

Intense frequency upconversion fluorescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped lithium-strontium-lead-bismuth glasses

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Infrared-to-visible upconversion fluorescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped lithium-strontium-lead-bismuth (LSPB) glasses for developing potential upconversion lasers has been studied under 975-nm excitation. Based on the results of energy transfer efficiency and upconversion spectra, the optimal Yb^{3+} - Er^{3+} concentration ratio is found to be 5:1. Intense green and red emissions centered at 525, 546, and 657 nm, corresponding to the transitions ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$, ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$, and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively, were observed. The quadratic dependence of the 525-, 546-, and 657-nm emissions on excitation power indicates that a two-photon absorption process occurs under 975-nm excitation. The high-populated ${}^4I_{11/2}$ level is supposed to serve as the intermediate state responsible for the upconversion processes. The intense upconversion luminescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped LSPB glasses may be a potentially useful material for developing upconversion optical devices.

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Erbium ion has been recognized as one of the most popular and efficient ions for obtaining frequency upconversion for their potential applications in areas such as optical data storage, lasers, sensors, and optical displays, as well as infrared emission for optical amplification at the third communication window (1.5 μm)^[1–5], with the commercialization of 980 and 800-nm solid state laser diodes (LDs). However, the two transitions of Er^{3+} , ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$ (at around 980 nm) and ${}^4I_{15/2} \rightarrow {}^4I_9/2$ (at around 800 nm), present weak ground state absorption. The sensitization of Er^{3+} doped materials with Yb^{3+} ions is a well-known method for increasing the optical pumping efficiency because of the efficient energy transfer from Yb^{3+} to Er^{3+} ions, but in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped glass, there exists optimal Yb^{3+} doping content. Pulsed and continuous wave laser actions have been demonstrated in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped glass lasers. Host material for Er^{3+} ions plays an important role in obtaining high-efficient upconversion signal, since glass host with low phonon energy can reduce non-radiative loss due to the multiphonon relaxation and thus realize strong upconversion luminescence. Upconversion is difficult to generate in conventional oxide glasses due to their high phonon energies, corresponding to the stretching vibrations of the oxide glass network former. However, oxide glasses have attractive properties, such as high chemical stability and ease of fabrication. Lead-bismuth glasses combine high mechanical strength, high chemical durability, and temperature stability with good transmission in the infrared region up to 8.5 μm , which make them promising materials for technological applications such as new lasing materials, upconverting phosphors, and optical waveguides^[6]. Recently, frequency upconversion emission of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped sodium-barium-strontium-lead-bismuth (NB-SPB) glasses has been reported^[2]. However, the NB-SPB glass temperature difference ΔT between the crystallization onset temperature T_x and the glass transition

temperature T_g is 105 °C, which is relatively smaller than that of $\text{R}_2\text{O-ZnO-TeO}_2$ glass^[6]. Glass with the molar composition (mol%) 10 $\text{Li}_2\text{O-10SrO-20PbO-60Bi}_2\text{O}_3$ ($\text{L}_{10}\text{S}_{10}\text{P}_{20}\text{B}_{60}$) is characterized by good glass stability, wide transmission region (0.44 – 8.5 μm), high density (7.6 g/cm³), and high refractive index (2.45), and the ΔT value is 190 °C. The long infrared cutoff edge indicated that the phonon energy of $\text{L}_{10}\text{S}_{10}\text{P}_{20}\text{B}_{60}$ glass is small compared with other conventional oxide glasses. In this letter, we report on the fabrication and characterization of novel $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped LSPB glasses. Intense upconversion fluorescence bands at around 525, 546, and 657 nm were observed under 975-nm excitation at room temperature, and the upconversion mechanisms were discussed and estimated.

The glasses used in this work were synthesized by conventional melting and quenching method. The starting materials are reagent-grade Li_2O , SrO , PbO , and Bi_2O_3 . The glass samples with the molar composition (mol%) 10 $\text{Li}_2\text{O-10SrO-20PbO-60Bi}_2\text{O}_3$ ($\text{L}_{10}\text{S}_{10}\text{P}_{20}\text{B}_{60}$) were doped with 0.5 mol% Er^{3+} and co-doped with 0.5, 1.5, 2, 2.5, 3, and 3.5 mol% Yb^{3+} , which were introduced as Er_2O_3 and Yb_2O_3 , respectively, with 99.99% purity. To measure the energy transfer efficiency, $\text{L}_{10}\text{S}_{10}\text{P}_{20}\text{B}_{60}$ glasses doped with 0.5, 1, 2, 2.5, 3, and 3.5 mol% Yb^{3+} were also prepared. About 20-g batches of the well-mixed raw materials were melted at 1000 °C for 20 – 30 min in covered aluminium oxide crucibles in an electronic furnace with O_2 atmosphere. When the melting was completed, the liquid was cast into stainless steel plate. The obtained glasses were annealed to room temperature, and then were cut and polished carefully in order to meet the requirements for optical measurements. UV-Vis/NIR absorption spectra were recorded between 400 and 1600 nm by a Perkin Elmer Lambda 900 spectrophotometer. The upconversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 975-nm LD with a maximum power of 2 W. In order to com-

