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1.55 μm emission and upconversion luminescence of Er^{3+}-doped strontium borate glasses

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Abstract

Er^{3+}-doped strontium borate glasses $10SrCO_3–2SrF_2–3Li_2CO_3–85H_3BO_3{:}xEr^{3+}$ ($x=0.5$, 1.0, 2.0 and 3.0) were synthesized via conventional melt quenching technique. The emission spectra, the luminescence decay curves and upconversion emission spectra were measured. Under the excitation of a 980 nm laser diode, 1.55 μm infrared fluorescence and efficient green and red upconversion fluorescence have been observed. The broad and intense emission positions centered at around 1550 nm show increasing red shift with the increase of Er^{3+} ions concentration. It can be noted that the full-width at half-maximum and the decay lifetimes of the 1.55 μm emission show the dependence of Er^{3+} ions concentration. A possible mechanism has also been proposed. It is worth noting that both the excited state absorption and the energy transfer of Er^{3+} ions are of great importance to the upconversion process.

Keywords: Borate glasses; Er^{3+}; Luminescence; Upconversion

1. Introduction

Glass materials have already proven to be attractive hosts for rare earth (RE^{3+}) ions for applications such as optical amplifiers [1] and infrared lasers [2]. In particular, trivalent erbium (Er^{3+}) doped glass hosts have been extensively investigated, since Er^{3+} is one of the most popular and efficient ions for obtaining near-infrared to visible upconversion as well as 1.5 μm infrared emission due to the main $^4I_{13/2}\rightarrow{}^4I_{15/2}$ NIR laser transition, which is useful for lasers and optical amplification in the third telecommunication window [3]. And the 1.5 μm wavelength is just located in 'eye safe' spectral region, hence Er^{3+}-doped glasses with a broad 1.5 μm emission band have attracted much attention for their potential applications in optical and planar waveguide amplifier for dense wavelength division multiplexing (DWDM) optical networks [4–6].

Meanwhile, the upconversion of Er^{3+} ions in glasses are also of great interest due to its potential applications for compact and high-power devices [7] etc., which is an attractive method to obtain compact solid-state visible-light sources. Up to now many kinds of glasses have been investigated, for instance, El-Mallawany et al. have observed strong green and red upconversion emission from Er^{3+}-doped tellurite glasses [8]. Amjad et al. have reported that the infrared to visible frequency upconversion emission under 797 nm excitation shows two emission bands green and red centered at 540 nm and 634 nm respectively, corresponding to Er^{3+} transitions in phosphate glass [9]. Zou et al. have researched the main mechanism of green upconversion in Er^{3+}-doped aluminate and gallate glasses [10].

Among different oxide glasses, borate glasses have the advantages of high transparency, high thermal stability, low melting point, different coordination numbers and good solubility of rare-earth ions [11,12]. Thus borate glasses doped with Er^{3+} ions seems to be very attractive systems for applications in optical devices of laser technology, they were also considered to be promising candidates for 1.5 μm broad band optical amplifier [13–15].

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The current study concerns the spectroscopic results of Er^{3+}-doped strontium borate glass systems with different concentrations. The emission spectra of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition and luminescence decay curves of the $^4I_{13/2}$ level were measured, several radiative and laser parameters such as the calculated and measured luminescence lifetime and the room-temperature peak stimulated emission cross-section were evaluated. In addition, upconversion luminescence was also measured using 980 nm excitation and a possible mechanism has been proposed to explain the process.

2. Experimental details

Er^{3+}-doped strontium borate glasses with the chemical composition $10SrCO_3$–$2SrF_2$–$3Li_2CO_3$–$85H_3BO_3$:xEr^{3+} ($x=0.5$, 1.0, 2.0 and 3.0) were prepared using the conventional melt quenching technique. All starting materials introduced were of analytic grade purity without further purification. These weighed chemicals (each batch composition of about 5 g) were mixed thoroughly and melted in porcelain crucibles at temperatures between 750 and 950 °C for 1 h. Then the homogeneous melts were poured onto a previously heated brass mold and held in a muffle furnace at 300 °C for 8 h to remove the formation of air bubbles, thermal strains and improve the mechanical strength. After that, the prepared glasses were cooled at a rate of 10 °C/h to room temperature and then polished on both sides before further optical measurements.

