<sup>3+</sup> ions is main objective in this work, the upper level <sup>4</sup>F<sub>9/2</sub> of the 3.5 μm emission is chosen to be directly pumped to improve the luminescence quantum efficiency. Based on the absorption peak of the Er<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> level in the 640 nm band, an in-house fabricated 638 nm LD was used as the pump source. The energy level diagram of Er<sup>3+</sup> ions under the excitation of a 638 nm pumping is shown in the inset of Fig. 1.

As shown in the inset Fig. 1, when the samples are excited by the 638 nm laser, the ions on the <sup>4</sup>I<sub>15/2</sub> ground level are pumped to the <sup>4</sup>F<sub>9/2</sub> level through ground state absorption (GSA). Then a portion of the ions on the <sup>4</sup>F<sub>9/2</sub> level transition back to the <sup>4</sup>I<sub>9/2</sub> level, producing fluorescence emission in the mid-infrared of 3.5 μm band and further returning to the <sup>4</sup>I<sub>15/2</sub> level with 800 nm radiation; while further portion of the ions relax to <sup>4</sup>I<sub>13/2</sub> level with 1150 nm emission. The ions that occupy the <sup>4</sup>I<sub>9/2</sub> level decay non-radiatively to the next level <sup>4</sup>I<sub>11/2</sub> as well as undergoing a further rapid decay to the <sup>4</sup>I<sub>13/2</sub> level, which in turn produces luminescence in the 2.7 μm band. Another portion of the ions in the <sup>4</sup>I<sub>11/2</sub> level relax to the ground level via radiative processes, yielding 980 nm emission.

Furthermore, most of the Er<sup>3+</sup> ions in the <sup>4</sup>I<sub>13/2</sub> level radiatively transition to the ground energy level and gave rise to 1550 nm fluorescence.

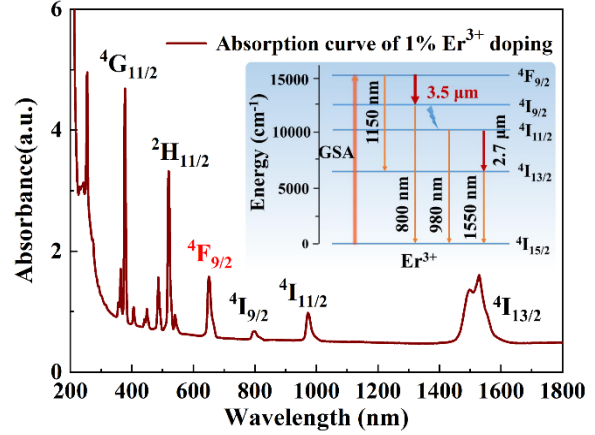


Fig. 1. Absorption spectrum of 1.0 mol% Er<sup>3+</sup> doped ZBYA glass; Inset: Er<sup>3+</sup> ion level diagram under λ~638 nm laser excitation.

Based on the measured absorption spectrum for Er<sup>3+</sup> ions, the Judd-Ofelt (J-O) intensity parameters Ω<sub>t</sub> (t=2, 4, 6) for Er<sup>3+</sup>-doped ZBYA glass were calculated as 2.373 × 10<sup>-20</sup> cm<sup>2</sup>, 0.288 × 10<sup>-20</sup> cm<sup>2</sup> and 1.977 × 10<sup>-20</sup> cm<sup>2</sup>, respectively. The J-O intensity parameters Ω<sub>t</sub> (t=2, 4, 6) for Er<sup>3+</sup> ions in several glass host matrices are listed in Table 1. In general, Ω<sub>2</sub> provides information on the local environment for rare earth ions sites and the point symmetry of the environment around the Er<sup>3+</sup> ions. Ω<sub>6</sub> reflects the photo-alkalinity of the matrix glass, a larger Ω<sub>6</sub> is associated with lower photo-alkalinity. Therefore, J-O analysis shows that the prepared Er: ZBYA glass has a stronger covalency and lower photo-alkalinity.

