Letter to the Editor

Green and red upconversion luminescence in ytterbium-sensitized erbrium-doped novel lead-free germanium–bismuth–lanthanum glass

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Received 16 November 2004
Available online 11 July 2005

Abstract

Structural and infrared-to-visible upconversion fluorescence properties in ytterbium-sensitized erbrium-doped novel lead-free germanium–bismuth–lanthanum glass have been studied. The structure of lead-free germanium–bismuth–lanthanum glass was investigated by peak-deconvolution of Raman spectrum, and the structural information was obtained from the peak wavenumbers. Intense green and red emissions centered at 525, 546, and 657 nm, corresponding to the transitions $^2\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^{4}\text{I}_{15/2}$, respectively, were observed at room temperature. The quadratic dependence of the 525, 546, and 657 nm emissions on excitation power indicates that a two-photon absorption process occurs under 975 nm excitation. This novel lead-free germanium–bismuth–lanthanum glass with low maximum phonon energy (~ 751 cm$^{-1}$) can be used as potential host material for upconversion lasers.

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PACS: 78.20.—e; 42.70.Ce; 32.70.Cs; 42.70.Hj

1. Introduction

Over the past few decades, there has been a significant interest in the production of new vitreous materials which find application as hosts in rare-earth doped infrared-to-visible upconverters. Optical properties of trivalent lanthanide ions such as Er$^{3+}$, Tm$^{3+}$, Ho$^{3+}$, and Nd$^{3+}$ in glasses have been extensively studied to develop upconversion visible or ultraviolet lasers which can be operated at room temperature [1–6]. Among the trivalent lanthanide ions, Er$^{3+}$ ion is the most studied, and the upconversion process of this ion in various kinds of host materials has been investigated [7]. The sensitization of Er$^{3+}$ doped materials with Yb$^{3+}$ ions is a well-known method for increasing the optical pumping efficiency because of the efficient energy transfer from Yb$^{3+}$ to Er$^{3+}$ ions [8,9]. Pulsed and continuous wave laser actions have been demonstrated in Er$^{3+}$/Yb$^{3+}$-co-doped glass lasers [10,11]. Host material for Er$^{3+}$ ions plays an important role in obtaining high-efficient upconversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR) and thus achieves strong upconversion luminescence. Though fluoride glasses have been studied due to low phonon energies, oxide glasses are more appropriate for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, heavy metal oxide (HMO) glasses containing PbO combine high mechanical strength, high chemical durability,
and temperature stability with good transmission, which make them promising materials for technological applications such as new lasing materials, upconverting phosphors, and optical waveguides [12–14]. However, in view of surrounding protection and preparation safety, lead-free HMO glass has more applications than lead glasses. Then, great efforts are still attracted to study other lead-free HMO glasses as suitable upconversion hosts.

In this paper, the structural and infrared-to-visible upconversion fluorescence properties of novel lead-free germanium–bismuth–lanthanum glass were investigated. Intense upconversion fluorescence bands at around 525, 546, and 657 nm have been observed, and the possible upconversion mechanisms are discussed and estimated.

2. Experimental

The glass used in this work was synthesized by conventional melting and quenching method. The starting materials are reagent-grade Bi₂O₃, La₂O₃, and high-purity GeO₂ (>99.999%). The glass sample studied has the following composition: (mol%) 92[GeO₂–Bi₂O₃]–8La₂O₃–0.5Er₂O₃–0.5Yb₂O₃ (GBLEY). Undoped (mol%) 92[GeO₂–Bi₂O₃]–8La₂O₃ (GBL) glass was also prepared to measure the Raman spectrum. About 20 g batches of the well-mixed raw materials were melted at 1300 for 20–30 min in covered aluminium oxide crucibles in an electronic furnace with O₂ atmosphere. When the melting was completed, the liquid was cast into stainless steel plate. The obtained glasses were annealed for several hours at the glass transition temperatures before cooling them to room temperature at a rate of 10 °C/h, and then were cut and polished carefully in order to meet the requirements for optical measurements.

