

Infrared luminescence and amplification properties of Bi-doped $\text{GeO}_2\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ glasses

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Bi, Ga, and Al codoped germanium glass was prepared and its optical properties were investigated by absorption, photoluminescence excitation (PLE), and photoluminescence spectra. Two active centers which occupy strong and weak crystal field environment are identified by using the PLE spectrum. The tunable and ultrabroadband luminescence properties are originated from electron transitions of these two active centers. Internal optical gain around 1300 and 1560 nm has been detected. The wavelength-dependent internal gains excited with 808 and 980 nm laser diodes show different characteristics, and the relative flat optical amplification can be realized by choosing 980 nm pumping. © 2008 American Institute of Physics. [DOI: 10.1063/1.2917303]

I. INTRODUCTION

All-solid-state broadband near infrared sources have attracted considerable attention since the reported tunable lasing operation in $\text{MgF}_2:\text{Ni}^{2+}$ in 1963 (Ref. 1) because of the fundamental applications in biomedics and telecommunications, e.g., solid-state tunable lasers, optical coherence tomography, and compact and versatile amplifiers. Many efforts have been dedicated to this kind of gain media, and the extensive researches were carried on the transition metals (TM) ions such as Ti^{3+} -, Ni^{2+} -, Co^{2+} -, Cr^{3+} -, Cr^{4+} -, and Mn^{6+} -doped crystal hosts,² glasses,³ and glass ceramics.⁴⁻⁸ However, broadband emission based on the $3d-3d$ transitions of TM ions is usually baffled by excited-state absorption and nonradioactive decay.^{9,10} These drawbacks impose an obstacle to overcome and they severely limited their actual applications.

Recently, an interesting kind of active ion (bismuth) doped silica glass is attracting people's interest because of its favorable properties such as high luminescence efficiency and broadband luminescence bandwidth.¹¹ In recent years, a number of hosts were investigated and broadband infrared luminescence was reported in silicate,^{12,13} germanium,¹⁴ phosphate,¹⁵ and barium borate glasses.¹⁶ It is exciting that optical amplification and lasing operation were also realized at present.¹⁷⁻²² Among the obtained results, an interesting phenomenon that was seldom observed in other active materials is the excitation wavelength sensitive luminescence, and the largest displacement of 200 nm was reported.¹² This special characteristic is significant since it offers the opportunity for realizing tunable and broadband lasers and amplifiers. Unfortunately, the origin of the phenomenon is still un-

known. On the other side, from the view point of practical application, the selection of appropriate pumping source for realizing high gain is another important issue which is necessary to be considered. It is urgent to provide more evidences related to the earlier-mentioned topics for further research.

Here we report the spectroscopic and amplification properties of Bi-activated, Ga and Al codoped germanium glass [(mol %) $96.5\text{GeO}_2-1.5\text{Ga}_2\text{O}_3-1.5\text{Al}_2\text{O}_3-0.5\text{Bi}_2\text{O}_3$ (GGAB)]. The glass matrix is selected since it shows excellent infrared luminescence property according to our recent investigation. The research results of the typical germanium glass are also helpful for further understanding of this kind of gain materials. Actually, there are few subsequent investigations after the observation of ultrabroadband infrared luminescence from Bi-doped germanium glass.¹⁴ The excitation spectra between 200 and 1000 nm are presented. Based on the result, the possible origin of excitation wavelength sensitive luminescence is discussed. Furthermore, broadband amplification property was also measured under excitation with 808 and 980 nm laser diodes (LDs).

II. EXPERIMENT

The glass samples were prepared by the conventional melting-quenching technique. Bi free glass sample (GGA) was also prepared for comparison. Starting materials were high-purity reagents GeO_2 (5 N), Ga_2O_3 (5 N), Al_2O_3 (4 N), and Bi_2O_3 (5 N). An approximately 30 g batch was mixed and then melted in a Pt-Rh crucible at 1600 °C for 30 min under an ambient atmosphere. The melt was then poured onto stainless steel. The obtained glass samples were cut to the thickness of 3 mm and polished for measurements. Absorption spectra were recorded by a double-beam spectrophotometer (JASCO FP-6500). Photoluminescence excitation (PLE) and photoluminescence spectra were measured by

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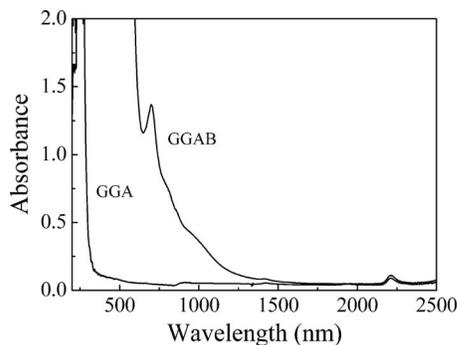


FIG. 1. Absorption spectra of GGAB and GGA glass.

exciting the samples with a 450 W Xe lamp and a double 0.22 m SPEX monochromator and were detected by an In-GaAs detector in the 1000–1800 nm wavelength region.