Table 1 Calculated J-O intensity parameters Ω<sub>t</sub> (t=2, 4, 6) (10<sup>-20</sup> cm<sup>2</sup>) of Er<sup>3+</sup> ion in various glass hosts

| Material             | Ω <sub>2</sub> | Ω <sub>4</sub> | Ω <sub>6</sub> |
|----------------------|----------------|----------------|----------------|
| Silicate [18]        | 4.23           | 1.04           | 0.61           |
| ZBLAN [18]           | 2.91           | 1.27           | 1.11           |
| Fluoroaluminate [19] | 2.021          | 1.194          | 1.239          |
| Fluorindate [20]     | 2.8815         | 2.2337         | 1.267          |
| ZBYA [This work]     | 2.373          | 0.288          | 1.977          |

Table 2 J-O calculated parameters for selected transitions of Er<sup>3+</sup> ion in ZBYA glass

| Transition  | Wavelength (nm) | A <sub>rad</sub> (s <sup>-1</sup> ) | β (%) | τ <sub>rad</sub> (ms) |
|---|-----------------|-------------------------------------|-------|-----------------------|
| <sup>4</sup> F <sub>9/2</sub> → <sup>4</sup> I <sub>9/2</sub>   | 3500            | 44.78                               | 2.4   | 0.54                  |
| → <sup>4</sup> I <sub>11/2</sub>                                | 1920            | 140.6                               | 7.55  |                       |
| → <sup>4</sup> I <sub>13/2</sub>                                | 1150            | 412.5                               | 22.14 |                       |
| → <sup>4</sup> I <sub>15/2</sub>                                | 660             | 1265.36                             | 67.91 |                       |
| <sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> I <sub>11/2</sub>  | 4500            | 2.04                                | 2.6   | 12.78                 |
| → <sup>4</sup> I <sub>13/2</sub>                                | 1700            | 14.28                               | 18.25 |                       |
| → <sup>4</sup> I <sub>15/2</sub>                                | 800             | 61.94                               | 79.15 |                       |
| <sup>4</sup> I <sub>11/2</sub> → <sup>4</sup> I <sub>13/2</sub> | 2800            | 44.03                               | 11.27 | 2.56                  |
| → <sup>4</sup> I <sub>15/2</sub>                                | 980             | 346.55                              | 88.73 |                       |
| <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> | 1500            | 183.19                              | 100   | 5.46                  |

Based on the J-O parameters, Table 2 summarizes the radiative parameters of ZBYA glass samples for different transfer processes, including the emission wavelength, spontaneous emission transition probability (A<sub>rad</sub>), fluorescence branching ratio (β) and theoretical radiative lifetime (τ<sub>rad</sub>). The spontaneous emission transition probability (A<sub>rad</sub>), fluorescence branching ratio (β) and theoretical radiative lifetime (τ<sub>rad</sub>) of the transition Er<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>9/2</sub> is calculated as 44.78 s<sup>-1</sup>, which is higher than that of ZBLAN glass (~26.3 s<sup>-1</sup>) [21], indicating that ZBYA glass has the potential to be an efficient candidate material for a fiber laser operating at λ~3.5 μm.

To examine the characteristics of λ~3.5 μm emission for potential laser applications, the emission cross-section (σ<sub>emi</sub>) and absorption cross-section (σ<sub>abs</sub>) of <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>9/2</sub> transition were calculated by Fuchtbauer-Ladenburg (FL) theory [22]:

$$\sigma_{emi}(\lambda) = \frac{A_{rad}}{8\pi cn^2} \times \frac{\lambda^5 I(\lambda)}{\int \lambda I(\lambda) d\lambda} \quad (1)$$

where λ is the center wavelength of the fluorescence spectrum, I(λ) is the emission intensity, A<sub>rad</sub> is spontaneous transition probability, c is the speed of the light, and n is the refractive index of the glass.

$$\sigma_{abs}(\lambda) = \sigma_{emi} \frac{Z_U}{Z_L} \exp\left[\frac{hc/\lambda - E_{ZL}}{k_B T}\right] \quad (2)$$

