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Investigations on bismuth and aluminum co-doped germanium oxide glasses for ultra-broadband optical amplification

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Abstract

The broadband luminescence covering 1.2–1.6 μm was observed from bismuth and aluminum co-doped germanium oxide glasses pumped by 808 nm laser at room temperature. The spectroscopic properties of GeO_2:Bi,Al glasses strongly depend on the glass compositions and the pumping sources. To a certain extent, the Al^{3+} ions play as dispersing reagent for the infrared-emission centers in the GeO_2:Bi,Al glasses. The broad infrared luminescence with a full width at half maximum larger than 200 nm and a lifetime longer than 200 μs possesses these glasses with the potential applications in broadly tunable laser sources and ultra-broadband fiber amplifiers in optical communication field.

PACS: 42.70.Km; 78.60.−b; 78.20.Ci; 42.60.Da

1. Introduction

The demand for the information transportation system with much higher transmission capacity and much faster bit rates results in the extraordinarily increasing utilization of the wavelength division multiplexing (WDM) system in the telecommunication field [1]. To achieve the more efficient WDM transmission network, one of attractive approaches is to increase the transmission-channel number through broadening the gain bandwidth of the laser sources and the fiber amplifiers. Therefore, exploration of new broadband luminescent materials especially covering the 1.2–1.6 μm region and possessing much larger full width at half maximum (FWHM) becomes a key step to further develop the broadband fiber amplifiers and the broadly tunable laser sources. In the past years, more studies have been performed on the rare earth ion, e.g., Er^{3+}, Tm^{3+} or Pr^{3+}, doped materials [2,3]. However, the work bandwidths of such materials hardly surpass 100 nm since the emissions in near infrared region are mainly initiated from the forbidden f–f transitions between the inner-shell 4f orbits of the rare earth ions. On the contrary, the broad emissions with FWHM larger than 100 nm can be easily achieved with transition-metal-ion-doped materials, because the emissions originate from the d–d transitions of transition-metal ions [4–6]. For example, broadband emission in 1.2–1.6 μm was observed with FWHM wider than 200 nm from Cr^{4+}- or Ni^{2+}-doped glasses [5,6]. Recently, Fujimoto and Nakatsuka reported a novel infrared luminescence from bismuth-doped silicate glass and realized its optical amplification

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at 1.3 μm with 0.8 μm excitation [7,8]. Subsequently, our group also observed the 1.3 μm emission with FWHM more than 300 nm in aluminum and bismuth co-doped germanium oxide glasses pumped by the 808 nm laser diode [9]. All the previous works have clearly demonstrated that co-doping of aluminum into bismuth-doped glasses is indispensable for the occurrence of the broadband infrared luminescence [7,9]. However, it is still unknown up to now what role the aluminum ion plays in the generation of infrared luminescence. In addition, no systematic investigations have been carried out on the effect of the principle glass composition on luminescent properties of GeO_2:Bi,Al glasses.

In this work, we firstly investigate the effects of the bismuth or aluminum concentrations and the pumping sources on the luminescent properties of GeO_2:Bi,Al glasses, and then study the possible role of aluminum in infrared luminescence of GeO_2:Bi,Al glasses and finally discuss the luminescent mechanism.

2. Experimental

The compositions of the glass samples prepared in this study are $(100 - x - y)GeO_2 \cdot xBi_2O_3 \cdot yAl_2O_3$ where $x = 0$, 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0 and $y = 0$, 1, 2, 3, 4, 5, 6, 8, respectively. Twenty grams batch for each sample was prepared from commercial powders of high-purity GeO_2 (99.999%), analytic reagent $Al(OH)_3$ and Bi_2O_3 by mixing homogenously in an agate mortar. Each batch was melted at 1540 °C in a high-pure alumina crucible for 20 min in air, and then quickly cast onto a stainless steel plate and finally annealed at 600 °C for 2 h. All the prepared and selected glass samples were transparent and bubble-free through the inspection by an optical microscope. The glass specimens were cut and polished into the appropriate shape and thickness for measurements.

