Mixed heavy metal effect on emission properties of Er^{3+}-doped borosilicate glasses

Jianhu Yang (杨建虎), Shixun Dai (戴世勋), Lei Wen (温 磊), Nengli Dai (戴能利), Lili Hu (胡丽丽), and Zhonghong Jiang (姜中宏)

Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800

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Er^{3+}-doped heavy metal borosilicate glasses were prepared using conventional melting and quenching method. The emission spectra of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were observed upon excitation at 974 nm and the lifetime of $^4I_{13/2}$ level of Er^{3+} was measured. Based on these data, the fluorescence properties of Er^{3+} are investigated on the emission and gain characteristics at the 1.5 μm bands. In particular, the effect of relative heavy metal content on fluorescence properties is discussed.

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How to expand the transmission capacity of wavelength division multiplexing (WDM) system is now becoming a hot topic in the fields of optical communications with the rapid development of computer networks and other data-transmitting services[1,2]. It is of great importance to shift the amplification bandwidth of Er^{3+}-doped fiber amplifier (EDFA) from conventional C band (1530 – 1565 nm) to L band (1570 – 1610 nm) because of its key function in the WDM system. However, the bandwidth of the traditional SiO_2-based EDFA is limited and the amplifier with a parallel configuration is complicated[3,4]. It is preferable to find a novel glass host for Er^{3+}-doped for amplifier to obtain an intrinsically broader gain bandwidth than that of SiO_2-based EDFA[5]. Heavy metal oxides glasses with high refractive indices have caught much attention since the stimulated emission cross section, an important parameter for amplifier, is proportional to the refractive index of the host ($\sigma_e \sim (n^2+2)^2/n$)[6–8]. Another important parameter is the full width at half maximum (FWHM) of the emission spectrum of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition because the gain bandwidth of an amplifier is mainly determined by the FWHM $\times$ σ_e product[9]. To the best of our knowledge, there is no detailed study on the influence of relative heavy metal content on emission properties of Er^{3+} in the glasses.

In this paper, we perform the bandwidth analysis for emission spectra of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition and the lifetime measurements of $^4I_{13/2}$ level of Er^{3+}. From these data, the effects of different PbO/Bi_2O_3 content on the emission properties, especially on the bandwidth and lifetime, are investigated.

Glass samples with the compositions of $55SiO_2-10B_2O_3-(30-x)Bi_2O_3-xPbO-5Na_2O-0.5Er_2O_3$ (x = 0, 5, 10, 15, 20, and 25 mol%) were prepared using the conventional melting and quenching method. The starting materials are reagent-grade SiO_2, H_3BO_3, Bi_2O_3, $PbSiO_3$, and Na_2CO_3. Er^{3+} was introduced as Er_2O_3 with high purity 99.99%. The obtained glasses were cut and polished carefully in order to meet the requirements for optical measurements.

The emission spectra of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were measured using a TRIAX550 spectrofluorimeter with the 970 nm excitation from a laser diode (LD). The lifetime of $^4I_{13/2}$ level of Er^{3+} was measured with light pulses of 974 nm LD.

Figure 1 illustrates the emission spectra of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in the glass samples. Because of the differences of the emission spectra in different glass hosts, FWHM of the spectrum is often used as a semi-quantitative indication of the bandwidth. Figure 2 shows the compositional dependence of FWHM of Er^{3+} in the glass samples. It can be seen that with an increase of PbO content, the FWHM first increases and reaches its maximum at PbO = 5 mol% and then decreases. According to Weber[10], the emission spectra of Er^{3+} in different glass hosts are mainly determined by the local ligand fields around Er^{3+} sites. Generally, the linewidth broadening of Er^{3+} in glasses is inhomogeneous broadening which is caused by the differences in the ligand field from Er^{3+} site to site, while in crystals only homogeneous broadening exists because of its periodic structure. Based on Raman spectroscopy, Husson *et al.* reported that Bi^{3+} and Pb^{2+} have similar properties in glasses, which play an intermediary role as glass network former or modifier[11]. From the IR and Raman measurements, the study of Kharlamov *et al.* showed that the two cations have different presentations in the glass network structure, Bi^{3+} presents in distorted BiO_6 octahedra while Pb^{2+} exists in distorted PbO_3 or PbO_4

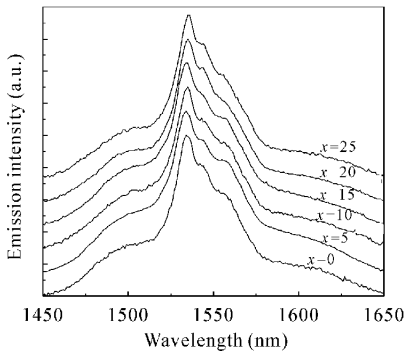

Fig. 1. Emission spectra of Er^{3+} in $55SiO_2-10B_2O_3-(30-x)Bi_2O_3-xPbO-5Na_2O-0.5Er_2O_3$ (x = 0, 5, 10, 15, 20, and 25 mol%) glasses.

