Enhanced 2.7 μ m Emission from Er³⁺/Tm³⁺/Pr³⁺ Triply Doped Fluoride Glass

Ying Tian,^{‡,§} Rongrong Xu,^{‡,§} Lili Hu,[‡] and Junjie Zhang^{‡,†}

[‡]Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, 201800, China

[§]Graduate School of Chinese Academy of Sciences, Beijing, 100039, China

The 2.7 µm emission has been obtained using 980 nm laser excitation in $\mathrm{Er}^{3+}/\mathrm{Tm}^{3+}/\mathrm{Pr}^{3+}$ triply doped $\mathrm{ZrF_4}$ -BaF₂-LaF₃-AlF₃-YF₃ glass. 2.7 µm emission characteristics and energy transfer are investigated. Population inversion between the ${}^{4}\mathrm{I_{11/2}}$ and ${}^{4}\mathrm{I_{13/2}}$ levels is significantly enhanced by way of Tm³⁺ and Pr³⁺ co-doping into Er^{3+} -doped fluoride glass. These results indicate that this $\mathrm{Er}^{3+}/\mathrm{Tm}^{3+}/\mathrm{Pr}^{3+}$ triply doped fluoride glass has potential applications in 2.7 µm laser.

I. Introduction

 $E\ r^{3+}$ -doped fiber lasers in the 2.7 μm band are generating great interests due to various useful applications including military, eye-safe laser radar, and medical surgery. $^{1-6}$ Despite the considerable amount of work on 2.7 μm laser emission from Er^{3+} singly doped glasses, the laser characteristics of the 2.7 $\mu m\ (^4I_{11/2}\rightarrow ^4I_{13/2})$ transition are not satisfactory since the $^4I_{11/2}$ level is self-terminating. Fortunately, co-doping of Pr^{3+} or Tm^{3+} with Er^{3+} has been demonstrated to overcome the population bottleneck. $^{7-9}$ It has been seen in a number of cases that glasses triply doped with certain rareearth ions often results in increased intensity of the desired emission. 10,11 But few results have been reported on the 2.7 $\mu m\ emission\ in\ Er^{3+}/Tm^{3+}/Pr^{3+}$ triply doped glasses.

 ${\rm Er}^{3+}$ -doped fluoride glass serves as a useful host for an efficient laser around 2.7 µm due to minimal absorption in the typical H₂O absorption band at 3 µm, low nonradiative decay rates, and high radiative emission rates.^{8,12} However, the problem of obtaining high quality and stable fluoride fiber has been raised, which stems from the nature of the glass compositions.¹³ In this article, we report the 2.7 µm emission properties and energy transfer mechanism between ${\rm Pr}^{3+}$, ${\rm Tm}^{3+}$, and ${\rm Er}^{3+}$ in a new kind of fluoride glass, ${\rm ZrF}_4$ -BaF₂-LaF₃-AlF₃-YF₃ (ZBLAY) glass, under 980 nm excitation. In addition, the spectroscopic investigation including absorption, emission spectra, and lifetime measurements has been performed for future applications in mid infrared lasers.

II. Experimental Procedure

The investigated glass has the following molar compositions: 50ZrF_{4} - 33BaF_{2} - $17(\text{LaF}_{3} + \text{AlF}_{3} + \text{YF}_{3})$ - 1ErF_{3} - 1PrF_{3} - 1TmF_{3} .

In addition, 1 mol% ErF_3 , 1 mol% TmF_3 , 1 mol% PrF_3 singly doped, 1 mol% $\text{PrF}_3/1$ mol% ErF_3 , 2mol% $\text{PrF}_3/1$ mol% ErF_3 , and 1mol% $\text{TmF}_3/1$ mol% ErF_3 co-doped ZBLAY glasses were prepared for the comparison of absorption and fluorescence spectra. Since YF_3 can increase the viscosity of the melt and so enhance the stability of the glass against crystallization, YF_3 is introduced into the fluoride matrix. ¹⁴ Samples were prepared by using high-purity ZrF_4 , BaF_2 , YF_3 , AlF_3 , LaF_3 , PrF_3 , TmF_3 , and ErF_3 powder. Well-mixed 25 g batches of the samples were placed in platinum crucibles and melted at 900°C for 30 min. Then, the melts were poured onto a preheated copper mold and annealed in a furnace around the glass transition temperature. The annealed samples were fabricated and polished to the size of 20 mm \times 10 mm \times 1 mm for the optical property measurements.

