



# Er<sup>3+</sup>-doped ZnF<sub>2</sub>-BaF<sub>2</sub>-SrF<sub>2</sub>-YF<sub>3</sub> fluoride glasses for 2.7 μm laser applications



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## ARTICLE INFO

### Article history:

Received 20 December 2017

Received in revised form 12 April 2018

Accepted 12 May 2018

Available online 14 May 2018

### Keywords:

ZnF<sub>2</sub>-BaF<sub>2</sub>-SrF<sub>2</sub>-YF<sub>3</sub> glasses

Er<sup>3+</sup>-doped fluoride glasses

2.7 μm emission properties

## ABSTRACT

Er<sup>3+</sup> doped ZnF<sub>2</sub>-BaF<sub>2</sub>-SrF<sub>2</sub>-YF<sub>3</sub> (ZBSY-e) glasses were prepared in a glove box. The absorption coefficient of residual hydroxyl in the glasses was calculated to be ~0.001 cm<sup>-1</sup> at 2.7 μm. Under 978 nm laser diode excitation, intense ~2.7 μm emissions were observed from the ZBSY-e glasses and the emission intensity was much stronger than that obtained in Er<sup>3+</sup>-doped fluoroindate, fluorozirconate or fluoroaluminate glasses for a same excitation power density. The efficient ~2.7 μm emission could be attributed to the relative low phonon energy (420 cm<sup>-1</sup>) of the ZBSY glass. Our results indicated that the ZBSY-e glass was a potential gain medium for ~2.7 μm lasers.

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## 1. Introduction

~3 μm lasers based on Er<sup>3+</sup> doped media have drawn much attention owing to their wide applications in fundamental research, atmosphere pollution monitoring, medical diagnosis and treatment [1,2]. Up to now, ~3 μm lasers have been realized in Er<sup>3+</sup>-doped crystals [3,4]. In the case of glass or glass fibers, ~3 μm lasers have only been obtained by using Er<sup>3+</sup>-doped ZrF<sub>4</sub>-BaF<sub>2</sub>-LaF<sub>3</sub>-AlF<sub>3</sub>-NaF (ZBLAN) glass or glass fibers as the gain media [5–7]. In 1999, T. Sandrock et al demonstrated ~2.8 μm lasing in Er<sup>3+</sup>-doped ZBLAN bulk glasses [5]. In 2015, Vincent et al. demonstrated a 30.5 W 2938 nm laser in Er<sup>3+</sup>-doped ZBLAN fiber [7]. Despite recent progress in this field, it is still necessary to explore new glass materials with low phonon energies and wide mid-infrared transmission windows for constructing ~3 μm lasers.

The ~3 μm emission is related to the transition <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>13/2</sub> of Er<sup>3+</sup> ions, which is a self-terminating transition [8]. Researchers have developed ways such as heavily Er<sup>3+</sup> doping [9], co-doping with Pr<sup>3+</sup> [10], and co-lasing of the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition at 1.6 μm [11] to deplete the lower laser level (<sup>4</sup>I<sub>13/2</sub>) for efficient laser operation. Except for those methods, developing glass matrixes with lower phonon energies would also be beneficial to enhance the luminous efficiencies of rare earth [12]. In addition, as the residual hydroxyl (OH<sup>-</sup>) would quench the ~3 μm emission, the OH<sup>-</sup> groups in the glass matrix should be completely removed.

Compared to fluorozirconate glasses, fluoride glasses based on ZnF<sub>2</sub> present have much lower phonon energies [13]. While, there are still no reports on the ~3 μm emission properties in zinc fluoride glasses up to now.

In this paper, we prepared Er<sup>3+</sup>-doped ZnF<sub>2</sub>-BaF<sub>2</sub>-SrF<sub>2</sub>-YF<sub>3</sub> (ZBSY-e) glasses by using conventional melt-quenching method in a glove box. Under 978 nm laser diode (LD) excitation, intense ~2.7 μm emission was observed in the ZBSY-e glasses. A comparison study on the 2.7 μm emission properties of ZBSY-e and Er<sup>3+</sup>-doped fluoroindate, fluorozirconate, fluoroaluminate glasses was carried out. In addition, the dependence of 2.7 μm emission intensities on the Er<sup>3+</sup> doping concentrations was also investigated.

