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Spectroscopic properties of Er^{3+}/Yb^{3+} co-doped Bi_2O_3–B_2O_3–GeO_2 glasses

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Abstract

Er^{3+}/Yb^{3+} co-doped $60Bi_2O_3$–$(40-x)B_2O_3$–$xGeO_2$ (BBG; $x = 0$, 5, 10, 15 mol%) glasses that are suitable for fiber lasers, amplifiers have been fabricated and characterized. The absorption spectra, emission spectra, and lifetime of the $^4I_{13/2}$ level and quantum efficiency of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were measured and calculated. With the substitution of GeO_2 for B_2O_3, both $\Delta\lambda_{eff}$ and σ_e decrease from 75 to 71 nm and 9.88 to 8.12×10^{-21} cm^2, respectively. The measured lifetime of the $^4I_{13/2}$ level and quantum efficiency of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition increase from 1.18 to 1.5 ms and 36.2% to 43.2%, respectively. The emission spectra of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was also analyzed using a peak-fit routine, and an equivalent four-level system was proposed to estimate the stark splitting for the $^4I_{15/2}$ and $^4I_{13/2}$ levels of Er^{3+} in the BBG glasses. The results indicate that the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} can be exhibit a considerable broadening due to a significant enhance the peak A, and D emission.

Keywords: Bi_2O_3–B_2O_3–GeO_2 glasses; Spectroscopic properties; Stark splitting; Four-level system

1. Introduction

Glasses doped with various rare-earth ions are important materials for fluorescent display devices, optical detector, bulk lasers, optical fibers, waveguide lasers and optical amplifiers [1,2]. With the demand in high transmission capacity of wavelength-division-multiplexing (WDM) networks increased, special attention is paid to erbium ion due to its emission band at 1.53 μm which makes it an ideal element for broadband applications. Spectroscopic properties of Er^{3+} ions have been studied in many glass hosts, such as silicate [3], germanate [4], phosphate [5], fluoride [6], sulphide [7] and tellurite glasses [8], as well as more complicated glasses systems like $Na_2O{\cdot}Ca_3Al_2Ge_3O_{12}$ [9], probably better suited for fiber amplifiers. Er^{3+}-doped tellurite glass exhibits a large stimulated emission cross-section and broad fluorescence width at half maximum (FWHM) at 1.5 μm bands, but its poor glass thermal stability and strong upconversion phenomenon made it difficult to be used in practice [10]. Recently, Chen et al. [11] reported that Er^{3+}-doped binary bismuth-borate glasses showed good broadband properties. Oprea et al. [12] also presented the glass formation range (25–65 mol% Bi_2O_3) and spectroscopic properties of bismuth-borate glasses. However, to knowledge of the authors, the lifetime of the $^4I_{13/2}$ level and quantum efficiency of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in bismuth-borate is relative lower with a large number of B–O bonds with high-phonon energy (~1400 cm^{-1}). Therefore, the design of a new ternary bismuth-borate glass host with relative higher lifetime and quantum efficiency is very important at present.

In this article, we firstly investigate the effect of the germanium concentrations on the spectroscopic properties of Er^{3+}/Yb^{3+} bismuth-borate glasses. Especially, the effect on the effective width of the emission line, the stimulated emission cross-section, the lifetime of the $^4I_{13/2}$ level and quantum efficiency of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition are analyzed and discussed.

2. Experiment

Reagent grade commercial oxides (>99.9% pure) were used as the starting materials. Each bismuth-borate glass listed in Table 1 was externally doped with 0.5 mol% Er_2O_3 as an active and 2.5 mol% Yb_2O_3 as a sensitizer in the batch. Mixed batches were melted in alumina crucibles at 1100–1200 °C for about 60 min. For reducing OH^- content drying procedures

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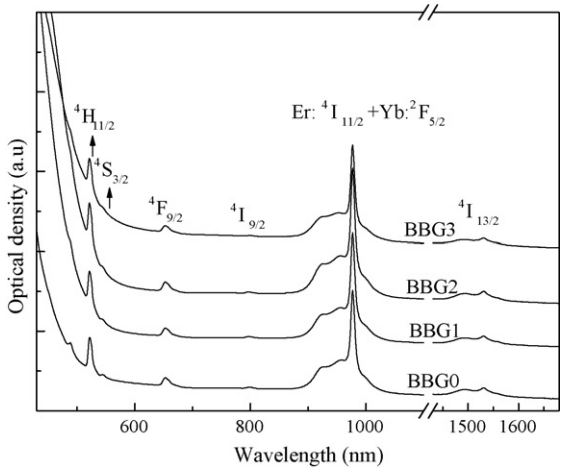

Fig. 1. Absorption spectra of Er^{3+}/Yb^{3+} co-doped BBG glasses.

were applied. Glass melt was bubbled with high purity oxygen. After completely melting, the glass liquids were poured into a stainless mold and then annealed to room temperature. The obtained glasses were cut and polished carefully to 10 mm × 10 mm × 1.2 mm in order to meet the requirements for optical measurements.

