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# Blue Cooperative Luminescence In $Yb^{3+}$-Doped Barium Gallogermanate Glass Excited At 976 nm

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**Abstract** The $Yb^{3+}$-doped barium gallogermanate glass has been prepared via the conventional melt method. The absorption spectra, the near infrared emission spectra, the upconversion emission spectra and the differential scanning calorimetry have been measured. Bright blue upconversion emission centered at 476 nm has been observed under the 976 nm laser diode excitation at room temperature. The blue upconversion emission mechanism has been discussed on the blue emission intensity and the measured lifetime. The slope of the log-log plot of the blue emission intensity versus the pump power is equal to 1.98, and the blue luminescence decay time is half of the near infrared fluorescence decay time, confirming that the blue emission comes from $Yb^{3+}$-$Yb^{3+}$ pairs cooperative upconversion mechanism. The result of differential scanning calorimetry suggests that this type of glass is suitable as a potential candidate for fiber drawing.

**Keywords** Cooperative upconversion · $Yb^{3+}$-doped glass · Barium gallogermanate glass

## Introduction

The study of blue-emitting laser sources for use in biomedical diagnostics, optical communication, high density optical data storage, sensors and three-dimensional (3D) display has become a focus of research in recent years [1–4]. Compared with other techniques for blue laser output, upconversion is of interest because it does not need either stringent constraint of phase matching or of high excitation wavelength stability and the output wavelength is not restricted to a given harmonic [5]. The frequency upconversion process is always achieved via multistep excitation due to classical excited state absorption (ESA), the photon avalanche effect, the efficient sequential energy transfer (ET) and the cooperative upconversion either between two ions or between a pair of ions and a third one in solids [6]. Among the rare-earth (RE) ions, upconversion blue emissions can be observed in the glasses doped with erbium ($Er^{3+}$), thulium ($Tm^{3+}$), holmium ($Ho^{3+}$) and ytterbium ($Yb^{3+}$), respectively. $Yb^{3+}$ is unique because it possesses only one electronic excited state that is located in the infrared region, which was always used as a sensitizer ion in RE co-doped system. Recent research illustrated that the blue cooperative upconversion of $Yb^{3+}$ for 3D display technology have the advantage over $Tm^{3+}$ which can significantly decrease the cost of multicolor display by using only one laser pumping beam in the infrared region [7]. In addition, using $Yb^{3+}$ instead of $Tm^{3+}$ can avoid the quenching of the upconversion luminescence at high doping levels caused by cross-relaxation [8]. Cooperative upconversion of $Yb^{3+}$ ions was first observed by Nakazawa and Shionoya in $YbPO_4$ [9]. During the past years, many reports have focused on this phenomenon in crystal [10–13], and some works have been done in fluorid, tellurite and silica glass hosts [7, 14, 15]. The glass fiber is an ideal medium for the integration and the miniaturization of the optical device, which are required for practical application. Thus RE-doped optical fibers based on excellent glass hosts have received considerable attention in recent years [16]. Among the glass hosts, the mechanical strength, chemical durability and

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thermal stability of fluoride glasses are generally less than those of oxide glasses, which hindered fluoride glasses for practical use. Among the oxide glasses, silica glass is not an ideal medium for obtaining intense upconversion emission due to its large nonradiative relaxation rates, and tellurite glass is also limited in the practical application for its bad mechanical property. Germanate glass is now considered as an important material for fiber drawing due to its good properties, such as good mechanical strength, excellent thermal stability, resistance against devitrification, good chemical durability and low phonon energy close to that of tellurite glass. Therefore, searching for an appropriate germanate glass host to obtain efficient upconversion fluorescence is necessary and valuable for developing blue emission fiber lasers at present.

In this work, we investigate the blue cooperative upconversion emission centered at 476 nm in $Yb^{3+}$-doped barium gallogermanate glass upon the 976 nm laser diode (LD) excitation. To the best of our knowledge, this is the first time that the cooperative upconversion blue emission is found in the $Yb^{3+}$-doped germanate glass. Additionally, the Differential scanning calorimetry (DSC) result suggests that this type of glass is a potential candidate for fiber drawing.