pare the luminescence intensity of Er³⁺/Yb³⁺ co-doped LSPB glasses as accurate as we can, the position and power (100 mW) of the pumping beam and the width (1 mm) of the slit to collect the luminescence signal were fixed under the same condition, and the sample was set at the same place in the experimental setup. The lifetimes for the ⁴I_{11/2} level of Er³⁺ in Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses were measured using a modulated 800-nm LD and a Tektronix TDS3052 digital oscilloscope controlled by a computer. The lifetime was calculated by fitting the exponential function to the decay data. All the measurements were performed at room temperature.

Figure 1 shows that the absorption spectra of Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses. Each assignment in Fig. 1 corresponds to the absorptions from the ground state ⁴I_{15/2} of Er³⁺ ions and ²F_{7/2} of Yb³⁺ ions to the excited states. The absorption band of Yb³⁺ for the ²F_{7/2} → ²F_{5/2} transition overlaps that of Er³⁺ for the ⁴I_{15/2} → ⁴I_{11/2} transition. Compared with Er³⁺ ions, the absorption of Yb³⁺ near 980 nm is predominant, as shown in Fig. 1, where the band intensity at around 980 nm obviously increases with Yb³⁺ ions content. When the excitation was performed at the ²F_{5/2} level with a diode laser of 975 nm, the emission from the ²F_{5/2} state of Yb³⁺ overlaps the absorption band for the ⁴I_{15/2} → ⁴I_{11/2} transition of Er³⁺ due to only one electronic excited state for Yb³⁺ ions. The energy transfer (ET) from Yb³⁺ to Er³⁺, ²F_{5/2}(Yb³⁺) + ⁴I_{15/2}(Er³⁺) → ²F_{7/2}(Yb³⁺) + ⁴I_{11/2}(Er³⁺), acts as indirect pumping of Er³⁺. So the energy transfer efficiency will play an important role in Er³⁺/Yb³⁺ co-doped system. The energy transfer efficiency (η) can be expressed as^[7]

$$\eta = 1 - \tau_{Yb} / \tau_{Yb}^0 \quad (1)$$

where τ_{Yb} and τ_{Yb}^0 were the ²F_{5/2} lifetimes of Yb³⁺ ions with and without Er³⁺ ions, respectively. Figure 2 shows the lifetimes of the ²F_{5/2} state and energy transfer efficiency from Yb³⁺ to Er³⁺ in Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses. The lifetimes of Yb³⁺ ions

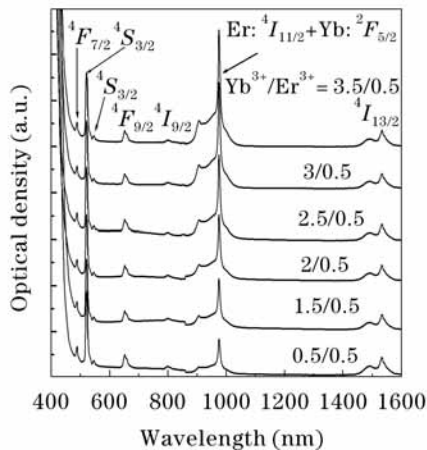


Fig. 1. Absorption spectra of L₁₀S₁₀P₂₀B₆₀ glasses doped with 0.5 mol% of Er³⁺ ions and different Yb³⁺ concentrations.

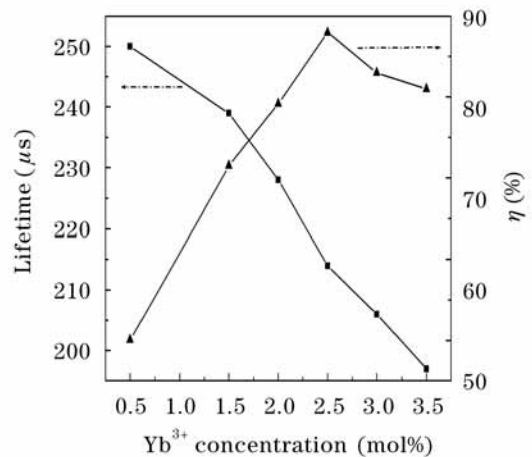


Fig. 2. Lifetimes of the ²F_{5/2} state and energy transfer efficiency from Yb³⁺ to Er³⁺ in Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses.

