

Enhanced broadband near-infrared emission from Bi-doped glasses by codoping with metal oxides

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An intense broadband and flat 1.3 μm emission from Bi-doped germanate glass has been measured upon excitation with a commercial laser diode, which makes the glasses more attractive for their use in broadband optical fiber amplifiers. The 1.3 μm emission exhibits a distinctive fine luminescence shape with four bands centered at 1225, 1320, 1370, and 1390 nm, respectively. It is noted that the addition of CeO_2 (2 mol %), As_2O_5 (2 mol %), or Y_2O_3 (1 mol %) into Bi-doped glasses could remarkably enhance the luminescence intensity by a factor of 4, 12, and 23, respectively. Whereas, no luminescence has been observed for the glass prepared under a controlled redox condition. The optical properties of the Bi-doped glasses and the possible mechanism involved have been explained. © 2008 American Institute of Physics. [DOI: 10.1063/1.2970167]

I. INTRODUCTION

Ever since Fujimoto and Nakatsuka¹ reported the ultra-broadband near-infrared (NIR) emission at 1.3 μm from Bi-doped silica glass, a great deal of research activity has been stimulated with a special focus on its luminescence properties, luminescence mechanism, and potential application in optical communication.^{2–5} Recently, Dianov *et al.*⁶ demonstrated Bi-doped optical fiber amplifier at 1.3 μm . Razdobreev *et al.*⁷ reported an efficient all-fiber Bi-doped laser with a slope efficiency as high as 24% at 1200 nm. Zhou *et al.*⁴ realized a broadband and an efficient optical amplification covering the whole 1.2–1.6 μm region. Unfortunately, however, the involved luminescence mechanism and the nature of the NIR emission at 1.3 μm still remain unclear. It is considered more important and vital to understand the intrinsic NIR emission mechanism in order to reveal the spectral feature shapes and also to explain the reason behind the enhanced NIR broadband emission from the potential Bi-doped glass.

Here in this paper, we report our results on the latest work pertaining to the spectral properties of Bi-doped germanate glasses. It is found that the 1.3 μm emission exhibits a distinct fine luminescence shape with four bands located at 1225, 1320, 1370, and 1390 nm, respectively, upon excitation with 808 and 980 nm laser diodes (LDs). It is noted that the addition of *MO* ($MO = \text{CeO}_2$, As_2O_5 , or Y_2O_3) will remarkably enhance the 1.3 μm luminescence intensity. Whereas, no luminescence has been obtained for the glass prepared under a controlled redox condition. The optical properties of the Bi-doped glasses and the possible mechanism involved have been discussed.

II. EXPERIMENTAL

The preparation process of the glass samples has been carried out by following the protocol of an ordinary melting-

quenching technique by using pure chemicals such as GeO_2 , $\text{Al}(\text{OH})_3$, Bi_2O_3 , CeO_2 , As_2O_5 , and Y_2O_3 as precursors. The chemical compositions and optical properties of these glasses are illustrated in Table I. For the preparation of GAYB(C), a mild reducing atmosphere was provided by burning carbon powder in a bigger crucible covered with a lid along with the reactants in a smaller alumina crucible, while a part of GAB sample was subjected to a reheating in pure oxygen at 1100 °C for 3 h, which was referred to as GAB(O_2). After annealing, samples for optical and spectral properties measurements were cut into rectangular $10 \times 10 \times 0.8 \text{ mm}^3$ shapes and optically polished. Room-temperature absorption spectra of the samples were recorded on a Perkin-Elmer Lambda-900 UV/vis/NIR spectrophotometer. The measurements of the photoluminescence spectra were carried out on a Jobin-Yvon Triax 320 spectrometer equipped with an In-GaAs photodetector by exciting samples with 808 and 980 nm LDs. The temporal decay curves of the fluorescence signals were stored after averaging 128 times using a Tektronix TDS3012B digital phosphor oscilloscope.

