



Broadband infrared luminescence in Bi-doped silicate glass



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ABSTRACT

Glasses having composition (0.5–5)Bi₂O₃-40SiO₂-40CaO-20MgO were synthesized by the conventional melt quenching technique. The amorphous nature of the glasses was confirmed by XRD studies. Absorption, transmittance, fluorescence, and XPS spectra were measured. Heavily Bi-doped (Bi ions up to 8 mol%) SiO₂-CaO-MgO glass can exhibit broadband NIR (Near-infrared) emission at about 1245 nm (under 808 nm excitation), and the FWHM (Full Width at Half Maximum) reach up to 300 nm. The measured fluorescent lifetime is several hundred microseconds. The XPS measurements of the Bi 4f region and decay time detection for the glass samples reveal that the NIR emission should be related to lower valence Bi ions (Bi⁺). After the Bi-doped glass was annealed in air atmosphere, the amount of luminescent active ions decreased.

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1. Introduction

Bismuth doped fiber/glass has been paid much attention because it was found to be a new medium for ultra-broadband optical fiber amplifier covering the entire telecommunications window [1–3]. The ultra-broadband infrared luminescence in Bi-doped glasses and fibers have been assigned to electronic transition of Bi⁵⁺, Bi²⁺, Bi⁺, Bi clusters [1, 4–7], or color centers [8], however, the origin of NIR emission in Bi-doped glasses is still controversial. The NIR broadband luminescence has been observed in bismuth-doped germanate [3,9,10], silicate [11–13], borate [14,15], and phosphate [16,17] glasses. Silica glass is a good host material for Bi luminescent centers due to the advantages of its chemical and thermal stability, appropriate mechanical properties and wide range of optical transmittance. However, pure silica or high silica content glass production requires very high temperatures (1600 °C or more), at so high temperature, the bismuth oxide is highly volatile and the glass composition should be non-stoichiometric.

In previous publications, NIR broadband luminescence was observed in (10–40)Bi₂O₃–(90–60)GeO₂ binary glasses, and the emission intensity increases monotonically until the ratio of Bi₂O₃ is up to 30 mol% (under 808 nm excitation), and then quenches rapidly [18], which indicates that concentration quenching of Bi ions might happen in Bi containing materials.

In this work, we plan to study the NIR spectroscopic properties of Bi-doped SiO₂-CaO-MgO (Bi up to 10 mol%, relative to sum of SiO₂ + CaO

+ MgO, unit: mol) glass. Adding CaO and MgO into silica glass, on one hand, the added oxides can decrease the production temperature; on the other hand, CaO and MgO have been used to avoid the quenching of luminescence [19]. (However, some scholars consider that the alkali and alkali earth metal oxides lead to quenching of the NIR luminescence [20]). The NIR emission and luminescence mechanism of Bi-doped SiO₂-CaO-MgO glass will be studied in this work.

2. Experiments

2.1. Sample preparation

The Bi-doped SiO₂-CaO-MgO glass samples were prepared by the conventional melt quenching procedure. The starting materials were 99.99% pure Bi₂O₃, SiO₂, CaO and MgO powders. We prepared 5 series of Bi-doped SiO₂-CaO-MgO glass raw materials with different components, 0.5Bi₂O₃-40SiO₂-40CaO-20MgO glass marked as G-Bi1, and 1.5Bi₂O₃-40SiO₂-40CaO-20MgO glass marked as G-Bi3, and so on, as presented in Table 1.

The raw materials were thoroughly mixed in a mortar, and then melted at 1320 °C (the heating rate is 10 °C/min) in platinum crucible (with the lid on top) for 45 min in air atmosphere. Consequently, the molten materials were pouring onto brass mold (which preheated at about 400 °C), and then slow cooling in air to the room temperature [21]. We observed that the Bi-doped SiO₂-CaO-MgO glasses were colored, and the color became darker with the increasing Bi content, but still transparent, see Fig. 1. The glass samples were of same thickness (3 mm) and high surface quality.

