Investigation of Tm3+/Yb3+ co-doped germanate-tellurite glasses for efficient 2 μm mid-infrared laser materials

Aoju Dou, Lingling Shen, Ning Wang, Yangjian Cai, Muzhi Cai, Yanyan Guo, Feifei Huang, Ying Tian, Shiqing Xu, Junjie Zhang

Investigation on Tm^{3+}/Yb^{3+} codoped germanate-tellurite glasses for efficient 2μm mid-infrared laser materials

Aoju Dou[1], Lingling Shen[1], Ning Wang[1],Yangjian Cai[1], Muzhi Cai[1,2], Yanyan Guo[3], Feifei Huang[1],Ying Tian[1], Shiqing Xu[1], Junjie Zhang[*1]

[1]College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P.R China

[2]Laboratory of Glasses and Ceramics, Institute of Chemical Science UMR CNRS 6226, University of Rennes 1, 35042 Rennes, France

[3]Collage of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, 130022, P.R China

Abstract:

The Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses with good thermal properties were prepared. Based on the absorption spectra and the Judd-Ofelt theory, the J-O intensity parameters (Ω_t), radiative transition probability ($276.78s^{-1}$), fluorescence lifetime (3.89ms) and absorption and emission cross sections (σ_e =$1.35\times10^{-20}cm^2$) were calculated. The ~2μm mid-infrared emission resulting from the $^3F_4\rightarrow{}^3H_6$ transition of Tm^{3+} sensitized by Yb^{3+} has been observed pumped by 980nm LD. Besides, the energy transfer mechanism between Yb^{3+} and Tm^{3+} was thoroughly discussed. Meanwhile, the measured ~2μm emission lifetime of Tm^{3+}/Yb^{3+} co-doped glass can reach as high as 2.38ms. The above results showed that Tm^{3+}/Yb^{3+}

* Corresponding author at: China Jiliang University, No. 555 Xueyuan Road, Jianggan Xiasha District, Hangzhou 310018 , China. Tel: +86138 1649 4960; Fax: +0571-87676298.
E-mail address: jjzhang@cjlu.edu.cn(J.J. Zhang)

co-doping glass could be expected to be a promising material to achieve high efficient ~2μm lasing with a 980nm LD pumping.

1. Introduction

Over the past several years, increasing efforts have been made to develop ~2.0μm fiber lasers driven by their wide applications such as remote sensing, laser surgery, environmental monitoring, and eye-safe light detection and ranging (LIDAR) [1-4].

Among the rare earth ions, Tm^{3+} and Ho^{3+} are well-known for the generation of ~2.0μm emission, due to Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ and Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$ transitions, respectively. In comparison with Ho^{3+}, Tm^{3+} is of special interests for its unsurpassed advantages, such as broad emission about 800nm suitable for tunable lasers [5] and high quantum efficiency be beneficial from the cross relaxation energy transfer ($^3H_4+{}^3H_6 \rightarrow {}^3F_4+{}^3F_4$) [6]. What is more, the $^3F_4$ level of Tm^{3+} can be populated using sensitizer ions such as Yb^{3+} and Er^{3+} [7, 8]. Yb^{3+} ion can be used as a sensitizer and it can be pumped by a more powerful and relatively inexpensive laser diode (LD) at 980nm. Because fast diffusion among the Yb^{3+} ions can enhance the efficiency of the nonresonant energy transfer from Yb^{3+} to Tm^{3+} ($^2F_{5/2}+{}^3H_6 \rightarrow {}^2F_{7/2}+{}^3H_5$). Yb^{3+} has a high absorption cross section and can effectively absorb excitation of commercial 980nm LD emission, and then transfer energy to Tm^{3+} ($^3H_5$ level) via non-resonant energy transfer process.

In order to research luminescence properties of rare-earth ions, it is very significant to select glass hosts for researchers. Since the first successfully Tm^{3+} doped silica fiber laser was demonstrated in 1988 by Southampton [9]. In 1999, Stuart

D. Jackson et al. proposed a theoretical model that describes the ion-pair dynamics relevant to the Tm-doped silica system, which can deduce equations for the steady-state intracavity photon density and for the steady-state population densities of the isolated and paired ions [10]. In 2009, Peter F. Moulton et al. used a piece of 25-μm-diameter and 0.08 numerical aperture (NA) core thulium-doped silica fiber to derive single mode laser output of the output powers of 300W and the slope efficiency as high as 64.5% for launched pump power [11]. Various host materials including fluoride [12], tellurite [13], germanate [6] and silicate glasses [14] have been successfully applied to achieve ~2.0μm fiber lasers with different efficiency. The obvious defects of silicate glasses are the low rare-earth solubility and high phonon energy. The fluoride glasses have the drawbacks of inferior mechanical and chemical properties. Germanate glasses have been intensively studied as promising candidates in mid-infrared optical applications, and high energy laser system [15-17]. Particularly, one system, Germanate-tellurite (GT) glass which has been practically applied in large infrared (IR) windows, because of the excellent combinations of superior IR transparency, comparatively low phonon energy, high rare-earth solubility, and good mechanical characteristics [18]. Tellurite glass has attracted a great deal of interest not only for its relatively lower maximum phonon energy (~760cm^{-1}) among all the oxide glasses, but also for the improvement in chemical and mechanical stability as well as the high refractive index, excellent infrared transmission [19]. Compared with germanate glass (~900cm^{-1}) [20], tellurite glass (~760cm^{-1}) [19] has much lower phonon energy, which is favorable for 2μm emission and that is helpful to reduce the

multi-phonon relaxation rate for Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ transition. However, tellurite glass has lower glass transition temperature (~350°C) than germanate glass (~600°C). Thus, tellurite glass has poor thermal stability to resist thermal damage at high pumping power. On the contrast, the thermal stability, chemical durability, resistance to thermal damage of germanate glass are superior. Therefore, germanate-tellurite glass combines the advantages from both germanate and tellurite glasses, i.e., good thermal stability, chemical durability, lower phonon energy, high rare earth solubility and high transparency in a wide wavelength range [21,22]. These features render germanate-tellurite glass as an ideal host for mid-infrared laser material. To the best of our knowledge, the fluorescence corresponding to the $^3F_4 \rightarrow {}^3H_6$ transitions of the Tm^{3+} has been under-reported sensitized by Yb^{3+} in germanate-tellurite glasses [23-25].

In this work, we report Tm^{3+}/Yb^{3+} codoped germanate-tellurite glasses for generating emission in the ~2.0μm wavelength band. Spectroscopic properties of Tm^{3+} and energy transfer mechanism between Tm^{3+} and Yb^{3+} ions were discussed in detail. Energy transfer microscopic parameters were calculated based on absorption spectra. Furthermore, the thermal properties are investigated and Judd-Ofelt intensity parameters have been determined to evaluate the radiative properties. In this paper, the lifetime and gain spectra have also been discussed. The results could verify that the Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses could be potential materials for mid-infrared lasers.