The emission spectra were measured by using a Ti–Sapphire ring laser (0.4-cm^{-1} line width) in the 1400–1660 nm range. The fluorescence was analyzed with a 0.22-m SPEX monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier and finally amplified by a standard lock-in technique. Lifetime measurements were performed by exciting the samples with a Ti–Sapphire laser pumped via a pulsed frequency doubled Nd:YAG laser (9-ns pulse width), and detecting the emission with a Hamamatsu R928 photomultiplier. Data were processed by a boxcar integrator.

3. Results and discussion

3.1. $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition emission

Fig. 1 presents the normalized emission cross-sections of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition for Er^{3+}-doped borate glasses with various concentrations of Er^{3+} ions (0.5, 1.0, 2.0, and 3.0 mol%). It is easy to see that the broad and intense emission positions (λ_p) are centered at around 1550 nm, which is associated with the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} ions. What is more, with the increase of Er^{3+} ions concentration, λ_p values show increasing red shift (~36 nm). This trends may be due to relative change in the stark level emissions of Er^{3+} ions caused by the phonon assisted energy transfer between Er^{3+} ions (energy migration) [16], which increases with Er^{3+} ions concentration.

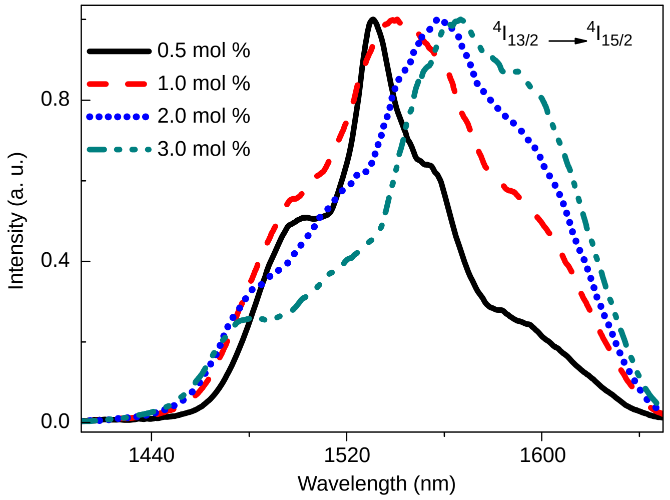

Fig. 1. Normalized emission cross-sections of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition for different concentrations (0.5, 1.0, 2.0, and 3.0 mol%) of Er^{3+}-doped strontium borate glasses ($\lambda_{ex}=980$ nm).

Full-width at half-maximum (FWHM) is an important luminescence property for optical amplifiers. It is calculated from Fig. 1 that the FWHM values increase from 66 to 108 nm when Er^{3+} ion concentration increases from 0.5 to 1.0 mol%, and then decrease to 103 nm for 2.0 mol% and 83 nm for 3.0 mol%. The observed changes in FWHM and cross-section at 1.55 μm with increasing Er^{3+} ions concentration could be due to two factors: The first is the radiative energy transfer between Er^{3+} ions induced by the overlapping of the absorption and emission bands. Another one is the energy migration [16] among Er^{3+} ions. These values are slightly larger than those reported materials commonly used for optical amplifiers, such as 40 nm for silicate glasses [10], 44 nm for phosphate glasses [17] and almost equal to the order of magnitude of tellurite glasses (93–121 nm) [8], and the larger value of FWHM could be interesting for wavelength division multiplexing applications [18].

Fig. 2 depicts the luminescence decay curves of the Er^{3+}-doped borate glasses due to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition measured at room temperature. The decay curves are single exponential for all the Er^{3+} ion concentrations, from the decay curves, lifetimes of the $^4I_{13/2}$ level have been determined by finding the first e-folding times. And lifetimes are found to decrease monotonically with increase in Er^{3+} ion concentrations from 5.21 ms to 1.10 ms.

