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Novel Bi-doped glasses for broadband optical amplification

Jianrong Qiu^{a,b,*}, Mingying Peng^b, Jinjun Ren^b, Xiangeng Meng^b, Xiongwei Jiang^b, Congshan Zhu^b

^a State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China ^b State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

Abstract

Broadband infrared luminescence is observed in various Bi-doped oxide glasses prepared by conventional melting-quenching technique. The absorption spectrum of the Bi-doped germanium oxide glass consists of five broad peaks at below 370, 500, 700, 800 and 1000 nm. The fluorescence spectrum exhibits a broad peak at about 1300 nm with full width at half maximum (FWHM) of more than 300 nm when excited by an 808 nm laser diode. The fluorescence lifetime at room temperature decreases with increasing Bi_2O_3 concentration. Influence of the glass composition and melting atmosphere on the fluorescence lifetime and luminescent intensity is investigated. The mechanism of the broadband infrared luminescence is suggested. The product of stimulated emission cross-section and lifetime of the Bi-doped aluminophosphate glass is about 5.0×10^{-24} cm² s. The glasses might be promising for applications in broadband optical fiber amplifiers and tunable lasers.

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1. Introduction

The demand for increasing transmission capacity of wavelength-division-multiplexing (WDM) system is indispensable due to the rapid development of computer network and optical telecommunication. As the number of information transmission channels depends strongly on the gain bandwidth of the optical amplifiers and laser sources, the gain bandwidth of optical amplifiers must be expanded in order to develop WDM systems with ultra large transmission capacity. Considerable efforts have been devoted to achieve broadband optical amplification in the past decades, which are mainly focused on the development of rare-earth ions (e.g. Er^{3+} , Pr^{3+} , and Tm^{3+}) doped opti-

E-mail address: qjr@zju.edu.cn (J. Qiu).

cal fiber amplifiers and Raman amplifiers [1–4]. However, in the case of rare-earth ions doped optical amplifiers, the gain bandwidth is less than 100 nm due to the f–f electronic transition nature of rare-earth ions. Even all the developed optical fiber amplifiers are combined in parallel or in series, we still can not fully use the ultra-low attenuation telecommunication windows of silica glass fiber.

It is well known that transition metal ions (e.g. Cr^{4+}) may yield broadband emission in the infrared wavelength region due to the d–d transitions, which have been paid much attention in the recent years. Widely tunable lasers, such as Cr^{4+} : YAG, have been developed for practical applications. But, it is difficult to control the valence state of Cr ion in glasses, and no net gain has been achieved in Cr ion-doped glasses up to now. Recently, Fujimoto et al. discovered broad band infrared luminescence in Bidoped silica glass and successfully realized its optical amplification at 1300 nm under 0.8 µm laser diode (LD)

^{*} Corresponding author. Address: State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China.

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excitation [5,6]. However, the mechanism of the broadband luminescence is still not clear, and it is also important to develop a multi-component glass with superior properties from the point view of practical application. We systematically studied the infrared luminescence properties of various Bi-doped oxide glasses [7,8]. Recently, we also have observed net gain at 1.3 μ m from Bi-doped germanate glasses [9].

In this article, we present our recent research development on Bi-doped glasses for broadband optical amplification. We report on Bi-doped germanium oxide glasses with the long fluorescence lifetime and broadband infrared luminescence at about 1300 nm with FWHM of more than 300 nm. The near infrared broadband emission of Bi-doped barium aluminoborate and aluminophosphate glasses was also investigated and compared. Based on our systematic investigations, we suggest that the infrared emission may be ascribed to transitions of Bi^+ ions. The product of stimulated emission cross-section and fluorescence lifetime of the glasses was also evaluated.

2. Experimental

Bi-doped oxide glass samples were prepared by the conventional melting-quenching technique. Analytical pure regents of GeO₂, Al(OH)₃, CaCO₃, BaCO₃, B₂O₃, NH₄H₂PO₄ and Bi₂O₃ were used as raw materials. The batch was mixed homogenously in an agate mortar, and then melted at 1550 °C in a high pure alumina crucible for 20 min in air. Consequently the molten was cast onto a stainless steel plate. The transparent and bubble-free samples were cut in the size of $10 \times 10 \times 1 \text{ mm}^3$ and polished for optical measurements.

The optical absorption spectra and the infrared luminescence spectra of the samples were measured using JASCO V-570 spectrophotometer and ZOLIX SBP300 spectrofluorometer with InGaAs as detector in 850–1800 nm with the excitation of the 808 nm laser diode (LD), respectively. The lifetime, τ , measurement was carried out by exciting the sample with a modulated 808 nm LD with a maximum power of 2 W. The signal detected by a PbS photodetector was recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were carried out at room temperature.

3. Results and discussions

3.1. Bi-doped germanium oxide glasses

Fig. 1 shows the transmittance spectrum of $96\text{GeO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3$ glass sample. There are five peaks at below 370, 500, 700, 800 and 1000 nm. The former four peaks were similar to, but the last one was absent in those of SiO₂:Al, Bi glass [5]. Since the band-gap absorption of glassy GeO₂ was at 5.63 eV (221 nm) [10] and the absorption edge of the Bi₂O₃-based glass was at about 475 nm



Fig. 1. Transmission spectrum of $96GeO_2 \cdot 3Al_2O_3 \cdot 1Bi_2O_3$ glass.

[11], the band at below 370 nm can therefore be assigned to the glass matrix.

Fig. 2 shows the fluorescence spectrum of $96\text{GeO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 1\text{Bi}_2\text{O}_3$ glass sample, excited by a GaAlAs laser diode with wavelength of 808 nm. A broad peak was observed at about 1300 nm with FWHM of 320 nm. The decay of the 1300 nm emission excited by the commercial 808 nm wavelength LD at room temperature is shown in Fig. 3. The fluorescence lifetime was measured to be about 254.5 μ s. The decay curve was close to the first-order exponential decay. The 808 nm-pumping scheme has offered a potential advantage of using high power semiconductor lasers, which are commercially available. Therefore, the broad emission with excitation source at 808 nm, as well as the long lifetime in the present Bi and Al codoping glasses, provided a significant route to develop the broadband fiber and planar laser and amplifiers.

As discussed in Ref. [5], the lifetime and the band-location in both absorption and emission spectra of Bi and Al codoping GeO₂ glasses were distinguishably different from not only Bi²⁺ ions but also Bi³⁺ ions doped materials. For example, the lifetimes of Bi³⁺-doped sodium borates or phosphates glasses were less than 4 µs [12]. Fujimoto and Nakatsuka [5] ascribed the absorption and the emission spectra of Bi and Al ions codoping silica glasses to the transitions between the ground state of ¹S₀ and the excited



Fig. 2. Fluorescence spectrum of $96GeO_2 \cdot 3Al_2O_3 \cdot 1Bi_2O_3$ glass excited by an 800 nm laser diode.

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