



Er³⁺-doped ZnF₂-BaF₂-SrF₂-YF₃ fluoride glasses for 2.7 μm laser applications

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ABSTRACT

Er³⁺ doped ZnF₂-BaF₂-SrF₂-YF₃ (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⁻¹ 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 Er³⁺-doped fluorindate, 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⁻¹) 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 Er³⁺ 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 Er³⁺-doped crystals [3,4]. In the case of glass or glass fibers, ~3 μm lasers have only been obtained by using Er³⁺-doped ZrF₄-BaF₂-LaF₃-AlF₃-NaF (ZBLAN) glass or glass fibers as the gain media [5–7]. In 1999, T. Sandrock et al demonstrated ~2.8 μm lasing in Er³⁺-doped ZBLAN bulk glasses [5]. In 2015, Vincent et al. demonstrated a 30.5 W 2938 nm laser in Er³⁺-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 ⁴I_{11/2} → ⁴I_{13/2} of Er³⁺ ions, which is a self-terminating transition [8]. Researchers have developed ways such as heavily Er³⁺ doping [9], co-doping with Pr³⁺ [10], and co-lasing of the ⁴I_{13/2} → ⁴I_{15/2} transition at 1.6 μm [11] to deplete the lower laser level (⁴I_{13/2}) 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⁻) would quench the ~3 μm emission, the OH⁻ groups in the glass matrix should be completely removed.

Compared to fluorozirconate glasses, fluoride glasses based on ZnF₂ 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 Er³⁺-doped ZnF₂-BaF₂-SrF₂-YF₃ (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 Er³⁺-doped fluorindate, fluorozirconate, fluoroaluminate glasses was carried out. In addition, the dependence of 2.7 μm emission intensities on the Er³⁺ 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 60ZnF₂-15BaF₂-10SrF₂-(15-x)YF₃-xErF₃ (x = 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, named as ZBSY-xe, respectively). The fluorindate, fluorozirconate and fluoroaluminate glasses have compositions of 31InF₃-19ZnF₂-17BaF₂-18SrF₂-8GaF₃-2CaF₂-5ErF₃, 50ZrF₄-33BaF₂-7AlF₃-5YF₃-5ErF₃, 37AlF₃-19CaF₂-21BaF₂-10YF₃-4SrF₂-4MgF₂-5ErF₃, 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 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 cm^{-1}), fluorozirconate (579 cm^{-1}) and fluoroaluminate (615 cm^{-1}) glasses [14,15]. In addition, the calculated multiphonon relaxation rates (W_{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_{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 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_{MPR} among the four fluoride glasses, and the values were 15.01, 22.01, 31.34 and 81.06 s^{-1} for an energy gap of 3743 cm^{-1} corresponding to the transition $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ of Er^{3+} in the ZBSY, fluoroindate, fluorozirconate and fluoroaluminate glasses, respectively. The relatively low W_{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 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 ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ (Er^{3+}); $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{9/2}$ (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 $^4\text{I}_{13/2}$ (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

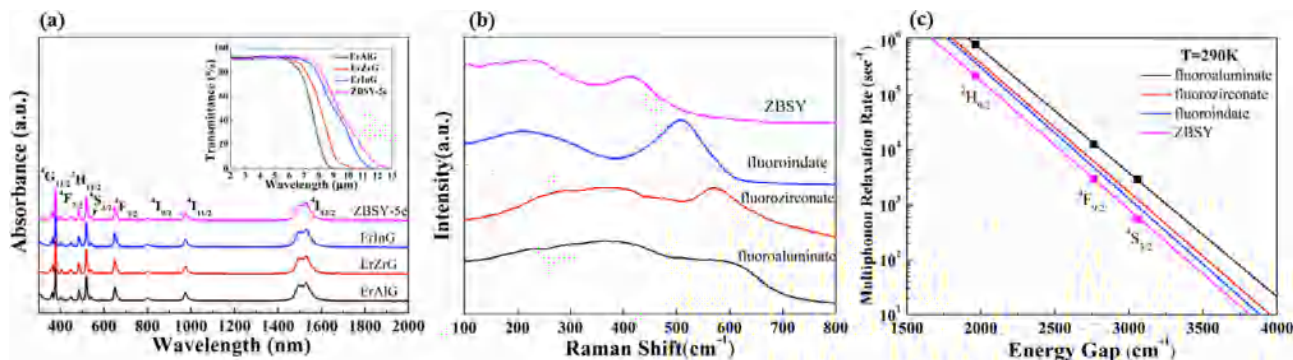


Fig. 1. (a) Absorption spectra of Er^{3+} -doped ZBSY-5e, ErInG, ErZrG and ErAlG glasses. Inset: IR transmission spectra of Er^{3+} -doped fluoride glasses. (b) Raman spectra of fluoroaluminate, fluorozirconate, fluoroindate and ZBSY glasses. (c) Dependence of multiphonon relaxation rates on the energy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

