



Energy transfer and 1.8 μm emission in $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses



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ABSTRACT

The 1.8 μm down-conversion emission properties of $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses are investigated under 980 nm laser diode (LD) excitation in this paper. The glass properties are systematically evaluated by DSC, XRD, Raman techniques. The spectroscopic properties of Er^{3+} and Tm^{3+} including infrared down-conversion (DC) and visible up-conversion (UC) emissions are studied in detail. Meanwhile, the up-conversion emissions at 542 nm, 654 nm of Er^{3+} are suppressed with a high amount of Tm_2O_3 added. The Judd-Ofelt parameters and spontaneous transition probability of Tm^{3+} are illustrated for radiative properties. Besides, the absorption and emission cross sections of Tm^{3+} in $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses are provided as potential candidates for mid-infrared applications. The possible energy transfer mechanism is investigated via simplified energy level diagram, and energy transfer efficiency from Er^{3+} to Tm^{3+} is as high as 85.9%. In addition, the energy transfer parameters between Er^{3+} and Tm^{3+} are analyzed by the phonon side-band theory. The results indicate that the $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses have potential applications in mid-infrared lasers.

1. Introduction

Nowadays, Tm^{3+} -doped glasses for $\sim 2 \mu\text{m}$ lasers have gained significant attentions because of their extensive applications in the high-resolution spectroscopy of gases, laser medicine surgery, eye-safe laser radar, and so on [1–3]. In order to obtain efficient 1.8 μm emission of Tm^{3+} ions, Yb^{3+} [4] is frequently used for enlarging the absorption efficiency of Tm^{3+} ions since Yb^{3+} is highly pumped by 980 nm laser diode (LD). However, intense up-conversion emissions of $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped glasses [4] blemish emitting efficiency of infrared down-conversion emissions, which restricts the applications of Yb^{3+} . As discussed in our previous work [5], Cr^{3+} ions offer a variety of selective pump wavelength for Tm^{3+} due to broad absorption bands ranging from near-ultraviolet to near-infrared. In addition, researchers also find out that $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped glasses pumped by 980 nm laser win over Tm^{3+} single-doped glasses excited at 800 nm laser because population reversion among the former is achieved more easily than the latter [6]. Therefore, there may be a new path of acquiring $\sim 2 \mu\text{m}$ emission [7–10] via co-doping $\text{Er}^{3+}/\text{Tm}^{3+}$. However, the strong up-conversion emissions of $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped glasses still need to be suppressed for applications in infrared field.

To date, $\sim 2.0 \mu\text{m}$ fiber lasers have been achieved from different

glasses mainly including silica, silicate, fluoride, tellurite, and germanate glasses [11–15]. Silica and silicate glasses have high maximum phonon energy (MPE) and multi-phonon decay becomes strongly competitive against radiative luminescence. Besides, the limited doping concentration of Tm^{3+} blocks the intention of tiny-sized lasers [11]. Fluoride glasses have low MPE and high luminous efficiency, however the preparation is difficult, their mechanical and chemical stabilities are poor. In contrast, germanate glasses have excellent thermal stability and a much higher doping concentration of rare earth ions, which supports the fabrication of highly compact devices [15].

According to previous research [16], Al_2O_3 is chosen as an important network intermediate instead of Ga_2O_3 in barium gallo-germanate glass to investigate its resistance to crystallization properties [17]. Then there is an effective approach to lowering the up-conversion emissions in the $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses via applying a high Tm^{3+} doping level. The Raman spectra are researched to find the MPE and OH^- content is studied by transmittance spectra. Besides, the spectroscopic properties and lifetime decay are followed to reveal the transitions properties of Tm^{3+} and Er^{3+} . To analyze the energy transfer mechanism between Tm^{3+} and Er^{3+} , simplified energy level diagram is showed and explained in detail. Additionally, the dipole-dipole energy transfer parameters are considered by the phonon

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Table 1
Representations of glass samples with x mol.% of ErF_3 and y mol.% of Tm_2O_3 .

