Broadband near-infrared luminescence and energy transfer in Bi singly-doped and Bi/Yb co-doped titanate glasses*

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Super-broadband near-infrared (NIR) emission from 1100 nm to 1600 nm is observed in Bi-doped titanate glasses at the excitation of 808 nm laser diode (LD). The effects of Bi content on the optical spectra are investigated. It is also found that the Bi-related emission intensity can be enhanced by Yb^{3+} co-doping at the excitation of 980 nm LD. It should be ascribed to the energy transfer from Yb^{3+} to active Bi ions. The energy transfer processes are studied based on the Inokuti-Hirayama (I-H) model, and the energy transfer of electric dipole-dipole interaction is confirmed to be dominant in Bi/Yb co-doped glasses.

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Owing to the rapid development of telecommunication networks, traditional rare-earth doped fiber amplifiers can not meet the demand because of the inherent limitations in gain bandwidth less than 100 nm[1,2]. In 2001, Fujimoto et al[3] found the Bi-doped silicate glass showing broadband near-infrared (NIR) emission in the 1200−1600 nm wavelength region. It suggests that Bi-doped glasses may be a promising material for broadband fiber amplifiers.

Since then a lot of Bi-doped glass hosts have been explored[4-8], but most of investigations were focused on silicate and germanate glass systems. In particular, the successful laser oscillation in Bi-doped silicate glass fiber[9-11] has motivated the search for new matrix glasses with acceptable optical performance as candidates for tunable lasers and optical fiber amplifiers.

Titanate glasses are of high refractive index, which have been applied widely in road illumination and decoration. TiO_2 has a similar molecular composition and chemical structure to SiO_2 and GeO_2, so it is possible to obtain broadband emission in Bi-doped titanate glasses. However, to our knowledge, there is no report on the broadband emission of Bi-doped titanate glasses. In this paper, we investigate the preparation of Bi singly-doped titanate glasses and the super-broadband emission of this Bi-doped glass system to obtain a novel favorable material for optical amplifiers and tunable lasers. Based on the observation of Bi singly-doped titanate glasses, we include Yb^{3+} into the titanate glasses to enhance Bi-related emission intensity at 980 nm excitation, which can overcome the emission intensity limitation of Bi singly-doped glasses[12].

Glasses with molar compositions of $50TiO_2$-$25BaO$-$15SiO_2$-$5B_2O_3$-$5Al_2O_3$-χBi_2O_3 (χ = 0.5, 1.5, 2.5 in mol%, designated as 0.5Bi, 1.5Bi, 2.5Bi) and $50TiO_2$-$25BaO$-$15SiO_2$- $5B_2O_3$-$5Al_2O_3$-$1.5Bi_2O_3$-ψYb_2O_3 (ψ = 1, 2.5, 4 in mol%, designated as 1.5Bi-1Yb, 1.5Bi-2.5Yb, 1.5Bi-4Yb) were prepared by the conventional melting-quenching method. Analytical reagents of TiO_2, $BaCO_3$, SiO_2, H_3BO_3, $Al(OH)_3$, Bi_2O_3, Yb_2O_3 were used as raw materials. Batches of materials (~20 g) were melted in platinum crucibles in air at 1550 ºC for 2 h. The melts were cast into preheated stainless steel plate and then annealed at 450 ºC for 2 h. The glasses were cut and polished into 2 mm in thickness for optical measurements.

The absorption spectra were measured by a Perkin-Elmer Lambda 950 UV/VIS spectrometer. The infrared emission spectra were measured by a TRIAX 550 spectrofluorometer excited by 808 nm and 980 nm LDs, respectively. The fluorescence decay curves of these glasses were registered by a Tektronix TDS 1012 digital storage oscilloscope. All measurements were carried out at room temperature.

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The absorption spectra of 0.5Bi, 1.5Bi and 2.5Bi samples in the range from 350 nm to 1100 nm are shown in Fig.1. Absorption bands centered at about 424 nm, 730 nm, 880 nm and 965 nm are observed, which should be ascribed to active Bi ions, in accordance with the results reported previously[13]. With the increase of Bi ion concentration, the absorption intensity becomes stronger gradually. However, there is no intense peak absorption from 800 nm to 1000 nm. For Bi-doped glasses and fibers, the absorption at the band from 808 nm to 980 nm is especially important, which can be pumped by low-cost commercial laser diodes (LDs). Hence, from the viewpoint of practical application, we should try to enhance the pumping efficiency of 808 nm and 980 nm LDs.