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Table 1
Component of Bi-doped SiO₂-CaO-MgO samples (raw materials).

Sample	Bi ₂ O ₃ (mol%)	SiO ₂ (mol%)	CaO (mol%)	MgO (mol%)
1, G-Bi1	0.5	40	40	20
2, G-Bi3	1.5	40	40	20
3, G-Bi6	3	40	40	20
4, G-Bi8	4	40	40	20
5, G-Bi10	5	40	40	20

2.2. Measurements

We have studied the Bi-doped SiO₂-CaO-MgO glass samples by means of the XRD (Rigaku D/max 2550 V X-ray diffractometer; radiation at 60 kV, 450 mA; resolution: 0.002°). A Perkin Elmer Lambda 900 UV/VIS spectrometer was used to measure the visible absorption spectra for the glass samples. The transmittance spectra were measured with a Spectrum 400 FT-IR and FT-NIR spectrometer (Perkin Elmer). The NIR emission spectra were taken with Princeton Instruments Trivista 557 (600 grooves/mm grating, electric cooling InGaAs point-type detector). XPS (X-ray photoelectron spectroscopy) spectra were recorded on multifunctional imaging electron spectrometer (Thermo Fisher Scientific, ESCALAB 250XI). The XPS had a monochromatic Al K α ($h\nu = 1486.6$ eV) source, and the peak positions were calibrated by carbon C1s line with a binding energy 284.8 eV.

3. Results and discussion

The Bi concentrations in the raw materials of samples no. 1, 2, 3, 4 and 5 were 1.0 mol%, 3.0 mol%, 6.0 mol%, 8.0 mol% and 10 mol% relative to sum of SiO₂ + CaO + MgO (unit: mol), while the concentrations of Bi in the obtained glasses were checked out 0.842 mol%, 2.51 mol%, 5.07 mol%, 6.81 mol% and 8.43 mol%, respectively, by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, Agilent 725 ICP-OES).

Fig. 2 displays the XRD patterns of Bi-doped SiO₂-CaO-MgO glasses. The broad humps (centered at $2\theta = 28.5^\circ$) confirm the amorphous nature of the prepared glasses. The glasses are remaining amorphous during incorporation of Bi ions (up to 10 mol%) without crystallization of other phases, which indicates that Bi doping has no distinct effect on SiO₂-CaO-MgO glass structure.

The visible absorption spectra of Bi-doped SiO₂-CaO-MgO glasses are shown in Fig. 3. These glass samples have the same absorption band at about 360 nm. The sample G-Bi8 exhibits absorption band peaking at about 470 nm, while the G-Bi10 has the similar absorption band shifting to 510 nm. These absorption bands (at 360 nm, 470 nm and 510 nm) lead to the color change of glass samples, and the similar absorption is usually observed in Bi-doped IR-luminescent materials [22,23]. As Fig. 3 shows, the visible absorption coefficient become bigger with the higher of Bi doping, which is the one reason why the color of the glass samples varied from light color to dark brown with increasing Bi content.

The NIR transmission spectra of Bi-doped SiO₂-CaO-MgO glasses are shown in Fig. 4. For all samples, there are broad band absorption peaking at 2120 cm⁻¹ and 3550 cm⁻¹, and the absorption intensity enhanced with the increasing Bi content. These NIR absorption bands were

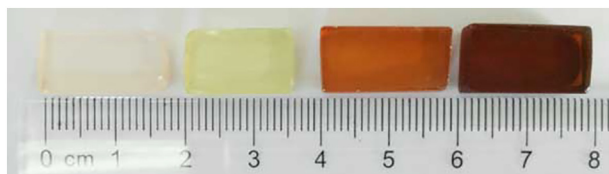


Fig. 1. Photos of the Bi-doped SiO₂-CaO-MgO glasses (from left: samples 2, 3, 4, 5).

