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Er³⁺/Tm³⁺ 共掺铋硅酸盐玻璃 2.0 μm 光谱性质

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摘 要: 用高温熔融法制备了 Er³⁺/Tm³⁺ 共掺杂无铅铋硅酸盐玻璃, 测试了玻璃的吸收光谱和荧光光谱, 分析和表征了 Er³⁺、Tm³⁺ 离子之间的能量传递机制和传递效率, 结果表明: 在 800 nm 和 1 550 nm 光源泵浦下, Er³⁺ 的掺入能够增强 Tm³⁺ 离子 1.8 μm 发光, 相应的最大发射截面分别为 6.7×10⁻²¹ cm² 和 7.3×10⁻²¹ cm², 荧光带宽达到 250 nm. 根据 Dexter-Foster 模型, 得到 Er³⁺:⁴I_{13/2} 能级到 Tm³⁺:³F₄ 能级的直接能量传递系数为 16.8×10⁻⁴⁰ cm⁶/s, 为 1 550 nm 泵浦下获得较强的 1.8 μm 发光奠定了基础.

关键词: 铋硅酸盐玻璃; 光谱性质; Er³⁺/Tm³⁺ 共掺杂; 2.0 μm 发光; 1 550 nm 泵浦

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Er³⁺ Sensitized Tm³⁺-Doped Lead-free Bismuth Silicate Glass for 2.0 μm Fiber Lasers

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Abstract: Er³⁺/Tm³⁺ codoped lead-free bismuth silicate glasses were successfully prepared by conventional melt-quenching method. The energy transfer mechanism and energy transfer efficiency between Er³⁺ and Tm³⁺ ions were investigated through absorption spectra and fluorescence spectra. The results show that the Tm³⁺:1.8 μm emission is enhanced by codoping Er³⁺ ions upon 800 nm and 1550 nm excitation. The corresponding maximum emission cross sections are estimated to be 6.7×10⁻²¹ cm² and 7.3×10⁻²¹ cm² on the basis of Fuchbauer-Ladenburger equation, respectively. Simultaneously, both values of 1.8 μm emission bandwidth are about 250 nm. The direct energy transfer microscopic parameter of Er³⁺:⁴I_{13/2}→Tm³⁺:³F₄ process is calculated to be 16.8×10⁻⁴⁰ cm⁶/s. This phenomenon results in the relatively stronger 1.8 μm emission using a 1550 nm pumping source.

Key words: Bismuth silicate glass, Optical properties; Er³⁺/Tm³⁺ co-doped; 2.0 μm Luminescence; 1550 nm pump

OCIS Codes: 160.2750, 160.0160, 070.4790, 260.2160

0 Introduction

Laser materials operating in the mid-infrared region have been gaining much interest due to their wide application in military, atmosphere pollution monitoring, pharmaceutical and medical industries^[1-2]. Recently, significant thrust has been driven on Rare Earth (RE) ions doped crystal and amorphous solid. Among these, ~2 μm emitting Tm³⁺ doped glass presently considered as one of the most promising

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candidates^[3]. Tm^{3+} serves as the active ion emitting 1.8 μm luminescence assigned to the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition, which exhibits the lower gain cross section and shorter radiative lifetime than Ho^{3+} ^[4]. To obtain intensive mid-IR emission from the Tm^{3+} doped glasses, the addition of the other rare earth ions was proposed as the energy sensitizer^[5]. Many studies have been concerning on some $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped glass, such as tellurite glass, fluorophosphate glass and bismuth glass^[6-8]. Except for Yb^{3+} ions, Er^{3+} ions have been used to sensitize the Tm^{3+} ions due to their strong absorption around 800 nm, 980 nm and 1550 nm^[5, 9].

Nowadays, a great number of glasses have been studied as matrix material for Tm^{3+} -doped, the most relevant work is still focusing on silica and silicate glass^[5, 10-13]. Among all kinds of glass hosts, silicate glass is qualified with distinguish thermal stability, excellent physical and chemical properties, strong glass-forming tendency and easy fiber-drawing ability. In 2016, Yang et al. have reported the $\sim 2 \mu\text{m}$ single mode laser performance using the Tm^{3+} -doped multi-component double cladding lead silicate glass fiber^[14]. Liu et al. realized 2 μm laser output from Tm^{3+} -doped lead silicate double cladding fiber^[15]. Enhanced 2 μm emission from $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluoride silicate glasses pumped at 800 nm and 980 nm were also observed^[9]. It is noted that the Maximum Phonon Energy (MPE) of silicate glass reaches up to 1 100 cm^{-1} which is harmful to the radiative transition of RE in glass.