## Experiments

### Glasses preparation

The glass sample was prepared by the conventional melt method. The starting materials for preparing the $Yb^{3+}$-doped barium gallogermanate glasses are analytic purity $BaCO_3$ (3N) and high purity $Ga_2O_3$ (5N), $GeO_2$ (5N) and $Yb_2O_3$ (5N). The composition of the glass is $15BaO–15Ga_2O_3–70GeO_2$ doped with 0.5 mol% and 4.5 mol% of $Yb_2O_3$. Batch of 20 g was melt in the covered platinum crucible at 1450°C for 20 min in a Si-Mo furnace. Finally the homogenous melts were cast on a stainless plate preheated at 230°C and hold in a muffle furnace at 640°C for 2 h and then cooled at a rate of 10°C/h to room temperature. The annealed samples were cut and polished carefully into 10 mm × 10 mm × 1.5 mm plates for optical measurements.

### Properties measurements

The absorption spectra was measured between 250 and 1800 nm using a Perkin-Elmer Lambda 900UV/VIS/NIR spectrophotometer with a resolution of 1.0 nm. The near infrared luminescence (800–1200 nm) and upconversion spectra (400–900 nm) were measured with a TRIAX320 type spectrometer (Jobin-Yvon Co., France) under the excitation of a multimode InGaAs laser diode stabilized with a pigtailed fiber at a wavelength of 976 nm, whose beam was focused to a 2.5 mm diameter spot on the glass plate. An InGaAs detector and a photomultiplier tube detector were used in the near infrared region and visible region, respectively. In order to compare the luminescence intensity of $Yb^{3+}$-doped barium gallogermanate glass with increasing pump power as accurate as we can, the position of the pumping beam and the width (0.5 mm) of the slit to collect the luminescence signal were fixed under the same condition. The wavelength calibration of the system from 400 to 900 nm was calibrated by using a standard continuous 450-W Xenon discharge lamp and the Raman scattering bands of the distilled water. The spectral response of the monochromator and detector was calibrated via a standard tungsten bulb lamp. The decay curve for the blue emission and the near infrared luminescence of $Yb^{3+}$ were taken by modulating the 976 nm LD and the decay time were obtained by fitting the decay data with a single-exponential decay function. The glass transition temperature ($T_g$) and the onset crystallization temperature ($T_x$) were analyzed with differential scanning calorimetry (DSC) at a heating rate of 10°C/min.

All the measurements were performed at room temperature.

## Results and discussion

### Absorption and near infrared emission spectra

The near infrared absorption spectra and the near infrared emission spectra of the $Yb^{3+}$-doped barium gallogermanate glass were shown in Fig. 1, and the inset diagram presents the absorption spectra in the range from 250 to 1800 nm of $Yb^{3+}$ ions. The recorded near infrared absorption shows two peaks centered at 935 and 975 nm, which corresponding to the transitions from the ground state multiplet $^2F_{7/2}$ into the various Stark levels of the excited state multiplet $^2F_{5/2}$, while the near infrared emission spectra presents a wide infrared emission band with two peaks centered at 973 and 1010 nm assigned to the transitions from the lowest level of the excited multiplet to the ground state multiplet. This spectrum was different from that of $Yb^{3+}$ in tellurite glass [15], which presents four peaks centered at 975, 1002, 1018, 1043 nm in the near infrared emission spectra. The other two peaks hardly observed in Fig. 1 may be due to the inhomogeneous broadening of the transitions [7]. The inset diagram of Fig. 1 account for the absorption spectra between 250 and 1800 nm, from which only the near infrared absorption band can be clearly observed. It is also found that the number of the absorption band is independent of $Yb^{3+}$ ions concentration.