The densities were measured according to the Archimedes principle. Refractive indices were measured with SPA-4000 (made in Korea) on prism by coupler method. Absorption spectrum was recorded on a Perkin-Elmer 900UV–VIS–NIR spectrophotometer. The emission spectra were measured with a TRIAX550 spectrophotometer on excitation at 970 nm laser diode (LD). The fluorescence lifetime of Er^{3+}:$^4I_{13/2}$ level was measured with light pulses of 970 LD. The pulse modulation was performed to obtain a light pulse with 5 μs width. The decay traces were recorded on a digital oscilloscope and fitted by single exponential functions to obtain the decay rates.

All the measurements were measured at room temperature.

3. Results and discussion

3.1. Absorption spectra

Table 1 shows some basic physical properties, Er^{3+}/Yb^{3+} concentrations, and the absorption cross-section and stimulated emission cross-section of Er^{3+} for the BBG glasses.

Fig. 1 illustrates the typical absorption spectra of our glass samples between 460 and 1670 nm. Due to the strong absorption of the host glasses at ultraviolet range, the absorption bands at wavelength shorter than 460 nm could not be distinguished. Each assignment corresponds to the excited level of Er^{3+}. The intense absorption of $^2F_{5/2}$ level of Yb^{3+} is also observed at the wavelength region from 900 to 1000 nm, whereas the absorption of the $^4I_{11/2}$ level of Er^{3+} is hidden in this broad and intense band [4].

Absorption cross-section of a ground state absorption, σ_a, is given by [8]

$$\sigma_a(\lambda) = \frac{2.303 \log(I_0/I)}{NL} \quad (1)$$

where $\log(I_0/I)$ is the absorbance, L the thickness of the glass sample in cm, and N is the rare earth (RE) concentration per cm^3 in the glass. As seen in Table 1, the absorption cross-section of Er^{3+}:$^4I_{15/2} \rightarrow {}^4I_{13/2}$ for the BBG glasses decreases monotonically with the increase of GeO_2 content. The reason may be attributed to decreasing B_2O_3 content [13].

3.2. Emission spectra and cross-section

To the best of our knowledge, the effective width of the emission band $\Delta\lambda_{eff}$ for Er^{3+} ions at 1.5 μm is an important parameter for the EDFA used in the WDM network system of optical communication. The definition of the effective width $\Delta\lambda_{eff}$ is [12]

$$\Delta\lambda_{eff} = \int \frac{I(\lambda)\,d\lambda}{I_{max}} \quad (2)$$

where $I(\lambda)$ is the emission intensity at wavelength λ and the I_{max} is the emission intensity at peak emission wavelength. Because the 1.5 μm emission band of Er^{3+} ions in glasses is asymmetric, choosing the effective width $\Delta\lambda_{eff}$ rather than the full width at half maximum (FWHM) one is more reasonable [14,15].

The normalized emission spectra of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for the BBG glasses are shown in Fig. 2. The dotted lines are the deconvolved Gaussian amplitude peaks fitted to BBG0 glass. The value of $\Delta\lambda_{eff}$, the peak wavelength, width and respective intensity of sub-components peak (A–D) emission of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for the BBG glasses are listed in Table 2. Obviously, it can be seen that the value of $\Delta\lambda_{eff}$ decreases slightly with the increase of GeO_2 content. The shorter wavelength, wider width and higher intensity of sub-components peak A and D emission can be inducing larger inhomogeneous broadening of Er^{3+}:$^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for the BBG glasses. The reason may be explained as follows: with the substitution of GeO_2 for B_2O_3, the number of the borate groups [BO_3] trigonal and [BO_4] tetrahedral units in the network structure decreases. Therefore the degree of structural disorder in the glass samples decreases with the increase of GeO_2 content [11]. As a result, the Stark level splitting of the Er^{3+} ions decrease and lead to the decrease of $\Delta\lambda_{eff}$.

Table 1
The compositions, refractive indices, densities, Er^{3+}/Yb^{3+} concentrations, and absorption cross-section and emission cross-section of Er^{3+} ions for the BBG glasses

Sample codes	Composition (mol%)	ρ (g cm^{-3})	n	N_{Er}/N_{Yb} ($\times10^{20}$ cm^{-3})	σ_a ($\times10^{-21}$ cm^2)	σ_e ($\times10^{-21}$ cm^2)
BBG0	$60Bi_2O_3$—$40B_2O_3$	7.188	2.384	1.407/7.037	8.88	9.88
BBG1	$60Bi_2O_3$—$35B_2O_3$—$5GeO_2$	7.007	2.388	1.363/6.817	7.87	8.71
BBG2	$60Bi_2O_3$—$30B_2O_3$—$10GeO_2$	6.981	2.393	1.349/6.749	7.44	8.29
BBG3	$60Bi_2O_3$—$25B_2O_3$—$15GeO_2$	6.413	2.397	1.232/6.616	7.23	8.12