It is clear that the lifetime of the $^4I_{13/2}$ level decreases with increasing Er^{3+} ion concentration, this could be attributed to energy transfer processes including both Er^{3+} ions and quenching centers such as OH^- groups [8,19,20]. With the increase of Er^{3+} ions concentration, the probability of energy migration among Er^{3+} ions increases, then it is easier to reach the OH^- ions which are the well known quenching centers of 1.54 μm infrared radiation in glass [21]. This is similar to the trend occurred in Er^{3+}-doped borate glasses, a large number of B–O

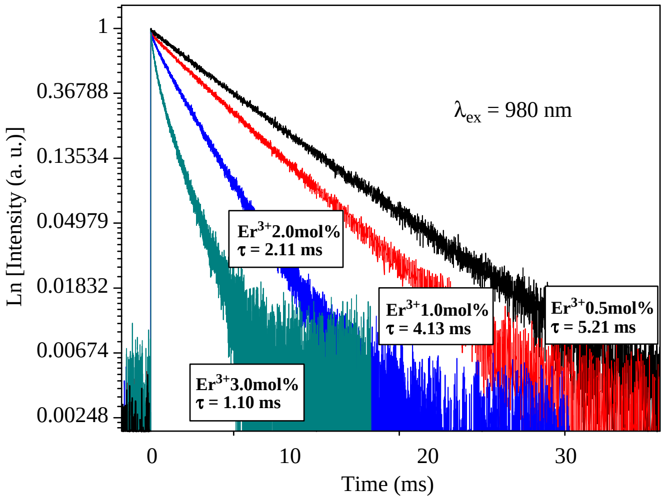

Fig. 2. Luminescence decay curves for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}-doped strontium borate glasses (0.5, 1.0, 2.0, and 3.0 mol% Er^{3+}).

bonds with high phonon energy (~1400 cm^{-1}) lead to high probability for non-radiative decay, and consequently shorten the lifetime of $^4I_{13/2}$ level from Er^{3+} ions, which was reported by Doo et al. [22].

3.2. The up-conversion luminescence

The emission spectra of the samples were recorded at room temperature with 980 nm radiation and are displayed in Fig. 3. It was found that the Er^{3+}-doped strontium borate glasses emit strong green emission along with weak red emission. These upconversion luminescence include three peaks at wavelength 530 nm, 550 nm and 670 nm, which are attributed to the Er^{3+}: $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions respectively.

As shown in Fig. 3, the intensity of 550 nm green upconversion emission increases rapidly from 0.1 to 1.0 mol% of Er^{3+} ions and reaches the maximum when the Er^{3+} ion concentration is 1.0 mol%, and then decreases from 1.0 to 2.0 mol%. The change in spectral profile of the green upconversion emission $((^2H_{11/2}+{}^4S_{3/2}) \rightarrow {}^4I_{15/2})$ with increase in Er^{3+} concentration could be due to energy migration [16] among Er^{3+} ions.

For the upconversion process in Er^{3+}-doped strontium borate glass under 980 nm excitation, this is probably induced by the process known as excited state absorption (ESA) and energy transfer upconversion (ETU) [23,24]. Fig. 4 shows a partial energy level diagram of Er^{3+} ions in strontium borate glass. Firstly, Er^{3+} ions are excited to the $^4I_{11/2}$ state from the ground $^4I_{15/2}$ state through ground state absorption (GSA) under 980 nm excitation. Then the exited ions may further reabsorb the incident 980 nm photon and promoted to the higher $^4F_{7/2}$ level through the ESA process, followed by non-radiative relaxation into the $^4S_{3/2}$ and $^2H_{11/2}$ levels. Because of the wide energy gap (3070 cm^{-1}) between the $^4S_{3/2}$ level and $^4F_{9/2}$ level, the multi-phonon relaxation rate from the $^4S_{3/2}$ level to the

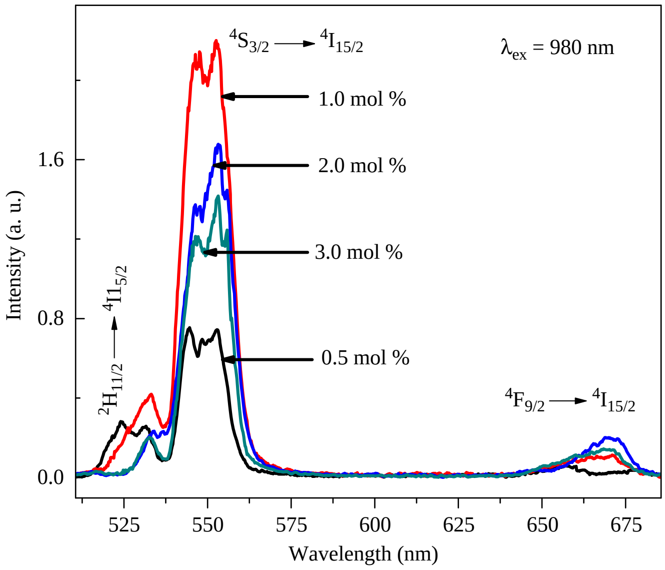

Fig. 3. Upconversion spectra for 0.5, 1.0, 2.0, and 3.0 mol% concentrations of Er^{3+}-doped strontium borate glasses ($\lambda_{ex}=980$ nm).