### The cooperative luminescence

The upconversion spectra of $15BaO–15Ga_2O_3–70GeO_2$-$0.5Yb_2O_3$ (in mol %) sample under the 976 nm LD excitation was depicted in Fig. 2, and the inset diagram shows

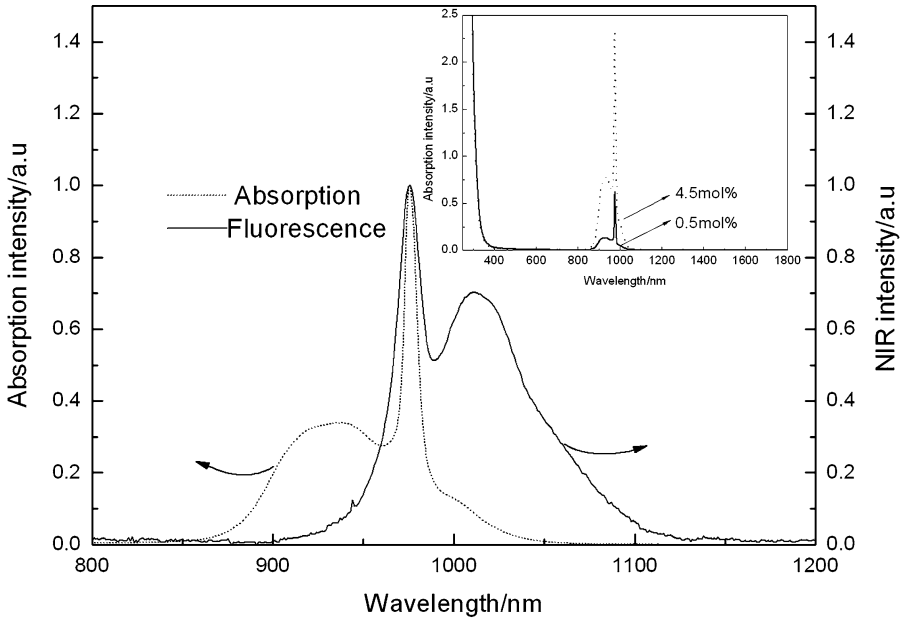


**Fig. 1** Absorption (doted line) and the near infrared emission (solid line) spectra of the $Yb^{3+}$-doped barium gallogermanate glass (1.0 mol%, $Yb^{3+}$) upon 976 nm LD excitation at room temperature. The inset shows the absorption spectra from 250 to 1800 nm of barium gallogermanate glasses with various $Yb_2O_3$ concentrations in mol%

the dependence of the blue emission intensity on the pump power. As can be seen from Fig. 2, an intense blue emission band centered at 476 nm is observed. It is important to point out that the blue emission can be easily seen by naked eyes at the pump power at 600 mW at room temperature. Three weak emission bands centered at 523, 547 and 652 nm, respectively, are also observed, which demonstrate that a bit $Er^{3+}$ impurity in the starting materials was introduced into the glass. From Fig. 2, we find no trace of impurity of $Tm^{3+}$ ions. The blue emission induced by $Tm^{3+}$ is contributed to a three-photon process, a log-log plot of the blue emission intensity as a function of the pump power was calculated, and the slope is equal to 1.98, as depicted in Fig. 2 inset. This result confirms that a double-photon excitation process is involved for the blue emission.

To elucidate the cooperative upconversion mechanism of the blue emission, the luminescence decay experiments of both the blue emission and the near infrared emission were performed, as shown in Fig. 3. The relation between the decay times of the cooperative luminescence ($\tau_{coop}$) and the near infrared emission ($\tau_2$) can be described employing a rate equation model [15, 17]. The rate equation for the energy