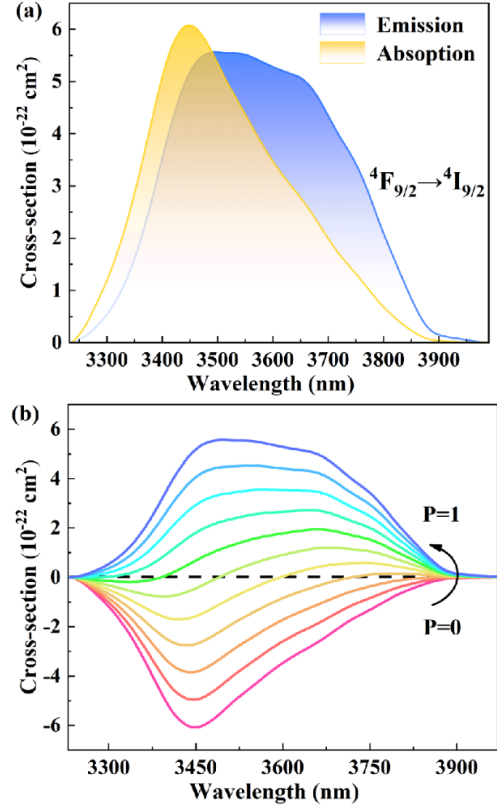


Fig. 2. (a) λ~3.5 μm emission and absorption cross-section and (b) gain cross-section.

where  $Z_L$  and  $Z_U$  are the partition functions of lower and upper levels, respectively.  $k_B$  is the Boltzmann constant,  $T$  represents the room temperature, and  $E_{ZL}$  represents the zero-line energy, which has the physical meaning of the free energy required to excite an ion from a low to a high energy level at temperature  $T$ . The gain coefficient  $G(\lambda)$  can be calculated by the equation:

$$G(\lambda) = P\sigma_{emi}(\lambda) - (1 - P)\sigma_{abs}(\lambda) \quad (3)$$

where  $P$  is the ratio of the population of the upper energy levels to the population of total energy levels. The calculated results are shown in Fig. 2 (a), the maximum emission cross section of  $5.5 \times 10^{-22} \text{ cm}^2$  is obtained at 3496 nm. The gain coefficients for various values of  $P$  ranging from 0 to 1 were also calculated for the  ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$  transition in ZBYA glass, the gain cross-section is shown in Fig. 2(b). It is evident that a positive gain is obtained when  $P > 0.3$ , which implies that a low pumping threshold can be achieved for laser operation based on the  ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$  transition [23].

To demonstrate the fluorescence characteristic of ZBYA glasses in the 3.5  $\mu\text{m}$  band with different  $\text{Er}^{3+}$  doping concentrations, mid-infrared emission spectra in the wavelength region 3200–4000 nm were measured under the excitation of a 638 nm LD, as depicted in Fig. 3. The luminescence intensity of the emission band is centered at 3496 nm, originating from the  $\text{Er}^{3+}$ :  ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$  transition. It shows a rising intensity with increases in the  $\text{Er}^{3+}$  ion doping concentration, furthermore.

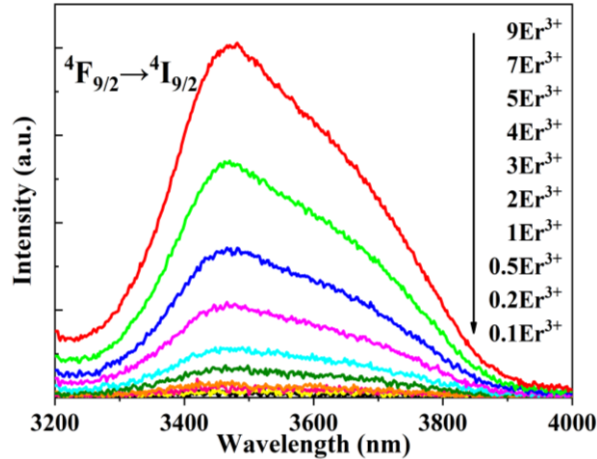


Fig. 3.  $\lambda \sim 3.5 \mu\text{m}$  mid-infrared luminescence spectra for different doping concentrations of  $\text{Er}^{3+}$  in ZBYA glasses under  $\lambda \sim 638 \text{ nm}$  laser excitation.

