

Structural and fluorescence properties of Ho3+/Yb3+doped germanosilicate glasses tailored by Lu2O3

W. Cao, F. Huang, R. Ye, M. Cai, R. Lei, J. Zhang, S. Xu, X.-H. Zhang

▶ To cite this version:

W. Cao, F. Huang, R. Ye, M. Cai, R. Lei, et al.. Structural and fluorescence properties of Ho3+/Yb3+ doped germanosilicate glasses tailored by Lu2O3. Journal of Alloys and Compounds, 2018, 746, pp.540-548. 10.1016/j.jallcom.2018.02.325. hal-01740148

HAL Id: hal-01740148 https://univ-rennes.hal.science/hal-01740148

Submitted on 6 Jul 2018 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Structural and fluorescence properties of Ho³⁺/Yb³⁺ doped germanosilicate glasses tailored by Lu₂O₃

Wenqian Cao¹, Feifei Huang^{1*}, Renguang Ye¹², Muzhi Cai¹², Ruoshan Lei¹, Junjie Zhang¹,

Shiqing Xu^{1*} and XiangHua Zhang²

1. College of Materials Science and Engineering, China Jiliang University, Hangzhou, 310018, China

2. Laboratoire Verres & Céramiques, UMR CNRS 6226, Université de Rennes 1, Campus Beaulieu,

35042 Rennes Cedex, France

* Corresponding author. huangfeifei@cjlu.edu.cn

shiqingxu@cjlu.edu.cn.

ABSTRACT: Structural and fluorescence properties of $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped germanosilicate glasses have been modified by tailoring the composition using lanthanide additive Lu₂O₃. Raman spectra and X-ray Photoelectron spectra reveal that the addition of Lu₂O₃ can change the structure by increasing non-bridging oxygens (NBO) in this glasses. Meanwhile, an improved thermal stability (Δ T: from 110 to 187 °C) has also been obtained via Lu³⁺ lanthanide contraction'. Futhermore, the positive effect of changed glass structure gives excellent fluorescence properties by the decreasing cross relaxation process which are proved by the experimental upconversion, near-infrared and mid-infrared fluorescence spectra. Additionally, a double enhancement of a 2.0 µm emission has been achieved successfully in this silica-germanate glass with 7 mol% Lu³⁺ addition, which possesses a larger emission cross section (4.41 × 10⁻²¹ cm²) at 2022 nm. These results indicate that the optimized emission of Ho³⁺ for optical fiber laser can be achieved by tuning the glass structure using lanthanide additive Lu₂O₃.

Keywords: Germanosilicate glasses; Lanthanide additive Lu₂O₃; NBO and BO; Energy transfer.

1. Introduction

Rare earth ions doped glass fibers that exhibit laser emission around ~2.0 μ m have been paid considerable attention due to their potential applications in eye safe laser radar, atmosphere pollution monitoring, measurement of water vapor and biomedicine, etc[1-5]. A number of experiments have proved that Tm³⁺ and Ho³⁺ perform well in achieving 2.0 μ m laser. Compared with Tm³⁺, the emission band of Ho³⁺ is broader and the stimulated emission cross section of Ho³⁺ is practically five times larger than that of Tm³⁺, which suggests that more efficient laser output can be achieved by Ho³⁺. Meanwhile, the longer fluorescence lifetime of Ho³⁺ is conducive to Q-switched lasers[6, 7]. However, Ho³⁺ cannot directly be pumped by 808 nm or 980 nm commercial laser diode (LD) source for lacking of a suitable ground absorption band. Traditionally, in order to solve this problem, other rare earth ions such as Er³⁺, Yb³⁺, Tm³⁺ and Nd³⁺ with obvious ground absorption under commercial LD excitations are usually introduced to sensitize the Ho³⁺[8-10]. Among all the sensitizers, Yb³⁺ ion with the simple energy level structure (ground state ²F_{7/2} and excited state ²F_{5/2}) and a broad absorption band in the wavelength region of 860-1060 nm can be a useful sensitizer[11, 12].

In order to develop more efficient fiber lasers for 2.0 μ m emission, besides the rare earth ions, the host material must be considered as well. Thus, searching for suitable host materials for mid-infrared lasers operating in this wavelength is quite necessary. Recent years have witnessed the great development of various glasses, such as silicate, heavy-metal oxide and fluoride glasses. Although the phonon energy of fluoride-based glass is low, its low mechanical strength limits its applications[13]. In parallel, the low loss and high physical strength of silicate glasses have made them remarkably useful hosts for rare-earth cations emitting in the 2.0 μ m region. However, compared with other glasses, the larger multiphonon relaxation rate induced by higher phonon energy in silicate glass (~1000 cm⁻¹)

lowers the quantum efficiency and causes thermal damage of the fiber laser[14]. Thus, the heavy-metal oxide glasses have become a new investigative hotspot of mid-infrared laser to achieve lower phonon energy. Germanate glass as the typical example of heavy-metal oxide glasses, is one of the most promising materials benefited from its high rare-earth solubility, superior infrared transparency, comparative low phonon energy (-900 cm⁻¹), strong mechanical and high damage threshold. Unfortunately, the high cost of GeO₂ causes its slow development in optical amplifiers[15-17]. So we try to research mixed germanosilicate (SG) glasses, which can compensate for the deficiencies of silicate and germanate glasses. The phonon energy has been decreased by introducing appropriate amount of GeO₂ into silicate glass, which can reduce the multiphonon relaxation rate and enhance the refractive index of the glass host and which is beneficial for improving the 2.0 μ m emission cross section[18, 19]. Therefore, germanosilicate glass which combines the merits of germanate and silicate glasses can be a suitable optical material for mid-infrared fiber lasers[20].