Representations	G0	GT1	GE1	GET0.1	GET0.5	GET1
ErF_3	0	0	1	1	1	1
Tm_2O_3	0	1	0	0.1	0.5	1

sideband theory.

2. Experiment

Based on glass forming region obtained via Thermodynamic Equilibrium Method, glasses with a nominal composition (in mol.%) of $65\text{GeO}_2\text{-}17\text{Al}_2\text{O}_3\text{-}12\text{BaF}_2\text{-}3\text{NaF}\text{-}3\text{La}_2\text{O}_3$ were prepared using the conventional melt-quenching technique. The glasses were doped with x mol.% of ErF_3 and y mol.% of Tm_2O_3 (x = 0, y = 0, 1.0; x = 1.0, y = 0, 0.1, 0.5, 1.0) and marked as G0, GT1, GE1, GET0.1, GET0.5, GET1, as listed at Table 1. All reagents ($\geq 99.99\%$) of NaF, BaF_2 , Al_2O_3 , GeO_2 , Tm_2O_3 , and ErF_3 were used as raw materials. The 15 g mixed batches were melted in alumina crucibles at 1350°C for 30 min and then poured onto a preheated steel plates (200°C), followed by annealing at 400°C for 2 h to remove internal stresses. The obtained glasses were cut into the size of $10 \times 15 \times 1.5 \text{ mm}^3$ then optically polished for measurements.

Differential scanning calorimeter (DSC) was carried out in N_2 as protected atmosphere at a heating rate of 10 K/min to evaluate the characteristic temperatures of glass transition and crystallization. To identify the glass phase, X-ray diffraction (XRD) measurements were performed on a powder diffractometer (X'Pert PROX, Cu-K α) operated at 40 kV and 40 mA with the scan range of $10\text{--}90^\circ$. The Raman spectrum was tested via Raman spectrometer. The absorption spectra were obtained on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer in the spectral range of 350–2000 nm with a resolution of 1 nm. The transmittance spectrum was measured using a Vector 33 Fourier transform infrared spectrophotometer (Bruker Corp.). Using a 980 nm laser diode as excitation source, the photoluminescence spectra were recorded on an iHR320 spectrometer (Jobin-Yvon Corp., Horiba Scientific). A digital oscilloscope (TDS3012C, Tektronix) equipped on the iHR 320 spectrometer was employed to collect the decay curves upon excitation with 980 nm and 808 nm pulsed LD. All the measurements were performed at room temperature.

3. Results and discussions

Glass Forming Region (marked as GFR) is the basis of preparing the glasses for researchers. However, lack of experimental GFR for $\text{BaO-Al}_2\text{O}_3\text{-GeO}_2$ puts obstacles for this study. As a reference, the calculated GFR of this glass system is theoretically obtained via thermodynamic

equilibrium method reported in our previous work [18]. As displayed in Fig. 1(a), the calculated GFR is located around eutectic points (T_1 , T_2 , T_3) surrounded with red lines, these points are acquired through points e_1 , e_2 , e_3 calculated corresponding to the binary phase diagram [18]. Furthermore, BaF_2 is used to take part of BaO in order to reduce the hydroxyl [19] in $\text{BaO-Al}_2\text{O}_3\text{-GeO}_2$ system, appropriate Al_2O_3 amount is added to increase the glass stability. Besides, the chosen point (marked as 1, composition $68\text{GeO}_2\text{-}17\text{Al}_2\text{O}_3\text{-}15\text{BaO}$) is located in calculated GFR. Then some NaF is added to lower the melting point of glass and La_2O_3 to enhance the refractive index. As an example of considering thermal properties of the glass, Fig. 1(b) demonstrates the DSC curve of GET1 glass, the glass characteristic temperatures T_g , T_c are determined as 504°C , 580°C , respectively. The T_g of GET1 is lower than that of lead-germanate and alkali-germanate glasses [20–21] and GET1 has a low fiber drawing temperature.