## 2. Experiments

In our experiments, all the fluoride glasses were prepared from high purity (99.99%) raw materials. Firstly, 20 g well mixed batches were melted in platinum crucible at 950 °C for 2 h. Then the samples were annealed in a copper mold near glass transition temperature for 5 h. The zinc fluoride glasses have a composition of 60ZnF<sub>2</sub>-15BaF<sub>2</sub>-10SrF<sub>2</sub>-(15-x)YF<sub>3</sub>-xErF<sub>3</sub> (x = 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, named as ZBSY-xe, respectively). The fluoroindate, fluorozirconate and fluoroaluminate glasses have compositions of 31InF<sub>3</sub>-19ZnF<sub>2</sub>-17BaF<sub>2</sub>-18SrF<sub>2</sub>-8GaF<sub>3</sub>-2CaF<sub>2</sub>-5ErF<sub>3</sub>, 50ZrF<sub>4</sub>-33BaF<sub>2</sub>-7AlF<sub>3</sub>-5YF<sub>3</sub>-5ErF<sub>3</sub>, 37AlF<sub>3</sub>-19CaF<sub>2</sub>-21BaF<sub>2</sub>-10YF<sub>3</sub>-4SrF<sub>2</sub>-4MgF<sub>2</sub>-5ErF<sub>3</sub>, and named as ErInG, ErZrG, ErAlG, respectively. All the above glasses were prepared in a glove box filled with nitrogen gas, and

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finally polished to the same thickness of 1 mm for optical measurements.

The absorption and transmission spectra of the fluoride glasses were recorded with a Shimadzu UV3600 spectrometer and a Nicolet 6700 FTIR spectrophotometer, respectively. The Raman spectra were measured by using a Horiba LabRAM HR Evolution spectrometer. The upconversion and downconversion emission spectra were measured by using a Hitachi F4500 spectrometer and a grating spectrometer equipped with an InSb detector, respectively. In our experiments, appropriate filters were used to block the undesired signals.

### 3. Results and discussions

Fig. 1(a) shows the absorption and transmission spectra of the ZBSY-5e, ErInG, ErZrG and ErAlG glasses. The infrared cutoff wavelength (with a transmittance of 50%) of ZBSY-5e glass was up to  $\sim 9.5 \mu\text{m}$ , which was longer than that of ErInG, ErZrG and ErAlG glasses (9.2, 8.2 and  $7.6 \mu\text{m}$ , respectively). The absorption coefficients of  $\text{OH}^-$  in the fluoride glasses were calculated to be as low as  $\sim 0.001 \text{ cm}^{-1}$  at  $\sim 3 \mu\text{m}$  by using the formula of  $\alpha_{\text{OH}} = \ln(T_0/T)/l$  [8], where  $l$  is the thickness of the sample and  $T_0, T$  are the incident and transmitted intensities, respectively. Fig. 1(b) shows the Raman spectra of ZBSY, fluoroindate, fluorozirconate and fluoroaluminate glasses. The phonon energy of ZBSY glass ( $\sim 420 \text{ cm}^{-1}$ ) was lower than that of fluoroindate ( $507 \text{ cm}^{-1}$ ), fluorozirconate ( $579 \text{ cm}^{-1}$ ) and fluoroaluminate ( $615 \text{ cm}^{-1}$ ) glasses [14,15]. In addition, the calculated multiphonon relaxation rates ( $W_{\text{MPR}}$ ) of the fluoroaluminate, fluorozirconate, fluoroindate and ZBSY glasses were shown in Fig. 1(c). The squares in Fig. 1(c) gave out the  $W_{\text{MPR}}$