Additionally, the structure properties of host glasses usually can be modified by tailoring the composition using lanthanide additives. Cations with higher coordination numbers and the higher field strength can enhance the structure of glass and increase glass transition temperature. Lanthanide cations with the high field strength are often used as network modifiers in the glass, which are incorporated in the space between Si-(O, N)x tetrahedral and strengthen the structure of glass[21]. Therefore, in 1994, Jewell J. et al. reported that the addition of La_2O_3 is able to improve glass forming ability and enhance thermal stability due to the larger molecular ratio and coordination number of La^{3+} ion, while Y_2O_3 component is able to improve thermal stability[22]. Since then, many authors have been using lanthanide as the modifier to tailor the optical properties of glasses. For example, in 2017,

Hao Y. et al. demonstrated the proper introduction of Y_2O_3 can enhance the luminescence properties of borosilicate glasses by decreasing the bridge oxygens of glass host[23]. At the same time, Wang X. et al also reported the influence of La₂O₃ on the structure and spectroscopy of Tm³⁺-doped Lanthanum aluminosilicate glasses[24]. Especially, the glass network with Lu³⁺ would have tighter structure and better properties than the glasses containing other lanthanides owing to its network with smaller atoms.[21]. Additionally, Lu³⁺ has a stronger ability for bonding with O²⁻ than Si⁴⁺ due to the oxyphilic character of Lu³⁺[25]. However, there is no detailed report on mid-infrared fluorescence of Lu₂O₃ modified germanosilicate glasses from the aspect of regulating its structure.

Thus, in this paper we investigated primarily different concentration of Lu₂O₃ in the Ho³⁺/Yb³⁺ co-doped SiO₂-GeO₂-Ga₂O₃-BaO-Li₂O (SG) glasses to analysis its structure and mid-infrared spectroscopic properties. The structure of glasses has been studied by X-ray Photoelectron Spectroscopy (XPS) and Raman spectra. The introduction of Lu₂O₃ improved the thermal stability and mid-infrared fluorescence in present system. Additionally, we researched the absorption spectra, and then calculated the J-O intensity parameters Ω_{λ} (t = 2, 4, 6), radiative parameters (such as spontaneous radiation transition probability A_{rad}, radiation lifetime τ_{rad}) of Ho³⁺ in present glass. Meanwhile, the absorption (σ_{abs}) and emission cross sections (σ_{em}) of Ho³⁺ at 2.0 µm have been calculated and discussed.

2. Experimental

Germanosilicate glasses with molar compositions of $(99-x)(SiO_2-GeO_2-20Ga_2O_3-BaO-Li_2O)-xYb_2O_3-1Ho_2O_3$ (x=0, 1, namely SG-Ho³⁺, and SG-Ho³⁺/Yb³⁺, respectively) and $98(SiO_2-GeO_2-(20-y)Ga_2O_3-yLu_2O_3-BaO-Li_2O)-1Yb_2O_3-1Ho_2O_3$ (y=0, 5, 7 and 9, named SG, SGLu5, SGLu7 and SGLu9, respectively) were fabricated by using reagent-grade SiO₂, GeO₂, Ga₂O₃, BaO,

Li₂CO₃, La₂O₃, Y₂O₃, Lu₂O₃ Yb₂O₃, and Ho₂O₃ as the starting materials. Batches of raw materials (15 g) were well-mixed and melted in a corundum crucible in a Si-Mo resistance electric furnace at 1520 °C for 40 min. Then, they were quenched on preheated stainless steel plate and annealed near the temperature of glass transition for 2 h before they were cooled to room temperature. The annealed samples were finally cut and optically polished to the size of 10 mm \times 10 mm \times 1 mm for the optical property measurements.

The characteristic temperatures (temperature of glass transition T_g and temperature of onset crystallization peak T_x) of samples were determined using a NetzschSTA449/C differential scanning calorimetry at a heating rate of 10 K/min with error limit of ±0.2%. The densities of samples were tested via the Archimedes principle using distilled water as the immersion medium with error of ± 0.001 g/cm³. Refractive indexes were measured by the prism minimum deviation method at the wavelength of 1053 nm with error limit of ±0.05%. The visible UC (500~800 nm) fluorescence spectra were obtained with a TRIAX550 spectrofluorimeter upon the excitation of 980 nm LD. Absorption spectra were obtained using a PerkinElmer Lambda 900UV-VIS-NIR spectrophotometer in the range of 300~2200 nm a resolution of 1 nm. The emission spectra (500~700 nm, 1100~1300 nm, 1800~2300 nm and 2700~300 nm) were measured via a Triax 320 type spectrometer upon excitation of 980 nm. The Raman spectra of the glasses were measured with a Renishaw invia Raman microscope in 200-1200 cm⁻¹ spectrum range using the 532 nm excitation line. The XPS measurements were conducted using a high-performance K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific, United States) in ultra high vacuum. Monochromatic Al Ka radiation (hu=1846.6 eV) was used with 15 kV accelerating voltage. The C-1s peak arising from pump oil impurities was used as an internal reference, with binding energy of 284.6 eV. The same experimental conditions for different

samples were maintained so as to get comparable results. All the measurements were carried out at room temperature. Additionally, the maximal measured error in binding energy is $\pm 0.5\%$.

3. Results and discussion

The Raman spectra of prepared glasses are measured at room temperature as shown in Fig.1. The spectrum of SG glass is deconvoluted into six peaks using Gaussian distribution. These six bands are denoted as 260, 465, 480, 670, 840 and 1020 cm⁻¹ bands. The obvious band C in Raman spectra is related to bending and stretching vibrations of the T-O-T (Ge or Ga) bond. The partial vibrations of Ge-O and Ga-O tetrahedron units the peak E is obtained[26]. Hence, in the Raman spectra the contribution of germanate bands is dominate, this is perhaps because of the higher polarizability of Ge4+ than Si4+ and therefore only the primary bands of germanate structures were observed[27, 28]. Especially, from the inset of Fig.1, two weak bands (Peak D and F in the SG glass) at 670 and 1020 cm⁻¹ may be assigned to the Si-O-Ge and Si-O-Si modes[29], and then, the two weak bands exhibit a sharp reduction in the relative intensity with the introduction of the Lu₂O₃. A possible mechanism for this reduction is related to the oxyphilic character of Lu^{3+} , and the Lu^{3+} is preference for bonding with O exceeds Si, which means that the Lu^{3+} will compete with Si for O²⁻[25]. Hence, in this paper, the introduction of Lu₂O₃ instead of Ga₂O₃ might break the primary structure of [SiO₄]/[GeO₄] and lead a change between the relative amount of NBO and BO. It will be detailedly researched to further understand the change of glass structure in the next.