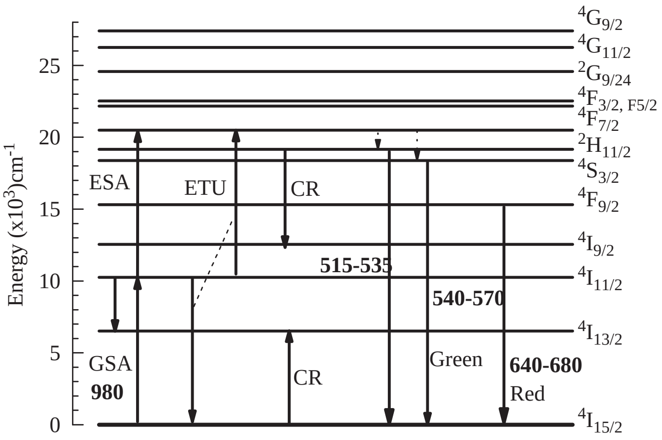

Fig. 4. Energy level diagram of Er^{3+} ions in strontium borate glass, showing the mechanism of upconversion emission under 980 nm excitation.

low-energy lying $^4F_{9/2}$ level is very low, this leads to the accumulation of population at the $^4S_{3/2}$ level, giving rise to very intense 550 nm green emission. Meanwhile, the $^2H_{11/2}$ level is also populated from the $^4S_{3/2}$ level by thermalization process between the levels, as the energy gap between them is around 770 cm^{-1}, which inturn decay to the ground state ($^2H_{11/2} \rightarrow {}^4I_{15/2}$) resulting in the weak green emission at 520–530 nm.

However, with the increase of Er^{3+} ions concentration, the phenomenon of energy transfer between two Er^{3+} ions through the $^4I_{11/2}$ level: $((^4I_{11/2}+{}^4I_{11/2}) \rightarrow {}^4I_{15/2}+{}^4F_{7/2})$ needs to be considered, which also populates the $^4F_{7/2}$ level and its contribution depends on the concentration of Er^{3+} ions. As shown in Fig. 3, the intensity of 550 nm green upconversion emission increases rapidly from 0.1 to 1.0 mol% of Er^{3+} ions, this is attributed to the upconversion mechanisms induced by the increasing Er^{3+} ions concentration. Then the 550 nm emission intensity decreases from 1.0 to 2.0 mol% and further declines in 3.0 mol% of Er^{3+} ions, this could be due to the onset and variation of the cross-relaxation (CR) energy transfer (non-radiative) process: $^2H_{11/2}+^4I_{15/2}\rightarrow ^4I_{9/2}+^4I_{13/2}$, between Er^{3+} ions [8].

Fig. 5 is the log–log plot of upconversion intensity as a function of the pump powers under 980 nm excitation at room temperature, the values of slopes, n, are close to 2.0 for strontium borate glasses with 0.5 and 1.0 mol% Er^{3+} concentration. This confirms that the upconversion is a two-photon process, the interaction of $Er^{3+}-Er^{3+}$ pairs involved for the green upconversion emission [25]. Then the n-values decreases to nearly 1.4 for the 2.0 mol% Er^{3+} concentration and nearly 1.3 for the 3.0 mol% Er^{3+}-doped sample. Such a decrease of n-value with the increasing Er^{3+} concentration has also been reported in Er^{3+}-doped chalcogenide glass [26], Er^{3+}-doped fluorozirconate glass [27] and Ho^{3+}–Yb^{3+} co-doped oxyfluoride glass [28], this could be due to the concentration quenching process.