In order to further explore the luminescence properties of  $\text{Er}^{3+}$ -doped ZBYA glasses, the fluorescence spectra at  $\lambda \sim 980 \text{ nm}$ ,  $\lambda \sim 1150 \text{ nm}$ ,  $\lambda \sim 1550 \text{ nm}$  and  $\lambda \sim 2.7 \mu\text{m}$  corresponding to the transition of  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ ,  ${}^4F_{9/2} \rightarrow {}^4I_{13/2}$ ,  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  and  ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ , respectively, were recorded and are shown in Fig. 4. In a similar manner to the 3.5  $\mu\text{m}$  case, luminescence intensity in each band increases with an increase in the doping concentration of  $\text{Er}^{3+}$  ions.

For the lifetimes testing, the glass samples were

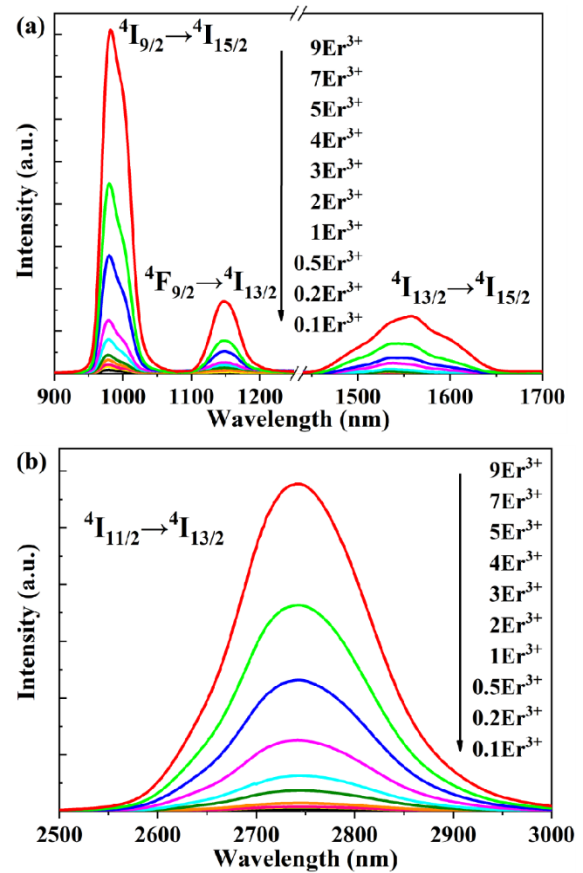


Fig. 4. (a) Near-infrared and (b)  $\lambda \sim 2.7 \mu\text{m}$  mid-infrared luminescence spectra of different doping concentration  $\text{Er}^{3+}$ -doped ZBYA glasses under  $\lambda \sim 638 \text{ nm}$  laser excitation.

excited at 630 nm in the experiment, the fluorescence decay curves at 660 nm, 980 nm and 1550 nm bands were monitored. As shown in Fig. 5 (a)-(c), the lifetimes of  ${}^4F_{9/2}$ ,  ${}^4I_{11/2}$  and  ${}^4I_{13/2}$  levels in the 1 mol%  $\text{Er}^{3+}$ -doped glass samples are 0.121 ms, 7.02 ms and 11.29 ms, respectively. Fig. 5 (d) shows the measured

lifetimes for  $^4I_{13/2}$ ,  $^4I_{11/2}$  and  $^4F_{9/2}$  levels as a function of  $Er^{3+}$  doping concentration. Based on the results, it can be seen that the lifetimes of  $^4I_{11/2}$  and  $^4F_{9/2}$  levels are almost constant with an increase in the  $Er^{3+}$  ion doping concentration, while the lifetimes for the  $^4I_{13/2}$  level show a modest upward trend with the increase of  $Er^{3+}$  ion doping concentration, reaching a maximum of 13.78 ms. The lifetime of  $^4I_{9/2}$  level is too short to be detected as a result of the equipment detection accuracy, but it is reported in the literature to be about 8  $\mu s$  [24].