The Raman spectrum was recorded on a FT-Raman spectrophotometer (Nicolet MODULE) within the range of 80–1000 cm⁻¹. The upconversion luminescence spectrum was obtained with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with a maximum power of 2 W. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Raman spectrum of GBL glass

Fig. 1 shows the Raman spectrum of GBL glass, and the spectrum is composed of three spectral regions: (i) low-frequency region (<270 cm⁻¹), attributed to the collective modes of local structures and heavy metal vibrational modes [15,16]; (ii) intermediate region (270–661 cm⁻¹), attributed to the deformation of vibrational modes of a glass network structure with bridged oxygen [17–20], and (iii) high-frequency region (>661 cm⁻¹), attributed to the stretching vibrational modes of the glass network former [19,20]. The Raman spectrum is developed through a deconvolution using Gaussian distribution and five bands appear at around 132, 208, 390, 567, and 751 cm⁻¹. The Raman spectrum of GBL glass shows only one high-frequency band around 751 cm⁻¹, and it has been well understood and is assigned to rather localized Ge–O stretching modes of the metagermanate units (interconnected tetrahedra with two non-bridges [GeO₄]²⁻) [21]. According to Miller et al. [22], the bridging-anion type Raman peaks, represented as cation–anion–cation configuration, have strongest intensities with large bond lengths, high valencies of the cation and anion, and low Raman frequency shift. Then the strongest 390 cm⁻¹ band could be attributed to Bi–O–La and Ge–O–La bridging vibrations [23], while the 567 cm⁻¹ band is from Bi–O–Bi and/or Ge–O–Ge stretching vibration [23–25]. The bands in low-frequency region could be attributed to vibrations involving Ge, Bi, and La atoms, respectively [16,17]. From Raman spectrum, we could observed that the maximum phonon energy of GBL glass matrix is around 751 cm⁻¹, which is lower than those of phosphate: 1100 cm⁻¹, silicate: 1000 cm⁻¹, germanate: 900 cm⁻¹, tellurite: 800 cm⁻¹ [26,27]. Therefore, it can be expected that the lead-free germanium–bismuth–lanthanum glass is better candidates for upconversion luminescence of Er³⁺ ions.

3.2. Upconversion fluorescence analysis

The room temperature upconversion spectrum of the GBLEY glass is shown in Fig. 2. The observed emissions correspond to transitions of Er³⁺ ions from excited states to ground state. The 512–539 and 539–577 nm green bands correspond to the ⁵H₁₁/₂ → ⁴I₁₅/₂ and
$^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions, respectively. The former was resolved into two part-overlapped Gaussian peaks at 525 and 533 nm, and the latter was resolved into two part-overlapped Gaussian peaks at 546 and 554 nm, respectively. The 634–694 nm red band corresponds to $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition, which was resolved into two part-overlapped Gaussian peaks at 657 and 670 nm. It is important to point out that the green upconversion fluorescence is bright enough to be observed by the naked eye at excitation power as low as 50 mW for GBLEY glass. This is because the integrated intensity ratio in percent between green (512–539 and 539–577 nm) and red (634–694 nm) is 61%:39%. In frequency upconversion process, the upconversion emission intensity $I_{up}$ increases in proportion to the $n$th power of infrared (IR) excitation intensity $I_{IR}$, that is