To elucidate the dominant mechanism of the green upconversion process, temporal behaviors of the 550 nm green upconversion emission and the Stokes green emission with direct excitation ($\lambda_{ex}=532$ nm) for 1.0 mol% Er^{3+}-doped borate glass were measured and are shown in Fig. 6. It can be seen clearly from inset of Fig. 6, that there is a rise time of around 4 μs at the beginning of the green emission process. Also, there is a large difference in the shapes and lifetimes of the green upconversion emission compared to the Stokes green emission ($\lambda_{ex}=532$ nm).

The lifetime under 532 nm excitation is fitted to be 11.38 ms; the decay profile for the $^4S_{3/2}\rightarrow ^4I_{15/2}$ emission is exponential with a longer lifetime of 23.63 ms, which is nearly two times the value of the Stokes green emission ($\lambda_{ex}=532$ nm). This provides a strong evidence for the contribution of the ETU process in the mechanism of upconversion, as illustrated in Fig. 4. This is also supported by the rapid increase in the 550 nm green emission intensity with increase in Er^{3+} ions concentration for low concentration samples. Hence, the above results suggest that energy transfer upconversion process is the dominant mechanism for green upconversion emission.

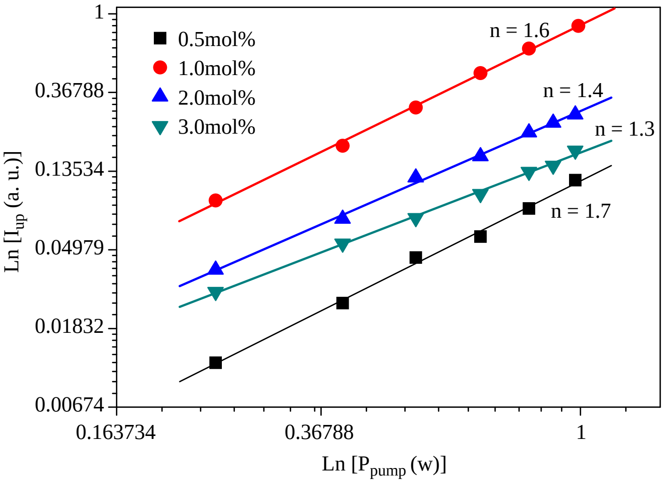

Fig. 5. The log–log plot of upconversion intensity as a function of the pump powers under 980 nm excitation at room temperature.

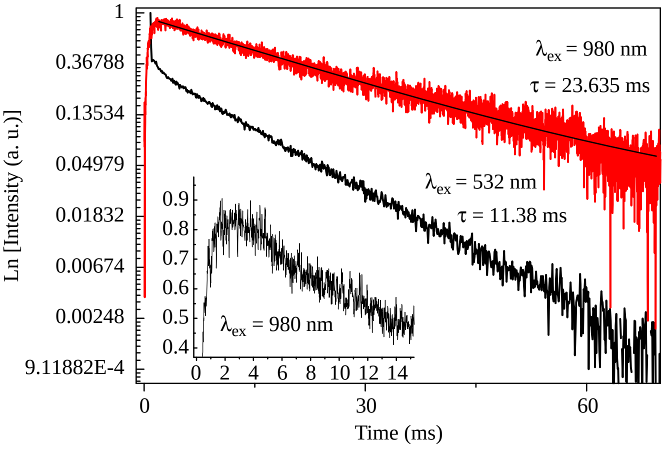

Fig. 6. Temporal behavior of 550 nm green upconversion emission and the Stokes green emission with direct excitation ($\lambda_{ex}=532$ nm) for 1.0 mol% Er^{3+}-doped strontium borate glass. Inset is the amplified figure at the initial time of the 550 nm green upconversion emission.

4. Conclusions

Er^{3+}-doped strontium borate glasses have been successfully prepared by conventional melt quenching technique. The samples show a broad 1.55 μm emission, and the FWHM values increase from 66 to 108 nm when Er^{3+} ion concentration increases from 0.5 to 1.0 mol%, and then decreases to 83 nm for 3.0 mol%. Concentration quenching of lifetime in Er^{3+}-doped borate glasses was investigated as a function of Er^{3+} concentration, the possible reason had been discussed in terms of energy transfer processes including both Er^{3+} ions and quenching centers. What is more, Er^{3+}-doped borate glasses give intense green and weak red upconversion fluorescence under 980 nm excitation. From the investigation of its temporal behavior, the green upconversion emission mainly comes from the energy transfer upconversion process.

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