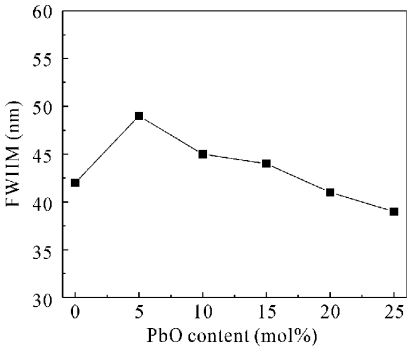

Fig. 2. Compositional dependence of FWHM of Er^{3+} in $55SiO_2-10B_2O_3-(30-x)Bi_2O_3-xPbO-5Na_2O-0.5Er_2O_3$ (x = 0, 5, 10, 15, 20, and 25 mol%) glasses.

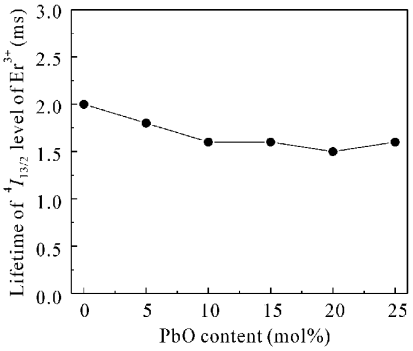

Fig. 3. Lifetime of $^4I_{13/2}$ level of Er^{3+} in $55SiO_2-10B_2O_3-(30-x)Bi_2O_3-xPbO-5Na_2O-0.5Er_2O_3$ (x = 0, 5, 10, 15, 20, and 25 mol%) glasses.

(trigonal or square) pyramids[12]. This means that Bi^{3+} and Pb^{2+} would have different effects on the variations of local ligand fields around Er^{3+} sites. The results suggest that the variation in ligand field around Er^{3+} sites in glasses first increases and reaches its maximum at PbO content = 5 mol% and then decreases. From the data obtained, we can see that the glasses with mixed heavy metal ions are preferable for Er^{3+} doped to realize broadband emission compared with the glasses with single heavy metal ions.

Figure 3 illustrates the measured lifetimes of $^4I_{13/2}$ level of Er^{3+} in the glasses. Apparently, with increasing PbO content, the lifetime only decreases slightly and almost keeps constant when PbO content is more than 10 mol%. The lifetime of $^4I_{13/2}$ level of Er^{3+} is an important parameter for an amplifier, since a critical factor in the success of Er^{3+}-doped fiber amplifiers in optical communications is the long lifetime of the metastable state which permits the required high population inversions to be obtained under steady-state conditions using modest pump powers[13]. The value of the lifetime of Er^{3+} is mainly determined by the refractive index and phonon energy of the glass host. Firstly, the radiative lifetime calculated by Judd-Ofelt theory is inversely proportional to the refractive index, and so is the measured lifetime. That is to say, the larger the refractive index of the host, the lower the value of the lifetime. Secondly, the measured lifetime decreases with an increase of phonon energy of the glass, since the non-radiative transition rate increases when increasing the phonon energy. The study of William *et al.* suggests that the substitution of PbO for Bi_2O_3 hardly change the refractive index of the glass hosts[14], while the infrared reflectance spectra study of heavy metal oxide glasses has shown that the vibration frequencies of Pb–O and Bi–O bonds, which are 400 and 470 cm^{-1}, respectively, are different only slightly[12]. In addition, free OH^- in the glass is also regarded as one of the important quenching centers in Er^{3+}-doped[15]. It is also clear that the lifetime of $^4I_{13/2}$ level of Er^{3+} in the glass is much lower than those in other conventional glass hosts ever known. This is attributed to the large refractive index of the glass host and the coupling of Er^{3+} with a number of B–O bonds with high phonon energy.

The effects of relative heavy metal content on emission properties of Er^{3+}-doped borosilicate glass were investigated on the emission and gain characteristic of 1.55 μm bands. The glasses with mixed heavy metal ions are preferable for Er^{3+} doped to realize broadband emission compared with the glasses with single heavy metal ions. The substitution of PbO for Bi_2O_3 almost does not change the lifetime of $^4I_{13/2}$ level of Er^{3+} due to their similar influence on the refractive index and the phonon energy of the glass hosts.

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