Give that the absence of any toxic species, the lead-free bismuth silicate glass (SBT) appears as an interesting candidate for mid-infrared active fiber laser in our previous work^[16]. Results demonstrate that the introduction of Bi_2O_3 can efficiently reduce the MPE of silicate glass system. The present work mainly aims to investigate the 1.8 μm emission transition of Tm^{3+} ions in as-designed glass matrix, especially when samples are pumped by 800 nm and 1550 nm Laser Diode (LD). The role of Er^{3+} co-doping on the enhancement of Tm^{3+} emission and possible energy transfer mechanisms were discussed in detail.

1 Experimental

The set of glass used in this paper has the following nominal molar composition: $64\text{SiO}_2\text{-}15\text{Bi}_2\text{O}_3\text{-}5\text{TiO}_2\text{-}8\text{Na}_2\text{O-}8\text{Li}_2\text{O-}0.3\text{Tm}_2\text{O}_3\text{-}x\text{Er}_2\text{O}_3$ ($x=0, 0.3, 0.6, 0.9, 1.2$ designated as T, E1T, E2T, E3T and E4T, respectively). The 0.3 mol% Er_2O_3 single doped sample was also prepared and designated as E. The raw materials were prepared from high-purity SiO_2 , Bi_2O_3 , TiO_2 , Na_2CO_3 , Li_2CO_3 , Er_2O_3 and Tm_2O_3 powder. Well-mixed raw materials (15 g) were placed in an alumina crucible and melted at 1 150°C for 30 min in an oxygen atmosphere. Bubbling dry oxygen gas in melt was used to minimize the hydroxyl groups. The melts were quickly poured into preheated stainless-steel molds and annealed for 2 h near the glass transition temperature (T_g). The annealed sample was fabricated and polished to a size of 20 mm \times 10 mm \times 1 mm for optical property measurements.

Refractive indices were detected at room temperature using a Metricon Model 2010/M Prism Coupler. The absorption spectra were recorded with a Perkin-Elmer Lambda 900UV/VIS/NIR spectrophotometer in 1-nm steps. The fluorescence spectra were measured by a TRIAX550 spectrophotometer with 800 nm LD and 1 550 nm LD as the excitation sources. All measurements were conducted at room temperature.

2 Results and discussion

2.1 Absorption spectra and Judd-Ofelt analysis

The absorption spectra of the glasses doped with Er_2O_3 , Tm_2O_3 and $\text{Er}_2\text{O}_3/\text{Tm}_2\text{O}_3$ co-doped in range of 400-2000 nm have been presented in Fig. 1. Typical absorption spectra of the co-doped samples containing different concentration Er_2O_3 are closely similar. Due to the smaller intrinsic energy band-gap, the ultraviolet visible absorption cut-off edge of as-made samples (412 nm) shift to the longer wavelength sideband in comparison with the normal silicate glass (386 nm)^[11]. This

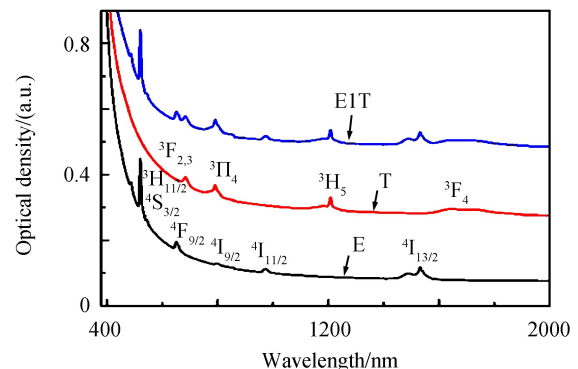


Fig.1 Absorption spectra of prepared samples

is mainly caused by the low chemical bonding strength of Bi-O bond^[2].

In Fig. 1, the characteristics absorption bands corresponding to Er³⁺, Tm³⁺ are labeled. The emerging three absorption bands around 800 nm, 980 nm and 1 550 nm are assigned to Er³⁺ ions. In optical absorption spectrum of co-doped glass, the shape and peak positions of each 4f-4f transitions remain almost unchanged as compared to the single doped sample, which confirms the sites of Er³⁺, Tm³⁺ are homogenous distributed in bismuth silicate glass network without cluster in the local surrounding. The most intense absorption bands near 800 nm and 1550 nm of Er³⁺ in co-doped sample suggest it can be efficiently pumped by 800 nm and 1 550 nm LD.