III. RESULTS AND DISCUSSION

The appearance of the germanium glass sample shows obvious change with the addition of Bi. The GGA sample is colorless, but the GGAB sample is a dark wine red color. Figure 1 shows the absorption spectra of GGA and GGAB samples. It can be seen that the GGAB glass shows band edge absorption characteristics with several imposed discrete peaks (700, 800, and 1000 nm) in the whole visible and near-infrared region. The band edge absorption in the GGAB sample is very similar to the absorption bands of colloid Bi nanoparticles acquired by experiment and calculation.^{23,24} This kind of narrow absorption edge might also be related to the charge transfer between Bi^{3+} and Bi^{5+} ions which was observed in the Bi mixed-valence oxides.²⁵ The imposed discrete peaks, which might be attributed to the isolated centers, are entirely different from the reported Bi^{3+} (with maximum at 250 nm) and Bi^{2+} (peaked around 500 nm) centers. They were ascribed to the electron transitions of infrared active centers.^{11,14} According to Ref. 15, the peaks at 700, 800, and 1000 nm are most probably originated from the transitions from the 3P_0 level to the 1D_2 , 3P_2 , and 3P_1 levels of the Bi^{3+} center.

Infrared luminescence properties under excitation with different wavelength light sources were investigated. Two typical peaks centered at 1110 and 1240 nm can be observed. The result is similar to the luminescence properties of Bi-doped silicate glass.¹² The corresponding PLE spectra were measured and shown in Fig. 2(a). It is noteworthy that the PLE spectra cover almost the entire 200–1000 nm range, indicative of efficient photoexcitation in a wide range of photon energy. This broadband excitation characteristic can be used to explain the phenomenon of broadband emission observed under excitation with various light sources. In order to further investigate the detailed attributions of these broadband bands, infrared luminescence excited by the selected wavelength in the whole 200–1000 nm region was measured. Acquired luminescence spectra can be classified into three major types, presented in Fig. 2(b). The first and the second types exhibit prominent peaks at 1110 and 1240 nm. The decay curves monitored at these two peaks show a fair consistency with the first-order exponential decay and the life-

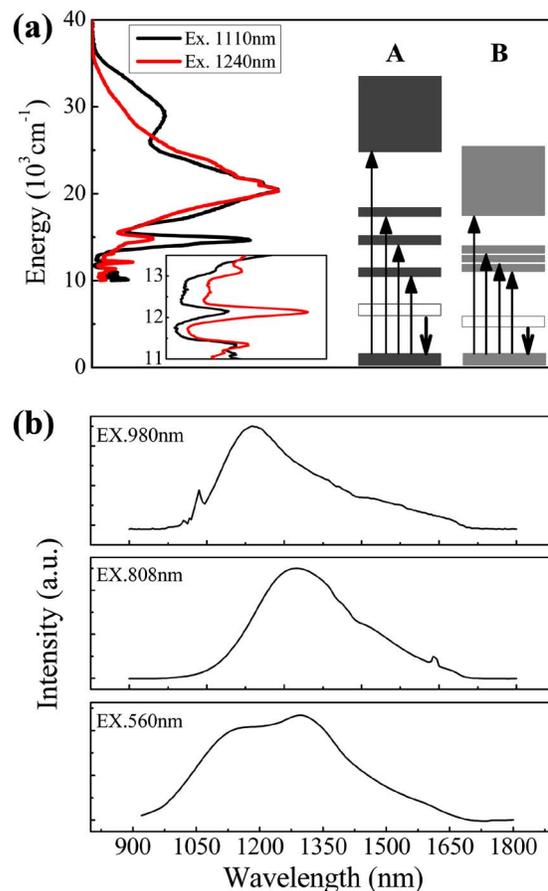


FIG. 2. (Color online) (a) The measured excitation spectra monitored at 1110 and 1240 nm (the inset shows the enlarge spectra between 1.1×10^4 and $1.35 \times 10^4 \text{ cm}^{-1}$). The energy level diagram was proposed based on the excitation spectra. (b) Fluorescence spectra of GGAB glass excited at 808, 980, and 560 nm.