Fig. 1 Deconvoluted Raman spectra of SG glass. The inset is Raman spectra of SG, SGLu5, SGLu7 and SGLu9 glasses.

A detailed analysis of the XPS binding energies was performed in order to get insight into the bonding in these glasses as a function of the rare earth. Fig.2 shows the O1S spectra of present glasses with a Shirley background subtraction. Each spectrum can be deconvoluted into two peaks according to the asymmetry of the shoulders and peaks. The low and high binding energy peaks of O1S spectra of prepared glasses are attributed to non-bridging (NBO) and bridging oxygens (BO), respectively[30, 31]. From Table 1, the area fraction F of NBO and BO are 0.33, 0.54, 0.70 and 0.71 in SG, SGLu3, SGLu7 and SGLu9 glasses, which suggests that the number of non-bridging oxygens increases in the glass network structures with the introduction of Lu₂O₃. A larger non-bridging oxygens number means the structure of primary glass changed and exhibits a lower extent of local Ho³⁺ clustering in the SGLU-X glasses[32]. Therefore, we can know that the addition of modifier Lu₂O₃ in this germanosilicate glass can change the structure of glasses to decrease the probability of rare-earth clustering, conducing to better fluorescence characteristic of germanosilicate glass.



Fig. 2 O1S spectrum of prepared glasses (a) SG; (b) SGLu5; (c) SGLu7; (d) SGLu9.

Glass samples	Binding energy(eV)	FWHM(eV)	F
SG	532.40	2.34	0.22
	531.00	2.17	0.55
SCI u5	532.21	1.98	0.54
SGLu5	531.42	2.11	0.34
SCL -7	531.73	2.13	0.70
SGLu7	531.05	2.21	0.70
SCIO	531.71	2.07	0.71
SULUY	530.79	2.73	0.71

Table 1 Binding energy (eV), FWHM (eV) and the area ratios F of NBO and BO in XPS spectra.

Fig. 3 shows the measured DSC curves for the prepared glasses. Table 2 lists the characteristic temperatures such as temperature of glass transition (T_g) , onset crystallization (T_x) and peak crystallization (T_p) as well as the calculated thermal stability parameters ΔT in prepared glasses. T_g is

an important factor for laser glass, which gives glass good thermal stability to resist thermal damage at high pumping intensities[33]. Meanwhile, ΔT has been frequently used for evaluating the thermal stability and forming ability of glass, a larger ΔT parameter means the better thermal stability against crystallization and nucleation process. Usually, ΔT should be more than 120 °C to minimize probability of crystallization during the fiber drawing process[34].



Fig. 3 DSC curves of prepared glasses.

Table 2 The glass transition temperature (T_e), onset crystallization temperature (T_x), top crystallization peak (T_p),

Sample	T _g (°C)	$T_x(^{\circ}C)$	$T_p(^{\circ}C)$	ΔT(°C)
SG	645	755	795	110
SGLu5	682	854	911	172
SGLu7	716	896	943	180
SGLu9	730	917	950	187

thermal stability parameters ΔT in prepared glasses.

As shown in Table 2, it can be found the glass transition temperature (T_g) increases from 645°C to

730°C which indicates that the introduction of lanthanide cations Lu^{3+} can improve the thermal stability of this germanosilicate glass system because of so called 'lanthanide contraction' [21]. In addition, the ΔT of SGLu5, SGLu7 and SGLu9 are 172, 180 and 187°C, respectively, which are much larger than that of SG glass. These results suggest that the introduction of Lanthanide cations Lu^{3+} with the high field strength in this germanosilicate glass can be a good way to improve the thermal stability, defined as the resistance to the permanent change of properties, particularly, the resistance against crystallization during heating[35]. Compared with the characteristic temperatures in Table 2 and Fig. 3, a conclusion can be drawn that the prepared germanosilicate glasses with the addition of Lu_2O_3 in this study possess a better thermal stability, which is good for crystal-free fiber drawing and fabrication.

Fig. 4 indicates the room temperature absorption spectra of Ho³⁺ singly and Yb³⁺/Ho³⁺ co-doped samples in the wavelength region of 300-2200 nm. The inset is the photo of prepared glasses. Referring to Ho³⁺ singly doped SG glass, the absorption spectrum consists of seven absorption bands centered at 1949, 1151, 644, 540, 487, 474 and 450 nm, corresponding to the transitions starting from the ⁵I₈ ground state to excited states ⁵I₇, ⁵I₆, ⁵F₅, (⁵F₄, ⁵S₂), (⁵G₆, ⁵F₁) and ⁵G₅, respectively. In addition, the broadband absorption with a strong peak at 980 nm can be observed in Ho³⁺/Yb³⁺ co-doped SG and SGLUX glasses due to the Yb³⁺: ²F_{5/2} transition, otherwise absorption spectra are similar. This suggests that there is no obvious change in the absorb sites of Ho³⁺ after the introduction of sensitizer Yb³⁺. It is implied that Yb³⁺/Ho³⁺ co-doped germanosilicate glass can be excited quite efficiently by a conventional 980 nm LD.



Fig. 4 Absorption spectra of the prepared glasses. The inset is the photo of prepared glasses.