2. Experiment

2.1. Material synthesis

The sample glasses were prepared by traditional melt-quenching method with using high-purity chemicals (99%-99.99+%). The investigated glasses of molar compositions:80(GeO_2+TeO_2)-(19.5-y)(K_2CO_3+Nb_2O_5+La_2O_3)-xYb_2O_3-yTm_2O_3(x=0.5; y=0.1, 0.25, 0.4, 0.5 and x=0; y=0.1) were placed in Al_2O_3 crucible and heated with a SiC-resistance electric furnace at 1200°C for 25min. The melts were then poured onto a preheated stainless mold, followed by annealing at 530°C for 5h to relinquish the inner stresses. Then it was allowed to cool slowly to room temperature. The cooled samples had been cut and polished to the size of 20×20×1.5mm^3 carefully, prepared for the optical property measurements.

2.2. Performance measurements

In this paper, the refractive index (1.73) and density (4.27g/cm^3) of 0.25Tm^{3+}/0.5Yb^{3+} co-doped sample were tested by prism minimum deviation method and Archimedes principle using distilled water as an immersion liquid. The maximum phonon energy of present germanate-tellurite glass is ~785cm^{-1}. The maximum phonon energy (~785cm^{-1}) is less than tellurite glasses (~900cm^{-1}) [16]. The characteristic temperatures of glass transition (T_g), onset crystallization peak (T_x) and top crystallization (T_p) were performed with 10K/min using the NETZSCH DTA 404 PC differential scanning calorimeter. Fluorescence spectra of the samples in the range of 1500-2400nm were measured by a liquid-nitrogen-cooled PbS detector using a

980nm laser diode (LD) as an excitation source. The absorption spectra measurements were performed by PerkinElmer Lambda 900 UV/VIS/NIR double beam spectrophotometer (Waltham, MA) in the range from 300 to 2100nm. The lifetime decay curves were measured and shown by TDS 3012C type Digital Phosphor Oscilloscope (100MHz, 1.25GS/S). For different samples, they were tested under the same experimental conditions. In addition, all the test results were carried out at room temperature.

3. Results and discussions

3.1. Thermal stability analysis

To correctly evaluate the thermal properties of the glasses，as shown in Fig.1, the DSC measurement of sample glasses were displayed. The figures of T_g, T_x, and T_p are 538°C, 726°C, and 750°C, respectively. T_g is a significant factor for laser glasses. The transition temperature (T_g) of the samples (538°C) is higher than those of bismuth (269°C) [26], tellurite (354°C) [27], tellurite(300°C) [13], germanate (526℃) [28] and fluoride glasses (332℃) [29]. The higher T_g is generally considered to possess better thermal properties to resist thermal damage at high pumping intensities. The ΔT (T_x-T_g) can usually be used to evaluate the thermal properties of glasses. A bigger ΔT reveals that the glass possesses an excellent thermal ability against the nucleation and crystallization as well. From Table 1, it is obvious that ΔT is 188°C, which is significantly larger than those of bismuthate (67°C) [26], tellurite (141°C) [27], germanate (129°C) [28] and fluoride glasses (76°C) [29], which reveals that

germanate-tellurite glasses could be potential materials for mid-infrared lasers. The above results indicate that germanate-tellurite glasses have better thermal performance in this paper. Hence, the prepared germanate-tellurite glasses have good anti-crystallization properties and could be selected as potential laser material.

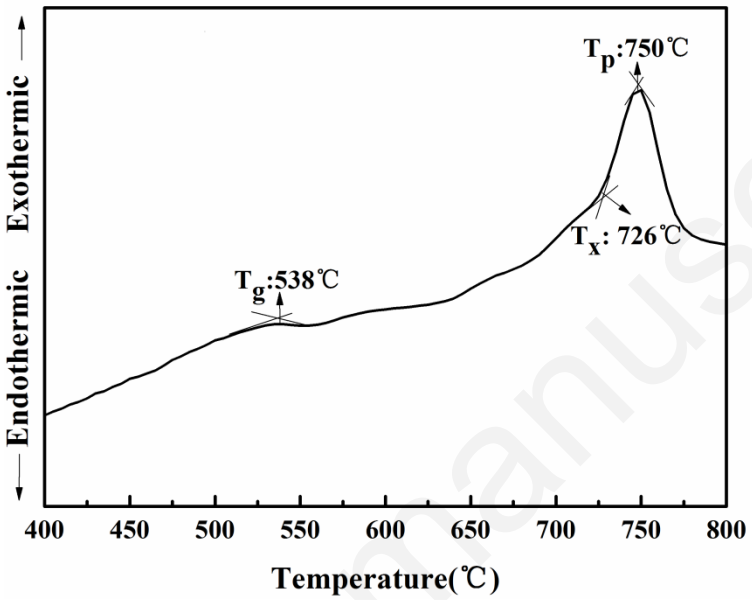

Fig.1. DSC curves of germanate-tellurite glass.

Table 1. The glass transition temperature (T_g), onset crystallization temperature (T_x), temperature of crystallization peak(T_p), thermal stability parameters ΔT in various glass hosts.

Glass samples	T_g(°C)	T_x(°C)	T_p(°C)	ΔT	References
GT	538	726	750	188	This work
Germanate	526	747	769	129	[28]
Tellurite	354	511	527	141	[27]
Bismuthate	269	336	358	67	[26]
Fluoride	332	408	426	76	[29]

3.2. Absorption spectra and J-O analysis

As shown in Fig.2, absorption spectra of 0.25Tm^{3+}, 0.5Yb^{3+} single doped and 0.25Tm^{3+}/0.5Yb^{3+} co-doped glass samples of thickness of 1.5mm is depicted in the wavelength range of 300-1750nm. For single Tm^{3+} doped the sample, in the range from 300 to 1750nm, It could be discerned five absorption bands centered at around 468、684、791、1208 and 1713nm, which correspond to the transitions from the $^3H_6$ ground state to excited levels $^1G_4$, $^3F_{2,3}$, $^3H_4$, $^3H_5$ and $^3F_4$, respectively, according to the absorption spectrum of Tm^{3+} single doped germanate glass. The shapes and the peak positions of each transition in Tm^{3+} single doped germanate-tellurite glasses nearly do not change when compared with the Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses and are very similar to those in other Tm^{3+}-doped glasses [30]. The phenomenon could be explained by the reason that the Tm^{3+} ions are

homogeneously incorporated into the glass network without clustering and any changes in the local ligand field [31]. In this paper, the 980nm LD is used as the pumping source. As we already know, the center of absorption peak of Yb^{3+} ions at 976nm is indeed more intense than all the absorption peaks of Tm^{3+}. The radiation wavelength of high power commercial 980nm LD can be matched with 976nm absorption peak of Yb^{3+} ions, showing that codoping with Yb^{3+} and Tm^{3+} is an efficient approach to enhance ~1.8μm emission from Tm^{3+}[32,33].