times fitted at about $460 \mu\text{s}$ (1110 nm) and $397 \mu\text{s}$ (1240 nm), respectively. They can be attributed to two different active centers and are represented as A and B. The ultrabroad luminescence characteristic of the third type observed under excitation with 560 nm is composed of two main peaks, possibly associated with the luminescence of centers A and B. It will be discussed later. In the absorption spectra (Fig. 1), the isolated absorption peaks are overlapped by the strong band edge absorption. In this case, the excitation spectra may give more detailed information about the electron transition process. On the basis of the corresponding emission band type, the excitation bands between 200 and 1000 nm are segmented into multiple bands. The results are illustrated in the inset of Fig. 2(a). The divided area from the excitation spectra can be considered as the simplified energy levels of luminescence centers. The emitting states [the unfilled strip in Fig. 2(a)] are also added by referring to the emission peak location of centers A and B. From the constructed energy levels, it can be confirmed that the excitation wavelength sensitive luminescence reported in the references might be the result of the alternate distribution of energy levels belonging to two active centers. Due to the complex characteristic of the shown energy levels, the level overlapping may occur at a special band region such as around 560 and 900

nm. This kind of overlapping is very beneficial to the process of coexcitation, and consequently, gives rise to the observed ultrabroadband emission.

In several references, the origin of infrared luminescence has been discussed and temporarily attributed to be the electron transition of Bi^{5+} , Bi^+ , clusters of Bi atoms, and $\{[\text{AlO}_4]_2^-, \text{Bi}^+\}$ complexes. It is still difficult to clarify the detailed origin based on the aforementioned results. However, it is interesting to note that both centers A and B seem to have a similar derivation since they show a similar energy level distribution. The major distinctive feature is the gap difference among various levels. Meng *et al.* found the infrared luminescence property of Bi-doped glass being dependent on the host composition.¹⁶ It can be supposed that the transition electrons probably play a role in the chemical bonding between the centers and the surrounding ligands, thus experiencing a strong electron-phonon coupling and local environment sensitive luminescence characteristic. In such conditions, the effect of crystal-field parameter, which may affect the energy levels distribution dramatically, must be considered. Herein, the observed two centers might be explained by the fluctuation of crystal-field strength which results in a strong-field configuration (center A) and another weak-field configuration (center B).

From the practical perspective, the selection of the pumping source is also an important topic. Especially when the gain materials are employed as fiber amplifiers, the commercial available cheap 800 or 980 nm lasers should be mainly considered. However, the relative evaluation has not been processed yet. Herein, we measured the amplification properties adopted by the traditional two-wave mixing geometry.²⁶ The internal gain is defined by $10 \log(I/I_0)$ where I and I_0 represent the optical signal with and without a pumping source, respectively.²⁷ In the process of gain measurement, it was observed that the continued laser irradiation may lead to a glass temperature rise. It may induce measurement error which was estimated to be about 0.2 dB. Figure 3(a) shows the internal gain properties at 1300 nm excited with 808 and 980 nm LDs. The internal gain increases with the excitation power and it reaches 5.44 dB (808 nm, 1.13 W) and 2.26 dB (980 nm, 1.12 W), respectively. The inset also gives an oscilloscope image of the amplification phenomenon with the excitation at 808 nm (1.13 W). Figure 3(b) shows the signal spectra with and without a pumping source. It can be seen that there are no obvious spurious modes in the vicinity of the signal, which corroborates the amplification phenomenon. According to these results, the 808 nm pumping scheme seems more efficient than the 980 nm pumping scheme.