Table 1 J-O intensity parameters Ω_t ($\times 10^{-20} \text{ cm}^2$) of Er³⁺, Tm³⁺ in various silicate glasses

Glass	Tm ³⁺			Er ³⁺			Reference
	Ω_2	Ω_4	Ω_6	Ω_2	Ω_4	Ω_6	
Silicate	3.31	1.21	0.48	3.8	0.6	0.3	[17, 18]
Aluminum silicate	3.36	1.25	0.75	3.91	0.67	0.17	[19, 20]
Lead silicate	4.51	0.69	0.74	4.72	1.19	0.85	[15, 21]
Lead bismuthsilicate	2.92	1.26	0.92	3.92	1.10	0.78	[5]
Bismuth silicate	3.17	0.36	0.54				[16]
Bismuth silicate	3.41	0.38	0.67	4.76	0.92	0.83	This work

Based on the absorption spectra (Fig. 1), Judd-Ofelt (J-O) analysis was applied to evaluate the important spectroscopic and laser parameters of Er³⁺, Tm³⁺ ions. The phenomenological intensity parameters (Ω_t , $t = 2, 4, 6$) in bismuth silicate glass were obtained in Table 1. When Er³⁺ ions are introduced with Tm³⁺ co-doped, these parameters doesn't exhibit the great changes, indicating the introduction of Er³⁺ doesn't drastically influence the local environment of Tm³⁺. Realistically, Ω_t parameters depend significantly on the glass composition and especially Ω_2 points the covalent degree of RE-ligands chemical bond^[22]. In addition, Ω_6 are closely related to the viscosity and rigidity of glass host. On the whole, the Ω_2 of Tm³⁺ in bismuth silicate glass is higher than that in silicate and aluminum silicate glass but lower than that in lead silicate glass, which is mainly caused by the high polarizability of Pb²⁺ and Bi³⁺. Similar, because the introduction of Pb²⁺ and Bi³⁺ destroy the silicate glass network to some extent, the viscosity of glass melt will decrease at the melting temperature. As a result, the Ω_6 of Tm³⁺ in bismuth silicate glass is higher than that in silicate glass but lower lead silicate and lead bismuth silicate glass. The root-mean-square error deviations (δ_{rms}) is 0.89×10^{-6} , which indicates the calculated results are reliable. For comparison, Table 1 also presents the Ω_t of Er³⁺, Tm³⁺ ions in the other glass system from the reference. In our previous work, Tm³⁺ single doped bismuth silicate glass were prepared and their intensity parameters were obtained^[16].

2.2 Emission spectra pumped at 800 nm and 1 550 nm

The emission spectra of as-made samples with various Er₂O₃ doping concentrations under 800 nm excitation are measured and shown in Fig. 2(a). The spectra exhibit three main emission bands centered at 1473 nm, 1531 nm and 1802 nm, which arises from the typical Tm³⁺: ³H₄ → ³F₄ transition, Er³⁺: ⁴I_{13/2} → ⁴I_{15/2} transition and Tm³⁺: ³F₄ → ³H₆ transition in oxide glass, respectively. Except for the increasing emission intensity, the shape of the 1.8 μm emission band is almost unaffected by the increasing Er³⁺ content confirming the small impact of the co-dopants on the sites of the Tm³⁺ ions. This phenomenon coincides with the changes of Judd-Ofelt intensity parameters after the introduction of Er³⁺. Taking into account the sensitizing effect, adjusting the erbium oxide concentration (E1T, E2T, E3T and E4T) results in the increasement of 1.53 μm emission intensity without concentration quenching, while the 1.47 μm emission intensity exhibits the erratic tendency. The enhanced 1.8 μm emission could be explained with the shorter distance among RE ions, which is favorable to the energy transfer from Er³⁺ to Tm³⁺. The detailed energy transfer mechanism will be discussed in following.