Fig. 2(a) denotes the XRD pattern of glass samples and they are completely amorphous without any sharp peaks. In the inset of Fig. 2(a), the obtained GE1, GT1, GET1 samples keep good transparency. Fig. 2(b) illustrates the Raman spectra of G0 glass. The Raman scattering bands around 475 cm^{-1} are corresponding to the various bending vibration modes of Ge-O-Ge and Al-O-Al [22], while the peaks around 814 cm^{-1} and 910 cm^{-1} are attributed to the stretching modes of Ge-O and Al-O structure units in the environment of bridging and non-bridging oxygen [22]. The MPE of the glass is $\sim 910 \text{ cm}^{-1}$, which is lower than those of bismuth silicate glass ($\sim 920 \text{ cm}^{-1}$) [23] and tungsten-tellurite glass ($\sim 926 \text{ cm}^{-1}$) [24]. More importantly, the non-radiative transition probability of Tm^{3+} will be suppressed by low vibrational phonon energy in the glass matrix and this low MPE glass matrix supports emission efficiency of $1.8 \mu\text{m}$ [23].

Fig. 3(a) displays the absorption spectra of $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses in the wavelength range from 300 to 2000 nm. There are labeled in the spectra with characteristic absorption bands corresponding to the transitions from the ground states to excited states of Er^{3+} and Tm^{3+} ions. The absorption transitions centered at 1650, 1209, 795, 682, 472 and 356 nm in GT1 are ascribed to the transitions from the ground state of $^3\text{H}_6$ to the excited states of $^3\text{F}_4$, $^3\text{H}_5$, $^3\text{H}_4$, $^3\text{F}_{2,3}$, $^1\text{G}_4$, and $^1\text{D}_2$, respectively. The absorption transitions belonging to Er^{3+} in GE1 are also marked in the Fig. 3(a). Here, absorption band around 1000 nm in GET1 matches with commercially available 980 nm LD and GET1 has the absorption possibility of 980 nm LD.

Fig. 3(b) demonstrates the transmittance spectra of GET1 from 2000 to 3200 nm and the maximum transmittance achieves as high as 90%. The broad absorption bands around 3000 nm are attributed to the stretching vibrations of free OH^- groups, and the OH^- absorption coefficient, α_{OH^-} (cm^{-1}) is obtained by Eq. (1) [26]:

$$\alpha_{\text{OH}^-} = \frac{1}{L} \ln \frac{T_0}{T} \quad (1)$$

where L is the thickness of the sample, T_0 and T are the transmittance at

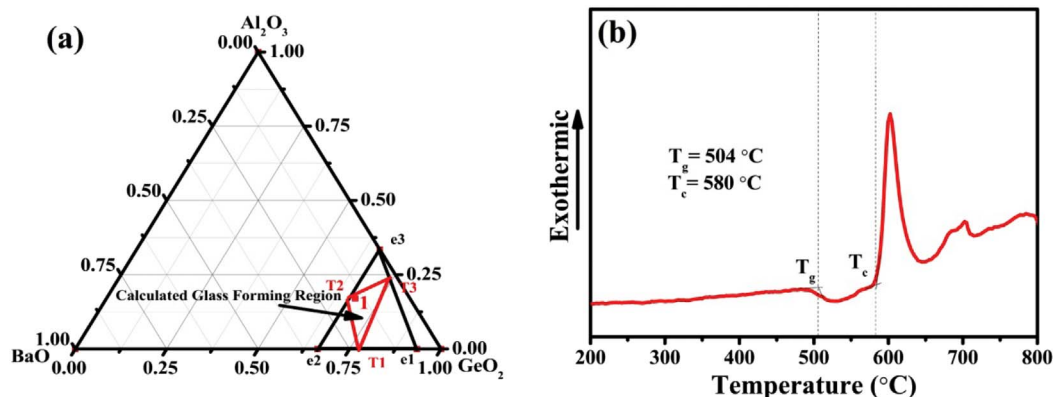


Fig. 1. (a) The calculated glass forming region of $\text{BaO-Al}_2\text{O}_3\text{-GeO}_2$. (b) DSC curve of GET1 glass.

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