$$I_{up} \propto I_{IR}^n,$$

where $n$ is the number of IR photons absorbed per visible photon emitted [28]. A plot of log $I_{up}$ vs log $I_{IR}$ yields a straight line with slope $n$. Fig. 3 shows such a plot for the 525, 546, and 657 nm emissions in GBLEY glass under 975 nm excitation. Values of 1.80, 1.85 and 1.93 were obtained for $n$ corresponding to the 525, 546, and 657 nm emission bands, respectively. The results indicate that a two-photon process populates the $^4S_{3/2}$, the $^2H_{11/2}$ and the $^4F_{9/2}$ levels. According to the energy matching and quadratic dependence on excitation power, the possible upconversion mechanisms for the emissions are discussed based on the simplified energy levels of Er$^{3+}$ and Yb$^{3+}$ presented in Fig. 4. For the green emissions, in the first step, the $^4I_{11/2}$ level is directly excited with 975 nm light (GSA) and/or by energy transfer (ET) process from $^2F_{5/2}$ level of Yb$^{3+}$: $^2F_{5/2}$(Yb$^{3+}$) + $^4I_{15/2}$(Er$^{3+}$) $\rightarrow$ $^2F_{7/2}$(Yb$^{3+}$) + $^4I_{11/2}$(Er$^{3+}$). Since Yb$^{3+}$ has a much larger absorption cross-section than Er$^{3+}$ in the 975 nm region, the ET process is dominant to the excitation of $^4I_{11/2}$ level. Thus, the second step involves the excitation processes based on the long-lived $^4I_{11/2}$ level as follows: cross-relaxation (CR), $^4I_{11/2}$(Er$^{3+}$) $\rightarrow$ $^4F_{7/2}$(Er$^{3+}$) + $^4I_{15/2}$(Er$^{3+}$); excited state absorption (ESA), $^4I_{11/2}$(Er$^{3+}$) + a photon $\rightarrow$ $^4F_{7/2}$(Er$^{3+}$); ET, $^2F_{5/2}$(Yb$^{3+}$) + $^4I_{11/2}$(Er$^{3+}$) $\rightarrow$ $^2F_{7/2}$(Yb$^{3+}$) + $^4F_{7/2}$(Er$^{3+}$). The populated Er$^{3+}$ $^4F_{7/2}$ level then relaxes rapidly and non-radiatively to the next lower levels $^2H_{11/2}$ and $^2S_{3/2}$ resulting from the small energy gap between them. Er$^{3+}$ ion at the $^2H_{11/2}$ state can also decay to the $^4S_{3/2}$ state due to multiphonon relaxation process. The estimated energy gap between the $^2H_{11/2}$ state and the next lower state $^4S_{3/2}$ is $\sim$800 cm$^{-1}$ [29]. Thus, multiphonon relaxation rate is very large and the 525 nm emission intensity is reduced.
The above processes then produce the two $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$ and $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$ green emissions centered at 525 and 546 nm, respectively. The red emission at 657 nm is originated from the $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$ transition. There exist two main possible pumping mechanisms for the red emission in GBLEY glass. The first pumping mechanism comprises the population of the $^{4}S_{3/2}$ state, by means of the process described previously, followed by a fast non-radiative decay through multiphonon interaction from the population $^{4}S_{3/2}$ level to $^{4}F_{9/2}$ level and then to the ground state. In the other possible mechanism, the population of $^{4}F_{9/2}$ is based on the processes as follows: ET from Yb$^{3+}$, $^{2}F_{5/2}(\text{Yb}^{3+}) + ^{4}I_{13/2}(\text{Er}^{3+}) \rightarrow ^{2}F_{7/2}(\text{Yb}^{3+}) + ^{4}F_{9/2}(\text{Er}^{3+})$; CR between Er$^{3+}$ ions, $^{4}I_{13/2} + ^{4}I_{11/2} \rightarrow ^{4}I_{15/2} + ^{4}F_{9/2}$; ESA, $^{4}I_{13/2} + \text{a photon} \rightarrow ^{4}F_{9/2}$. The $^{4}I_{13/2}$ level is populated owing to the non-radiative relaxation from the upper $^{4}I_{11/2}$ level.

4. Conclusions

We have studied the structure of GBL glass by peak-deconvolution of Raman spectrum, and the structural information was obtained from the peak wavenumbers. The Raman spectrum investigation indicates that GBL glass has the maximum phonon band at ~751 cm$^{-1}$. Infrared-to-visible upconversion fluorescence in GBLEY glass has also been observed under continuous wave excitation at 975 nm at room temperature. The intense 525, 546, and 657 nm upconversion fluorescence emissions, corresponding to the $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$, $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$, and $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$ transitions, respectively, are due to two-photon absorption processes. Intense upconversion fluorescence of GBLEY glass and relatively low maximum phonon energy of the glass matrix indicates this lead-free germanium–bismuth–lanthanum glass can be used as potential host material for upconversion lasers.

Acknowledgements

This work was financially supported by the ‘Qiming-xing’ Project of Shanghai Municipal Science and Technology Commission (04QNX1448), Shanghai Science and Technology Foundation (022261046), and Chinese National Science Foundation (60207006).

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