



Effects of copper ions on the near-infrared luminescence in Bi doped silicate glass via copper for sodium ion exchange



Xijia He^{a,b}, Xuhui Xu^a, Dacheng Zhou^a, Cuiqiong Yan^b, Jianbei Qiu^{a,*}

^a College of Materials Science and Engineering, Kunming University of Science and Technology, Xuefu RD, Kunming 650093, Yunnan, China

^b College of Physics and Electronic Engineering, Qujing Normal University, Sanjiang RD, Qujing 655011, Yunnan, China

ARTICLE INFO

Article history:

Received 12 March 2015

Received in revised form 9 April 2015

Accepted 11 April 2015

Available online 21 April 2015

Keywords:

Bismuth;

Near infrared luminescence;

Copper for sodium ion exchange

ABSTRACT

The copper (Cu) atoms were incorporated into the bismuth (Bi) doped silicate glasses by the copper for sodium (Cu–Na) ion exchange method. After the ion exchange process, the Cu ions were introduced into the glass matrix with different copper valence states, namely, Cu⁰, Cu⁺, and Cu²⁺. Bi³⁺ ions could be reduced to lower valence states of Bi containing Bi near infrared (NIR) active centers with the incorporation of the Cu ions, resulting in the enhancement of the Bi NIR luminescence intensity. During the heat treatment process, some lower valence states of Bi containing Bi NIR active centers could be oxidized, resulting in the attenuation of the NIR luminescence of Bi. Our research may extend the understanding of chemical environment modulation in Bi valence states and offer a valuable way to enhance the NIR luminescence intensity of Bi in glasses.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Due to the rapid development of telecommunication technology, which demands for optical amplifier with a wide and flat gain spectrum in the telecommunication window, bismuth (Bi) doped glasses with broad near infrared luminescence (NIR) gain in the telecommunication window have been widely studied over the past decade [1–8]. Though the origin of the Bi NIR active center(s) is still controversial [6,9–13], which impedes the application of the Bi doped materials, much of the current work put weight on Bi with low valence state(s) as the NIR active center(s), such as Bi⁺ [13–15].

Usually, Bi NIR active centers co-exist with other valence states of Bi ions. There is no effective way to prepare glasses doped with single Bi NIR active center [16–18]. It is reasonable to believe that the valence state distribution profiles of Bi in materials depend on their chemical environments [13,17,19,20], so the NIR emission profile may be tuned by modulating the chemical environment of the glass matrices. Ion exchange is a method to modify the local environment of the glass [21–26]. However, there is sparse investigation about the effect of ion exchange on the NIR luminescence properties of Bi doped glasses.

In this work, the chemical environment of Bi was adjusted by the copper for sodium (Cu–Na) ion exchange method in the Bi doped silicate glass. After the ion exchange process, the Cu ions were introduced into the glass matrix with different copper valence states, namely, Cu⁰, Cu⁺, and Cu²⁺. The Bi NIR emission was adjusted by the Cu

ion exchange process and the subsequent heat treatment process. The possible mechanisms were discussed in detail.

2. Experiments

Glass sample with the composition (in mol%) of 60SiO₂·10Al₂O₃·20CaO·10Na₂O·1Bi₂O₃ was prepared by the melt-quenching method. High grade reagents silicon dioxide (SiO₂, 4 N, Aladdin Industrial Corporation), aluminum oxide (Al₂O₃, 4 N, Aladdin Industrial Corporation), calcium carbonate (CaCO₃, 4 N, Sinopharm Chemical Reagent Co., Ltd.), sodium carbonate (Na₂CO₃, analytical reagent, Aladdin Industrial Corporation), and bismuth oxide (Bi₂O₃, 4 N, Xingju Mineral Resource Development Co. Ltd.) were selected as raw materials. The 50 g batches were mixed homogeneously in an agate mortar. Then they were melted in a corundum crucible at 1550 °C for 1 h in air. The melt was cast onto a stainless steel plate and heat treated at 520 °C for 8 h in air. Finally, the obtained glass was cut and polished into the same size. The Cu–Na ion exchanged glass samples were obtained by immersing the glasses in different molten baths of CuSO₄/Na₂SO₄, with a copper sulfate molar concentration of 40%, 50% and 60%, and the corresponding samples were hereafter indicated as BiCu40, BiCu50 and BiCu60, at 550 °C for 1.5 h in air. The reference sample (indicated as Bi) did not undergo the Cu–Na ion exchange process. The mixed salts were contained in a silica crucible hold in a vertical furnace, in which the temperature was controlled to within ±1 °C. After inter-diffusion, samples were removed from the molten bath and washed with distilled water and alcohol to remove copper sulfate adhering to their surface. Then a part of the samples was further heat-treated at a temperature of 500 °C for 4 h in air, and the corresponding samples were hereafter indicated as BiCu40HT, BiCu50HT