The broadband amplification properties were also measured. Figure 4 shows the internal gain as a function of different seed beam wavelengths from 1272 to 1348 nm under excitation with 808 nm (1.13 W) and 980 nm (1.12 W) LDs. Points and curves represent experimental measurements and fluorescence spectrum under 808 and 980 nm excitations. The highest gain at 1272 nm of the GGAB glass sample pumped by 808 and 980 nm reaches 5.62 and 2.11 dB, respectively. These values are larger than the reported results in Bi-doped silica glass.¹⁷ The optical amplification with 77

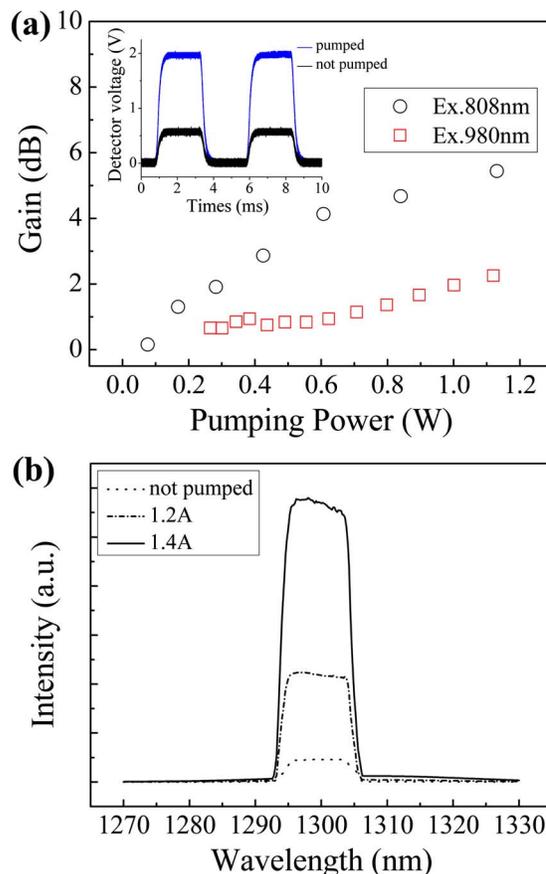


FIG. 3. (Color online) (a) Internal optical gain properties at 1300 nm excited at 808 and 980 nm. The inset shows an oscilloscope image of the amplification phenomenon. (b) The amplified spontaneous emission spectra.

nm bandwidth implies the GGAB glass can overcome the disadvantages of the present praseodymium-doped fluoride fiber amplifiers such as brittle and narrow amplification bandwidth (25 nm).^{28,29} Furthermore, it is significant to point out that the amplification phenomenon at 1560 nm is also observed. It means that the superwide amplification covering whole *O*, *E*, *S*, *C*, and *L* bands could be potentially realized in the GGAB glass system. According to Refs. 17–19, the reported amplification and lasing operation of the Bi-doped matrix were mainly focused around 1.2 μm which can be ascribed to the relative narrower emission width of Bi-doped

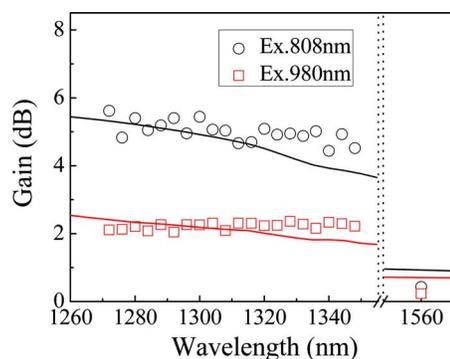


FIG. 4. (Color online) Internal gain as a function of different seed beam wavelength from 1272 to 1348 nm under excitation with 808 nm (1.13 W) and 980 nm (1.12 W) LDs.

silica glass compared with germanium glass. The results demonstrate that the GGAB glass system could be an excellent broadband near-infrared source. On the other hand, it is interesting that the wavelength dependent internal gain under 980 nm excitation is flatter than that under 808 nm. This kind of flat amplification characteristic is important since gain excursion over the whole spectral width can be minimized when the materials are used as broadband optical amplifiers in the Wavelength-Division Multiplexing (WDM) system. Although the gain value under excitation with 980 nm is smaller than that under 800 nm, which might be ascribed to the relative low absorption cross section of active centers at 980 nm, the amplification performance could be expected to be improved by codoping sensitization ions (e.g., Yb).³⁰

IV. SUMMARY

In summary, the optical properties of Bi, Ga, and Al codoped germanium glass were investigated. The origin of excitation wavelength sensitive and ultrabroadband luminescence is discussed. Superwide amplification was realized in the glass system pumped by commercial 800 and 980 nm LDs. The obtained glass has potential application as solid-state broadband near-infrared sources and optical amplifiers. The results show that the 808 nm pumping scheme is more efficient than the 980 nm pumping scheme, but the latter scheme shows flatter gain than the former. They provide good reference for practical applications.

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