Absorption spectra were recorded with a JASCO V-570 UV/VIS spectrophotometer (JASCO International Co. Ltd., Tokyo, Japan). in the range of 400-2000 nm and the emission spectra were measured with a FLSP920 fluorescence spectrophotometer (Edinburgh Analytical Instruments Ltd., Edinburgh, U.K.) excited by 980 nm laser diode (LD). To accurately compare the intensity of 2.7 µm luminescence, the position and power (0.5 W) of the 980 nm excitation and the width (0.1 nm) of the slit to collect the luminescence signal were fixed to the same conditions. In addition, samples were set at the same place in the experimental setup. The fluorescence lifetime of the Er^{3+} : ${}^{4}I_{13/2}$ level was measured by the instrument FLSP920 fluorescence spectrophotometer (Edinburgh Analytical Instruments Ltd.) and the same experimental conditions for different samples were maintained so as to get comparable results. All the measurements were carried out at room temperature.

III. Results and Discussions

The absorption spectra of Er^{3+} , Pr^{3+} , Tm^{3+} singly doped and $\text{Er}^{3+}/\text{Tm}^{3+}/\text{Pr}^{3+}$ triply doped samples at room temperature in the wavelength region of 400–2000 nm, respectively, are shown in Fig. 1. Absorption bands for the three kinds of ions corresponding to transitions from ground state to higher levels are labeled. For triply doped sample the shape and peak positions of each transition are similar to those of Er^{3+} , Pr^{3+} , and Tm^{3+} singly doped samples and generally there is no shift in the wavelength of the absorption peaks. Therefore, it can be inferred that Er^{3+} , Pr^{3+} , and Tm^{3+} ions are homogeneously incorporated into the glassy network without cluster in the local ligand field. The emergence of the absorption band around 980 nm due to the Er^{3+} : ${}^{4}\text{I}_{15/2} \rightarrow {}^{4}\text{I}_{11/2}$ and Pr^{3+} : ${}^{3}\text{H}_{4} \rightarrow {}^{4}\text{G}_{1}$ transitions in the $\text{Er}^{3+}/\text{Tm}^{3+}/\text{Pr}^{3+}$ triply doped sample indicate that this glass can be excited efficiently by 980 nm LD.

The fluorescence spectra of the Er^{3+} -doped ZBLAY glasses were measured as shown in Fig. 2. 2.7 µm emissions

P. Wysocki-contributing editor

Manuscript No. 29184. Received January 12, 2011; approved April 19, 2011.

This work is financially supported by National Natural Science Foundation of China (No. 60937003 and No. 50902137) and GF Innovation Project (No. CXJJ-11-M23 and CXJJ-11-S110).

[†]Author to whom correspondence should be addressed. e-mail: jjzhang@mail.siom. ac.cn



Fig. 1. Absorption spectra of prepared samples.



Fig. 2. Fluorescence spectra of prepared samples in the wavelength of 2600–2800 $\mu m.$

with different peak intensities of the prepared samples can be observed from the Er^{3+} : ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ transition. For all samples, the emission bands are inhomogeneously broadened due to the site-to-site variation in the local ligand field which leads to the deviation of the fluorescence peaks. The enhancement of 2.7 µm fluorescence can be obtained in the 1 mol% $Pr^{3+}/1$ mol% Er^{3+} doubly doped sample. Through the energy transfer Er^{3+} : ${}^{4}I_{13/2} \rightarrow Pr^{3+}$: ${}^{3}F_{3,4}$ process, the lifetime of the Er^{3+} : ${}^{4}I_{13/2}$ level is quenched, which is beneficial to the population inversion between the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ levels. The fluorescence intensity of 2.7 um in the 1 mol% $Tm^{3+}/1$ mol% Er^{3+} doubly doped sample is higher than that in the Er^{3+} singly doped sample, which indicates that Tm^{3+} ions could also deactivate the Er^{3+} : ${}^{4}\text{I}_{13/2}$ level. However, the enhanced effect of 1 mol% Pr^{3+} ions is more obvious than that of 1 mol% Tm³⁺ ions as a result of smaller energy gap between the Pr³⁺: ${}^{3}F_{3,4}$ and Er³⁺: ${}^{4}I_{13/2}$ levels than that of Tm³⁺ ions(Er³⁺: ${}^{4}I_{13/2} \rightarrow$ Tm³⁺: ${}^{3}F_{4}$). Increasing Pr³⁺ ions concentration, 2.7 µm fluorescence intensity in the 2 mol% Pr³⁺/1 mol% Er³⁺ sample is lower than that in the other samples. Since the energy gap between the Pr^{3+} : ${}^{4}G_{1}$ and Er^{3+} : ${}^{4}I_{11/2}$ levels is as small as that between the Pr^{3+} : ${}^{3}F_{3,4}$ and Er^{3+} : ${}^{4}I_{13/2}$ levels, relatively a large amount of Pr^{3+} ions in present system will accelerate the energy transfer process of Er^{3+} : ${}^{4}\mathrm{I}_{11/2} \rightarrow \mathrm{Pr}^{3+}$: ${}^{4}\mathrm{G}_{1}$ as well as Er^{3+} : ${}^{4}\mathrm{I}_{13/2} \rightarrow \mathrm{Pr}^{3+}$: ${}^{3}F_{3,4}$. Consequently, population of the lower and upper laser levels are depleted, which is not beneficial to 2.7 um fluorescence. Considering larger energy gap between the Tm: ${}^{3}H_{5}$