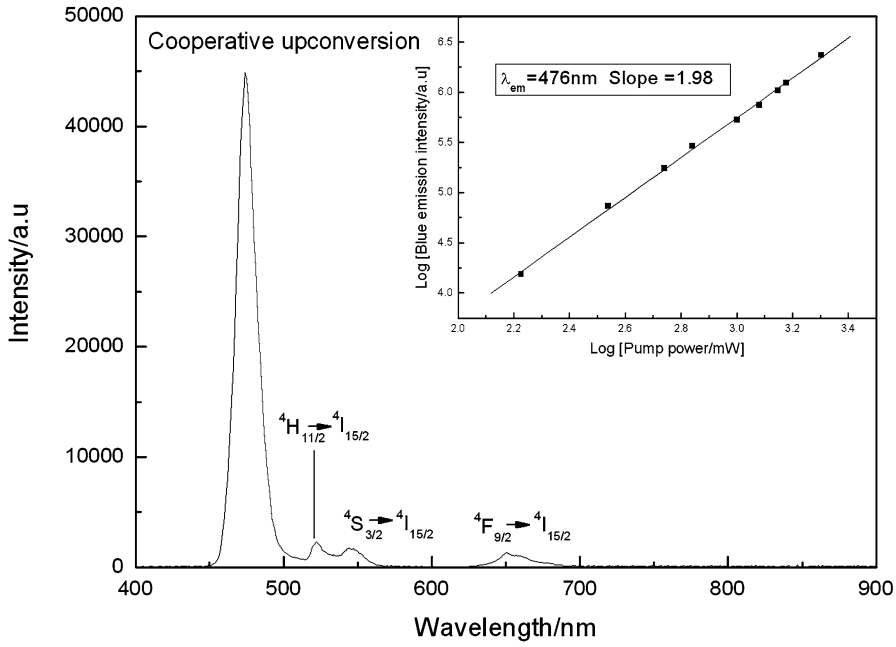


**Fig. 2** The upconversion spectra in the range from 400 to 900 nm in the $Yb^{3+}$-doped barium gallogermanate glass (1.0 mol%, $Yb^{3+}$) upon 976 nm LD excitation. The inset presents the log-log plot of the blue emission intensity as a function of the pump power under the 976 nm LD excitation at room temperature

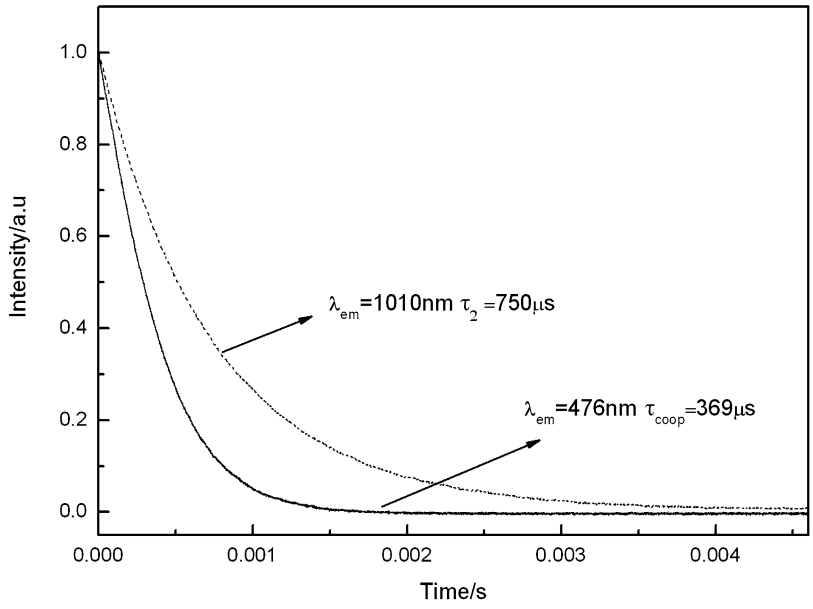


**Fig. 3** The decay curve of blue luminescence (476 nm) and near infrared fluorescence (1010 nm) in $Yb^{3+}$-doped barium gallogermanate glass (1.0 mol%, $Yb^{3+}$), excited by a 976 nm LD beam at room temperature

level of $Yb^{3+}$ has the following form:

$$\frac{dN_2}{dt} = RN_1 - \frac{N_2}{\tau_2} - CN_2^2 \quad (1)$$

where $N_1$ and $N_2$ are the population densities of the ground state and the excited state levels of $Yb^{3+}$, R is the pump rate, C is the cooperative luminescence rate constant. Decay formula of the near infrared intensity ($I_{NIR}$) and cooperative luminescence intensity ($I_{coop}$) can be expressed respectively as:

$$I_{NIR} \propto N_2 \propto \exp\left(\frac{-t}{\tau_2}\right) \quad (2)$$

and

$$I_{coop} \propto N_2^2 \propto \exp\left(\frac{-t}{\tau_2/2}\right) \quad (3)$$

As can be seen from Fig. 3, the near infrared and cooperative luminescence decay curves were fitted with a single exponential decay function, with a constant of 750 $\mu$s $\pm$ 5 and 369 $\mu$s $\pm$ 5, respectively, The cooperative luminescence decay time is half of the near infrared decay time, which agrees very well with the rate equation model given above, confirming that the blue emission comes from $Yb^{3+}$ -$Yb^{3+}$ cooperative upconversion mechanism, as illustrated in Fig. 4.