The Judd-Ofelt theory is commonly applied to evaluate the important spectroscopic and laser properties of rare-earth ions doped glasses[36]. According to the J-O theory, absorption spectrum and other parameters, some spectroscopic parameters of rare earths in solids, such as intensity parameters Ω_{λ} radiative transition probability A_{rad} , and radiative lifetime τ_{rad} can be calculated. Table 3 shows the J–O intensity parameters (Ω_2 , Ω_4 , and Ω_6) of Ho³⁺ ions in various glass hosts. Previous studies proved that the parameter Ω_2 closely depends on the ligand symmetry of local environments of Ho³⁺ ion sites, and is strongly related to the amount of covalent bonds[37]. As is showed in Table 3, it can be obtained that Ω_2 in SGLuX is lower than that of SG glass, the results illustrated that the presence of Lu³⁺ in the glass structure reduces the covalent of rare earth ions. So, the germanosilicate glass with the addition of Lu₂O₃ has lower asymmetry and covalent environment around Ho³⁺ ions. On the other hand, the Ω_6 parameter is a vibronic dependent parameter and the radio of Ω_4/Ω_6 determines the spectroscopy quality of the materials[38]. The Ω_4/Ω_6 values of prepared glasses are showed in Table 3. The larger Ω_4/Ω_6 value means the higher lasing efficiency for the laser transition of Ho³⁺ ions in a given matrix. From results as shown in Table 3, it can be found that the Ω_4/Ω_6 value increases when the Lu₂O₃ is introduced in primal germanosilicate glass host. It turns out that the Lu₂O₃ contents in germanosilicate glass can improve the efficiency of laser and be a useful modifier for mid-infrared emission. Besides, the radiative transition probabilities for Ho³⁺: ${}^{5}I_{7}\rightarrow {}^{5}I_{8}$ level can be evaluated via J–O parameters. The radiative transition probability A_{rad} of prepared sample which possesses highest Ω_4/Ω_6 value (SGLu7) is calculated (103.42 s⁻¹), which is larger than those of silicate glass (78.71s⁻¹)[39] and germanate glass (70.15 s⁻¹) [40]. High spontaneous transition probability is beneficial for high gain and more opportunity to achieve laser action.

Sample	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6
SG	5.28±0.2	3.93±0.1	1.25±0.05	3.14
SGLu5	5.08±0.2	3.84±0.1	1.19±0.05	3.23
SGLu7	4.76±0.2	3.62±0.1	1.08 ± 0.05	3.35
SGLu9	4.52±0.2	3.44±0.1	1.03±0.05	3.33

Table 3 The J–O intensity parameters Ω_{λ} (λ =2, 4, 6) (×10⁻²⁰ cm²) of Ho³⁺ in prepared glasses.

To research the effect of addition of Lu₂O₃ on the mid-infrared emission properties in Ho³⁺/Yb³⁺ co-doped germanosilicate glass, the 2.0 μ m fluorescence spectra of Ho³⁺/Yb³⁺ co-doped SG and SGLU glasses were measured upon 980nm LD and revealed in Fig.5 (a), it can be seen that an obvious emission peak centered near 2.0 μ m in all samples, which is corresponding to the Ho³⁺: ⁵I₇ \rightarrow ⁵I₈ transition. Meanwhile, the concentrations of Ho³⁺/Yb³⁺ remain unchanged, and it can be found that the relative emission intensity of 2.0 μ m firstly increases and then decreases with the increasing Lu₂O₃ concentration. Additionally, the maximum fluorescence peak intensity for prepared glasses is observed around 7 mol % Lu₂O₃. Although the 2.0 μ m emission intensity of SGLu9 decreases, it is still higher

than original SG glass.



Fig. 5 Fluorescence spectra around (a)2.0 μm (b)2.8 μm (c)up-conversion (d) near-infrared spectra of prepared glasses.

In order to clearly elucidate the 2.0 μ m emission phenomenon, the 2.8 μ m, near-infrared and up-conversion fluorescence spectra were tested. As shown in Fig. 5(b), (c) and (d), we can find the emissions at 2800, 552, 652, and 1200 nm have the uniform change with the 2000 nm emission. Therefore, the energy level diagram and energy transfer mechanism of Ho³⁺/Yb³⁺ are showed in Fig.6 so as to further comprehend the relation of mid-infrared (2.0 and 2.8 μ m), near-infrared and up-conversion emissions. The electrons of Yb³⁺ ions at ²F_{7/2} are excited to Yb³⁺:²F_{5/2} by ground state absorption (GSA) when the sample is pumped by 980 nm LD. Then the energy transfers from the ions on the excited Yb³⁺ to the ⁵I₆ state of Ho³⁺ by ET: Ho³⁺:⁵I₈ +Yb³⁺: ²F_{5/2}→Ho³⁺:⁵I₆ +Yb³⁺: ²F_{7/2}. On one hand, some of the electrons at Ho³⁺:⁵I₆ level are excited to the ⁵F₄, ⁵S₂), the decay of the ions from these states (⁵F₄, ⁵S₂) to the ground state Ho³⁺:⁵I₈ result in the green emission (⁶F₄, ⁵S₂→Fl₈+662 nm). Due to the small energy gap between ⁵F₄, ⁵S₂ and ⁵F₅ level, ions of ⁵F₄, ⁵S₂ level relax non-radiative to the next ⁵F₅ level, the 552 nm radiations take place according to the ⁵F₅-5⁵I₈ transition. On the other hand, a part of ions on the Ho³⁺: ⁵I₆ level decay to the next lower Ho³⁺:⁵I₇ and ⁵I₈ states,

leading to the 2.8 and 1.2 μ m emissions, respectively. Finally, the ions in ⁵I₇ level decay radiatively to the ground state ⁵I₈ and 2.0 μ m emission occurs. According to Fig.5, it can be obtained that the intensity of 2.8 μ m, near-infrared and up-conversion emissions are in good agreement with the behavior of 2.0 μ m fluorescence spectra. It might be attributed to the difference of local environment around Ho³⁺/Yb³⁺ ions and, hence, leading to different fluorescence behaviors between SGLUX and SG glasses. It means that a moderate quantity of Lu³⁺ can decrease clustering of rare-earth (Ho³⁺) ions in this glass, therefore decrease the cross relaxation among rare-earth (Ho³⁺) ions and enhance the emission intensity of Ho³⁺. Additionally, the maximum fluorescence peak intensity for all fluorescence spectra is observed in SGLu7, which indicates that for fluorescence characteristic the optimum Lu₂O₃ adding concentration is around 7% mol in this germanosilicate glass.



Fig. 6 Energy level diagrams and energy transfer mechanism between Yb³⁺ and Ho³⁺ ions.