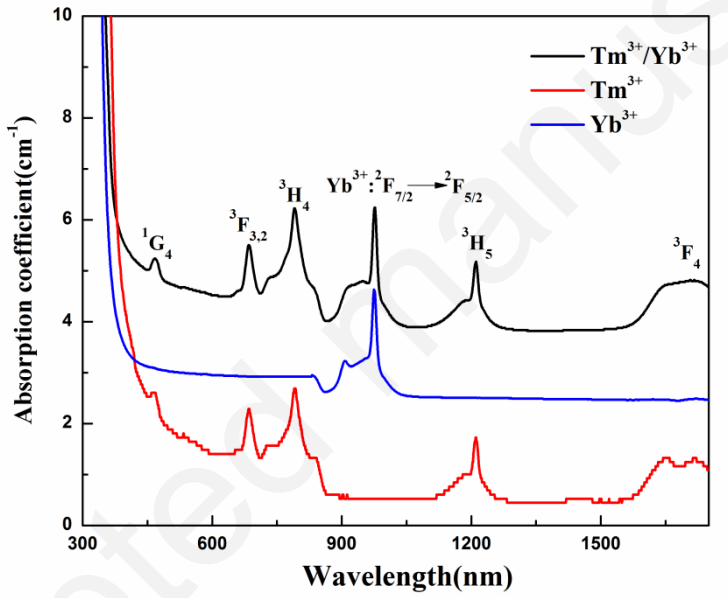

Fig.2. Absorption spectra of Tm^{3+},Yb^{3+} single doped and Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses.

The Judde-Ofelt (J-O) theory [34,35] plays a significant role in analyzing the spectroscopic properties (radiative lifetimes, intensity parameters Ω_t (t=2, 4, 6), spontaneous emission probabilities and so on) for rare earth ions doped glasses.

From Table 2, it compares the Judde-Ofelt parameters of Tm^{3+} ions in germanate, tellurite and bismuthate glasses. The Ω_2 parameter is intensively dependent on local

environment of the rare earth ions. The value of Ω_2 (4.45×10^{-20} cm^2) of Tm^{3+} is relatively large, which is higher than those of silicate (3.70×10^{-20} cm^2) [36], tellurite (3.30×10^{-20} cm^2) [37] glasses. On the one hand, it is straightly related to the symmetry of rare earth ions with ligand formation. On the other hand, the polarization of the localstructure and the covalent nature of the chemical bonds result in the formation of rare earth ions with ligands. A large field strength is mainly attributed to a high polarizability of oxygen at the rare earth site. For the crystal field parameter, the value of Ω_2 might also be affected by the asymmetry of the rare earth sites. The Ω_2 is an important factor to obtain good spectral properties of the host materials. From Table 2, the value of Ω_6 is larger than silicate glasses (0.60×10^{-20} cm^2) [36], but smaller than tellurite (1.28×10^{-20} cm^2) [37] and germanate (1.92×10^{-20} cm^2) [38] glasses. At the same time, comparison with Ω_2, Ω_6 doesn't depend on the environment but is more dependent on the overlap integrals of the 4f and 5d orbits [39].

Table 2. Comparison of J-O intensity parameters of Tm^{3+} ions in various glass hosts.

Glass	Ω_2	Ω_4	Ω_6	Reference
	($\times10^{-20}$ cm^2)			
GTT	4.45	0.84	0.93	This work
Germanate	8.13	2.32	1.92	[38]
Silica	3.70	2.30	0.60	[36]
Tellurite	3.30	2.38	1.28	[37]
Bismuthate	6.51	2.11	1.52	[40]

From the Table 3, full understanding of the radiation characteristics of the prepared glasses, the radiative lifetimes (τ_{rad}), spontaneous transition probabilities (A_{rad}) and fluorescence branching ratios (β) were calculated. The radiative transition probability (A_{rad}) of Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ transition is calculated to be 276.78s^{-1}. The higher spontaneous radiative transition probability provides larger opportunity to achieve better laser action, so the prepared glasses could be a promising candidate for mid-infrared laser [41]. It is known from other papers that the radiative transition probability (A_{rad}) of Tm^{3+} in sample is higher than those of tellurite and germanate glass [42,43]. We can see that the radiative lifetime of $^3F_4 \rightarrow {}^3H_6$ transition is as long as 3.89ms, which is longer than that of tellurite (1.64ms) and germanate (0.859ms) glass [42,43]. The high efficient ~2μm radiations can be achieved in the prepared glass.

Table 3. The spontaneous emission probabilities, branching ratios and radiative lifetimes of Tm^{3+} in the samples.

Transition	Final state	S_{ed} (10^{-20} cm^2)	A_{ed} (s^{-1})	A_{md} (s^{-1})	β	τ_{rad} (ms)
$^3F_4$	$^3H_6$	3.353	276.780	0	1	3.89
$^3H_5$	$^3H_6$	1.266	224.027	77.898	98.57%	3.26
	$^3F_4$	0.561	4.386		1.43%	
$^3H_4$	$^3H_6$	1.588	1240.053		90.58%	0.73
	$^3F_4$	0.862	99.750		7.29%	
	$^3H_5$	0.474	15.134	14.009	2.13%	
$^3F_3$	$^3H_6$	1.048	1635.344		74.58%	0.46
	$^3F_4$	0.169	57.322	93.308	6.87%	
	$^3H_5$	3.089	403.103		18.38%	
	$^3H_4$	0.939	3.741		0.17%	
$^3F_2$	$^3H_6$	0.241	634.031		36.14%	0.57
	$^3F_4$	1.356	874.099		49.82%	
	$^3H_5$	0.792	217.764		12.41%	
	$^3H_4$	1.610	28.417		1.62%	
	$^3F_3$	0.080	0.046	0.155	0.01%	
$^1G_4$	$^3H_6$	0.279	1032.915		46.20%	0.45
	$^3F_4$	0.089	125.596		5.62%	
	$^3H_5$	0.874	743.923		33.27%	
	$^3H_4$	1.119	275.795		12.34%	
	$^3F_3$	0.422	47.050		2.10%	
	$^3F_2$	0.148	10.439		0.47%	