Thermal stability of the glass sample

Figure 5 shows the DSC curve of $Yb^{3+}$-doped barium gallogermanate glass, the difference between the glass transition temperature and the onset crystallization temperature ($\Delta T = T_x - T_g$), $\Delta T$, has been frequently adopted as a rough indicator of the glass thermal stability against devitrification. To achieve a wide working range of temperature for fiber drawing, it is desirable for a glass host to have a $\Delta T$ as large as possible [16, 18]. For drawing a glass fiber, $\Delta T > 120$C is necessary. It can be seen that $Yb^{3+}$-doped barium gallogermanate glass exhibits a $\Delta T = 172$C, which suggests that it is suitable as a potential candidate for fiber drawing [19].

## Conclusions

The $Yb^{3+}$-doped barium gallogermanate glass has been prepared by the conventional melt method. The absorption, the near infrared emission, the upconversion spectra and the

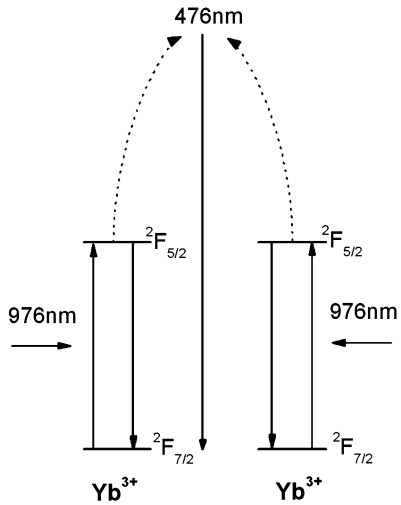


**Fig. 4** The simplified energy level diagram of $Yb^{3+}$-$Yb^{3+}$ pairs under the 976 nm LD excitation

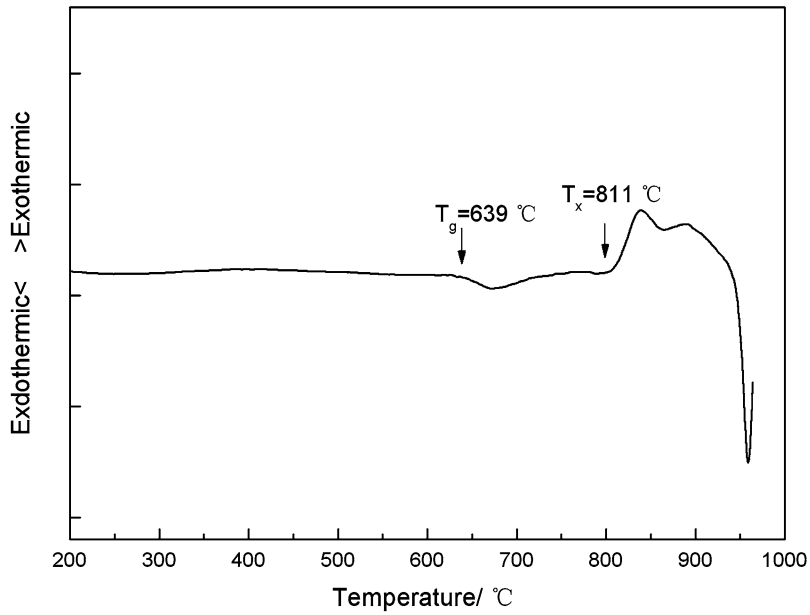


**Fig. 5** The DSC curve of $Yb^{3+}$-doped barium gallogermanate glass (1.0 mol%, $Yb^{3+}$)

differential scanning calorimetry have been measured. Bright blue upconversion emission centered at 476 nm has been observed under the 976 nm LD excitation at room temperature. The blue luminescence decay lifetime is half of the near infrared fluorescence decay lifetime, which demonstrated that the blue emission is originated from $Yb^{3+}$-$Yb^{3+}$ cooperative upconversion. This glass exhibits a $\Delta T = 172$℃, which suggests that it is suitable as a potential candidate for fiber drawing.

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