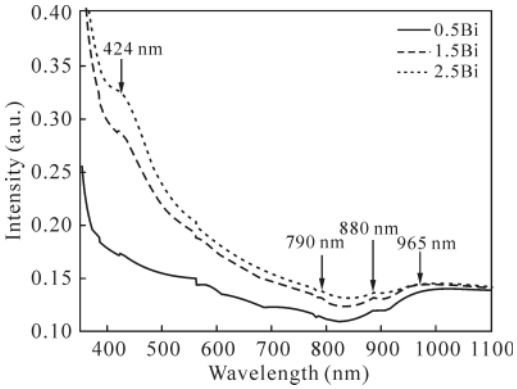

Fig.1 Absorption spectra of 0.5Bi, 1.5Bi and 2.5Bi samples

Fig.2 shows the emission spectra of Bi-doped glasses excited by 808 nm LD at room temperature, and the inset shows the relationship between emission intensity and Bi doping concentration. All glass samples exhibit broadband emission in the 1000−1600 nm wavelength region. The full width at half maximum (FWHM) is about 300 nm, which is wider than that of Bi-doped germanate glasses[14]. It can be seen from the inset that as Bi-dopant concentration is increased, the emission intensity increases rapidly initially and then decreases. When Bi_2O_3 concentration is 1.5 mol%, the highest emission intensity can be obtained. The decrease of emission intensity can be ascribed to the concentration quenching when the Bi_2O_3 concentration is over 1.5 mol%.

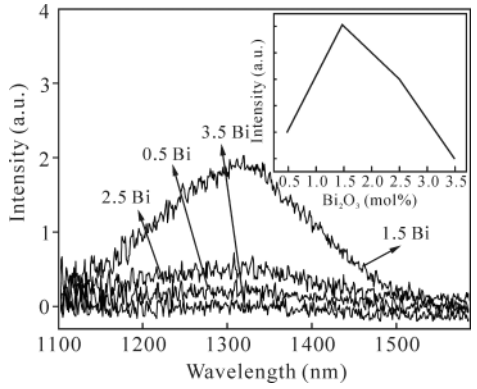

Fig.2 Emission spectra of Bi-doped glasses under 808 nm excitation

By assuming a Gaussian-shaped emission band, the stimulated emission cross-section σ_p at the band center can be estimated by[13]:

$$\sigma_p = \frac{\lambda_c^4}{4\pi n^2 \tau c}\left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} \frac{1}{\Delta\lambda} \quad , \tag{1}$$

where λ_c is the band center wavelength, $\Delta\lambda$ is the FWHM of the emission, n is the refractive index, τ is the fluorescence lifetime, and c is the speed of light in vacuum. The optical parameters of various Bi-doped glasses are shown in Tab.1. The value of σ_p is 0.73×10^{-20} cm^2 in the 1.5Bi glass at 808 nm excitation. This value is comparable to the reported values in Bi-doped germanate and phosphate glasses[6,14].

Tab.1 Optical parameters of various Bi-doped glasses

Samples	n	λ_c (nm)	$\Delta\lambda$ (nm)	τ (μs)	σ_p ($\times 10^{-20}$ cm^2)
$50TiO_2$-$25BaO$-$15SiO_2$ -$5B_2O_3$-$5Al_2O_3$-$1.5Bi_2O_3$	1.90	1320	300	490	0.73
$96GeO_2$-$3Al_2O_3$-$0.5Na_2O$ -$0.5Bi_2O_3$ [14]	1.62	1220	195	280	1.93
$85P_2O_5$-$15Al_2O_3$ -$1Bi_2O_3$ [15]	1.53	1300	300	500	1.00

The product of the stimulated emission cross-section and the lifetime, $\sigma_p \times \tau$, is an important parameter to characterize laser materials, because the laser threshold is proportional to $(\sigma_p \times \tau)^{-1}$. The value of $(\sigma_p \times \tau)$ for the 1.5Bi sample is 3.57×10^{-24} cm^2•s, which is much larger than that of Ti^{3+}:Al_2O_3 (1.4×10^{-24} cm^2•s)[6]. It indicates that Bi-doped titanate glasses prepared in this work are promising materials for optical amplifiers and tunable lasers.

The dependence of emission intensity of active Bi ions on Yb_2O_3 concentration is also presented in the inset of Fig.3. The amount of Bi is constant (1.5 mol%), while the concentration of Yb^{3+} is changed from 0 mol% to 4 mol%. Two emission peaks are observed in Bi/Yb co-doped glasses, which should be ascribed to the Yb^{3+} transition of $^2F_{5/2} \rightarrow {}^2F_{7/2}$ at 1020 nm and Bi-related centers at 1210 nm, respectively. The Bi-related emission centered at 1210 nm is highly enhanced in Bi/Yb co-doped glasses in comparison with that of the Bi singly-doped glass. And with the increase of Yb^{3+} concentration, the intensity of active Bi increases gradually. It can be ascribed to efficient energy transfer from Yb^{3+} to active Bi ions.