3.3. Emission spectra and cross section

In the past studies [44], the energy transfer process between Yb^{3+} and Tm^{3+} is recognized by researchers, and the efficiency of the process is very high. As shown in Fig.3.(a), with the increase of Tm^{3+} concentration, the Tm^{3+}:~1.8μm emission is also enhanced as well. And the fluorescence spectra of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glass pumped by 980nm LD is displayed. From Fig.3.(b), we can find that there is no fluorescence when Tm^{3+} singly doped in germanate-tellurite

glasses. With the assistance of Yb^{3+} ions, the ~1.8μm emission peak of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses are excited by 980nm LD. This confirms that the lack of Tm^{3+} absorption band near 976nm and the existence of energy transfer from Yb^{3+} to Tm^{3+}. In addition, with the increase of Tm^{3+} ions concentration, the fluorescence intensities of Tm^{3+}/Yb^{3+} co-doped glass samples increases initially, and then rapidly decreases. When the concentration of Tm^{3+} is 0.25mol%, the intensity of fluorescence emission reaches the maximum in these four sets of glass samples. So the optimum concentration of Tm^{3+} is 0.25mol%. The reason is that the energy transfer probability between Yb^{3+}:$^2F_{5/2}$ and Tm^{3+}:$^3H_5$ ions is enhanced. Subsequently, this emission intensity decreases gradually with the increase of Tm^{3+} ions concentration, because of the concentration quenching [45]. Therefore, the optimum concentration ratio between Tm^{3+} ions and Yb^{3+} ions is 1:2, the results can show that the Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses could be potential materials for mid-infrared lasers.

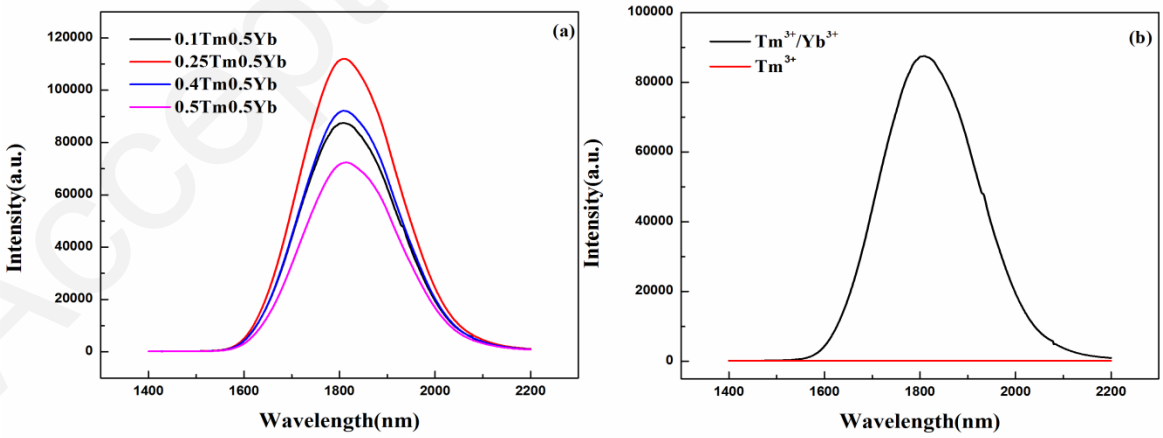

Fig.3.(a). Emission spectra of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses; **(b).** Emission spectra of Tm^{3+} doped and Tm^{3+}/ Yb^{3+} co-doped germanate-tellurite glasses.

Furthermore, emission cross section is an important parameter to estimate the possibility for achieving laser action. According to the above measured absorption spectra, the absorption cross section can be expressed as Beer–Lambert equation

$$\sigma_{abs} = \frac{2.303}{N \times l} OD(\lambda) \quad (1)$$

where N is the density of rare-earth ion (ions/cm^3), l is the thickness of the polished sample glass, $OD(\lambda)$ is the optical density, the value of the optical density is equal to the spectra intensity.

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

where λ is the wavelength, A_{rad} is the spontaneous transition probability, I(λ) is the emission intensity, c and n is the light speed in vacuum and refractive index, respectively.

As shown in figure Fig.4(a), the values of emission and absorption cross sections of Yb^{3+} are 0.87×10^{-20}cm^2 and 0.59×10^{-20}cm^2 in the sample glasses, respectively. From Fig.4(b), the value of emission and absorption cross section of Tm^{3+} are 1.35×10^{-20}cm^2 and 0.56×10^{-20}cm^2 at 1.8μm, respectively. We can see that the emission cross section (1.35×10^{-20}cm^2) of Tm^{3+} is larger than those of silicate (0.2×10^{-20}cm^2) [46], tellurite (0.86×10^{-20}cm^2) [42], tellurite (0.96×10^{-20}cm^2) [13] and bismuthate glasses (0.71×10^{-20}cm^2) [47]. For a laser material, in generally, the high stimulated emission cross section is helpful to increase the gain. A larger gain results in better amplification behavior.

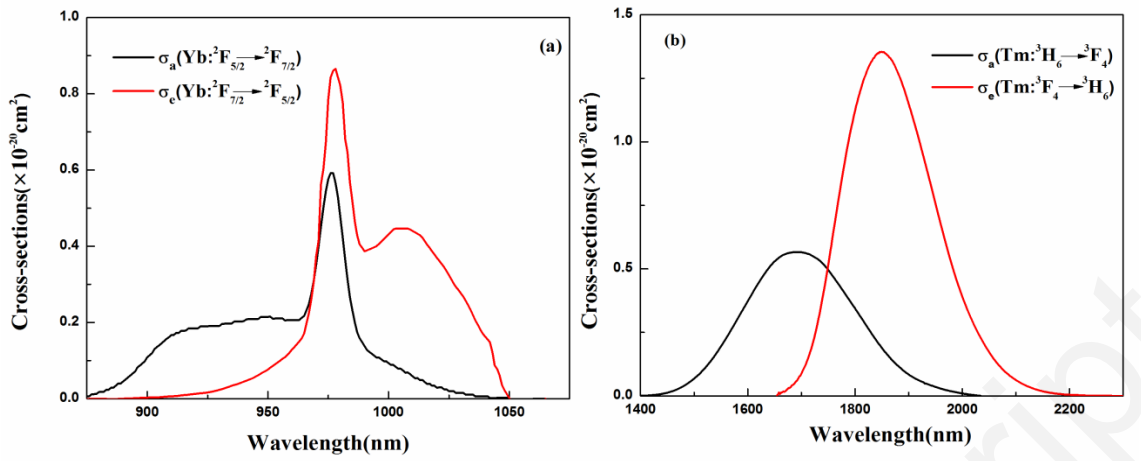

Fig. 4.(a)Absorption and emission cross sections corresponding to Yb^{3+}: $^2F_{5/2}\rightarrow{}^2F_{7/2}$.(b) Absorption and emission cross sections corresponding to Tm^{3+}: $^3F_4\rightarrow{}^3H_6$.