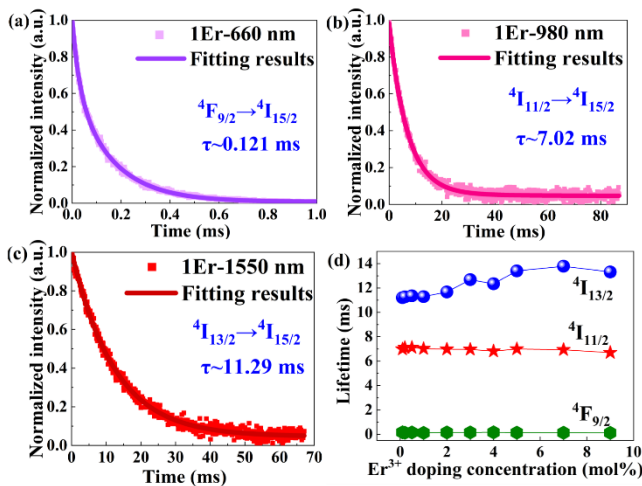


Fig. 5. Energy level lifetime of (a) 660 nm:  $^4F_{9/2} \rightarrow ^4I_{15/2}$ , (b) 980 nm:  $^4I_{11/2} \rightarrow ^4I_{15/2}$  and (c) 1550 nm:  $^4I_{13/2} \rightarrow ^4I_{15/2}$  in the 1 mol%  $Er^{3+}$ -doped sample; (d) Energy level lifetimes of  $Er^{3+}$ :  $^4I_{13/2}$ ,  $^4I_{11/2}$ ,  $^4F_{9/2}$  levels as a function of  $Er^{3+}$  doping concentration under  $\lambda \sim 630$  nm laser.

The quantum efficiency  $\eta$  is usually used to assess the ability of lasing for glass gain materials. In practical experiments, the quantum efficiency is connected with the maximum phonon energy of the substrate glass.  $\eta$  can be calculated by following equation [25]:

$$\eta = \frac{\tau_{mea}}{\tau_{rad}} \times 100\% \quad (4)$$

where  $\tau_{mea}$  is the spontaneous radiative lifetime calculated from J-O parameters and  $\tau_{rad}$  is the measured fluorescence lifetime. The quantum efficiency of  $Er^{3+}$ -doped ZBYA glass for the 3.5  $\mu m$  band is calculated as 27.78%, the result is higher than fluorindate glass (25.0%) [20], which confirms the considerable potential application of Er: ZBYA glass as a gain medium for  $\lambda \sim 3.5$   $\mu m$  fiber lasers.

## 4. Conclusion

In conclusion, intense 3.5  $\mu m$  MIR luminescence emission has been demonstrated in  $Er^{3+}$ -doped ZBYA glasses for the first time. The gap between the upper and lower energy levels is small for the 3.5  $\mu m$  band transition, which results in an inefficient lasing radiation due to high quantum defect in the matrix with a high phonon energy. The low phonon energy of the ZBYA glass material in this experiment can reduce the non-radiative relaxation process of multiple phonons in the matrix, and the  $^4F_{9/2}$  upper energy level is directly excited by a 638 nm laser, which in turn can improve the fluorescence quantum efficiency of the 3.5  $\mu m$  band. The absorption, emission and gain cross-sections were determined, yielding a maximum emission cross-section of  $5.5 \times 10^{-22} \text{ cm}^2$  at 3496 nm. The quantum efficiency for the 3.5  $\mu m$  band is calculated as 27.78%. As a consequence of these favorable spectroscopic characteristics, it is possible to assert that  $Er^{3+}$ -doped ZBYA glasses are strong candidates as host materials for 3.5  $\mu m$  MIR fiber lasers.