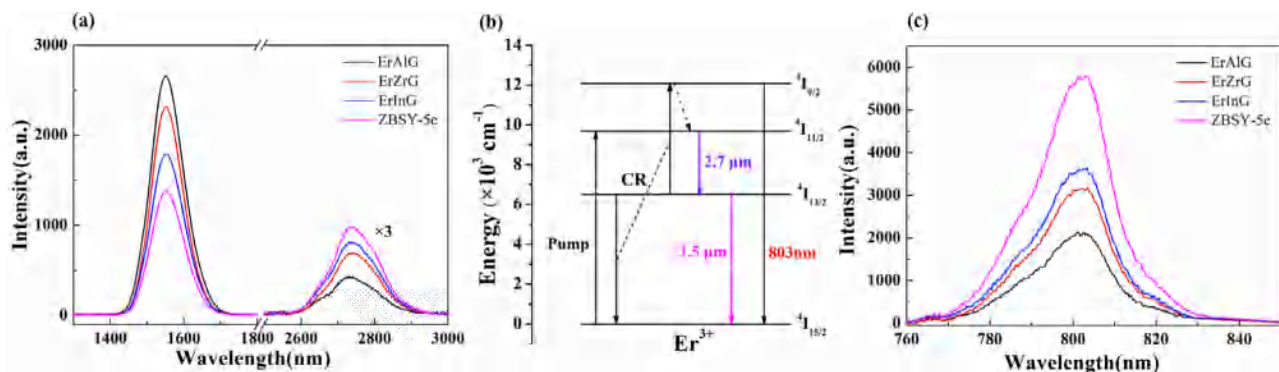


Fig. 2. (a) 1550 nm and 2740 nm emission spectra of ZBSY-5e, ErInG, ErZrG and ErAlG glasses. (b) Energy level diagram and emission mechanism of Er^{3+} . (c) 803 nm emission spectra of ZBSY-5e, ErInG, ErZrG and ErAlG glasses.

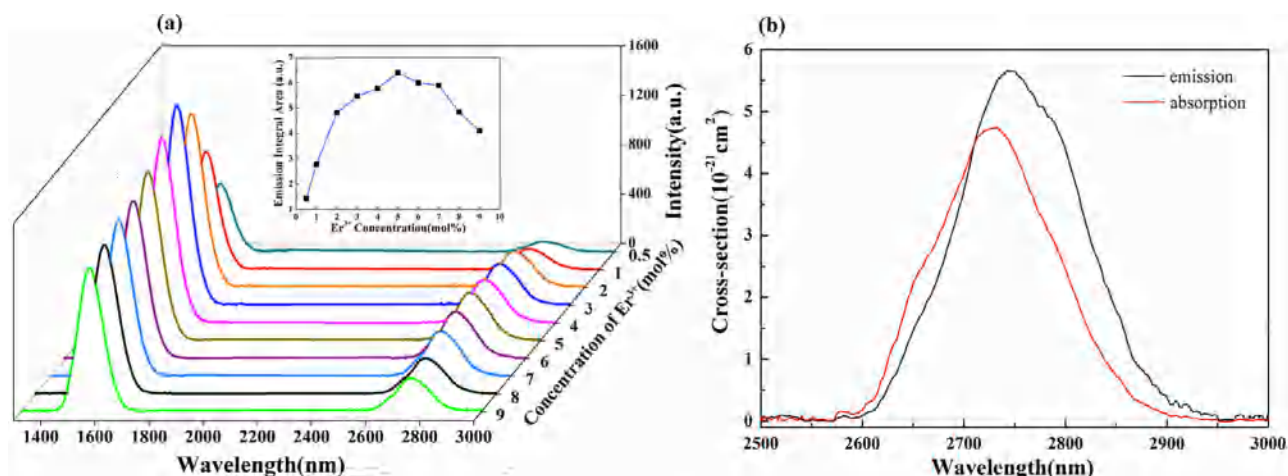


Fig. 3. (a) 1.5 μm and 2.7 μm emission spectra of ZBSY-e glasses with different Er^{3+} concentrations. Inset: Dependence of the 2.7 μm emission intensities on Er^{3+} concentrations. (b) Calculated stimulated emission and absorption cross sections of the transition $^4\text{I}_{13/2} \leftrightarrow ^4\text{I}_{15/2}$ of 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 W/cm².

In addition, the dependence of emission intensities on the 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 W/cm², the 2740 nm emission intensities increased monotonously as the increase of 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 ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ (Er^{3+}): $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{9/2}$ (Er^{3+})) at higher 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 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 ~ 2.7 μm emission for potential laser applications, we calculated the emission cross section (σ_{em}) by using Fuchtbauer-Ladenburg equation [17]. The σ_{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 ~ 2.7 μm 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 Er^{3+} in ZBSY glass [8,19]. These results indicate that the ZBSY-5e glass could be used for ~ 2.7 μm 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, fluoroaluminosilicate and fluoroindate glasses for a fixed excitation power density. The efficient ~ 2.7 μm emission could be attributed to the relative low phonon energy (420 cm⁻¹) of the ZBSY glass. Our results showed that the ZBSY glass was a promising candidate for highly efficient ~ 2.7 μm laser applications.

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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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