The process of energy transfer between Tm^{3+} and Yb^{3+} ions is presented in Fig.5. As shown in Fig.5, the efficient energy transfer between $Tm^{3+}$and Yb^{3+} can be obtained through the transfer of phonons, and a main energy transfer process in the Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glass has was shown. The Yb^{3+} is pumped by 980nm LD and excited from the ground state ($^2F_{7/2}$) to the upper level ($^2F_{5/2}$), following a energy transfer process from Yb^{3+}:$^2F_{5/2}$ to Tm^{3+}:$^3H_5$ (ET: Yb^{3+}:$^2F_{5/2}$+Tm^{3+}:$^3H_6\rightarrow Yb^{3+}$:$^2F_{7/2}$+Tm^{3+}:$^3H_5$). And the process is assisted by phonons. The Tm^{3+} ion in the $^3H_5$ level relaxes very quickly to the $^3F_4$ level, then particle is transferred from $^3F_4$ level to $^3H_6$ level. Yb^{3+} ion as a sensitizer can greatly improve upconversion efficiency through energy transfer (ET), which is due to strong absorption of Yb^{3+} ion around 980 nm when Tm^{3+}/Yb^{3+}-codoped glasses are excited by 980 nm laser. The simplified energy level diagram exhibit distinct the

upconversion centered at 476nm, 650nm and 689 nm which are assigned to the $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$ and $^3F_{2,3} \rightarrow {}^3H_6$ transitions of Tm^{3+} ions, respectively.

The microscopic parameter based on the evaluation of the overlap integral between the absorption and emission cross sections can be obtained using the following equations:

$$C_{DA} = \frac{6cg_{low}^{D}}{(2\pi)^4 n^2 g_{up}^{D}} \sum_{m=0}^{\infty} e^{-(2\bar{n}+1)S_0} \frac{S_0^m}{m!} (\bar{n}+1)^m \int \sigma_{ems}^{D}(\lambda_m^+) \sigma_{abs}^{A}(\lambda) d\lambda \quad (3)$$

The g^D_{low} and g^D_{up} are the degeneracies of the respective lower and upper levels of the donor, respectively. $\bar{n} = 1/\left(e^{\hbar w_0/KT} - 1\right)$ is the average occupancy of the phonon mode at T. S_0 is Huang-Rhys factor.

The Table 4 has listed the energy transfer microscopic parameters of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glass. It's clearly shown that effective energy transfer takes place between Tm^{3+} and Yb^{3+} ions. As shown in Table 4, the energy transfer coefficient between Yb^{3+}:$^2F_{5/2}$ level and Tm^{3+}:$^3H_5$ level can be as high as $1.3826\times10^{-40}cm^6/s$. It is worth mentioning that the above energy transfer process is non-resonant and mainly assisted by one phonon (39.076%), two phonons (27.785%) and three phonons (1.696%). This circumstance mainly results from low phonon energy of germanate-tellurite glass. Besides, with increasing Tm^{3+} concentration, the energy transfer process can difficultly happen from Yb^{3+}:$^2F_{5/2}$ to Tm^{3+}:$^3H_5$. As shown in Fig.6, the decay curves can confirm this process. Hence, it is very important for mid-infrared materials to select suitable Tm^{3+} concentration.

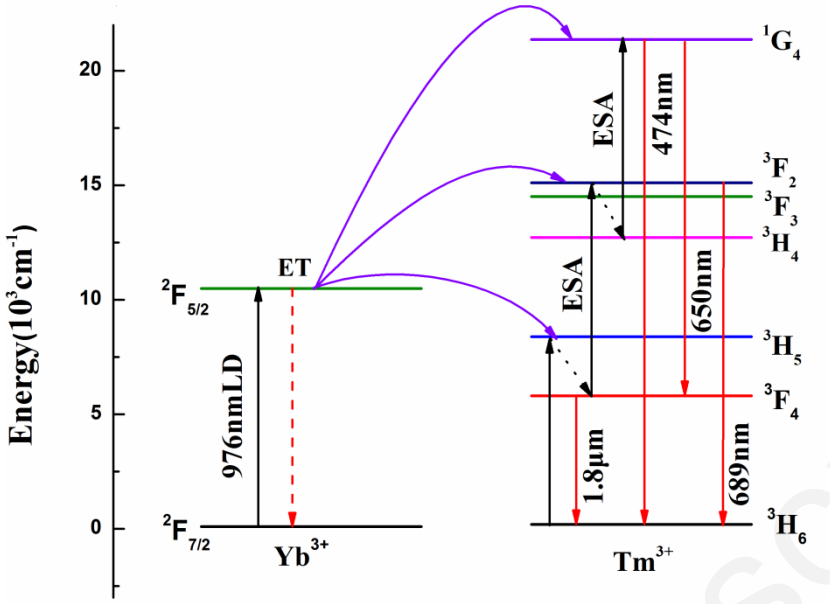

Fig.5. Simplified energy level diagram of the Tm^{3+}/Yb^{3+} co-doped system.

Table 4. Energy transfer parameters between Tm^{3+} and Yb^{3+} in glass sample

Energy transfer	N(number of phonons)(%phonon assisted)				Coefficient(cm^6/s)
$Yb^{3+}(^2F_{5/2})\rightarrow Tm^{3+}(^3H_5)$	0	1	2	3	1.3826×10^{-40}
	30.708	39.076	27.785	1.696	

3.4. Fluorescence lifetimes and gain coefficient

As shown in Fig.6, the 1.8μm highest lifetime (2.38ms) of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses sample is obtained, and is significantly larger than those of silicate (1.42ms) [48] and germanate (0.36ms) glass [49]. The lifetime of Tm^{3+}/Yb^{3+} in co-doped is longer than that in Tm^{3+} single doped germanate-tellurite glass. It indicates that there is an effective energy transfer between Tm^{3+} and Yb^{3+}. We can see that the lifetime of $^3F_4$ level decrease gradually with increasing Tm^{3+} concentration. The reduced lifetime isn't beneficial for upconversion process. The decreased

upconversion process contributes to population aggregation of Tm^{3+}:$^3F_4$ and might enhance Tm^{3+}:$^3H_5 \rightarrow {}^3F_4$. Here the stronger upconversion process is due in part to the excited state absorption (ESA), while the excited state absorption process reduces the $^3F_4$ level number of particles, which is detrimental to the 1.8μm lifetime. Therefore, the decrease in the conversion process is beneficial to the 1.8μm lifetime of Tm^{3+}. In addition, the relatively long lifetime generally enhances the luminous efficiency of glasses and it generally reduces the laser oscillation threshold. Hence, the emission lifetimes (2.38ms) indicate that Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glass is a promising materials for ~2.0μm fiber laser.