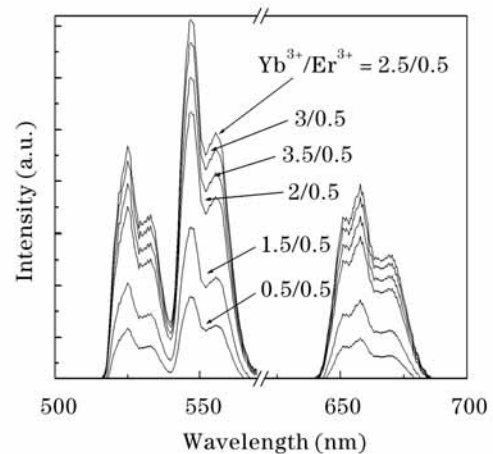


Fig. 3. Upconversion fluorescence spectra of Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses under 975-nm excitation.

monotonically decreases in the co-doped glasses, while the energy transfer efficiency was found to increase first and then decrease with the increase of Yb³⁺ concentration. The maximum energy transfer efficiency was found to be 88% in Yb³⁺/Er³⁺ (2.5/0.5) co-doped L₁₀S₁₀P₂₀B₆₀ glass.

Figure 3 shows the room temperature upconversion spectra of Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses. The observed emissions correspond to transitions of Er³⁺ ions from excited states to ground state. Intense green and red emission bands at around 525-, 546-, and 657-nm wavelength are attributed to the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2}, and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively. It is important to point out that the green emission is bright enough to be observed by the naked eye at excitation power as low as 60 mW for Er³⁺/Yb³⁺ co-doped L₁₀S₁₀P₂₀B₆₀ glasses. The emission intensity of green and red emissions increases at first, and then slightly decreases with the increase of Yb³⁺ concentration, which is mainly due to the intense backward energy transfer from Er³⁺ to Yb³⁺. From Fig. 3, it is predictable that the optimal Yb³⁺ doping content is 2.5 mol%, which is a reasonable value when compared with other results^[8] and consistent with the results of ET efficiency in Fig. 2.

In frequency upconversion process, the upconversion emission intensity I_{up} increases in proportion to the n th power of infrared (IR) excitation intensity I_{IR} , that is, $I_{up} \propto I_{IR}^n$, where n is the number of IR photons absorbed per visible photon emitted. A plot of $\log I_{up}$ versus $\log I_{IR}$ yields a straight line with slope n . Figure 4 shows such a plot for the 525-, 546-, and 657-nm emissions in Er^{3+}/Yb^{3+} co-doped $L_{10}S_{10}P_{20}B_{60}$ glass under 975-nm excitation. Values of 1.87, 1.89, and 1.86 were obtained for n corresponding to the 525-, 546-, and 657-nm emission bands, respectively. The results indicate that a two-photon process populates the $^4S_{3/2}$, the $^2H_{11/2}$ and the $^4F_{9/2}$ levels. According to the energy matching and quadratic dependence on excitation power, the possible upconversion mechanisms for the emissions are discussed based on the simplified energy levels of Er^{3+} and Yb^{3+} presented in Fig. 5. For the green emissions, in the first step, the $^4I_{11/2}$

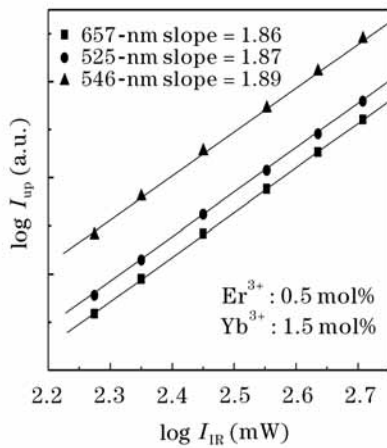


Fig. 4. Dependence of upconversion fluorescence intensity on excitation power under 975-nm excitation for Er^{3+}/Yb^{3+} co-doped $L_{10}S_{10}P_{20}B_{60}$ glass.