## Funding

National Key Scientific Instrument and Equipment Development Projects of China (61727816); Shenzhen Fundamental Research Program (JCYJ20190808140805488, JCYJ20190808173401660, JCYJ20190808173619062); Basic and Applied Basic Research Foundation of Guangdong Province (2019A1515110320); National Natural Science Foundation of China (11874332, 62105217).

## References

- [1] M. Ebrahim-Zadeh, Mid-infrared optical parametric oscillators and applications, in Mid-Infrared Coherent Sources and Applications. 2008, Springer. p. 347-375.
- [2] J. Allain, M. Monarie and H. Poignant, Erbium-doped fluorozirconate single-mode fibre lasing at 2.71  $\mu m$ . Electronics Letters, 1989. 1(25): p. 28-29.
- [3] R. Woodward, M. Majewski, G. Bharathan, D. Hudson, A. Fuerbach and S. Jackson, Watt-level dysprosium fiber laser at 3.15



- $\mu\text{m}$  with 73% slope efficiency. *Optics letters*, 2018. 43(7): p. 1471-1474.
- [4] Y.O. Aydin, V. Fortin, F. Maes, F. Jobin, S.D. Jackson, R. Vallée and M. Bernier, Diode-pumped mid-infrared fiber laser with 50% slope efficiency. *Optica*, 2017. 4(2): p. 235-238.
- [5] S. Jia, C. Li, Z. Zhao, C. Yao, Z. Jia, G. Qin, Y. Ohishi and W. Qin,  $\text{Er}^{3+}$ -doped  $\text{ZnF}_2\text{-BaF}_2\text{-SrF}_2\text{-YF}_3$  fluoride glasses for 2.7  $\mu\text{m}$  laser applications. *Materials Letters*, 2018. 227: p. 97-99.
- [6] Y. Wang and H. Luo, Wavelength-tunable, linearly polarized Q-switched and gain-switched polarization-maintaining  $\text{Er}^{3+}$ -doped fluoride fiber laser in the range of 2.7~2.83  $\mu\text{m}$ . *Optics Communications*, 2022. 504: p. 127482.
- [7] X. Zhu and N. Peyghambarian, High-Power ZBLAN Glass Fiber Lasers: Review and Prospect. *Advances in OptoElectronics*, 2010, (2010-3-29), 2010. 2010: p. 149-154.
- [8] G.A. Newburgh and M. Dubinskii, Power and efficiency scaling of Er: ZBLAN fiber laser. *Laser Physics Letters*, 2021. 18(9): p. 095102.
- [9] O. Henderson-Sapir, J. Munch and D.J. Ottaway, Mid-infrared fiber lasers at and beyond 3.5  $\mu\text{m}$  using dual-wavelength pumping. *Optics letters*, 2014. 39(3): p. 493-496.
- [10] V. Fortin, F. Maes, M. Bernier and R. Vallée. Erbium-doped all-fiber laser operating at 3.44  $\mu\text{m}$ : Experimental and numerical studies. in *CLEO: Science and Innovations*. 2016. Optica Publishing Group.
- [11] H. Tobben, Room temperature CW fibre laser at 3.5  $\mu\text{m}$  in  $\text{Er}^{3+}$ -doped ZBLAN glass. *Electronics Letters*, 1992. 14(28): p. 1361-1362.
- [12] O. Henderson-Sapir, J. Munch and D.J. Ottaway, New energy-transfer upconversion process in  $\text{Er}^{3+}$ : ZBLAN mid-infrared fiber lasers. *Optics Express*, 2016. 24(7): p. 6869-6883.
- [13] M. Lemieux-Tanguay, V. Fortin, T. Boilard, P. Paradis, F. Maes, L. Talbot, R. Vallée and M. Bernier, 15 W monolithic fiber laser at 3.55  $\mu\text{m}$ . *Optics Letters*, 2022. 47(2): p. 289-292.