Besides, in order to further evaluate the performance of the samples, the fluorescence quantum efficiency has been estimated from the lifetime values by the following equation.

$$\eta = \frac{\tau}{\tau_{rad}} \times 100\% \quad (4)$$

where τ is the measured fluorescence lifetime of the sample ($0.5Tm^{3+}/0.1Yb^{3+}$), and τ_{rad} is the theoretical lifetime the sample ($0.5Tm^{3+}/0.1Yb^{3+}$). The measured $^3F_4$ lifetime (2.38ms) for Tm^{3+} is shorter than the calculated lifetime (3.89ms), which is due to non-radiative quenching. It can be found that the fluorescence quantum efficiency is high as 61.18%, which is higher than that of silicate glass (13.0%) [50]. Therefore, Tm^{3+}/Yb^{3+} codoped germanate-tellurite glass is a more promising material for improving the Tm^{3+} 2.0μm fiber laser performance.

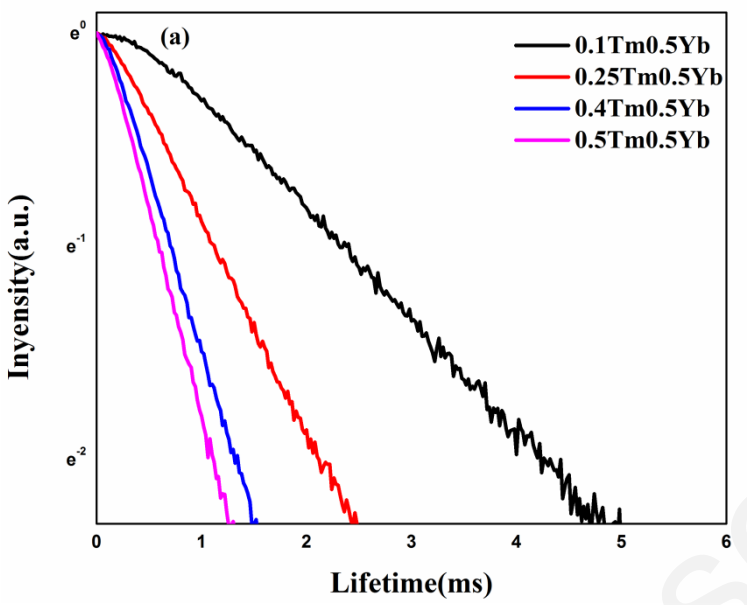

Fig.6. Decay curve of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses.

Another important parameter to evaluate the gain performances of prepared sample quantitatively is gain coefficient. In order to calculate the gain ability of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses, the gain coefficient *G(λ,P)* of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses is calculated. The room temperature gain coefficient (*G(λ,P)*) can be simply denoted as

$$G(\lambda, P) = N[P \sigma_{em}(\lambda) - (1-P)\sigma_{abs}(\lambda)] \quad (5)$$

where *N* is the doping concentration of the rare-earth ion, *P* is the population inversion.

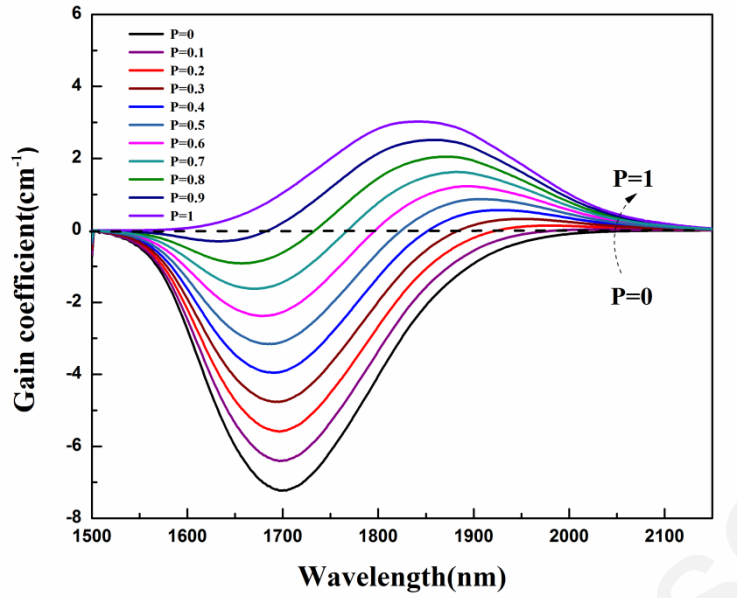

Fig. 7. Gain coefficient of Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ transitions in germanate-tellurite glasses.

The Fig.7 shows the calculated gain coefficients of Tm^{3+} and Yb^{3+} transitions as the function of wavelength. The gain coefficients results are calculated by setting the P ranging from 0 to 1 in interval of 0.1. We can see that the gain coefficient is increasing as the value of P continues to increase. As shown in Fig.7, the maximum gain coefficients of Tm^{3+} reach 3.02cm^{-1}, furthermore the concentrations of Tm^{3+} and Yb^{3+} are 0.1mol% and 0.5mol%, respectively. Besides when the P is more than 0.4, the value $G(\lambda,P)$ of the Tm^{3+}:$^3F_4 \rightarrow {}^3H_6$ transitions becomes positive number. In addition when the P is less than 0.4, it becomes negative number. The above results show that Tm^{3+}/Yb^{3+} co-doped GeO_2-TeO_2-K_2CO_3-Nb_2O_5-La_2O_3 glass has high gain and low pumping threshold for the laser, and is an outstanding gain host material for ~2μm mid-infrared laser.

4. Conclusions

In a word, efficient ~1.8μm emissions have been achieved in Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses. The energy transfer process between Yb^{3+} and Tm^{3+} has been investigated in detail. The thermal stability, absorption and emission cross sections，lifetimes have been analyzed. Results indicated that Tm^{3+} in the prepared glasses had not only superior thermo-mechanical stability (T_g =538°C, ΔT=188°C), but also large emission cross section ($1.35\times10^{-20}cm^2$). The measured lifetime of Tm^{3+}/Yb^{3+} co-doped germanate-tellurite glasses is as high as 2.38ms. It also possesses superior gain performance for Tm^{3+}:$^3F_4\rightarrow{}^3H_6$ and Yb^{3+}:$^2F_{5/2}\rightarrow{}^2F_{7/2}$ transitions. All of the results indicate that the prepared germanate-tellurite glass is a promising candidate for ~2.0μm mid-infrared laser materials applications.