Fig. 3. (a) Upconversion spectrum of the $\mathrm{Er^{3+}/Tm^{3+}/Pr^{3+}}$ triply doped ZBLAY glass pumped by 980 nm LD. (b) Infrared emission spectrum of the sample pumped by 980 nm LD. The inset is the emission around 980 nm of the sample pumped by 800 nm LD.

and Er: ${}^{4}I_{11/2}$ levels, Tm^{3+} ions have a lesser impact on the Er^{3+} : ${}^{4}I_{11/2}$ level than that of Pr^{3+} ions. As a result, 1 mol% Tm^{3+} and 1 mol% Pr^{3+} ions are introduced into the system simultaneously to combine the advantages of these two ions. As expected, the $Er^{3+}/Tm^{3+}/Pr^{3+}$ triply doped sample emits the strongest 2.7 μm fluorescence. Therefore, this $Er^{3+}/Tm^{3+}/Pr^{3+}$ ZBLAY glass can be a promising host material to achieve intense 2.7 μm laser from the $Er^{3+}:{}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ transition.

In Fig. 3(a), upconversion fluorescence at wavelengths of 522, 541, and 652 nm, arising from the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively, is demonstrated. Moreover, the green emission signal could readily be seen by the naked eye. It is noted that some other important infrared emissions can be observed simultaneously in present glass. As is shown in Fig. 3(b), broad emission band around 1.5 µm can be ascribed to the Er^{3+} : ${}^{4}\mathrm{I}_{13/2} \rightarrow {}^{4}\mathrm{I}_{15/2}$ and Tm^{3+} : ${}^{3}\mathrm{H}_{4} \rightarrow {}^{3}\mathrm{F}_{4}$ transitions. In addition, the Tm^{3+} : ${}^{3}\mathrm{F}_{4} \rightarrow {}^{3}\mathrm{H}_{6}$ and Tm^{3+} : ${}^{3}\mathrm{H}_{4} \rightarrow {}^{3}\mathrm{H}_{5}$ transitions yield emisssions around 1.8 and 2.3 µm. The sharp fluorescence around 1.96 µm can be attributed to the second-order contribution of laser emission from 980 nm LD. Whereas the width of this fluorescence may result from the second-order contribution of 0.98 μm emission due to the $Er^{3\,+}\colon {}^4I_{11/2}{\rightarrow} {}^4I_{15/2}$ transition, shown in the inset of Fig. 3(b). From a practical point of view, emissions around 1.5 µm are desired for developing S-band amplifiers; meanwhile, 1.8, 2.3, and 2.7 µm emissions of present glass have potential applications in eye-safe medical laser. Thus, this $Er^{3+}/Tm^{3+}/Pr^{3+}$ ZBLAY glass is a good potential candidate for mid-infrared lasers.