Fig. 2(b) shows the emission spectra of Er³⁺/Tm³⁺ co-doped bismuth silicate glasses in the region of 1600-2200 nm under excitation of a 1550 nm LD. The emission spectra are dominated by an intense broadband emission band around 1.8 μm of Tm³⁺. The intensity of the band appears to be greatly dependent on the Er₂O₃ concentration. Since the high absorption intensity of Er³⁺ at 1550 nm practically

feeds the population density of the $\text{Er}^{3+} : ^4\text{I}_{13/2}$ excited state favoring an efficient energy transfer from Er^{3+} to Tm^{3+} in present matrix

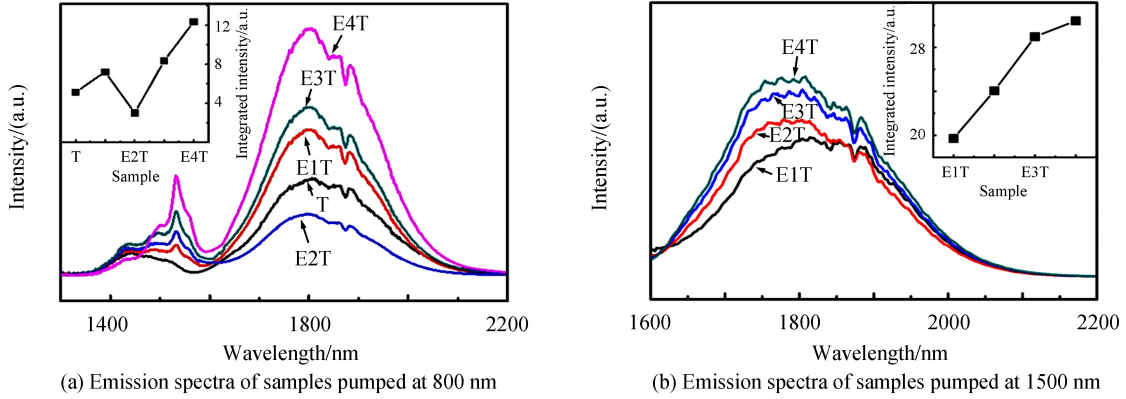


Fig.2 Emission spectra of samples pumped at 800 nm and 1 550 nm

According to the Fuchtbauer-Ladenburg theory and emission spectra, the $1.8 \mu\text{m}$ emission cross-section (σ_{em}) can be calculated as follows^[23]

$$\sigma_{\text{em}} = \frac{\lambda^4 A_{\text{rad}}}{8\pi c n^2} \times \frac{\lambda I(\lambda)}{\int \lambda I(\lambda) d\lambda} \quad (1)$$

where λ represents the wavelength, c and n are the light speed and the index of refraction, A_{rad} represents the spontaneous transition probability corresponding to the $\text{Tm}^{3+} : ^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition, and $I(\lambda)$ is the emission intensity. The maximum emission cross-section at $1.8 \mu\text{m}$ in the $\text{Er}^{3+}/\text{Tm}^{3+}$ -doped bismuth silicate glass pumped at 800 nm is $6.7 \times 10^{-21} \text{ cm}^2$, and this value is $7.3 \times 10^{-21} \text{ cm}^2$ when the sample is pumped at 1550 nm . The relatively high emission cross section is probably related to the high refractive index as a result of the introduction of heavy metal oxide Bi_2O_3 . Additionally, the Full Width at Half Maximum (FWHM) of $1.8 \mu\text{m}$ emission is about 250 nm pumped at 800 nm or 1550 nm , which is lower than that of silicate glass but higher than that of chalcogenide and germanate glass^[9, 24, 25]. The high band width is great beneficial to the ultra-broadband tunable laser sources. The inhomogeneous broadening of Tm^{3+} in bismuth silicate glass is related to the multisite character of Tm^{3+} luminescence centers. Based on the Raman analysis, the bismuth silicate glass is mainly composed of $[\text{SiO}_4]$ tetrahedron, $[\text{BiO}_6]$ octahedron and $[\text{BiO}_3]$ tetrahedron^[16]. The disorder of glass networker gives rise to the ensemble of Tm^{3+} centers in host.

2.3 Energy transfer mechanism and quantitative analysis

The partial energy level diagram illustrated in Fig. 3 exhibits the observed Near Infrared (NIR) and Middle Infrared (MIR) emission transitions with the possible energy transfer channels in the present host.