Acknowledgment

This research was financially supported by the Chinese National Natural Science Foundation (No.61775205, 61605192 and 51502022).

References

[1] G. X Chen, Q. Y Zhang, G. F Yang , Z. H Jiang, Mid-Infrared Emission Characteristic and Energy Transfer of Ho3+-Doped Tellurite Glass Sensitized by Tm^{3+}. J.Fluoresc. 17(3), 301-307 (2007)

[2] F. Amzajerdian, J. Geng, Q. Wang, T. Luo, Single-frequency narrow-linewidth Tm-doped fiber laser using silicate glass fiber. Opt. Lett. 34(22), 3493-3495 (2009)

[3] Yuen H. Tsang, Ashraf F. El-Sherif, Terence A. King, Broadb and amplified spontaneous emission fibre source near 2.0 μm using resonant in-band pumping. J.Mod.Opt. 52(1), 109-118 (2005)

[4] W. J. Zhang, Q. Y. Zhang, Q. J. Chen, Q. Qian, Z. M. Yang, J. R. Qiu, P. Huang, Y. S. Wang, Enhanced 2.0 μm emission and gain coefficient of transparent glass ceramic containing BaF_2: Ho^{3+},Tm^{3+} nanocrystals. Opt. Express. 17(23), 20952-20958 (2009)

[5] S. Agger, J. H. Povlsen, and P. Varming, Single-frequency thulium-doped distributed-feedback fiber laser. Opt. Lett. 29(13), 1503–1505 (2004)

[6] J. F. Wu, Z. D. Yao, J. Zong, S. B. Jiang, Highly efficient high-power thulium-doped germanate glass fiber laser. Opt. Lett. 32(6), 638-640 (2007)

[7] S. F. León-Luis, J. Abreu-Afonso, J. Peña-Martínez, J. Méndez-Ramos, A. C. Yanes, J. del-Castillob, V. D. Rodrígueza, Up-conversion and colour tuneability in Yb^{3+}-Er^{3+}-Tm^{3+} co-doped transparent nano-glass-ceramics. J. Alloys Compd. 479(1), 557-560 (2009)

[8] D. Zhou, Z. Song, G. Chi, J. Qiu, NIR broadband luminescence and energy transfer in Er^{3+}-Tm^{3+}co-doped tellurite glasses. J. Alloys Compd. 48(1), 881-884 (2009)

[9] D. C. Hanna, I. M. Jauncey, R. M. Percival, I. R. Perry, R. G. Smart, P. J. Suni, J. E. Townsend, A. C. Tropper, Continuous-wave oscillation of a monomode thulium-doped fiber Laser. Electron. Lett. 24(19), 1222–1223 (1988)

[10] S. D. Jackson and T.A. King, Dynamics of the output of heavily Tm-doped double-clad silica fiber lasers, Opt. Lett.16(12), 2178-2189 (1999)

[11] P. F. Moulton, Tm-Doped Fiber Lasers: Fundamentals and Power Scaling, Journal of the selected topics in quantum electronics, 15(1), 85-92 (2009)

[12] R. M. Percival, D. Szebesta, S. T. Davey, Highly efficient and tunable operation of two colour Tm-doped fluoride fibre laser. Electron. Lett. 28(7), 671-673 (1992)

[13] K. F. Li, G. Zhang, L. L. Hu, Watt-level ~2.0 μm laser output in Tm^{3+} doped tungsten-tellurite glass double-cladding fiber. Opt. Lett. 35(24), 4136–4138 (2010)

[14] Q. Wang, J. Geng, T. Luo, S. Jiang, Mode-locked 2.0 μm laser with highly thulium-doped silicate fiber. Opt.Lett. 34(23), 3616–3618 (2009)

[15] J. F. Wu, Z. D. Yao, J. Zong, S. B. Jiang, Highly efficient high-power thulium-doped germanate glass fiber laser. Opt. Lett. 32(6), 638–640 (2007)

[16] N. P. Barnes, B. M. Walsh, D. J. Reichle, R. J. DeYoung, S. B. Jiang, Tm: germanate fiber

laser: tuning and Q-switching. Appl. Phys. B. 89(2-3), 299–304 (2007)

[17] F. Fusari, A. A. Lagatsky, G. Jose, S. Calvez, A. Jha, M. D. Dawson, J. A. Gupta, W.Sibbett, C. T. Brown, Femtosecond mode-locked Tm^{3+} and Tm^{3+}-Ho^{3+} doped 2.0 μm glass Lasers. Opt. Express. 18(21), 22090–22098 (2011)

[18] R. Xu, M. Wang, Y. Tian, L. Hu , J. Zhang, 2.05 μm emission properties and energy transfer mechanism of germanate glass doped with Ho^{3+}, Tm^{3+}, and Er^{3+}. J. Appl. Phys. 109(5), 285 (2011)

[19] Y. Y. Guo. M. Li, Y. Tian, R. R. Xu, L. L. Hu, J. J. Zhang. Enhanced 2.7 μm emission and energy transfer mechanism of Nd^{3+}/Er^{3+} co-doped sodium tellurite glasses. J. Appl. Phys. 110(1), 013512-013516 (2011)

[20] M. D. Di, L. F. Santos, A. C. Marques. Vibrational spectra and structure of alkali germanate glasses. J. Non-Cryst. Solids. 293, 394-401 (2001)

[21] G. Monteiro, L. F. Santos, J. Pereira, R. M. Almeida, Optical and spectroscopic properties of germanotellurite glasses. J. Non-Cryst. Solids. 357(14), 2695-2701 (2011).

[22] M. Jayasimhadri, E. J. Cho, K. W. Jang, H. S. Lee, S. I. Kim, Spectroscopic properties and Judd-Ofelt analysis of Sm^{3+} doped lead-germanate-tellurite glasses. J. Phys. D: Appl. Phys. 41(17), 175101-175104 (2008).