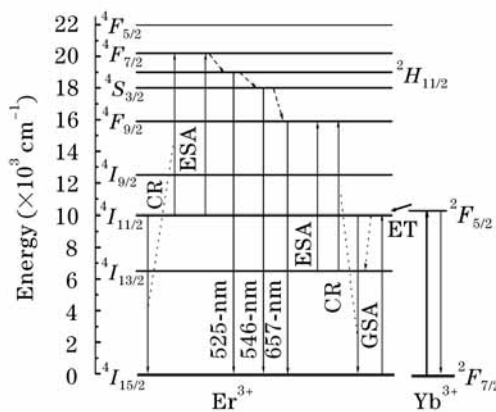


Fig. 5. Simplified energy level diagram of Er^{3+} and Yb^{3+} ions and possible transition pathways in Er^{3+}/Yb^{3+} co-doped $L_{10}S_{10}P_{20}B_{60}$ glasses.

level is directly excited with 975-nm light and/or by ET process from $^2F_{5/2}$ level of Yb^{3+} : $^2F_{5/2}(Yb^{3+}) + ^4I_{15/2}(Er^{3+}) \rightarrow ^4F_{7/2}(Yb^{3+}) + ^4I_{11/2}(Er^{3+})$. Since Yb^{3+} has a much larger absorption cross-section than Er^{3+} in the 975-nm region, the ET process is dominant to the excitation of $^4I_{11/2}$ level. The measured lifetimes of $^4I_{11/2}$ level for $L_{10}S_{10}P_{20}B_{60}$ ($Yb^{3+}/Er^{3+}=0.5/0.5, 1.5/0.5, 2/0.5, 2.5/0.5, 3/0.5$) glasses are shown in Table 1, which are much longer than those in other oxide glasses^[9]. Thus, the second step involves the excitation processes based on the long-lived $^4I_{11/2}$ level as follows: cross-relaxation (CR), $^4I_{11/2}(Er^{3+}) + ^4I_{11/2}(Er^{3+}) \rightarrow ^4F_{7/2}(Er^{3+}) + ^4I_{15/2}(Er^{3+})$; excited state absorption (ESA), $^4I_{11/2}(Er^{3+}) + \text{a photon} \rightarrow ^4F_{7/2}(Er^{3+})$; ET, $^2F_{5/2}(Yb^{3+}) + ^4I_{11/2}(Er^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^4F_{7/2}(Er^{3+})$. The populated $^4F_{7/2}$ level of Er^{3+} then relaxes rapidly and nonradiatively to the next lower levels $^2H_{11/2}$ and $^4S_{3/2}$ resulting from the small energy gap between them. Er^{3+} ion at the $^2H_{11/2}$ state can also decay to the $^4S_{3/2}$ state due to multiphonon relaxation process. The estimated energy gap between the $^2H_{11/2}$ state and the next lower state $^4S_{3/2}$ is $\sim 800 \text{ cm}^{-1}$ ^[10]. Thus, multiphonon relaxation rate is very large and the 525-nm emission intensity is reduced. However, it is also considered that the $^2H_{11/2}$ excited level is easily thermally populated from $^4S_{3/2}$ level by a fast thermal equilibrium between $^2H_{11/2}$ and $^4S_{3/2}$ levels and subsequently contributes to the radiative relaxation in this spectral range at room temperature (see Fig. 3)^[11]. The above processes then produces the two $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ green emissions centered at 525 and 546 nm, respectively. The red emission at 657 nm is originated from the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition and the population of $^4F_{9/2}$ is based on the processes as follows: ET from Yb^{3+} , $^2F_{5/2}(Yb^{3+}) + ^4I_{13/2}(Er^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^4F_{9/2}(Er^{3+})$; CR between Er^{3+} ions, $^4I_{13/2} + ^4I_{11/2} \rightarrow ^4I_{15/2} + ^4F_{9/2}$; ESA, $^4I_{13/2} + \text{a photon} \rightarrow ^4F_{9/2}$. The $^4I_{13/2}$ level is populated owing to the nonradiative relaxation from the upper $^4I_{11/2}$ level. Besides, the nonradiative process from $^4S_{3/2}$ state, which is populated by means of the process described previously, to $^4F_{9/2}$ level also contributes to the red emission.

In conclusion, we have studied the frequency upconversion fluorescence of LSPB glasses under continuous wave excitation at 975 nm at room temperature. Based on the results of energy transfer efficiency, it was found that the optimal Yb^{3+} doping content is 2.5 mol% when the Er^{3+} doping content is 0.5 mol%. The intense 525, 546, and 657-nm upconversion fluorescence emissions, corresponding to the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions, respectively, are due to two-photon absorption processes. The discussion

Table 1. The Lifetimes of $^4I_{11/2}$ Level of Er^{3+} in $L_{10}S_{10}P_{20}B_{60}$ Glasses with Different Yb^{3+} Concentrations

Yb^{3+}/Er^{3+} (mol%)	0.5/0.5	1.5/0.5	2/0.5	2.5/0.5	3/0.5	3.5/0.5
Lifetime (μs)	220	251	276	290	284	278

of upconversion mechanisms reveals that the long-lived $^4I_{11/2}$ level plays an important role in the upconversion processes for both green and red emissions. $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped LSPB glasses with intense upconversion fluorescence can be used as potential host material for upconversion lasers.

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