In absence of Er^{3+} , the 800 nm laser diode perfectly matches with the $\text{Tm}^{3+} : ^3\text{H}_6 \rightarrow ^3\text{H}_4$ absorption. While, for the $1.8 \mu\text{m}$ emission, the Tm^{3+} presents the relatively low pumped efficiency under excitation of an 800 nm LD. Moreover, the undesirable NIR emission and upconversion luminescence won't be avoided. In presence of Er^{3+} as a sensitizer, the 800 nm laser light excites efficiently the Er^{3+} to $^4\text{I}_{9/2}$ level in glass, in subsequent stage, being transferred to neighboring Tm^{3+} ions through resonant energy transfer shortcut. In this process, the sensitized Tm^{3+} ions jump to its $^3\text{H}_4$ excited state. Then, the ions on

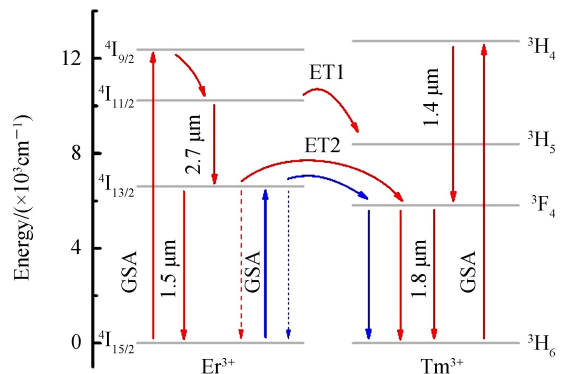
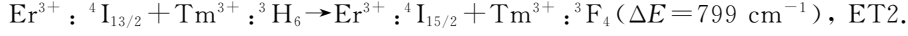
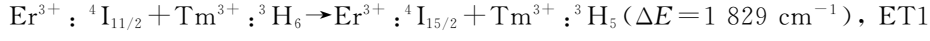


Fig.3 Simplified energy diagram of Er^{3+} and Tm^{3+} with possible energy transfer channels.

Tm³⁺:³H₄ come down to the ³F₄ and ³H₆ states, yielding 1.47 μm and 1.8 μm emission, respectively.

Two phonon-assisted non-resonant energytransfer channels play an important role in energy transfer mechanism (ΔE=energy mismatch):



It has been verified that the resonant Er³⁺:⁴I_{9/2}→Tm³⁺:³H₄ process is the most probable microscopic process to take place in contrast with the above two non-resonant processes^[26]. It is difficult to take place once two or more than two phonons generation are needed to participate the non-resonant process. In view of the greater energy mismatch of ET1 process, the probability rate of ET2 process is larger than that of ET1 process. When the samples are pumped by an 800 nm LD, the Er³⁺:⁴I_{9/2}→Tm³⁺:³H₄ process, Er³⁺:⁴I_{11/2}→Tm³⁺:³H₅ process and Er³⁺:⁴I_{13/2}→Tm³⁺:³F₄ process could take place resulting in the waste of excitation energy along with the undesirable visual, NIR and MIR luminescence. Therefore, the adoption of a 1550 nm LD is a feasible approach to obtain the 1.8 μm emission.

Dexter and Förster calculate the energy transfer rate between RE ions diluted in solid matrix in terms of emission (absorption) cross section of the donor (acceptor)^[27]. The energy transfer microparameter can be expressed to describe the donor-acceptor interaction model,

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

$$C_{\text{AD}} = \frac{6cg_{\text{low}}^{\text{A}}}{(2\pi)^4 n^2 g_{\text{up}}^{\text{A}}} \sum_{k=0}^N e^{-2nS_0} \frac{S_0^k}{k!} (n)^k \times \int \sigma_{\text{em}}^{\text{A}}(\lambda_k^-) \sigma_{\text{abs}}^{\text{D}}(\lambda) d\lambda \quad (3)$$

where $g_{\text{low}}^{\text{D}}$ and g_{up}^{D} are the degeneracy of the lower and upper levels of the donor, respectively. n is the average occupancy, m and k is the number of the phonons participating in the energy transfer, S_0 is the Huang-Rhys factor, and λ_m^+ and λ_k^- are the wavelength with m phonons and k phonons, respectively. It has been observed that the Er³⁺:⁴I_{13/2}→Tm³⁺:³F₄ microscopic energy transfer channel is more effective than the Er³⁺:⁴I_{11/2}→Tm³⁺:³H₅ channel^[28]. In this work, values of C_{DA} and C_{AD} of the ET2 process in bismuth silicate glass are listed in Table 2 using Eq. (2)~(3). The related spectral superposition between the Er³⁺:⁴I_{13/2}→⁴I_{15/2} emission and the fundamental Tm³⁺:³H₆→³F₄ absorption in bismuth silicate glass are exhibited in Fig. 4. The break lines represent the one- and two-phonons emission sidebands of Er³⁺.