All the samples were confirmed to be amorphous by X-ray diffraction (XRD) patterns recorded on a Bruker D4 X-ray diffractometer at 40 kV/20 mA with Cu Kα1 ($\lambda = 1.5405$ Å) as a radiation source. Absorption spectra were recorded with JASCO V-570 spectrophotometer from 400 to 1500 nm using the sample with a thickness of approximately 1 mm. Infrared emission spectra were measured using ZOLIX SBP300 spectrofluorometer with InGaAs as detector in 850–1800 nm. A 50 mW double frequency YAG: Nd laser with 532 nm wavelength, a 50 mW He–Ne laser with 632.8 nm wavelength and a 135 mW InGaAs semiconductor laser diode with 808 nm wavelength were chosen as the excitation sources. Lifetime measurements were carried out by exciting the sample with a modulated 808 nm laser diode with a maximum power of 2 W. The signal detected by an InGaAs photodetector in TRIAX550 was recorded using a Tektronix TDS3052 storage digital oscilloscope. X-band ESR spectra in the case of $v = 9.82$ GHz were obtained with a Bruker model ER200D-SRC spectrometer under microwave power of 20 MW. The polished glass sample hardness was measured using a HXD-1000 microhardness instrument under an applied load of 100 g. The refractive index was measured on the prism minimum deviation method. All the above measurements were taken at room temperature. Differential thermal analysis (DTA) curve was measured with a CRY-Z Differential Thermal Analyzer at a heating rate of 10 °C min^{-1} using aluminum oxide ceramic pans.

3. Results

3.1. Effect of bismuth concentration

Figs. 1 and 2 show the absorption and fluorescent spectra of $(97 - x)GeO_2 \cdot xBi_2O_3 \cdot 3Al_2O_3$ ($x = 0.01$, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0) glasses, respectively. As can be seen from Fig. 1, there are four absorption peaks at about 500, 700, 800 and 1000 nm, respectively. With the bismuth concentration increasing, the peak of the 500 nm band shifts towards shorter wavelength from about 560 nm gradually to 500 nm while the peak of the 700 nm band shifts towards the reverse direction. And the latter two bands remain almost unshift. At the same time, as shown in Fig. 2, the strongest emission peak moves towards longer wavelength, viz. 1100 nm for $x = 0.01 \rightarrow 1254$ nm for $x = 0.05 \rightarrow 1260$ nm for $x = 0.1 \rightarrow 1284$ nm for $x = 0.5 \rightarrow 1300$ nm for $x = 1.0 \rightarrow 1305$ nm for $x = 1.5 \rightarrow 1310$ nm for $x = 2.0$. Furthermore, with increasing x value, the fluorescent intensity monotonically increases until $x = 0.5$, and then decreases, showing that the critical dopant concentration is about 0.5 mol%.

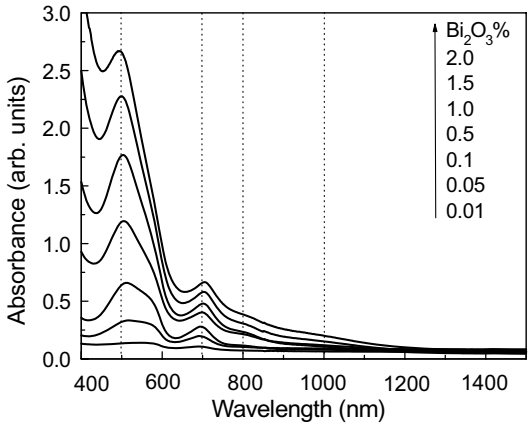

Fig. 1. Absorption spectra of $(97 - x)GeO_2 \cdot 3Al_2O_3 \cdot xBi_2O_3$ ($x = 0.01$, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0) glasses.