for the transitions  ${}^2\text{H}_{9/2} \rightarrow {}^4\text{F}_{3/2}$ ,  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{9/2}$ , and  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{F}_{9/2}$  of  $\text{Er}^{3+}$  in ZBSY and fluoroaluminate glasses, respectively. The detailed procedures were described in the [Supplementary information](#). It was obvious that the ZBSY glass had the lowest  $W_{\text{MPR}}$  among the four fluoride glasses, and the values were 15.01, 22.01, 31.34 and  $81.06 \text{ s}^{-1}$  for an energy gap of  $3743 \text{ cm}^{-1}$  corresponding to the transition  ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$  of  $\text{Er}^{3+}$  in the ZBSY, fluoroindate, fluorozirconate and fluoroaluminate glasses, respectively. The relatively low  $W_{\text{MPR}}$  would be beneficial for obtaining high luminous efficiency at  $\sim 2.7 \mu\text{m}$ .

Under the excitation of a 978 nm laser, intense emissions centered at 1550 nm and 2740 nm were observed from the fluoride glasses, as shown in Fig. 2(a). The 2740 nm emission intensity obtained from the ZBSY-5e glass was higher than that obtained from the other three glasses for a fixed excitation power density of  $0.53 \text{ W/cm}^2$ , which was consistent with the above analysis that glass matrices with lower phonon energies would be beneficial to enhance the luminous efficiencies of rare earth ions. The quantum efficiencies of the  $\sim 2.7 \mu\text{m}$  emission in ErAlG, ErZrG, ErInG and ZBSY-5e glasses were calculated to be 11.1%, 13.6%, 14.0% and 16.7%, respectively (see in [Supplementary Information](#)). In contrast, the 1550 nm emission intensity obtained from the ZBSY-5e glass was the lowest among the four fluoride glasses. This might be because that the cross relaxation (CR) process ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  ( $\text{Er}^{3+}$ ):  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{9/2}$  ( $\text{Er}^{3+}$ )) (shown in Fig. 2(b), which would quench the 1550 nm emission and enhance the 2740 nm emission, might be more effective in matrixes with lower phonon energies for a longer lifetime of the level  ${}^4\text{I}_{13/2}$  ( $\text{Er}^{3+}$ ) [16]. The assumption was further confirmed by the measured 803 nm emission (corresponding to the  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}$  transition) properties of the

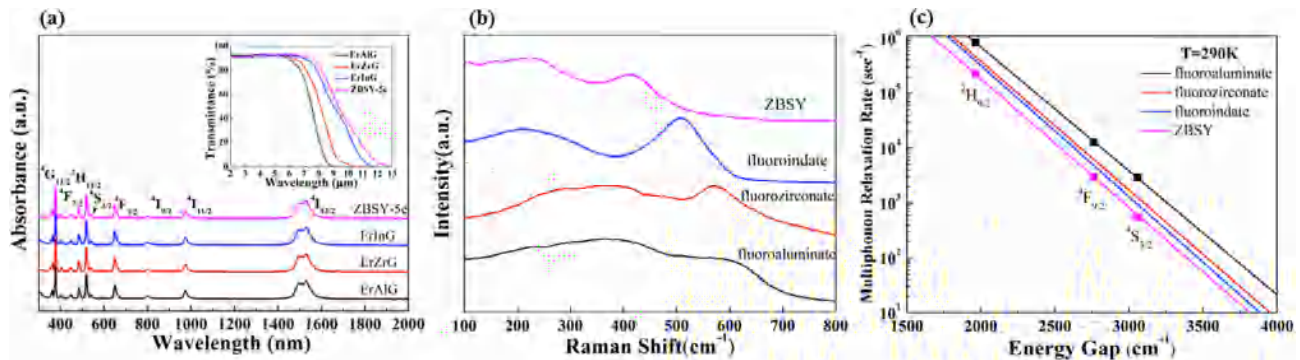


Fig. 1. (a) Absorption spectra of  $\text{Er}^{3+}$ -doped ZBSY-5e, ErInG, ErZrG and ErAlG glasses. Inset: IR transmission spectra of  $\text{Er}^{3+}$ -doped fluoride glasses. (b) Raman spectra of fluoroaluminate, fluorozirconate, fluoroindate and ZBSY glasses. (c) Dependence of multiphonon relaxation rates on the energy gap between the upper and lower energy levels for ZBSY, fluoroindate, fluorozirconate and fluoroaluminate glasses at room temperature.