When one phonon is released to assist the energy transfer, the absorption and emission cross-section spectra of the Tm³⁺ and Er³⁺ ions, respectively, overlap strongly, so that the C_{DA} value (direct energy transfer) is almost 25 times larger than C_{AD} (back energy transfer). In addition, it is noted the number of phonons participated the ET2 process in present glass is smaller than that in bismuth germanate glass, which is mainly caused by the relatively larger phonon energy of bismuth silicate glass. The results again support the rationality of adoption of a 1550 nm LD pumping source.

Table 2 Calculated microparameters C_{DA} , C_{AD} for the Er³⁺→Tm³⁺ energy transfer processes (ET2). Number (#) of phonons needed to assist energy transfer, as well as the percentage of each phonon participation (%) in the process

Energy transfer	N (# of phonons) (% phonon-assist)	$C_{\text{DA}}/$ ($\times 10^{-40}\text{ cm}^6 \cdot \text{s}^{-1}$)	N (# of phonons) (% phonon-assist)	$C_{\text{AD}}/$ ($\times 10^{-40}\text{ cm}^6 \cdot \text{s}^{-1}$)
Er ³⁺ : ⁴ I _{13/2} → Tm ³⁺ : ³ F ₄	0, 1 (16, 84)	16.8	1, 2, 3 (56, 39, 5)	0.65

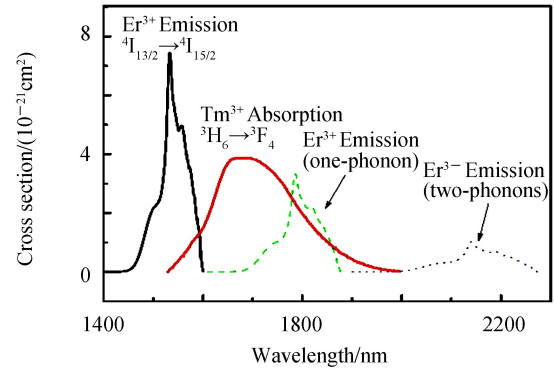


Fig.4 Excited state absorption spectrum of Tm³⁺:³F₄ and emission spectra of Er³⁺:⁴I_{13/2} in present host.

2.4 Fluorescent decay curves

The fluorescent decay curves of $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level in E4 and E4T glasses were measured and are shown in Fig. 5. As shown in Fig. 5, the measured lifetime of $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level obviously decreases in $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped glass (E4T) in comparison with the Er^{3+} singly-doped ones (E4), which indicates the existence of energy transfer from Er^{3+} to Tm^{3+} . In general, the energy transfer efficiency η can be evaluated by the following equation^[29]

$$\eta = 1 - \frac{\tau}{\tau_0} \quad (4)$$

where τ and τ_0 represent the fluorescence lifetimes of $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level in $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped and Er^{3+} singly doped glasses, respectively. The τ and τ_0 were measured to be 5.31 ms and 1.23 ms in E4T and E4 glasses. The obtained η of ET2 is up to 76.8%, which is benefit to enhance the 1.8 μm emission of Tm^{3+} ions.

3 Conclusions

Only Tm^{3+} , only Er^{3+} and (Er^{3+} , Tm^{3+}) co-doped lead-free bismuth silicate glasses were prepared and their spectroscopic properties are studied with two LDs; one with the wavelength of 800 nm and the other with the wavelength of 1550 nm, in order to contrast the 1.8 μm emission capability. An intense broadband mid-infrared emission spectrum with the largest simulated emission cross section of $7.3 \times 10^{-21} \text{ cm}^2$ is obtained with the excitation source of 1550 nm. The correlation between the energy transfer mechanism and the $\text{Tm}^{3+} : ^3\text{F}_4$ population was found and explained. The increasing Er^{3+} doping level efficiently enlarge the energy transfer probability from Er^{3+} to Tm^{3+} . Based on the Dexter-Föster analysis, the calculated direct energy transfer microparameter of $\text{Er}^{3+} : ^4\text{I}_{13/2} \rightarrow \text{Tm}^{3+} : ^3\text{F}_4$ process is up to $16.8 \times 10^{-40} \text{ cm}^6/\text{s}$. All these data indicate that the lead-free bismuth silicate glasses with $\text{Er}^{3+}/\text{Tm}^{3+}$ codoped are promising materials for 2 μm fiber lasers.