In order to investigate the energy transfer between active Bi ions and Yb^{3+}, the fluorescent decays for Yb ions near 1020 nm in Bi singly-doped and Bi/Yb co-doped glasses were

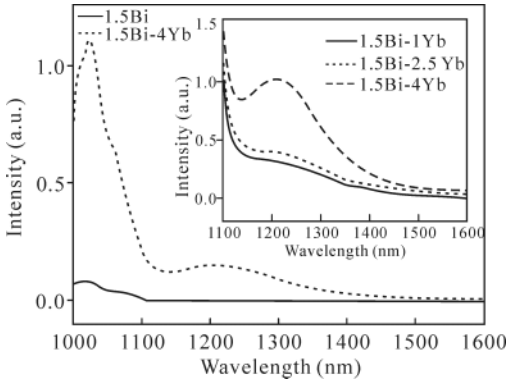

Fig.3 Emission spectra of 1.5Bi and 1.5Bi-4Yb glasses under 980 nm excitation

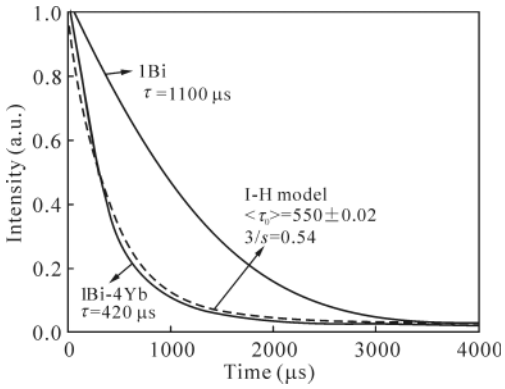

Fig.4 Fluorescence decay curves of active Bi ions near 1320 nm in Bi singly-doped and Bi/Yb co-doped glasses

measured at 808 nm excitation, and are shown in Fig.4 as solid lines. From the fluorescence decays, the average fluorescent lifetime can be calculated by[15]:

$$\tau_{\text{avg}} = \frac{\int I(t)t\,\mathrm{d}t}{\int I(t)\mathrm{d}t}\ , \tag{2}$$

where $I(t)$ is the luminescence intensity as a function of time t. In the Yb singly-doped sample, the decay of luminescence can be fitted to a nearly single exponential decay with the average lifetime of 1100 μs. However, when the Bi ions are introduced, the decay curves become nonexponential with the average lifetime, declining rapidly from 1100 ìs for Bi singly-doped sample to 420 ìs for Bi(1 mol%)/Yb(4 mol%) co-doped sample.

It is well known that the nonexponential fluorescent decay follows the Inokuti-Hirayama (I-H) model[16], in which the fluorescent decay can be expressed as

$$I(t) = I(0)\exp[-\frac{t}{\tau_0} - \frac{4}{3}\pi\Gamma(1-\frac{3}{s})R_0^3 N(\frac{t}{\tau_0})^{\frac{3}{s}}]\ , \tag{3}$$

where s=6, 8 and 10, denotes the electric dipole-dipole, dipole-quadruple and quadruple-quadruple interactions between luminescent centers, respectively, N is the doping concentration, $\tilde{A}(1\text{-}3/s)$ is a Gamma function, R_0 is the critical transfer distance, and $\acute{o}_0$ is the intrinsic radiative transition lifetime. The fitting curves are shown in Fig.4 as dotted lines. In the fitting processes, the value of $3/s$ is also obtained to be 0.54, that is to say that s is close to 6. This indicates that the energy transfer of electric dipole-dipole interaction is dominant in Bi/Yb co-doped glass.

The similar behaviors are also observed in Bi/Yb co-doped silicate glasses. Jian et al[12] has provided a possible mechanism of the energy transfer process between Bi ions and Yb ions in Bi/Yb co-doped silicate glasses. According to the absorption and emission spectra, a reasonable near emission mechanism is suggested in the following. Fig.5 shows the energy level diagram for Bi/Yb co-doped titanate glasses. At 980 nm excitation, Yb^{3+} ions are excited to $^2F_{5/2}$ level, and the energy is transferred to the excited state of active Bi ions, and then returns to the ground state. Hence, the enhanced emission of Bi-related centers at 1210 nm is observed.

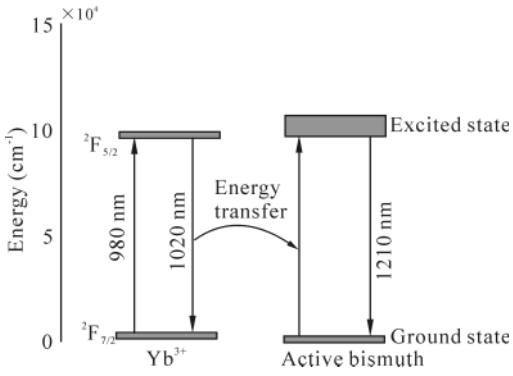

Fig.5 Possible energy transfer process of Bi/Yb co-doped titanate glasses excited by 980 nm

In conclusion, novel Bi-doped titanate glasses possess long fluorescence lifetime, broad FWHM and large product of the stimulated emission cross-section and the lifetime at 808 nm excitation. The addition of Yb_2O_3 can enhance the Bi-related emission intensity at 980 nm excitation. It should be ascribed to the energy transfer from Yb^{3+} to active Bi ions. The energy transfer of electric dipole-dipole interaction is dominant between active Bi ions and Yb^{3+} ions according to the I-H model. Bi-doped titanate glasses may be potential materials for broadband fiber amplifiers and tunable lasers.

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