



# Effect of cerium oxide and niobium oxide addition on absorption and emission properties of bismuth doped silicate glasses



Jinyan Li, Lei Liao, Yingbo Chu, Peng Liu, Haiqing Li, Jinggang Peng, Nengli Dai \*

Wuhan National Laboratory for Optoelectronics, School of Optoelectronics Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

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## ABSTRACT

Ce/Bi and contrastive Nb/Bi co-doped silicate glasses were prepared to investigate the effects of  $\text{CeO}_2$  and  $\text{Nb}_2\text{O}_5$  on the absorption and emission properties. Based on the spectrum measurement, interestingly it was found that the changes about valance state of Bi ions in  $\text{SACB-xCeO}_2$  and  $\text{SCB-yNb}_2\text{O}_5$  are different. Furthermore, near-infrared (NIR) emission intensity all decreased with the addition of oxidizing agents. It may provide an evidence for the low valance state bismuth ( $\text{Bi}^+$ ,  $\text{Bi}^0$ ) ions being the broadband NIR active center. According to the spectral changes, we also discussed the existence form of Ce ions and Nb ions in the chemical environment around NIR active center and the possible energy level transformations of NIR emission.

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## 1. Introduction

Owing to the rapid development of data traffic in telecommunication, broadband amplifiers and tunable lasers for telecommunication widows are indispensable for dense wavelength division multiplexing (DWDM) network systems. For another, numerous applications in the spectral region of 1150–1500 nm desired some efficient solid-state (fiber) laser sources. Generally speaking, Raman fiber lasers can achieve laser at any wavelength with appropriate pump sources [1]. However, Raman fiber lasers also have some inevitable drawbacks, such as the other harmful nonlinearity and limitations in the pulse-mode operation. Thus, bismuth doped materials are promising as a new medium for fiber lasers and ultra-broadband optical fiber amplifier covering the entire telecommunication window, since the broadband NIR luminescence in Bi-doped silica glass was discovered in 2001 [2]. Over the past decade, there has been increasing interest in the development of many Bi-doped glasses (silicate, germanate, aluminophosphate, aluminoborate) [2–8] and Bi-doped fiber lasers [9–13]. Though significant progress has been achieved in this field, the origin of near-infrared photoluminescence remains still unclear. There are some papers that attribute the origin to  $\text{Bi}^{5+}$  [2],  $\text{Bi}^+$  [5], Bi clusters [14], or Bi dimmers [15]. Concerning the question as to which bismuth-related species is the NIR emission

center, experimental evidence presently exists for both sides, that is, bismuth in higher or lower valance state [2,5,16]. With our previous research, it is found that Si powder added into a glass component can strengthen effectively the NIR emission from Bi-doped glass [17]. Because the Si powder has reducibility, it can be speculated that the enhancement of NIR emission derives from the bismuth ions to the transition of the lower valance state. However, it is difficult to illustrate that the NIR emission of bismuth glasses results from low bismuth valance state, just depending on this phenomenon. It seems to be necessary to research the variation of bismuth valance state in bismuth doped silicate glasses added a small quantity of oxidizing agent.

As we know, the rare earth element of cerium is usually used as an oxidizing agent [18]. Therefore, bismuth doped silicate glasses with a small quantity of cerium oxide were prepared. However, just a kind of oxidizing agent added to glasses is a little hard to cause plentiful existence of bismuth valance states. Considered in this situation, another kind of bismuth doped silicate glasses with a large number of niobium oxide was prepared to contrast with the bismuth doped silicate glasses with cerium oxide. According to this idea, in our works, Ce/Bi and Nb/Bi co-doped silicate glasses were prepared, and the effects of  $\text{CeO}_2$  and  $\text{Nb}_2\text{O}_5$  addition on absorption and emission properties of the bismuth-doped silicate glasses were investigated. By analyzing the variations of bismuth valance state and combining with the former research on the effect of Si powder, it may be valid evidence that proves that the lower valance bismuth is the active center of NIR luminescence in

\* Corresponding author.

E-mail address: [dainl@mail.hust.edu.cn](mailto:dainl@mail.hust.edu.cn) (N. Dai).

bismuth silicate glasses. Furthermore, according to the relations between the absorption and emission spectra and energy-level diagrams for the two kinds of lower valence state bismuth ( $\text{Bi}^0$ ,  $\text{Bi}^+$ ), the NIR emissions corresponding to energy level transition are discussed.