References

- [1] BALAJI S, GUPTA G, BISWAS K, *et al.* Role of Yb^{3+} ions on enhanced $\sim 2.9 \mu\text{m}$ emission from Ho^{3+} ions in low phonon oxide glass system[J]. *Scientific Reports*, 2016, **6**: 29203.
- [2] RAGIN T, ZMOJDA J, KOCHANOWICZ M, *et al.* Enhanced mid-infrared 2.7 μm luminescence in low hydroxide bismuth-germanate glass and optical fiber co-doped with $\text{Er}^{3+}/\text{Yb}^{3+}$ ions[J]. *Journal of Non-Crystalline Solids*, 2017, **457**: 169-174.
- [3] TAN Lin-ling, KANG Shi-liang, PAN Zhi-wen, *et al.* Topo-chemical tailoring of tellurium quantum dot precipitation from supercooled polyphosphates for broadband optical amplification[J]. *Advanced Optical Materials*, 2016, **4**(10): 1624-1634.
- [4] HUANG Fei-fei, CHENG Ji-meng, LIU Xue-qiang, *et al.* $\text{Ho}^{3+}/\text{Er}^{3+}$ doped fluoride glass sensitized by Ce^{3+} pumped by 1550 nm LD for efficient 2.0 μm laser applications[J]. *Optic Express*, 2014, **22**(17): 20924-20935.
- [5] WANG Xin, LI Zhi-lan, LI Ke-feng, *et al.* Spectroscopic properties and energy transfer in Er-Tm co-doped bismuth silicate glass[J]. *Optical Materials*, 2013, **35**(12): 2290-2295.
- [6] LI Ke-feng, ZHANG Qiang, BAI Gong-xun, *et al.* Energy transfer and 1.8 μm emission in $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped lanthanum tungsten tellurite glasses[J]. *Journal of Alloys and Compounds*, 2010, **504**(2): 573-578.
- [7] FANG Yong-zheng, ZHAO Guo-ying, XU Jia-yue, *et al.* Energy transfer and 1.8 μm emission in $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped bismuth germanate glass[J]. *Ceramics International*, 2014, **40**(4): 6037-6043.
- [8] TIAN Ying, XU Rong-rong, HU Li-li, *et al.* Mid-infrared luminescence and energy transfer of $\text{Tm}^{3+}/\text{Yb}^{3+}$ doped fluorophosphate glass[J]. *Materials Chemistry and Physics*, 2012, **133**(1): 340-345.
- [9] CAO Rui-jie, LU Yu, TIAN Ying, *et al.* 2 μm emission performance in $\text{Tm}^{3+}/\text{Er}^{3+}$ codoped silicate glasses under 800nm and 980nm excitation[J]. *Infrared Physics & Technology*, 2017, **81**: 21-26.
- [10] PENG Ming-ying, ZHANG Na, WONGRACZEK L, *et al.* Ultrabroad NIR luminescence and energy transfer in Bi and Er/Bi co-doped germanate glasses[J]. *Optic Express*, 2011, **19**(21): 20799-20807.

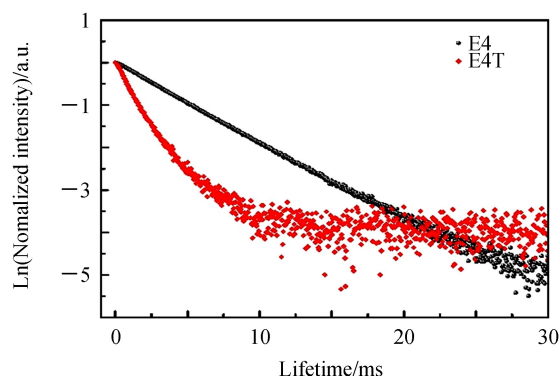


Fig.5 Fluorescence decay curves of $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level in E4 and E4T glasses