The mechanism of the infrared and visible emissions of $Er^{3+}/Tm^{3+}/Pr^{3+}$ ZBLAY glass can be explained by the energy sketch shown in Fig. 4. Firstly, ions of the Er^{3+} :⁴I_{15/2} state are excited to the ${}^{4}I_{11/2}$ state by ground state absorption (GSA) when sample is pumped by 980 nm LD. A part of the ions in the ${}^{4}I_{11/2}$ level undergo the energy transfer upconversion (ETU1) process, subsequently the ${}^{4}F_{7/2}$ level is populated. Population of the ${}^{4}F_{7/2}$ level decay non-radiatively to the next-lower ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ levels. Then the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions take place with green emissions centered at 522 and 541 nm, respectively. Ions in the ${}^{4}S_{3/2}$ level can also decay to the ${}^{4}F_{9/2}$ level, resulting in red emission around 655 nm which is originated from the ${}^4F_{9/2}{\rightarrow}{}^4I_{15/2}$ transition. The other part of ions in the $Er^{3+}{}^4I_{11/2}$ level experience several complicated processes: decay radiatively to the next-lower ${}^{4}I_{13/2}$ level with 2.7 µm emission or the ${}^{4}I_{15/2}$ level with 0.98 µm emission, transfer their energies to the Pr^{3+} : ${}^{1}G_{4}$ (ET1) and Tm^{3+} : ${}^{3}H_{5}$ (ET2) levels; decay non-radiatively to the ${}^{4}I_{13/2}$ level. As to the ${}^{4}I_{13/2}$ level, possible energy transfer processes are as follows: 1.55 µm emission is caused by the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition. Another energy transfer upconver-



Fig. 4. The energy level diagram and energy transfer sketch map of the $Er^{3+}/Tm^{3+}/Pr^{3+}$ triply doped ZBLAY glass when pumped at 980 nm.



Fig. 5. Decay curves of the Er^{3+} :⁴ $I_{13/2}$ level in prepared samples.

sion process (ETU2: ${}^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{15/2} + {}^4I_{9/2}$ increases population of the ${}^4I_{9/2}$ level.⁸ Then, the ${}^4I_{11/2}$ level can be populated by a fast multiphonon decay from the ${}^{4}I_{9/2}$ level, which leads to an increase of 2.7 μ m emission.⁸ In the Er³⁺/ Tm^{3+}/Pr^{3+} triply doped sample, some energy of the ${}^{4}I_{13/2}$ level is transferred to the Pr^{3+} : ${}^{3}F_{3,4}$ (ET3) and Tm^{3+} : ${}^{3}F_{4}$ (ET4) levels. Since there is no obvious absorption band of Tm³⁺ around 980 nm as shown in Fig. 1, it can be deduced that the 1.8 and 2.3 μ m emissions of Tm³⁺ shown in Fig. 3(b) stem from the energy transfer ET4 and ET5 $(Er^{3+}F_{9/2} \rightarrow Tm^{3+}F_3)$ processes, respectively, as shown in Fig. 4. By means of above energy transfer processes, population of the Er^{3+} : ${}^{4}\mathrm{I}_{13/2}$ level is significantly reduced.

As mentioned previously, since the fluorescence lifetime (τ) of the upper laser level (⁴I_{11/2}) is shorter than that of the lower laser level (${}^{4}I_{13/2}$), population of the ${}^{4}I_{11/2}$ level in Er³⁺ singly doped glass is smaller than that of the ${}^{4}I_{13/2}$ level, which consequently affects the 2.7 µm emission. Figure 5 shows decay curves of the ${}^{4}I_{13/2}$ level in Er^{3+} singly,

 ${\rm Er^{3\,+}/Tm^{3\,+}},~{\rm Er^{3\,+}/Pr^{3\,+}}$ co-doped and ${\rm Er^{3\,+}/Tm^{3\,+}/Pr^{3\,+}}$ triply doped samples as well as the lifetime. With the introduction of Tm^{3+} or Pr^{3+} ions, reduction in lifetime indicates the energy transfer between Er^{3+} and Tm^{3+} or Pr^{3+} ions. More-over, the lifetime of the ${}^{4}\mathrm{I}_{13/2}$ level drops significantly from 14.6 ms in Er^{3+} singly doped sample to 4.4 ms in Er^{3+} Tm³⁺/Pr³⁺ triply doped sample, which indicates that a better quenching effect can be achieved by the introduction of \tilde{F}^+ and \tilde{Pr}^{3+} ions simultaneously. Since lifetime quench-Tm² ing of the ${}^4\mathrm{I}_{13/2}$ level is beneficial to the population inversion and intense 2.7 μ m emission, doping the system with Tm³⁺, Pr³⁺, and Er³⁺ is a preferred technique for a diode-pumped 2.7 µm fiber laser.

IV. Conclusion

The $Er^{3+}/Tm^{3+}/Pr^{3+}$ triply doped fluoride glass with the chemical composition of 50ZrF₄-33BaF₂-17(LaF₃ + AlF₃ + YF_3) is investigated. Intense emission at 2.7 µm is obtained due to the efficient energy transfer between Er^{3+} , Tm^{3+} , and Pr^{3+} ions. With the introduction of Tm^{3+} and Pr^{3+} into the Er^{3+} doped system, the lifetime of the Er^{3+} :⁴ $I_{13/2}$ level is significantly reduced and the population inversion between the $^4I_{11/2}$ and $^4I_{13/2}$ levels becomes more possible. The present results suggest that the $Er^{3\,+}/Tm^{3\,+}/Pr^{3\,+}$ ZBLAY glass can be considered as a promising material for a 2.7 µm laser.