## 2. Experimental

The glass samples were prepared by the melting-quenching technique. The high-purity reagents  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CeO}_2$  and  $\text{Nb}_2\text{O}_5$  were selected as raw materials. The batch corresponding to the composition of  $65\text{SiO}_2-10\text{Al}_2\text{O}_3-25\text{CaCO}_3-2\text{Bi}_2\text{O}_3-x\text{CeO}_2$  ( $x = 0$  mol%, 0.05 mol%, 0.1 mol%, 0.2 mol%, designated as SACB- $x\text{CeO}_2$  glasses) and  $(70-y)\text{SiO}_2-30\text{CaCO}_3-1.5\text{Bi}_2\text{O}_3-y\text{Nb}_2\text{O}_5$  ( $y = 0$  mol%, 10 mol%, 15 mol%, 20 mol%, designated as SCB- $y\text{Nb}_2\text{O}_5$  glasses) were mixed homogeneously in an agate mortar. Then the batch melted at  $1550^\circ\text{C}$  in an alumina crucible for 2 h. Consequently the melt was quickly cast onto a stainless steel plate and annealed in an electric furnace at  $550^\circ\text{C}$  for 1.5 h to release stress induced during the quenching process. The prepared samples were cut into the size of  $15\text{ mm} \times 15\text{ mm} \times 2\text{ mm}$  and polished for optical measurements.

The absorption spectra in the wavelength range of 200–1100 nm were measured by a PerkinElmer Lambda 35 spectrophotometer. The fluorescence spectra in the range of 300–850 nm were measured by a Jasco FP-6500 fluorescence spectrophotometer. The fluorescence spectra in the wavelength range of 800–1650 nm were measured on a ZOLIX SBP300 spectrophotometer. The fluorescence lifetime measurements were carried out by exciting the samples with a modulated 808 nm LD at 1290 nm. The signals detected by an InGaAs photodetector in a TRIAX550 spectrofluorometer were recorded using a storage digital oscilloscope (Tektronix TDS3052). All the measurements were carried out at room temperature in air.

## 3. Results and discussion

### 3.1. Absorption spectra

Figs. 1 and 2 show the absorption spectra of the SACB- $x\text{CeO}_2$  ( $x = 0$  mol%, 0.05 mol%, 0.1 mol%, 0.2 mol%) glasses and the SCB- $y\text{Nb}_2\text{O}_5$  ( $y = 0$  mol%, 5 mol%, 10 mol%, 15 mol%, 20 mol%) glasses, respectively. As can be seen from Fig. 1, there are five obvious absorption peaks at about 300, 473, 700, 808 and 980 nm, respectively. The strong absorption at 300 nm can be considered to be the absorption edge of bismuth-doped glasses [19]. With the introduction of oxidizing agent  $\text{CeO}_2$  and the increment of concentration, the absorption intensity at 473, 700, 800 and 980 nm related to Bi active centers weakens gradually, and

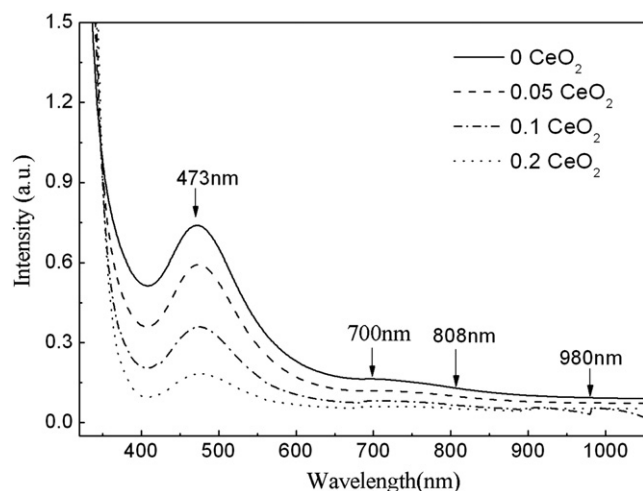


Fig. 1. Absorption spectra of the SACB- $x\text{CeO}_2$  ( $x = 0$  mol%, 0.05 mol%, 0.1 mol%, 0.2 mol%) glasses.