* Corresponding author.

E-mail address: qiu@kmust.edu.cn (J. Qiu).

and BiCu60HT. The base glass (indicated as Base) was prepared with the composition (in mol%) of $60\text{SiO}_2 \cdot 10\text{Al}_2\text{O}_3 \cdot 20\text{CaO} \cdot 10\text{Na}_2\text{O}$, and the Cu–Na ion-exchanged and heat-treated glass samples were hereafter indicated as Cu50, and Cu50HT.

Absorption spectra were recorded using a HITACHI U-4100 type spectrophotometer. The visible spectra were collected using a HITACHI F-7000 fluorescence spectrophotometer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a PHI 5000 VersaProbe spectrometer, and the binding energies (BE) were referenced to the adventitious C1s line at 284.8 eV. The NIR luminescence spectra were obtained by a Zolix SBP300 spectrofluorometer with an InGaAs detector excited with an 808 nm laser diode. All measurements were carried out at room temperature.

3. Results

3.1. Ion-exchanged samples

The XPS spectra give direct information on the charge state of atoms in materials. Unluckily, due to the fact that the content of the incorporated Cu ions is very little, the XPS spectra of Cu can hardly be distinguished from the background signal in our samples. However, the trace of Cu ions can be observed in the absorption spectra. The absorption spectra of the ion-exchanged samples are shown in Fig. 1. The absorption intensity increases with the introduction of the Cu ions in glass. The inset is the difference of the absorption of the sample BiCu50 from that of the sample Bi. The absorption at the ultraviolet (UV) region may arise from the d–s transition of Cu^+ ions [27,28]. The absorption peak at ~570 nm, corresponding to the surface plasmon resonance (SPR) of Cu NPs, and the transmission electron microscope (TEM) image of glass BiCu50 (Fig. 2) indicate that there are Cu NPs formed in the ion exchange process [29,30]. The faint absorption in the range of 650–1000 nm can be attributed to the d–d transition of Cu^{2+} [31,32]. So we can conclude that the Cu ions are introduced into the glass matrix with different copper valence states, namely, Cu^0 , Cu^+ , and Cu^{2+} .

Usually, the characteristic emission peaks of Bi^{3+} occur in the UV region, blue or green wavelength region with variation of host materials [33–37]. Fig. 3 shows that the UV–visible luminescence intensity attenuates with the Cu concentration increase. The attenuation may be caused by the energy transfer from Bi^{3+} to Cu ions and/or the decreasing amount of Bi^{3+} . As can be seen in Fig. 3, the characteristic visible emission of Cu^+ ions is enhanced in the Cu/Bi co-doped sample

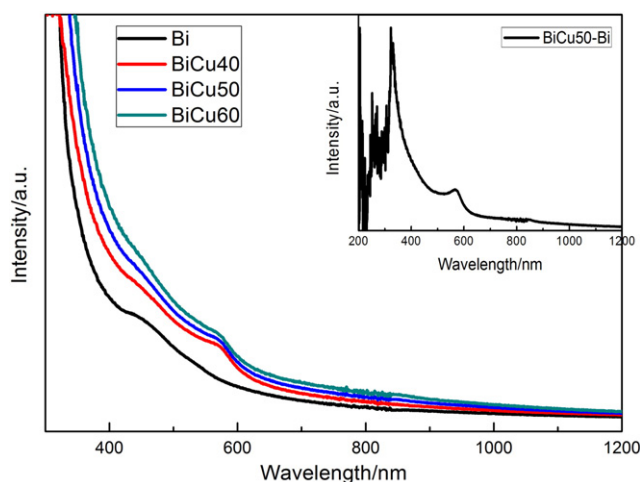


Fig. 1. Absorption spectra of samples Bi, BiCu40, BiCu50 and BiCu60. The inset is the difference of the absorption of the sample BiCu50 from that of the sample Bi.