- [11] WANG Xin, FAN Xiao-kang, GAO Song, *et al.* Spectroscopic properties of Tm³⁺-Ho³⁺ codoped SiO₂-Al₂O₃-CaO-SrO glasses[J]. *Ceramics International*, 2014, **40**(7, Part A): 9751-9756.
- [12] DING Jia, ZHAO Guo-ying, TIAN Ying, *et al.* Bismuth silicate glass: A new choice for 2μm fiber lasers[J]. *Optical Materials*, 2012, **35**(1): 85-88.
- [13] BAI Gong-xun, GUO Yan-yan, TIAN Ying, *et al.* Light emission at 2 μm from Ho-Tm-Yb doped silicate glasses[J]. *Optical Materials*, 2011, **33**(8): 1316-1319.
- [14] TANG Guo-wu, ZHU Ting-ting, LIU Wang-wang, *et al.* Tm³⁺ doped lead silicate glass single mode fibers for 2.0 μm laser applications[J]. *Optical Materials Express*, 2016, **6**(6): 2147-2157.
- [15] LIU Xue-qiang, WANG Xin, WANG Long-fei, *et al.* Realization of 2μm laser output in Tm³⁺-doped lead silicate double cladding fiber[J]. *Materials Letters*, 2014, **125**: 12-14.
- [16] ZHAO Guo-ying, TIAN Ying, WANG Xin, *et al.* Spectroscopic properties of 1.8μm emission in Tm³⁺ doped bismuth silicate glass[J]. *Journal of Luminescence*, 2013, **134**: 837-841.
- [17] PENG Bo, IZUMITANI T. Optical properties, fluorescence mechanisms and energy transfer in Tm³⁺, Ho³⁺ and Tm³⁺-Ho³⁺ doped near-infrared laser glasses, sensitized by Yb³⁺ [J]. *Optical Materials*, 1995, **4**(6): 797-810.
- [18] LE N L, JIANG Shi-bin, HWANG B C, *et al.* Effect of relative alkali content on absorption linewidth in erbium-doped tellurite glasses[J]. *Journal of Non-Crystalline Solids*, 1999, **255**(1): 97-102.
- [19] XU Rong-rong, WANG Meng, TIAN Ying, *et al.* 2.05 μm emission properties and energy transfer mechanism of germanate glass doped with Ho³⁺, Tm³⁺, and Er³⁺ [J]. *Journal of Applied Physics*, 2011, **109**(5): 053503.
- [20] WANG Xin, LI Ke-feng, YU Chun-lei, *et al.* Effect of Tm₂O₃ concentration and hydroxyl content on the emission properties of Tm doped silicate glasses[J]. *Journal of Luminescence*, 2014, **147**: 341-345.
- [21] LIU Xue-qiang, HUANG Fei-fei, CHENG Ji-meng, *et al.* Investigation on Er³⁺/Ho³⁺ co-doped silicate glass for ~ 2μm fiber lasers[J]. *Journal of Luminescence*, 2015, **162**: 197-202.
- [22] PADLYAK B V, LISIECKI R, RYBA-ROMANOWSKI W. Spectroscopy of the Er-doped lithium tetraborate glasses [J]. *Optical Materials*, 2016, **54**: 126-133.
- [23] WEBER M J, ZIEGLER D C, ANGELL C A. Tailoring stimulated emission cross sections of Nd³⁺ laser glass: Observation of large cross sections for BiCl₃ glasses[J]. *Journal of Applied Physics*, 1982, **53**(6): 4344-4350.
- [24] TIAN Ying, XU Rong-rong, HU Li-li, *et al.* 2.7μm fluorescence radiative dynamics and energy transfer between Er³⁺ and Tm³⁺ ions in fluoride glass under 800nm and 980nm excitation[J]. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2012, **113**(1): 87-95.
- [25] WEI Tao, CHEN Fang-ze, JIANG Xu-feng, *et al.* Structure and spectroscopic properties of Er³⁺ doped germanate glass for mid-infrared application[J]. *Solid State Sciences*, 2014, **31**(5): 54-61.
- [26] TARELHO L, GOMES L, RANIERI I. Determination of microscopic parameters for nonresonant energy-transfer processes in rare-earth-doped crystals[J]. *Physical Review B*, 1997, **56**(22): 14344-14351.
- [27] DE SOUSA D F, LEBULLENGER R, HEMANDES A C, *et al.* Evidence of higher-order mechanisms than dipole-dipole interaction in Tm³⁺ → Tm³⁺ energy transfer in fluoroindogallate glasses[J]. *Physical Review B*, 2002, **65**(9): 094204.
- [28] ZHAO Guo-ying, KUAN Pei-Wen, FAN Hui-yan, *et al.* Enhanced green and red upconversion and 2.7μm emission from Er³⁺/Tm³⁺ co-doped bismuth germanate glass[J]. *Optical Materials*, 2013, **35**(5): 910-914.
- [29] SHENG Qiu-chun, WANG Xiao-lin, CHEN Dan-ping, *et al.* Enhanced broadband 2.0μm emission and energy transfer mechanism in Ho-Bi co-doped borophosphate glass[J]. *Journal of the American Ceramic Society*, 2012, **95**(10): 3019-3021.

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