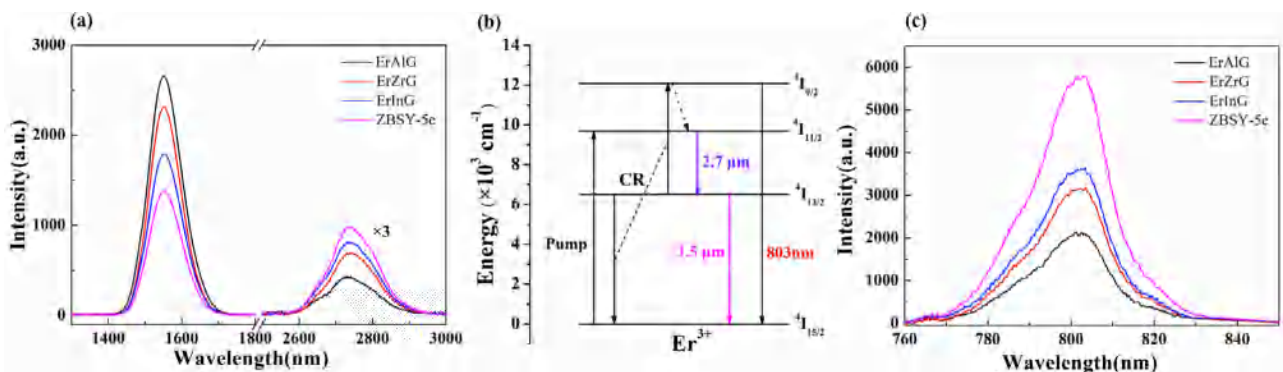
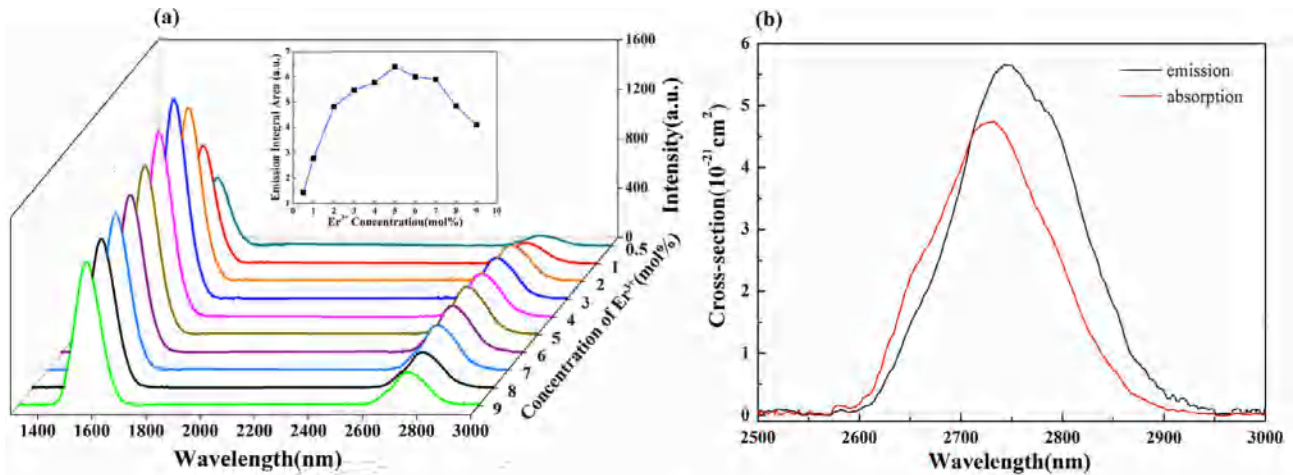


Fig. 2. (a) 1550 nm and 2740 nm emission spectra of ZBSY-5e, ErInG, ErZrG and ErAlG glasses. (b) Energy level diagram and emission mechanism of  $\text{Er}^{3+}$ . (c) 803 nm emission spectra of ZBSY-5e, ErInG, ErZrG and ErAlG glasses.



