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Spectroscopic properties of Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses

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ABSTRACT

We report on the fabrication and characterization of Nd-doped Bi_2O_3-GeO_2/SiO_2 glass. The glass samples were synthesized by melt quenching procedure and characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Near-infrared (NIR) emission was found at about 1065 nm under 590 nm and 808 nm laser diodes (LDs) excitation. The highest stimulated emission cross-section (ECS, σ_{em}) for the luminescence of 1065 nm can reach up to 3.89×10^{-20} cm^2. The markedly increased absorption at 808 nm contributes to the strong emission at 1065 nm (808 nm pump) in Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses. The Nd-doped Bi_2O_3-GeO_2/SiO_2 glass can be exploited as a good optical laser material.

1. Introduction

Recently, rare earth (RE) doped glass laser sources have promising applications in science and industry because of their good optical properties and their capability of being doped with considerable amounts of metal ions with high uniformity [1–3]. RE ions can induce special spectroscopic properties in glass matrix for their outer-shell electrons of 4f–4f transitions [4]. The absorption and emission of RE active ions in glasses depend on the chemical composition and network of host glass matrix, furthermore, the emission cross-sections (σ_{em}), effective band-width ($\Delta\lambda_{eff}$), and fluorescence decay time (τ) also depend on the surrounding ligand field of active ions and the host materials [5]. Nowadays, considerable work has been done in evaluating the effect of various host materials on spectroscopic properties of rare earth active ions.

Bi ions often act as the NIR (near infrared) emission centers in glass materials [6–8], moreover, researchers usually discuss the valence state of Bi ion when Bi emit NIR light [9–13]. Up to now, the optical properties of many Bi containing glasses of different composition were investigated, however, the optical amplification and lasing were mostly obtained in Bi-doped (with low concentrations) optical fibers based on silica glass [14]. The 4-level Nd^{3+}:Glass lasers generally exhibit very low pump threshold and are particularly interesting for operation with low pump power levels. Nd-doped glasses have been widely examined and they possess many advantages that make them very considerable materials to be used as laser media and can substitute for single crystals.

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Table 1
Component of Nd-doped Bi_2O_3-GeO_2/SiO_2 glass samples (raw materials).

Sample	Bi_2O_3 (mol%)	GeO_2 (mol%)	SiO_2 (mol%)	Nd_2O_3 (mol%)
BG	70	30	0	0
BGN-0.3	70	30	0	0.3
BGN-0.6	70	30	0	0.6
BGN-1.0	70	30	0	1.0
BSN-0.3	70	0	30	0.3
BSN-0.6	70	0	30	0.6
BSN-1.0	70	0	30	1.0

In previous publications, the $Bi_4Ge_3O_{12}$:Nd and $Bi_{12}SiO_{20}$:Nd crystals had been studied, and the researchers found that there is a radiative energy transfer between the host lattice and the Nd impurity ion [15]. In this work, we introduce Nd to the Bi_2O_3-GeO_2/SiO_2 glass system to investigate the infrared emission of Nd and the potential interaction between Nd and Bi ions. It is well known that the Bi_2O_3 and GeO_2 (or SiO_2) are easy to form the glass, and such glass does give the emission in the visible and NIR region which may be helpful in increasing the photoluminescence output of Nd^{3+} ions, moreover, the phonon losses in these glasses are expected to be very minimal because of their high density. In this work, the infrared spectroscopic properties of Nd-doped $70Bi_2O_3$–$30GeO_2$/SiO_2 glasses have been studied.

2. Methods

2.1. Sample preparation

The analytical reagent of Bi_2O_3, GeO_2, SiO_2 and Nd_2O_3 (99.99% purity) were used as starting materials. Seven batches of Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses were acquired by the conventional melt quenching method. The $70Bi_2O_3$-$30GeO_2$ glass marked as BG, $70Bi_2O_3$-$30GeO_2$-(0.3-1.0)Nd_2O_3 glasses were simplified as BGN-(0.3-1.0), and $70Bi_2O_3$-$30SiO_2$-(0.3-1.0)Nd_2O_3 glasses marked as BSN-(0.3-1.0), as presented in Table 1.

Various glass samples were prepared by melting in alumina crucible (with the lid on top) in an electrically-heated furnace at 1150 °C in air atmosphere. When the melting was completed, the liquid was poured on a preheated brass mold and then annealed at 400 °C for 2 h to release internal stresses, and then slow cooling in air to the room temperature [16]. The obtained glasses were brown colored, but still transparent. The glass samples were cut to 2.5 mm thickness and their surface were polished.

2.2. Measurements

The XRD patterns were done in a Rigaku D/max 2550V X-ray diffractometer (radiation at 60 kV, 450 mA; resolution: 0.002°). The absorption spectra for the glass samples were measured by a Perkin Elmer Lambda 900 UV/VIS spectrometer. The NIR emission spectra were taken with Princeton Instruments Trivista 557 (600 grooves/mm grating, electric cooling InGaAs point-type detector). Raman spectra were acquired on a LabRam-1B Spectrometer (Jobin Yvon, France) using He-Ne laser (at 632.8 nm) as the light source. XPS spectra were recorded with a Thermo Fisher Scientific (ESCALAB 250XI) multifunctional imaging electron spectrometer. The XPS had a monochromatic Al Kα ($h\nu$ = 1486.6 eV) source, and the binding energies reported here were calibrated with reference to C1s peak at 284.8 eV.

3. Results and discussion

The amorphous structure of the glass was investigated on an X-ray diffractometer in the 2θ range from 10° to 80°, see Fig. 1. The diffraction patterns of undoped as well as Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses show similar broad humps (centered at 2θ = 28.5°), which confirms the absence of any long range structural order in the as-obtained glasses. The XRD patterns of these glasses are similar to that of previous publications ($2Bi_2O_3$-$3GeO_2$ glasses) [17], which indicates that there is no significant change in the XRD patterns of the Bi_2O_3-GeO_2 glasses, even if the Bi_2O_3/GeO_2 proportion changes or add Nd.

Fig. 2 presents the optical absorption spectra of Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses, that of undoped glass (sample BG) is shown for the sake of comparison in the same figure. It can be seen that the samples have the same absorption edge at about 520 nm. The absorption peaking at about 587 nm, 749 nm, 808 nm, and 878 nm are attributed to transitions from ground state $^4I_{9/2}$ to the higher excited states $^4F_{3/2}$, ($^4F_{5/2}$, $^2H_{9/2}$), ($^4F_{7/2}$, $^4S_{3/2}$), and ($^2G_{7/2}$, $^4G_{5/2}$) respectively in $4f^3$ electronic configuration of Nd^{3+} [5]. To some extent, the absorption band at near 808 nm increases with increasing of Nd^{3+} doping, and the absorption coefficient is higher than that of Nd_2O_3 doped (with low concentrations: 0.1 mol%) $Bi_4Ge_3O_{12}$ and $Bi_{12}SiO_{20}$ crystals [15], which indicates that with the introduction of more Nd^{3+} ions, the absorption under 808 nm excitation can be dramatically improved (especially in the samples BGN-1.0 and BGN-0.6).

Fig. 3 shows emission spectra of Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses (λ_{ex} = 590 nm), and the spectra were measured under identical conditions. All samples emitted at about 900 nm, 1065 nm and 1330 nm, which can be assigned to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ of Nd^{3+} ions [18,19], respectively. It can be seen that the emission intensity increased with