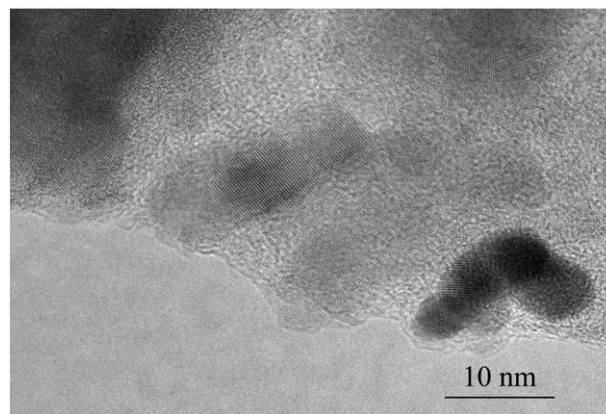


Fig. 2. Transmission electron microscope (TEM) image of glass BiCu50.

BiCu50, so the energy transfer from Bi^{3+} to Cu ions is an attenuate factor. However, the possible reduction of Bi^{3+} cannot be ruled out directly.

In order to reveal the variation of valence states, we measured the XPS spectra of Bi ions in samples Bi and BiCu50 (Fig. 4). The XPS spectrum of Bi in sample BiCu50 shifts to lower binding energy compared with that of Bi in the sample Bi [38,39], which indicates that the introduction of Cu ions into the glass matrix could reduce the higher valence states of Bi ions to lower valence species in glasses. That is the Cu–Na ion exchange could modulate the valence states of Bi in the glasses.

Fig. 5 shows the NIR luminescence spectra of samples Bi, BiCu40, BiCu50 and BiCu60 excited at 808 nm. Excitingly, with the increase of the Cu concentration, the NIR luminescence intensity of Bi is enhanced.

3.2. Heat-treated samples

Heat treatment was applied on a group of the ion-exchanged samples. The absorption spectra of samples Bi, BiCu50 and BiCu50HT are shown in Fig. 6. The inset is the difference of the absorption of the sample BiCu50HT from that of the sample BiCu50. The obvious dip at the situation of the SPR band indicates the dissolution of the Cu NPs during the heat treatment process. And the TEM images in Figs. 2 and 7 confirm this speculation. On the other hand, as can be seen in Fig. 8, the characteristic emission of Cu^+ is enhanced in the single Cu ion exchanged

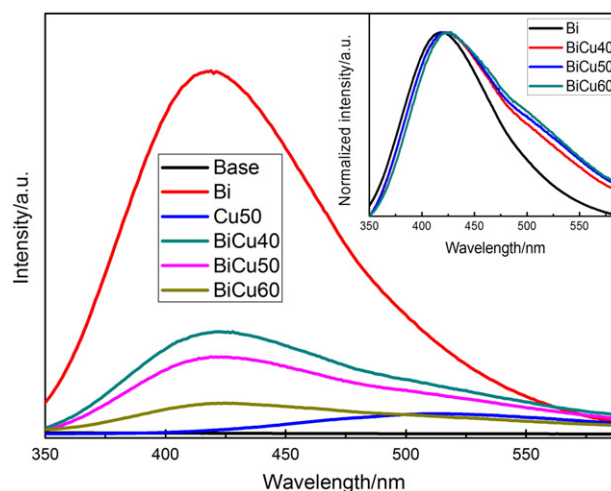


Fig. 3. Visible photoluminescence spectra of samples Base, Bi, Cu50, BiCu40, BiCu50 and BiCu60 excited at 310 nm. The inset is the normalized luminescence spectra of samples Bi, BiCu40, BiCu50 and BiCu60 excited at 310 nm.

Download English Version:

<https://daneshyari.com/en/article/1480619>

Download Persian Version:

<https://daneshyari.com/article/1480619>

[Daneshyari.com](https://daneshyari.com)