[23] H. Lin, Y. Y. Zhang, E. Y. B. Pun, Fluorescence investigation of Ho^{3+} in Yb^{3+} sensitized mixed-alkali bismuth gallate glasses. Spectrochim.Acta. Part A. 71(4), 1547-1550 (2008)

[24] L. Huang, S. Shen, A. Jha, Near infrared spectroscopic investigation of Tm^{3+}-Yb^{3+} co-doped tellurite glasses. J. Non-Cryst. Solids. 345-346(20), 349-353 (2004)

[25] D. Di Martino, L.FSantos, A.CMarques, R.MAlmeida, Vibrational spectra and structure of alkali germanate glasses. J. Non-Cryst. Solids. 293-295(1), 394-401 (2001)

[26] E. R. Shaaban, M. Shapaan, Y. B. Saddeek, Structural and thermal stability criteria of Bi_2O_3-B_2O_3 glasse. J. Phys. Condens. Matter. 20(20), 155108 (2008)

[27] D. D. Chen, Q. Y. Zhang, G. F. Yang, Z. H. Jiang, Thermal stability and spectroscopic properties of Er^{3+}doped niobium tellurite glasses for broadband amplifiers. Mater. Chem. Phys.90(1), 78-82 (2005)

[28] T .Wei , F. Chen , Y. Tian, S. Xu, 1.53 μm emission properties in Er^{3+} doped Y_2O_3 and Nb_2O_5 modified germanate glasses for an optical amplifier. J. Lumin. 154(154), 41-45 (2014)

[29] Y. Tian, R. Xu, L. Hu, J. Zhang, 2.7 μm fluorescence radiative dynamics and energy transfer between Er^{3+} and Tm^{3+} ions in fluoride glass under 800nm and 980nm excitation. J Quant Spectrosc Radiat Transf. 113(1), 87-95 (2012)

[30] A. A. El-Maaref, K. H. S. Shaaban, M. Abdelawwad, Y. B. Saddeek, Optical characterizations and Judd-Ofelt analysis of Dy^{3+} doped borosilicate glasses. Opt. Mater. 72, 169-176 (2017).

[31] G. C. Ram, T. Narendrudu, S. Suresh, D. Krishna Rao, Investigation of luminescence and laser transition of Dy^{3+} ion in P_2O_5 PbO Bi_2O_3 R_2O_3 (R=Al, Ga, In) glasses. Opt. Mater. 66, 189-196 (2017).

[32] F. Huang, Y. Ma, W. Li, X. Liu, L Hu, D. Chen, 2.7μm emission of high thermally and chemically durable glasses based on AlF_3. Sci.Rep. 4, 3607 (2014)

[33] B. R. Judd, Optical Absorption Intensities of Rare-Earth Ions. Phys. Rev. 127(3), 750-761 (1962)

[34] G.S.Ofelt, tensities of Crystal Spectra of Rare-arth Ions, J. Chem. Phys. 37, 511-520 (1962)

[35] H.Sun, L. Zhang, L. Wen, M. Liao, J. Zhang , Effect of $PbCl_2$ addition on structure, OH^- content, and upconversion luminescence in Yb^{3+}/Er^{3+} co-doped germanate glasses. Appl.Phys. B. 80(7), 881-888 (2005)

[36] R. Cao, M. Cai, Y. Lu, Y. Tian, F. Huang, S. Xu, J. Zhang, Ho^{3+}/Yb^{3+} codoped silicate glasses for 2 μm emission performances. Appl. Opt. 55(8), 2065-2070 (2016)

[37] S. Xu, Z. Yang, S. Dai, G.Wang, L. Hu, Z. Jiang, Upconversion fluorescence spectroscopy of Er^{3+}doped lead oxyfluoride germanate glass. Mater. Lett. 58(6), 1026-1029 (2004)

[38] R. Xu, Y. Tian, L. Hu, J. Zhang, Broadband 2 μm emission and energy-transfer properties of thulium-doped oxyfluoride germanate glass fiber. Appl. Phys. B. 104(4), 839-844 (2011)

[39] K. Li, H. Fan, G. Zhang, G. Bai, S. Fan, J. Zhang, L. Hu , Broadband near-infrared emission in Er^{3+}-Tm^{3+} co-doped bismuthate glasses. J. Alloys Compd. 509(6), 3070-3073 (2011)

[40] E. R. Shaaban, M. Shapaan, and Y. B. Saddeek, Structural and thermal stability criteria of Bi_2O_3–B_2O_3 glasses. J. Phys. Condens. Matter. 20(20),155108 (2008)

[41] K. Dieckmann, Laser Spectroscopy[M], World Scientific Publishing Co Pte Ltd. 1, 10 (2008)

[42] J. Yuan, W. C .Wang, D. D. Chen, M. Y. Peng , Q. Y. Zhang, Z. H. Jiang, Enhanced 1.8μm emission in Yb^{3+}/Tm^{3+}codoped tungsten tellurite glasses for a diode-pump 2.0 μm laser. J. Non-Cryst. Solids. 402(17), 223-230 (2014)

[43] C. Zhu, X. Zhao, Z. Wang, H. Lin, Upconversion photon quantification in Tm^{3+}/Yb^{3+}dopedaluminum germanate glasses for waveguide-typedirradiation light sources. Optik. 127(23), 11544-11552 (2016).

[44] G. Bai ,Y. Guo, Y. Tian, L. Hu, J. Zhang, Light emission at 2.0 μm from Ho-Tm-Yb doped silicate glasses. Opt. Mater. 33(8), 1316-1319 (2011)

[45] Y. Guo, Y. Ma, F. Huang, Y. Peng, L. Zhang, J. Zhang, 2.7 μm emission properties of Er^{3+} doped tungsten-tellurite glass sensitized by Yb^{3+} ions.Spectrochim. Acta.A. 111(111), 150-153 (2013)

[46] G. Bai, Y. Guo, Y. Tian, L. Hu, J. Zhang, Light emission at 2.0 μm from Ho^{3+}-Tm^{3+}-Yb^{3+} doped silicate glasses. Opt. Mater. 33(8), 1316-1319 (2011)

[47] K. Li, S. Fan, L. Zhang, Q. Zhang, J. Zhang, L. Hu, Spectroscopic properties of the 1.8 μm emission of Tm^{3+}/Yb^{3+} codoped TeO_2-ZnO-Bi_2O_3 glasses with efficient energy transfer. J. Non-Cryst. Solids. 357(11-13), 2417-2420 (2011)

[48] R. Cao, Y. Lu, Y. Tian, F. Huang, Y. Guo, S. Xu, J. Zhang, Mid-infrared luminescence and energy transfer of Tm^{3+} in silicate glasses by codoping with Yb^{3+} ions, Opt. Laser Technol. 94, 106-111 (2017).

[49] Y. Tian, R. Xu, L. Hu, J. Zhang, Efficient 2μm emission and energy transfer mechanism of Ho^{3+} doped barium gallium germanate glass sensitized by Tm^{3+} ions, Appl. Phys. B. 108(3), 597-602 (2012)

[50] X. Q. Liu, M. Li, X. Wang, F. F. Huang, L. L. Hu, D. P. Chen. ~2 μm Luminescence properties and nonradiative processes of Tm^{3+} in silicate glass. J. Lumin. 150, 40-45 (2014).