References

¹M. Pollnau and S. D. Jackson, "Energy Recycling Versus Lifetime Quench-ing in Erbium-Doped 3 µm Fiber Lasers," *IEEE J. Quantum Electron.*, 38,

^{162–9} (2002). ²J. Wu, S. Jiang, T. Qua, M. Kuwata-Gonokami, and N. Peyghambarian, "2 µm Lasing From Highly Thulium Doped Tellurite Glass Microsphere," Appl. Phys. Lett., **87**, 211118–3 (2005). ³Y. Tsang, A. El-Taher, T. King, and S. Jackson, "Efficient 2.96 μm

Dysprosium-Doped Fluoride Fibre Laser Pumped With a Nd: YAG Laser Operating at 1.3 µm," Opt. Lett., 29, 334–6 (1999).

L. Schweizer, D. w. Hewak, B. N. Samson, and D. N. Payne, "Spectro-scopic Data of the 1.8-, 2.9, and 4.3-μm Transitions in Dysprosium-Doped Gallium Lanthanum Sulfide Glass," *Opt. Lett.*, **21**, 1594–6 (1996). ⁵J. Schneider, C. Carbonnier, and U. B. Unrau, "Characterization of a Ho³⁺ -Doped Fluoride Fiber Laser With a 3.0 µm Errichter With T. Schweizer, D. W. Hewak, B. N. Samson, and D. N. Payne, "Spectro-

-Doped Fluoride Fiber Laser With a 3.9-µm Emission Wavelength," Appl. Opt., 36, 8595-600 (1997).

D. F. de Sousa, L. F. C. Zonetti, M. J. V. Bell, J. A. Sampaio, L. A. O. Nunes, M. L. Baesso, A. C. Bento, and L. C. M. Miranda, "On the Observation of 2.8 μ m Emission From Diode-Pumped Er³⁺- and Yb³⁺-Doped low Silica Calcium Aluminate Glasses," Appl. Phys. Lett., 74, 908-10 (1999).

⁷Y. G. Choi, K. H. Kim, B. J. Lee, Y. B. Shin, Y. S. Kim, and J. Heo, "Emission Properties of the Er^{3+} .⁴I_{11/2}-⁴I_{13/2} Transition in Er^{3+} . and Er^{3+} . Transition in Er^{3+} . Ber Ge-Ga-As-S Glasses," J. Non-Cryst. Solids, **278**, 137-44 (2000).

⁸P. S. Golding, S. D. Jackson, T. A. King, and M. Pollnau, "Energy Trans-fer Processes in Er³⁺-Doped and Er³⁺, Pr³⁺-Codoped ZBLAN Glasses," Phys. Rev. B, 62, 856-64 (2000).

⁹Y. Tian, R. Xu, L. Zhang, L. Hu, and J. Zhang, "Observation of 2.7µm Emission From Diode-Pumped Er3+/Pr3+-Codoped Fluorophosphate Glass,'

Def. Lett., **36**, 109–11 (2011). ¹⁰L. F. Johnson, L. G. Van Uitert, J. J. Rubin, and R. A. Thomas, "Energy Transfer From Er^{3+} to Tm^{3+} and Ho^{3+} Ions in Crystals," *Phys. Rev.*, **133**, A494-8 (1964).

¹¹C. Y. Chen, R. R. Petrin, D. C. Yeh, W. A. Sibley, and J. L. Adam, - and Tm² "Concentration-Dependent Energy-Transfer Processes in Er³ Doped Heavy-Metal Fluoride Glass," Opt. Lett., 14, 432-4 (1989).

 12 S. D. Jackson, T. A. King, and M. Pollnau, "Diode-Pumped 1.7-W Erbium 3-µm Fiber Laser," *Opt. Lett.*, **24**, 1133–5 (1999). 13 S. A. Pollack and M. Robinson, "Laser Emission of Er³⁺ in ZrF₄-Based

Fluoride Glass," Electron. Lett., 24 320-2 (1988).

⁴M. Koide, K. Matusita, and T. Komatsu, "Viscosity of Fluoride Glasses at Glass Transition Temperature," J. Non-Cryst. Solids, 125, 93-7 (1990).