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Super broadband near-infrared emission and energy transfer in Bi–Er co-doped lanthanum aluminosilicate glasses

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1. Introduction

The demanding for increasing transmission capacity of the wavelength division-multiplexing (WDM) system is indispensable due to the rapid development of computer network and optical telecommunication. Expending the gain bandwidths of the fiber amplifiers and the laser sources seems to be an effective method. However, it is difficult for the gain bandwidth of traditional rare-earth ions doped optical fiber amplifiers (e.g., Er³⁺, Pr³⁺, Tm³⁺) to be surpassed 100 nm due to the f-f electronic transition nature of rare-earth-ions [1,2]. Although Er³⁺-doped fiber amplifier (EDFA) was available, its bandwidth was limited in silicate hosts to a maximum of 40 nm at the C band. Er³⁺-Tm³⁺ co-doped glasses which were proposed for the broadband amplification in the S+C bands [3–5]. However, the bandwidth of all these rare-earth-doped glasses could not cover the whole low-loss optical fiber transmission window. This has provoked intense research on novel types of amplifier materials with broader emission bandwidth at the best covering of the ultra-low attenuation telecommunication windows of silica glass fiber.

Recently, Fujimoto had reported a new broadband infrared emission from Bi-doped silica glasses and realized 1300 nm optical amplification with 800 nm excitation, which provided a promising candidate for broadband optical fiber amplifiers and tunable lasers [6,7]. Subsequently, a wide variety of traditional glass hosts containing Bi were not only investigated so far, mainly silicates

ABSTRACT

The Bi–Er co-doped lanthanum aluminosilicate glasses, which exhibited a broadband near-infrared emission, were developed and observed in using the optical absorption and photoluminescence spectra. A super broadband near-infrared emission extending from 1.0 to 1.8 μ m with a full-width at half-maximum of 450 nm which covered the whole O, E, S, C and L bands, was observed in Bi–Er co-doped samples under 808 nm excitation, as a result of the overlap of the Bi-related emission band (1270 nm) and the emission from Er^{3+ 4}I_{13/2} \rightarrow ⁴I_{15/2} transition (1545 nm). This report will discuss about a possible mechanism for energy transfer between Bi-related centers and Er³⁺ ion.

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[8–10] and germinate [11–13] but also phosphates [14] and borates [15]. For their intriguing spectral properties, research on Bidoped devices has rapidly progressed from the first demonstration of lasing to efficient all-fiber optical amplifiers and lasers [16–18].

In recent years, rare-earth and Bi co-doped glasses had received some attention. Few reports had observed the ultra-broadband near-infrared (NIR) emission from 1000 to 1600 nm, including all the O. E. S. C and L bands in rare-earth and Bi co-doped glasses [19-22]. Compared with other glass hosts, silicate glasses were more remarkable for their compatibility with the commercial silica fiber network. They could potentially be easier to incorporate into existing silica fiber networks and had the potential for low-loss transmission. In addition, silicate glasses had the most chemically and mechanically stable and could be fabricated into various shapes such as a rod and optical fiber [23]. On the other hand, compared with M-O bond-strengths of alkali- and alkali earth-based glasses, La-O bonds are stronger due to the high field-strength of La³⁺ ions. Lanthanum aluminosilicate glasses exhibited high glass transition temperatures ranging from 800 to 900 °C, which was virtually independent of the composition [24]. The excellent physical properties and lower optical basicity made lanthanum aluminosilicate glasses to be potential hosts for bismuth doping.

Based on all above considerations, in this study, we report on broadband NIR luminescence properties in Bi–Er co-doped $10La_2O_3-30Al_2O_3-60SiO_2$ (LAS) glasses, the observation of emission with an FWHM of 450 nm covering the whole O, E, S, C and L bands using the pump excitation at 808 nm, and the discussion of possible energy transfer processes between Bi⁺ and Er³⁺ ions.





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2. Experimental details

Sample glasses were prepared by a conventional melting method with compositions of $(10 - x)La_2O_3-30Al_2O_3-60SiO_2-1Bi_2O_3-xEr_2O_3$ (LASBE-1) (in mol%, x = 0, 0.02, 0.05, 0.08 and 0.12) and 9.9La_2O_3-30Al_2O_3-60SiO_2-yBi_2O_3-0.1Er_2O_3 (LASBE-2) (in mol%, y = 0, 1, 1.5 and 2). Reagents of SiO_2 (99.99%), Al_2O_3 (99.99%), La_2O_3 (99.99%), Bi_2O_3 (99.99%) and Er_2O_3 (99.99%) were used as raw materials. The mixtures (about 10 g), which compacted into a platinum crucible, were set in an electric furnace. After holding at 1600 °C for 1 h under air atmosphere, the melts were quenched by putting it onto a polished plate of stainless steel. All the glasses were annealed at 600 °C for 6 h to remove thermal strains. The samples were cut into the size of 10 mm × 10 mm × 2 mm and polished for optical measurements.

The HITACHI U-4100 spectrophotometer was used to measure the optical absorption spectra at the wavelength range from 400 to 2000 nm, and the ZOLIX SBP300 spectrophotometer with an InGaAs detector with pumping excitation under 808 nm was used to measure the fluorescence spectra at the wavelength range from 900 to 1800 nm. All the spectral measurements were performed at the ambient temperatures.

3. Results and discussion

Fig. 1 shows the absorption spectra of Bi–Er co-doped glasses. The inset is absorption spectrum of un-doped LAS glass. Comparing with the un-doped glass, two strongly pronounced peaks at 500 and 700 nm and a shoulder at 800 nm were observed in Bi-doped glasses (Fig. 1a), which indicated that the absorption band might be from the transitions of Bi ions. The nature of Bi-related luminescence properties was still controversial. Hypotheses of the near IR luminescence origin from Bi⁺, Bi clusters, elemental clustering such as Bi_2^-/Bi_2 , interstitial negative charged Bi dimers ${}^2Bi_2^-/Bi_2^{--}$ and others have been studied [14,25-29]. However, there were no direct proofs to confirm any of these hypotheses until now. In this study, we inclined to ascribe the origin of the luminescence to Bi⁺ ion [14,22,25]. Accordingly, the absorption bands centered at ${\sim}500$ nm, ${\sim}700$ nm and ${\sim}800$ nm might correspond to the transitions from the ground state of ³P₀ to the excited states ¹S₀, ¹D₂, ³P₂ respectively, and the ~1300 nm emission was due to the ${}^{3}P_{1} \rightarrow {}^{3}P_{0}$ transition [19].



Fig. 1. Absorption spectra of (a) LAS: $1 \text{ mol}\% \text{ Bi}_2\text{O}_3$, (b) LAS: $0.1 \text{ mol}\% \text{ Er}_2\text{O}_3$ and (c) LAS: $1 \text{ mol}\% \text{ Bi}_2\text{O}_3$, $0.1 \text{ mol}\% \text{ Er}_2\text{O}_3$. Inset is absorption spectrum of un-doped glass.



Fig. 2. Fluorescence spectra of (a) 10La₂O₃-30Al₂O₃-60SiO₂-1Bi₂O₃, (b) 9.95La₂O₃-30Al₂O₃-60SiO₂-0.05Er₂O₃ and (c) 9.95La₂O₃-30Al₂O₃-60SiO₂-1Bi₂O₃-0.05Er₂O₃.



Fig. 3. Fluorescence spectra of LASBE-1 glasses under the excitation of 808 nm LD.



Fig. 4a. Fluorescence spectra of LASBE-2 glasses under the excitation of 808 nm LD.

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