To research the number of photons involved in the up-conversion luminescence process of this glass, the up-conversion of SGLu7 excited at 980 nm with different pump power has been measured and shown in Fig.7 (a). The result clearly illustrates that the up-conversion increases with pump power increasing. It is known that for the up-conversion process, the number of photons required to populate the upper emitting state can be described by the following relation[41, 42]

(1)

where I is the up conversion luminescence intensity, P is the pump laser intensity, and n is the number of pump photons required. Fig.7 (b) shows the logarithm-logarithm plots for the up conversion green (552 nm) and red emission (662 nm) intensities of SGLu7 as function of excitation power. The plots are well fitted linearly($R^2 = 0.998$), giving out the slope for ${}^5F_5 \rightarrow {}^5I_8$ and ${}^5F_4 \rightarrow {}^5I_8$ transitions are 1.41 ± 0.02 and 1.47 ± 0.02, respectively. This indicates that a two-photon absorption process is responsible for the up conversion emission.



Fig. 7 (a) Up-conversion of SGLu7 excited at 980 nm with different pump power (mW) in the region of 200–700 nm, (b) Integrated up-conversion intensity at ~552 and 662 nm of SGLu7 vs the pump power.

Fluorescence lifetime is an important parameter to estimate the ions behavior of the excited state. According to the measured and fitted decay curves, the fluorescence lifetime can be determined by the time of the intensity of 1/e. R-square of the single exponential fittings in prepared glass are all above 0.998. The coincidence between the measured and fitted decay curves suggests that energy level ${}^{5}I_{7}$ in these glasses single-exponentially. Hence, from Fig.8 and Table.4, it can be found the fluorescence lifetime of Ho³⁺: ${}^{5}I_{7}$ level becomes longer with increasing Lu₂O₃ concentrations. Higher lifetime suggests that the upper level of 2.0 μ m emission for SGLuX is more favorable for ions accumulation, and SGLuX is more helpful for population inversion between upper level and lower level than SG glass. The lifetime results further proved that the cross relaxation among rare-earth (Ho³⁺) ions has been

decreased with the addition of Lu^{3+} , and hence, fluorescence lifetime of Ho^{3+} : ${}^{5}I_{7}$ level increased owing to the reduction of multistep energy transfer among rare-earth ions. Moreover, the longer radiation lifetime is beneficial for reducing the laser oscillation threshold[43]. Therefore, this Ho^{3+}/Yb^{3+} co-doped germanosilicate glass with the addition of $Lu_{2}O_{3}$ can be considered as an appropriate medium to achieve 2.0 µm laser.



Fig. 8 Decay curves of 2.0 µm emission in prepared glasses excited by 980 nm LD. The solid lines represent the

singly fitted decay curves.

			,, r .r	6
Sample	SG	SGLu5	SGLu7	SGLu9

616 µs

485 µs

Lifetime

Table 4 Measured fluorescence lifetimes of the Ho³⁺: ⁵I₇ level of prepared glasses.

707 µs

691 µs

The fluorescence decay curves of Yb^{3+} ions at the wavelength of 1064 nm in Yb^{3+} singly, and Yb^{3+}/Ho^{3+} co-doped glasses were measured to research the energy transfer process. From Fig.9, it can be found the fluorescence lifetime of Yb^{3+} becomes longer with the Lu₂O₃ addition, which further proved that the cross relaxation among rare-earth ions (Yb^{3+}) has been decreased with the addition of Lu³⁺. Additionally, the fluorescence lifetime of the SG and SGLu7 samples both show obvious

decrease with the addition of Ho³⁺. According to the following equation,

$$\eta = 1 - \frac{\tau}{\tau_0} \tag{2}$$

where τ and τ_0 are the measured lifetimes of Yb³⁺ with and without the co-doping of Ho³⁺ ions, respectively. The calculated energy transfer efficiencies of SG and SGLu7 are as high as 73.5% and 72.6 %, respectively, which indicates that the energy transfer from Yb³⁺ to Ho³⁺ is efficient. The decrease of energy transfer efficiency might be due to the increase of average distances for Ho³⁺-Yb³⁺.



Fig. 9 Decay curves of 1064 nm emission in prepared glasses excited by 980 nm LD (a) SG sample,

(b)SGLu7 sample.

The average distance of rare earth ion pairs is related to the cross relaxation and energy transfer among rare earth ions. Hence, the average distance for Ho^{3+} – Ho^{3+} and Yb^{3+} – Ho^{3+} are counted using the following equation[44]

$$R_{i} = \left(\frac{M}{N_{A}\rho X}\right)^{1/3}$$
(3)

where N_A is the Avogadro number, ρ is the density of prepared glass, M is the mean molecular weight of glass, and x is the total concentration of the Yb³⁺–Ho³⁺ or Ho³⁺–Ho³⁺ ions. The calculated values are listed in Table 5. The change of average distances is in line with the above discussion. The increasing average distance of Yb³⁺–Ho³⁺ slightly decreases the energy transfer efficiency. However, the increasing average distance of Ho^{3+} – Ho^{3+} also results in the decrease of cross relaxation, which can enhance the fluorescence emission of Ho^{3+} ions.

Based on the above results, the ideal net structure diagram of the prepared glasses in short range

Table 5 The average distances of Yb^{3+} –Ho³⁺ or Ho³⁺–Ho³⁺ ion pairs

has been proposed as shown in Fig.10.

Average distance (Å)	SG	SGLu5	SGLu7	SGLu9
Yb ³⁺ –Ho ³⁺	10.48	10.60	10.69	10.77
$Ho^{3+}-Ho^{3+}$	13.20	13.35	13.47	13.57



Fig. 10 The ideal net structure diagram of the prepared glasses in short range (a) without Lu₂O₃ (b) with Lu₂O₃.