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the absorption spectra of GAB, GAYB, GAAB, GACB, and GAYB(C) glasses. Intense absorption bands centered at 480 and 700 nm as well as a weak peak around 800 nm are measured from the GAB, GAYB, GAAB, and GACB glasses, and those are assigned to the electronic transitions of Bi ions.² Different absorption bands thus observed could provide a possibility in choosing a relevant pump source for optical amplifications. The GAYB(C) glass prepared under the reductive atmosphere exhibits only a weak absorption around 700 nm due to the strong absorption of the host material at the visible wavelength. With an extrapolation-to-zero transmittance at the steepest slope, it is noticed that the cutoff wavelength for GAB, GAYB, GAAB, GACB, and GAYB(C) glasses are 452, 536, 558, 677, and 696 nm, respectively. The absorption edge of the Bi-doped glasses could be expressed by $\beta(\nu) = A(h\nu - E_{\text{opt}})^2/h\nu$,⁸ where

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TABLE I. Chemical compositions and optical properties of glass samples.

Samples	Chemical composition (mol %)	Peak wavelength (nm)	FWHM (nm)	Lifetime (μ s)	
				A band 1225 nm	B band 1320 nm
GAB	95.5GeO ₂ -4Al ₂ O ₃ -0.5Bi ₂ O ₃	1216	286
GAB(O ₂)	95.5GeO ₂ -4Al ₂ O ₃ -0.5Bi ₂ O ₃	1223	294	132	410
GACB	93.5GeO ₂ -4Al ₂ O ₃ -2CeO ₂ -0.5Bi ₂ O ₃	1230	274	85	255
GAAB	93.5GeO ₂ -4Al ₂ O ₃ -2As ₂ O ₅ -0.5Bi ₂ O ₃	1238	315	94	271
GAYB	94.5GeO ₂ -4Al ₂ O ₃ -1Y ₂ O ₃ -0.5Bi ₂ O ₃	1230	276	94	273
GAYB(C)	95.5GeO ₂ -4Al ₂ O ₃ -0.5Bi ₂ O ₃ (C)

β , E_{opt} , and $h\nu$ denote the absorption coefficient, optical band gap, and photon energy, respectively. Following is the trend in the glass series GAYB(C) \rightarrow GACB \rightarrow GAAB \rightarrow GAYB \rightarrow GAB based on the absorption edge results which range is given here: 1.78 \rightarrow 1.83 \rightarrow 2.22 \rightarrow 2.31 \rightarrow 2.74 eV, as shown in the inset of Fig. 1.

Figure 2 shows the NIR emissions for all samples upon excitation of 808 nm LD. The emission signal detected in single Bi-doped GAB glass is more noisy in nature due to its weak fluorescence as illustrated in the inset of Fig. 2(a), and is characterized by peak at 1225 nm with a full width at half maximum (FWHM) of about 286 nm. It is noted that an intense 1.3 μ m emission with FWHM of 294 nm has been obtained in Bi-doped germanate glass prepared under an oxide condition. The luminescence intensity of GAB(O₂) glass is three times higher than that of GAB, and it is decipherable that this luminescence emission consists of two broadbands located at 1225 and 1320 nm, respectively. Whereas, no luminescence has been obtained for the GAYB(C) glass prepared under a controlled redox condition in our experiment. This result is quite different from the recently reported in Ref. 5 in which an unambiguous and broadband NIR emission has been achieved from a colorless Bi-doped soda-lime-silica glass prepared under redox conditions with 800 nm excitation, which might be due to the high soda-lime con-

tents of the silica glass. The complex glass composition might also be disadvantageous to judge the influence of the redox condition on bismuth ions.

It should be mentioned here that the addition of MO into the Bi-doped glasses remarkably enhances the luminescence intensity. The luminescence intensity in GAYB, GAAB, and GACB glasses exceed that of single Bi-doped sample (GAB) by a factor of 23, 12, and 4, respectively. Clearly, the Bi-doped GAYB glass codoped with Y₂O₃ exhibits a stronger NIR emission. Taking into account the glass-making conditions and the 1.3 μ m emission intensity sequence, which could be presented in the order of $I_{\text{GAYB}} > I_{\text{GAAB}} > I_{\text{GACB}} > I_{\text{GAB(O}_2\text{)}} > I_{\text{GAB}}$, as shown in the Fig. 2, we understand that the emission center might be related to the higher valence Bi ion. Previously, the literature has confirmed that the primary existing forms of Bi ions as Bi³⁺ and Bi⁵⁺ in Bi_{0.7}Y_{0.3}O_{1.5} polycrystals^{3,9} would offer a possible chemical surrounding that is preferable for the formation of higher valence Bi ions. It is interesting to note that the 1.3 μ m emission exhibits a distinct fine luminescence shape with four bands centered at 1225, 1320, 1370, and 1390 nm, respectively (that are labeled as A, B, C, and D), which is quite different from those