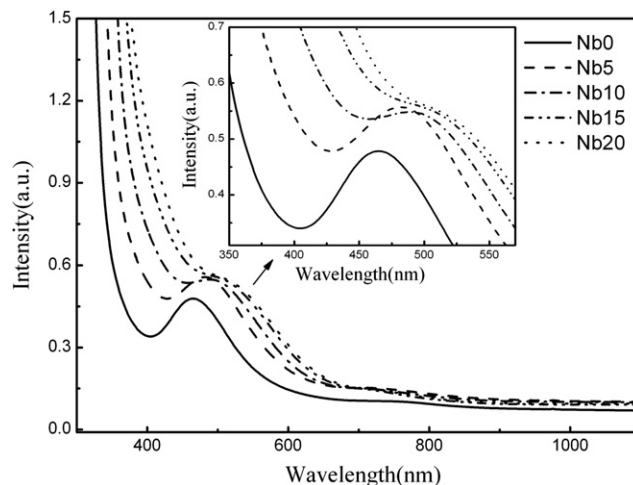


Fig. 2. Absorption spectra of the SCB- $y\text{Nb}_2\text{O}_5$  ( $y = 0$  mol%, 5 mol%, 10 mol%, 15 mol%, 20 mol%) glasses.

simultaneously the colors of the glass samples change gradually from reddish-brown to a light color. At the same time, as showed in Fig. 2, the five parallel absorption peaks are observed. However, since the concentration of  $\text{Nb}_2\text{O}_5$  in SCB- $y\text{Nb}_2\text{O}_5$  is much higher than the concentration of  $\text{CeO}_2$  in SACB- $x\text{CeO}_2$ , the background loss caused by  $\text{Nb}_2\text{O}_5$  would be the main factor that affects the absorption spectra. So with the increment of  $\text{Nb}_2\text{O}_5$  concentration, the absorption peaks have a few enhancements, especially at around 473 nm, and the ultraviolet absorption edge and the above-mentioned peak shift toward longer wavelength. Meanwhile, there is a tendency that the absorption peak at 473 nm is covered up by the ultraviolet absorption edge. Inset of Fig. 2 presents the magnified patterns of Fig. 2 at the range of 350–600 nm. According to research from Mizoguchi [20], the red shift of absorption edge is originated from the increment of the  $\text{Bi}^{5+}$  concentration. In Fig. 1, the analogous phenomenon of red shift is not observed. It can be explained that the oxidizing atmosphere in SACB- $x\text{CeO}_2$  is not intense compared with the oxidizing atmosphere in SCB- $y\text{Nb}_2\text{O}_5$ . Because of the lower oxidability, it is difficult to oxidize the bismuth to the  $\text{Bi}^{5+}$  ions in the glasses. But the significantly weaker absorption bands at 473 nm related to bismuth NIR active centers can prove that the bismuth NIR active centers reduce because of the addition of oxidizing agent  $\text{CeO}_2$ . Meanwhile, in Fig. 2 with a large number of  $\text{Nb}_2\text{O}_5$  added to the glasses, we observe that a majority of bismuth in the glasses are oxidized into the  $\text{Bi}^{5+}$  ions that lead to the red shift of absorption edge.

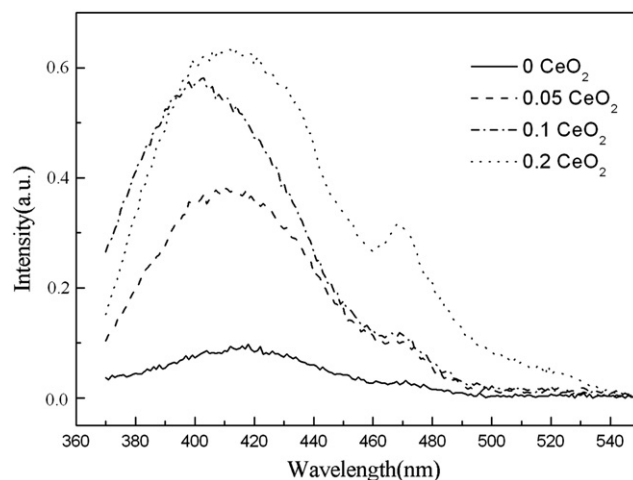


Fig. 3. Fluorescence spectra of the SACB- $x\text{CeO}_2$  ( $x = 0$  mol%, 0.05 mol%, 0.1 mol%, 0.2 mol%) glasses when excited by 280 nm.

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