From the discussions above, we can conclude that SGLu7 possesses optimal fluorescence characteristic. So we calculated the absorption, emission and gain cross sections of SGLu7 sample in order to further research its possibility as mid-infrared laser material. The emission cross section (σ_{em}) of 2.0 µm fluorescence spectra can be calculated according to Fuchtbauer–Ladenburg (FL) equation[45]

$$\sigma_{em}(\lambda) = \frac{\lambda^4 A_{rad}}{8\pi cn^2} \times \frac{\lambda I(\lambda)}{\int \lambda I(\lambda) d\lambda}$$
(4)

where A_{rad} is the spontaneous radiative transition probability of $Ho^{3+}:{}^{5}I_{7} \rightarrow {}^{5}I_{8}$ transition, λ is the emission wavelength, n is the refractive index of glass host, c is the velocity of light in vacuum, $\int I(\lambda) d\lambda$ is the integrated fluorescence intensity, and $I(\lambda)$ is the 2.0 µm fluorescence spectra intensity.

Based on emission cross section, absorption cross section can be obtained by using the

McCumber (MC) formula[46]

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \times \frac{Z_l}{Z_u} \times \exp\left[\frac{hc}{kt} \times \left(\frac{1}{\lambda_{ZL}} - \frac{1}{\lambda}\right)\right]$$
(5)

where Z_1 and Z_u are the respective partition functions of the lower and the upper levels involved in the considered optical transition is equal to 17/15. Parameter K and T are the Boltzmann constant (1.38 $\times 10^{-23}$ J/K) and the temperature (here it is the room temperature), respectively. λ_{ZL} =2014 nm is the zero-phonon line which means the wavelength for the transition between the lower Stark sublevels of the emitting multiplets and the lower Stark sublevels of the receiving multiplets.

The absorption and emission cross sections of Ho^{3+} in SGLu7 sample are shown in Fig.11 (a). It can be seen that the maximum emission cross section σ_{em} for Ho^{3+} : ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$ is $4.41 \times 10^{-21} \text{cm}^{2}$ at 2022 nm, which is higher than those of germanate-tellurite $(4.36 \times 10^{-21} \text{ cm}^{2})[47]$ and silicate $(3.07 \times 10^{-21} \text{ cm}^{2})[48]$ glasses. Thereby, the prepared SGLu7 glass possessing higher emission cross section might be a superior laser material for achieving intense 2.0 µm laser.

In addition, gain coefficient is another characteristic parameter to evaluate 2.0 μ m emission properties quantitatively. Therefore, the gain spectra G (λ) can be calculated by

$$G(\lambda) = N[P\sigma_{em}(\lambda) - (1 - P)\sigma_{abs}(\lambda)]$$
(6)

where P is the population inversion given by the ratio between the population of $Ho^{3+}SI_7$ level and the total Ho^{3+} concentration and N is the total concentration of Ho^{3+} Fig.11 (b) indicates the gain spectra of 2.0 µm of SGLu7 glasses. Obviously, when the population inversion P>0.4, the gain cross sections in the range of 1700-2300 nm become positive. It is suggested that the prepared Ho^{3+}/Yb^{3+} co-doped SGLu7 glass would be a suitable optical material to obtain 2.0 µm infrared emission thanks to the excellent gain properties.



Fig. 11 (a) The calculated absorption and emission cross sections (b) gain coefficient for prepared glass (SGLu7).

4. Conclusions

This study investigated the structure and fluorescence characteristic in the Ho^{3+}/Yb^{3+} co-doped germanosilicate glasses by using lanthanide additives Lu₂O₃. The introduction of Lu₂O₃ improves the thermal stability of glass system owing to the oxyphilic character of Lanthanide cations Lu³⁺. And Lu₂O₃ changes the structure of glass to decrease the probability of rare-earth clustering (Ho³⁺), conducing to the fluorescence characteristic of germanosilicate glass. Meanwhile, the J-O intense parameters and radiative lifetimes of Ho³⁺/Yb³⁺ co-doped germanosilicate glass with different concentration Lu₂O₃ are calculated and discussed. The results of test and discussion indicate that SGLu7 possesses optimal fluorescence characteristic. The emission cross section at 2.0 µm reaches as high as 4.41 ×10⁻²¹ cm² in SGLu7 glass. According to the experimental results, the germanosilicate glass with the modification of Lu₂O₃ might be a promising candidate for 2.0 µm laser.

Acknowledgements

This research was financially supported by the Chinese National Natural Science Foundation (Nos. 61605192, and 51472225), the Natural Science Foundation of Zhejiang Province (LY18E020008), and the open Fund of the Guangdong Engineering Technology Research Development Center of Special Optical Fiber Materials and Devices (South China University of Technology).

References

 J. Geng, Q. Wang, Z. Jiang, T. Luo, S. Jiang, G. Czarnecki, Kilowatt-peak-power, single-frequency, pulsed fiber laser near 2 µm, Opt. Lett. 36 (2011) 2293-2295.

[2] Z. Zheng, D. Ouyang, J. Zhao, M. Liu, S. Ruan, P. Yan, J. Wang, Scaling all-fiber mid-infrared supercontinuum up to 10W-level based on thermal-spliced silica fiber and ZBLAN fiber, Photon. Res. 4 (2016) 135-139.

[3] F. Qi, F. Huang, L. Zhou, Y. Tian, R. Lei, G. Ren, J. Zhang, L. Zhang, S. Xu, Long lifetime of Er^{3+} : ⁴I_{11/2} in low phonon-energy fluoro-chloride glasses for mid-infrared optical applications, J. Alloys Compd. 731 (2018) 418-422.

[4] Y. Sun, Q. Yang, H. Wang, Q. Zhang, Y. Shao, Preparation and mid-infrared 2.7 μ m luminescence property of high content Er³⁺-doped (Y_{0.9}La_{0.1})₂O₃ transparent ceramics pumped at 980nm, Ceram. Int. 44 (2018) 1812-1816.

[5] A. Yang, J. Qiu, M. Zhang, H. Ren, C. Zhai, S. Qi, B. Zhang, D. Tang, Z. Yang, Mid-infrared luminescence of Dy³⁺ ions in modified Ga-Sb-S chalcogenide glasses and fibers, J. Alloys Compd. 695 (2017) 1237-1242.

[6] R. Xu, J. Pan, L. Hu, J. Zhang, $2.0\mu m$ emission properties and energy transfer processes of Yb³⁺/Ho³⁺ codoped germanate glass, J. Appl. Phys. 108 (2010) 043522.