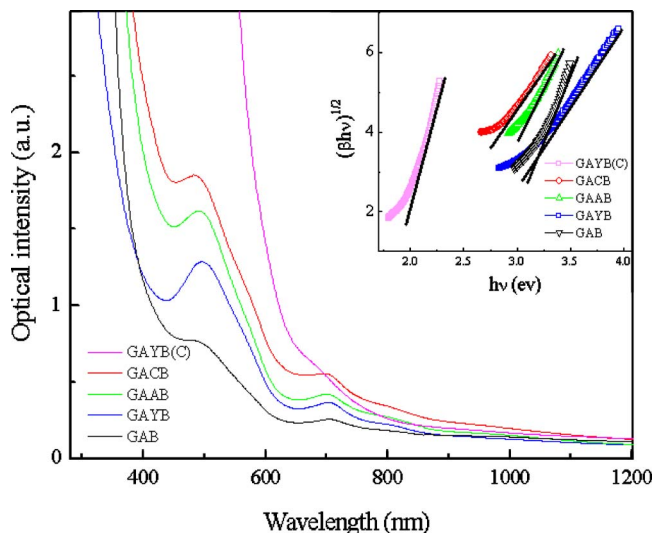


FIG. 1. (Color online) Absorption spectra of GAB, GAYB, GAAB, GACB, and GAYB(C) glasses. The inset shows $(\beta h\nu)^{1/2}$ vs photon energy and $h\nu$ of samples.

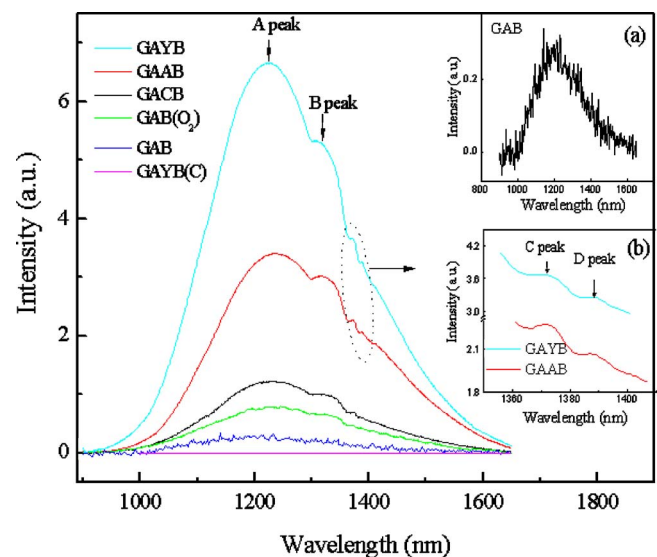


FIG. 2. (Color online) Emission spectra of GAB, GAYB, GAAB, GACB, GAB(O₂), and GAYB(C) glasses with excitation of 808 nm LD. (a) The inset shows the enlarged NIR emission of GAB. (b) The inset displays the part of the enlarged fluorescence spectra of GAYB and GAAB samples from 1350 to 1410 nm, which show two emissions centered at between 1370 and 1390 nm.