- [14] Z. Qin, Y. Zhou, G. Xie, P. Yuan, J. Ma and L. Qian, Red-diode-clad-pumped CW and mode-locked Er:ZBLAN fiber laser at 3.5  $\mu\text{m}$ . *Optics Express*, 2022. 30(7): p. 11174-11180.
- [15] H. Zhao, R. Wang, X. Wang, S. Jia, Y. Fan, E. Lewis, G. Farrell, S. Wang and P. Wang, Intense mid-infrared emission at 3.9  $\mu\text{m}$  in  $\text{Ho}^{3+}$ -doped ZBYA glasses for potential use as a fiber laser. *Optics Letters*, 2020. 45(15): p. 4272-4275.
- [16] C. Xu, J. Zhang, M. Liu, H. Zhao, F. Ling, S. Jia, G. Farrell, S. Wang and P. Wang, Recent advances in luminescence and lasing research in ZBYA glass. *Optical Materials Express*, 2022. 12(4): p. 1542-1554.
- [17] C. Xu, J. Zhang, X. Zhao, H. Zhao, F. Ling, S. Jia, G. Farrell, S. Wang and P. Wang, Two-watt mid-infrared laser emission in robust fluorozirconate fibers. *Optics Letters*, 2022. 47(6): p. 1399-1402.
- [18] X. Zou and T. Izumitani, Spectroscopic properties and mechanisms of excited state absorption and energy transfer upconversion for  $\text{Er}^{3+}$ -doped glasses. *Journal of Non-Crystalline Solids*, 1993. 162(1): p. 68-80.
- [19] J. Zhang, R. Wang, X. Wang, W. Li, M. Liu, S. Jia, L. Wang, Y. Ning, H. Peng and G. Brambilla, Efficient 3.5  $\mu\text{m}$  mid-infrared emission in heavily  $\text{Er}^{3+}$ -doped fluoroaluminate glasses and its emission mechanism. *Journal of Luminescence*, 2021. 238: p. 118301.
- [20] P. Wang, J. Zhang, J. Zhang, S. Jia, L. Wang, Y. Ning, H. Peng, G. Farrell, S. Wang and R. Wang, 3.5  $\mu\text{m}$  emission in  $\text{Er}^{3+}$  doped fluoroindate glasses under 635 nm laser excitation. *Journal of Luminescence*, 2021. 237: p. 118200.
- [21] S. Ivanova and F. Pellé, Strong 1.53  $\mu\text{m}$  to NIR-VIS-UV upconversion in  $\text{Er}^{3+}$ -doped fluoride glass for high-efficiency solar cells. *Journal of the Optical Society of America B*, 2009. 26(10).
- [22] L. Tarelho, L. Gomes and I. Ranieri, Determination of microscopic parameters for nonresonant energy-transfer processes in rare-earth-doped crystals. *Physical Review B*, 1997. 56(22): p. 14344.
- [23] Y. Xu, Y. Li, Y. Tian, Y. Hua, F. Huang and J. Zhang, Excellent Luminescence Performance of  $\text{Ho}^{3+}$  Ions Based on a New System of Oxyhalide Glass.
- [24] C. Wang, H. Luo, J. Yang, J. Li and Y. Liu, Watt-Level~ 3.5  $\mu\text{m}$   $\text{Er}^{3+}$ -Doped  $\text{ZrF}_4$  Fiber Laser Using Dual-Wavelength Pumping at 655 and 1981 nm. *IEEE Photonics Technology Letters*, 2021. 33(15): p. 784-787.
- [25] D. Tang, Q. Liu, X. Liu, X. Wang, X. Yang, Y. Liu, T. Ying, Y. Renguang, X. Zhang and S. Xu, High quantum efficiency of 1.8  $\mu\text{m}$  luminescence in  $\text{Tm}^{3+}$  fluoride tellurite glass. *Infrared Physics & Technology*, 2022: p. 104055.