[7] W. Li, D. Chen, Q. Zhou, L. Hu, Watt-level output rectangular-core neodymiun-doped silicate glass fiber laser, Chin. Opt. Lett. 14 (2016) 01140201-01140203.

[8] G. Bai, Y. Guo, Y. Tian, L. Hu, J. Zhang, Light emission at 2 μm from Ho–Tm–Yb doped silicate glasses, Opt. Mater. 33 (2011) 1316-1319.

[9] G. Gao, L. Hu, H. Fan, G. Wang, K. Li, S. Feng, S. Fan, H. Chen, J. Pan, J. Zhang, Investigation of 2.0 μ m emission in Tm³⁺ and Ho³⁺ co-doped TeO₂–ZnO–Bi₂O₃ glasses, Opt. Mater. 32 (2009) 402-405. [10] M. Li, Y. Guo, G. Bai, Y. Tian, L. Hu, J. Zhang, ~2 μ m Luminescence and energy transfer characteristics in Tm³⁺/Ho³⁺co-doped silicate glass, J. Quant. Spectrosc. Radiat. Trans. 127 (2013) 70-77.

[11] B. Zhou, L. Tao, C. Yat-Yin Chan, W. Jin, Y.H. Tsang, E. Yue-Bun Pun, Near- and mid-infrared photoluminescence in Ho^{3+} doped and $Ho^{3+}-Yb^{3+}$ codoped low-phonon-energy germanotellurite glasses, J. Lumin. 137 (2013) 132-137.

[12] S. Ye, J. Song, D. Wang, Y. Tian, J. Qu, H. Niu, Reduced photon quenching in Ce-doped NaYF₄:Yb/Ho upconversion nanoparticles with core/shell structure, Opt. Lett. 14 (2016) 21601-21605.

[13] D. He, S. Kang, L. Zhang, L. Chen, Y. Ding. Q. Yin, L. Hu, Research and development of new neodymium laser glass, High Power Laser Sci. Eng. 5 (2017) e1

[14] M. Li, G. Bai, Y. Guo, L. Hu, J. Zhang, Investigation on Tm³⁺-doped silicate glass for 1.8μm emission, J. Lumin. 132 (2012) 1830-1835.

[15] G. Bai, L. Tao, K. Li, L. Hu, Y.H. Tsang, Enhanced light emission near 2.7μm from Er–Nd co-doped germanate glass, Opt. Mater. 35 (2013) 1247-1250.

[16] S.S. Bayya, G.D. Chin, J.S. Sanghera, I.D. Aggarwal, Germanate glass as a window for high energy laser systems, Opt. Express. 14 (2006) 11687-11693.

[17] W.J. Zhang, Q.J. Chen, J.P. Zhang, Q. Qian, Q.Y. Zhang, L. Wondraczek, Enhanced NIR emission from nanocrystalline LaF₃:Ho³⁺ germanate glass ceramics for E-band optical amplification, J. Alloys Compd. 541 (2012) 323-327.

[18] S.S. Bayya, G.D. Chin, G. Villalobos, J.S. Sanghera, I.D. Aggarwal, VIS-IR transmitting windows,

Proc. SPIE 5786 (2005) 262-271.

[19] T. Wei, F. Chen, Y. Tian, S. Xu, Broadband 1.53µm emission property in Er³⁺ doped germa-silicate glass for potential optical amplifier, Opt. Commun. 315 (2014) 199-203.

[20] T. Wei, C. Tian, M. Cai, Y. Tian, X. Jing, J. Zhang, S. Xu, Broadband $2\mu m$ fluorescence and energy transfer evaluation in Ho³⁺/Er³⁺ codoped germanosilicate glass, J. Quant. Spectrosc. Radiat. Trans. 161 (2015) 95-104.

[21] F. Lofaj, R. Satet, M.J. Hoffmann, A.R. de Arellano López, Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses, J. Eur. Ceram. Soc. 24 (2004) 3377-3385.

[22] J. M. Jewell, P.L. Higby, I.D. Aggarwal, Properties of BaO– R_2O_3 – Ga₂O₃–GeO₂ (R = Y, Al, La, and Gd) Glasses, J. Am. Ceram. Soc. 77 (1994) 697-700.

[23] Y. Hao, Y. Dai, Influence of Y_2O_3 on the structure and luminescence of Eu^{2+} doped borosilicate glasses, J. Non-Cryst. Solids. 474 (2017) 32-36.

[24] X. Wang, S. Kang, S. Fan, S. Wang, C. Yu, D. Chen, L. Hu, Influence of La/Al ratio on the structure and spectroscopy of Tm^{3+} doped Al_2O_3 -La₂O₃-SiO₂ glasses, J. Alloys Compd. 690 (2017) 583-588.

[25] V. Fouquet-Parry, F. Paumier, M.J. Guittet, M. Gautier-Soyer, R. Satet, M.J. Hoffmann, P.F. Becher, G.S. Painter, Composition and local bonding in RE–Si–M–O–N (M=Mg, Al ; RE=La, Lu) glasses, Appl. Surf. Sci. 254 (2008) 4665-4670.

[26] T. Wang, F. Huang, F. Qi, Y. Tian, J. Zhang, S. Xu, Spectroscopic properties and energy transfer process in Tm³⁺-doped Silica-germanate glasses, J. Lumin, 187 (2017) 205-210.

[27] H. Verweij, Raman study of the structure of alkali germanosilicate glasses (I): Sodium and potassium metagermanosilicate glasses, J. Non-Cryst. Solids. 33 (1979) 41-53.

[28] R. Chen, Y. Tian, B. Li, X. Jing, J. Zhang, S. Xu, H. Eckert, X. Zhang, Thermal and luminescent properties of 2 μm emission in thulium-sensitized holmium-doped silicate-germanate glass, Photon. Res. 4 (2016) 214-221.

[29] S.K. Sharma, D.W. Matson, J.A. Philpotts, T.L. Roush, Raman study of the structure of glasses along the join SiO₂-GeO₂, J. Non-Cryst. Solids. 68 (1984) 99-114.