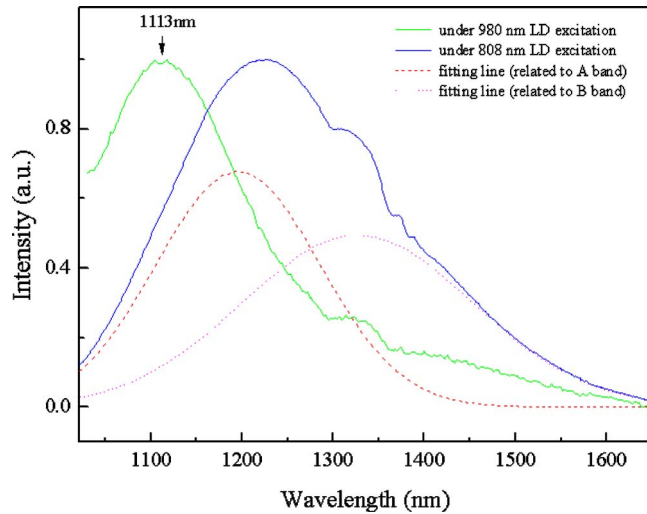


FIG. 3. (Color online) Normalized NIR emission spectra of GAYB glass upon excitation of 980 and 808 nm LDs, respectively. Dotted curves are results of double peak Gaussian fits.

reported earlier in literature.^{4,6,10} The distinct multippeak emissions could possibly be revealing the properties of the actual energy levels of the emission center.^{11–13} The addition of MO into Bi-doped germanate glasses could change only the concentration of the NIR emission center, indicating that the four fine luminescence peaks come from the single species.

Figure 3 shows a normalized NIR emission spectra of GAYB glass upon excitation of 980 and 808 nm LDs, respectively. It is interesting that the peak wavelength and width of the NIR emission could be controlled drastically by the excitation wavelength. Intense NIR emissions at 1113 nm with FWHM of 265 nm have been clearly observed upon excitation with 980 nm from a LD. However, by varying the excitation wavelength from 980 to 808 nm, an obvious redshift from 1113 to 1225 nm has been observed, meanwhile the FWHM of the emission increases from 265 to 305 nm. A double exponential model has been obtained to fit well to the experimental decay curves at the two main emission bands, which are corresponding to A and B bands as shown in Fig. 3 (dotted curves). The lifetime of the glasses studied are also summarized in Tables I and II. The measured lifetime of the GAYB glass is 94 and 273 μs for the emission bands centered at 1225 and 1320 nm, respectively. The stimulated emission cross sections (σ_e) corresponding to the two main bands at 1225 and 1320 nm could be estimated from the Fuchtbauer–Ladenburg equation by assuming a Gaussian-shaped emission band:¹⁴

TABLE II. Optical properties of the two main bands A and B in the emission spectrum of GAYB.

	A	B
λ_0 (nm)	1225	1320
FWHM (nm)	235	302
τ (μs)	94	273
σ_e (cm^2)	4.435×10^{-20}	1.785×10^{-20}
$\sigma_e \times \tau$ ($\text{cm}^2 \text{s}$)	4.17×10^{-24}	4.87×10^{-24}

$$\sigma_e = \frac{\lambda_0^4}{4\pi n^2 c \tau} \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta\lambda}, \quad (1)$$

where λ_0 , n , τ , and $\Delta\lambda$ denote the peak wavelength, the refractive index of the host material, the emission lifetime, and the FWHM of the emission, respectively. The properties and the stimulated emission cross sections of the two main emission bands in GAYB glass are given in Table II. The products of the stimulated emission cross section and the decay lifetime $\sigma_e \times \tau$, which is proportional to the amplification gain and inversed laser oscillation threshold,^{5,14,15} were 4.17×10^{-24} and $4.87 \times 10^{-24} \text{ cm}^2 \text{ s}$ for the emission peak at 1225 and 1320 nm, respectively. The values are larger than that of Ti:sapphire ($\sigma_e \times \tau = 1.4 \times 10^{-24} \text{ cm}^2 \text{ s}$), which suggest that the Bi-doped germanate glass has got a good potential for the broadband gain media toward the development of optical amplifiers and tunable lasers.

IV. CONCLUSION

In summary, we conclude that spectral properties of Bi-doped germanate glasses have been investigated. An intense 1.3 μm emissions with a FWHM of 294 nm in Bi-doped germanate glass prepared under oxide condition has been obtained upon excitation with an 808 nm LD. Whereas, no luminescence has been observed for the glass prepared under a controlled redox condition. Incorporation of the codopants (MO) into the Bi-doped germanate glasses has remarkably enhanced the 1.3 μm luminescence performance. The 1.3 μm emission exhibits a distinctly fine luminescence shape with four bands centered at 1225, 1320, 1370, and 1390 nm, respectively.

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