**Fig. 3.** (a) 1.5  $\mu\text{m}$  and 2.7  $\mu\text{m}$  emission spectra of ZBSY-e glasses with different  $\text{Er}^{3+}$  concentrations. Inset: Dependence of the 2.7  $\mu\text{m}$  emission intensities on  $\text{Er}^{3+}$  concentrations. (b) Calculated stimulated emission and absorption cross sections of the transition  ${}^4\text{I}_{13/2} \leftrightarrow {}^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$  in ZBSY-5e glass.

four fluoride glasses, as shown in Fig. 2(c). The 803 nm emission intensity obtained from the ZBSY-5e glass was also higher than that obtained from the other three glasses for a fixed excitation power density of  $0.53 \text{ W/cm}^2$ .

In addition, the dependence of emission intensities on the  $\text{Er}^{3+}$  doping concentrations in ZBSY-e glasses was also investigated, and the result was shown in Fig. 3(a). When the excitation power density was fixed at  $0.53 \text{ W/cm}^2$ , the 2740 nm emission intensities increased monotonously as the increase of  $\text{Er}^{3+}$  doping concentration from 0.5 to 5 mol%, as shown in the inset of Fig. 3 (a). This could be attributed to the more effective CR process ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  ( $\text{Er}^{3+}$ ):  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{9/2}$  ( $\text{Er}^{3+}$ )) at higher  $\text{Er}^{3+}$  concentrations [16], which could increase the fraction of ions in level  ${}^4\text{I}_{11/2}$  and enhance the 2740 nm emission. With further increasing the  $\text{Er}^{3+}$  doping concentration to 9 mol%, the 2740 nm emission intensities decreased gradually, which might be caused by concentration quenching effect [17]. To examine the characteristics of  $\sim 2.7 \mu\text{m}$  emission for potential laser applications, we calculated the emission cross section ( $\sigma_{em}$ ) by using Fuchtbauer-Ladenburg equation [17]. The  $\sigma_{em}$  of ZBSY-5e glass was calculated to be  $\sim 5.67 \times 10^{-21} \text{ cm}^2$  at 2744 nm, as shown in Fig. 3(b), which was similar to that reported in ZBLAN glass ( $5.7 \times 10^{-21} \text{ cm}^2$ ) [18]. The full widths at half maximum (FWHM) for the  $\sim 2.7 \mu\text{m}$  emission obtained from the ZBSY-5e glass was 142 nm, which was larger than that obtained from ZBLAN glass (113 nm) [18]. This could be ascribed to the more permitted doping sites and higher doping concentration of  $\text{Er}^{3+}$  in ZBSY glass [8,19]. These results indicate that the ZBSY-5e glass could be used for  $\sim 2.7 \mu\text{m}$  laser applications.

#### 4. Conclusion

In summary, we prepared low hydroxyl erbium doped ZBSY glasses and obtained intense 2740 nm emission from them under the excitation of a 978 nm laser. The emission intensity was higher than that obtained from erbium doped fluoroaluminate, fluorozirconate and fluoroindate glasses for a fixed excitation power density. The efficient  $\sim 2.7 \mu\text{m}$  emission could be attributed to the relative low phonon energy ( $420 \text{ cm}^{-1}$ ) of the ZBSY glass. Our results showed that the ZBSY glass was a promising candidate for highly efficient  $\sim 2.7 \mu\text{m}$  laser applications.

#### Acknowledgements

This work was supported by the NSFC (Grant Nos. 61527823, 61378004, 61605058, 11774132 and 11474132), the Opened Fund of the State Key Laboratory on Integrated Optoelectronics, and Tsinghua National Laboratory for Information Science and Technology Cross-discipline Foundation, the Key Technology Research and Development Project of Jilin Province (No. 20180201120GX), the Major Science and Technology Tendering Project of Jilin Province (No. 20170203012GX), the Joint Foundation from Equipment Pre-research and Ministry of Education (No. 6141A02022413), and the Outstanding Young Talent Fund Project of Jilin Province (No. 20180520188JH).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.matlet.2018.05.062>.

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