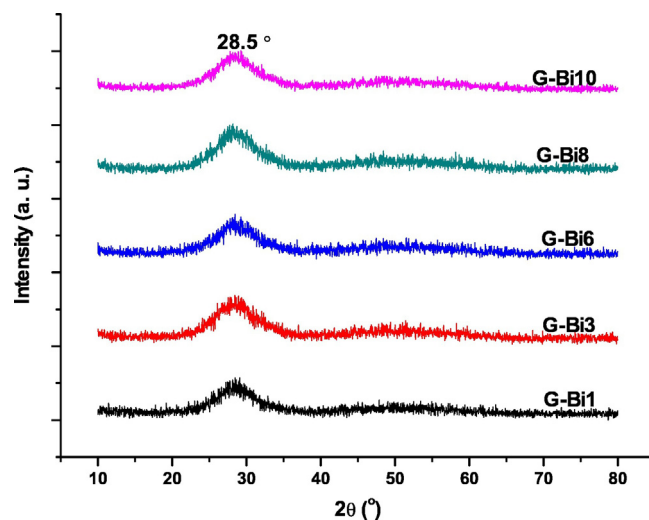


Fig. 2. X-ray diffraction patterns of Bi-doped SiO₂-CaO-MgO glasses.

likely to be the characteristic absorption of the Bi-doped SiO₂-CaO-MgO glasses (the absorption at 3550 cm⁻¹ may also be superposition of the OH group band in this region).

NIR emission are detected under 808 nm, 940 nm and 980 nm LDs excitation in (before and after annealing) Bi-doped SiO₂-CaO-MgO glass samples, as shown in Figs. 5,6 and 8. The emission measurements were performed at room temperature and all the emission spectra were corrected for the setup characteristic.

NIR emission spectra under excitation at 808 nm are shown in Fig. 5. The broadband emission peaking at 1245 nm can be observed, and the FWHM reach up to 300 nm (sample G-Bi8). To some extent, the emission intensity increases with increasing Bi content (up to 8 mol%). The emission at 1245 nm should be attributed to Bi ions [24]. Some researchers had studied various Bi-doped (with low concentrations) glasses, and found that the NIR luminescence is undoubtedly caused by the presence of bismuth in the glass composition [25,26], however, its lineshape of emission spectra differs from that of our results. In previous publications, the NIR luminescence of Bi-doped glass is often ascribed to reduced Bi states (e.g. Bi⁺/Bi²⁺ and various clusters [27–29]).

As Fig. 6 shows, sample G-Bi8 exhibits a noticeable emission band centered at about 1235 nm and 1460 nm under 940 nm LD excitation, and only an emission peaking at 1235 nm was observed under 980 nm LD excitation. Furthermore, the NIR emission intensity was weaker than the intensity under 808 nm LD pumping (in Figs. 5,6, the

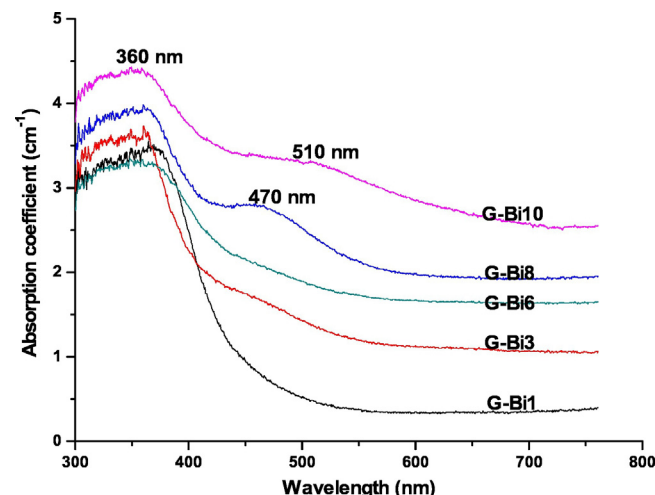


Fig. 3. Absorption spectra of Bi-doped SiO₂-CaO-MgO glasses.

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