[30] B.V.R. Chowdari, Z. Rong, The role of Bi_2O_3 as a network modifier and a network former in $xBi_2O_3 \cdot (1 - x)LiBO_2$ glass system, Solid State Ionics. 90 (1996) 151-160.

[31] T. Honma, R. Sato, Y. Benino, T. Komatsu, V. Dimitrov, Electronic polarizability, optical basicity and XPS spectra of Sb₂O₃–B₂O₃ glasses, J. Non-Cryst. Solids. 272 (2000) 1-13.

[32] L. Wang, L. Tan, Y. Yue, M. Peng, J. Qiu, Efficient Enhancement of Bismuth NIR Luminescence by Aluminum and Its Mechanism in Bismuth-Doped Germanate Laser Glass, J. Am. Ceram. Soc. 99 (2016) 2071-2076.

[33] N.H. Chan, R.K. Sharma, D.M. Smyth, Nonstoichiometry in Acceptor-Doped BaTiO₃, J. Am. Ceram. Soc. 65 (1982) 167-170.

[34] Z. Yang, T. Luo, S. Jiang, J. Geng, P. Lucas, Single-mode low-loss optical fibers for long-wave infrared transmission, Opt. Lett. 35 (2010) 3360-3362.

[35] B. Burtan-Gwizdala, M. Reben, J. Cisowski, R. Lisiecki, W. Ryba-Romanowski, B. Jarzabek, Z. Mazurak, N. Nosidlak, I. Grelowska, The influence of Pr^{3+} content on luminescence and optical behavior of TeO₂–WO₃–PbO–Lu₂O₃ glass, Opt. Mater. 47 (2015) 231-236.

[36] B.R. Judd, Optical Absorption Intensities of Rare-Earth Ions, Phys. Rev. 127 (1962) 750-761.

[37] M. Wang, L. Yi, G. Wang, L. Hu, J. Zhang, emission performance in Ho^{3+} doped fluorophosphate glasses sensitized with Er^{3+} and Tm^{3+} under 800 nm excitation, Solid State Commun. 149 (2009)

1216-1220.

[38] P.R. Watekar, S. Ju, W.T. Han, Optical properties of Ho-doped alumino-germano-silica glass optical fiber, J. Non-Cryst. Solids. 354 (2008) 1453-1459.

[39] R. Cao, M. Cai, Y. Lu, Y. Tian, F. Huang, S. Xu, J. Zhang, Ho³⁺/Yb³⁺ codoped silicate glasses for 2 μm emission performances, Appl. Opt. 55 (2016) 2065-2070.

[40] J. Fan, Y. Fan, Y. Yang, D. Chen, L. Calveza, X. Zhang, L. Zhang, Spectroscopic properties and energy transfer in Yb³⁺–Ho³⁺ co-doped germanate glass emitting at 2.0μm, J. Non-Cryst. Solids. 357 (2011) 2431-2434.

[41] Z. Dong, T. Wei, Y.J. Ma, T.B. Zhang, X.X. Lian, Y.Y. Guo, F.M. Yang, D.M. An, Influence of erbium substitution on structural, electrical, and up-conversion photoluminescence properties of unfilled tungsten bronze oxides $Ba_{3.75}La_{0.833-x}Er_xNb_{10}O_{30}$, J. Alloys Compd. 681 (2016) 240-252.

[42] C. Zhao, X. Kong, X. Liu, L. Tu, F. Wu, Y. Zhang, K. Liu, Q. Zeng, H. Zhang, Li^+ ion doping: an approach for improving the crystallinity and upconversion emissions of NaYF₄:Yb³⁺, Tm³⁺ nanoparticles, Nanoscale. 5 (2013) 8084-8089.

[43] T. Wei, Y. Tian, F. Chen, M. Cai, J. Zhang, X. Jing, F. Wang, Q. Zhang, S. Xu, Mid-infrared fluorescence, energy transfer process and rate equation analysis in Er^{3+} doped germanate glass, Sci. Rep. 4 (2014) 6060.

[44] X.Y. Sun, D.G. Jiang, Y.Z. Sun, X. Zhang, Q.L. Hu, Y. Huang, Y. Tao, Eu^{3+} -activated B₂O₃-GeO₂-RE₂O₃ (RE=Y³⁺, La³⁺ and Gd³⁺) borogermanate scintillating glasses, J. Non-Cryst. Solids. 389 (2014) 72-77.

[45] S.A. Payne, L.L. Chase, L.K. Smith, W.L. Kway, W.F.E.D.B.J.G.A.H.T. Krupke, W. Krupke, Infrared cross-section measurements of the Er³⁺, Tm³⁺, and Ho³⁺ ions in crystals, Conference on Lasers and Electro-Optics, 28 (1991) 2619-2630.

[46] F. Qi, F. Huang, T. Wang, R. Lei, J. Zhang, S. Xu, L. Zhang, Influence of Tm^{3+} ions on the amlification of $\text{Ho}^{3+}:{}^{5}\text{I}_{7}-{}^{5}\text{I}_{8}$ transition in fluoride glass modified by $Al(PO_{3})_{3}$ for applications in mid-inrared optics, Chin. Opt. Lett. 15 (2017) 05160401-05160406.

[47] Y. Peng, Y. Guo, J. Zhang, L. Zhang, Ho³⁺/Yb³⁺-codoped germanate-tellurite glasses for 2.0μm emission performance, Appl. Opt. 53 (2014) 1564-1569.

[48] M. Li, Y. Guo, G. Bai, Y. Tian, L. Hu, J. Zhang, ~2μm Luminescence and energy transfer characteristics in Tm³⁺/Ho³⁺co-doped silicate glass, J. Quant. Spectrosc. Radiat. Trans. 127 (2013) 70-77.

Highlights:

- 1. Structural and fluorescence properties of germanosilicate glasses were researched.
- 2. The addition of Lu_2O_3 increases ΔT to improve the thermal stability of glass host.
- 3. The increase of NBO can decrease the cross relaxation effect among RE-RE ions.
- 4. Fluorescence properties of Ho^{3+} have been improved due to the increase of NBO.