

SCIENTIFIC REPORTS

OPEN

Optical characterization of Tm³⁺ doped Bi₂O₃-GeO₂-Ga₂O₃ glasses in absence and presence of BaF₂

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Received: 09 February 2016

Accepted: 14 July 2016

Published: 10 August 2016

In this paper, Two new Bi₂O₃-GeO₂-Ga₂O₃ glasses (one presence of BaF₂) doped with 1mol% Tm₂O₃ were prepared by melt-quenching technique. Differential thermal analysis (DTA), the absorption, Raman, IR spectra and fluorescence spectra were measured. The Judd–Ofelt intensity parameters, emission cross section, absorption cross section, and gain coefficient of Tm³⁺ ions were comparatively investigated. After the BaF₂ introduced, the glass showed a better thermal stability, lower phonon energy and weaker OH⁻ absorption coefficient, meanwhile, a larger ~1.8 μm emission cross section σ_{em} ($7.56 \times 10^{-21} \text{ cm}^2$) and a longer fluorescence lifetime τ_{mea} (2.25 ms) corresponding to the Tm³⁺: ⁴F₃ → ³H₆ transition were obtained, which is due to the addition of fluoride in glass could reduce the quenching rate of hydroxyls and raise the cross-relaxation (³H₆ + ³H₄ → ³F₄ + ³F₄) rate. Our results suggest that the Tm³⁺ doped Bi₂O₃-GeO₂-Ga₂O₃ glass with BaF₂ might be potential to the application in efficient ~1.8 μm lasers system.

Over the past decade, Tm³⁺-doped fiber lasers have attracted growing attention in numerous areas owing to their very broad transition linewidth over ~1.7 to 2.1 μm wavelength^{1–4}. As we know, near-infrared lasers at the eye-safe 2 μm region have many potential applications in medicine, remote sensing, and atmospheric pollutant monitoring^{4,5}. Recently, the long-wavelength window around 1700 nm has attracted attention for OCT imaging⁶. Wavelengths near ~1720 nm are of interest for targeting fat/lipid-rich tissues due to the high absorption coefficient of human fat and low water scattering and absorption⁷. Nicholas G. Horton. *et al.* were put forward expectations that a wavelength-tunable source that covers the entire “low attenuation” spectral window from 1650 to 1850 nm can be obtained, which will further increase the number of accessible fluorophores and fluorescent proteins for Three-photon fluorescence microscopy (3PM) in the 1700 nm spectral window⁸. In addition, they can operate as pump sources for achieving 3.0~5.0 μm mid-infrared fiber lasers output at room-temperature, for national defense and commercial applications^{9,10}. A typical work on Tm³⁺-Tb³⁺ co-doped tunable fiber ring laser for 1716 nm lasing was pumped by a 1.21 μm laser diode¹¹. Another type of Tm-doped silica fiber laser with narrow-linewidth and output wavelength near 1750 nm has been reported, by using a 1550 nm Er-doped fiber laser pump source and a volume Bragg grating (VBG)¹².

Tm³⁺ is a better solution to ~2 μm emissions because of its absorption band near 808 nm matching well with commercially available and high power laser diode¹³. Due to the cross-relaxation (³H₆ + ³H₄ → ³F₄ + ³F₄) process between Tm³⁺ ions, the ideal quantum efficiency of Tm³⁺: ³F₄ can reach 200%^{14,15}. To date, in order to get powerful infrared emissions from Tm³⁺ ions, various kinds of glass hosts have been investigated including silicate¹⁶, tellurite¹⁷, germanate¹⁸, and fluorophosphates¹⁹ glasses. Yin-Wen Lee, *et al.* reported an 18-dB 2013-nm amplifier which was demonstrated in a 50-cm 7 wt% Tm³⁺-doped double-clad silicate fiber²⁰. Xin Wen, *et al.* reported a multilongitudinal-mode fiber laser at 1.95 μm has also been achieved in a 10 cm long as-drawn active fiber, yielding a maximum laser output power of 165 mW and a slope efficiency of 17%²¹. Zhi-Xu Jia reported a supercontinuum generation in Tm³⁺ doped tellurite microstructured fibers pumped by a 1.56 μm femtosecond fiber laser²². However, few researches have been paid on the bismuth germanate glass and fiber.

Among the oxide glasses, the bismuthate glass has a lower phonon energy (~440 cm⁻¹)^{23,24} compared with silicate (~1000 cm⁻¹)¹⁶, germanate (~900 cm⁻¹)¹³ and tellurite (~750 cm⁻¹)¹⁷ glasses, which is very useful to enhance the luminescence quantum efficiency²³ of Tm³⁺ ions and reduce the multiphonon relaxation²⁴. In addition, compared with silicate and other heavy metal oxide glasses, the bismuthate glass possesses many other material

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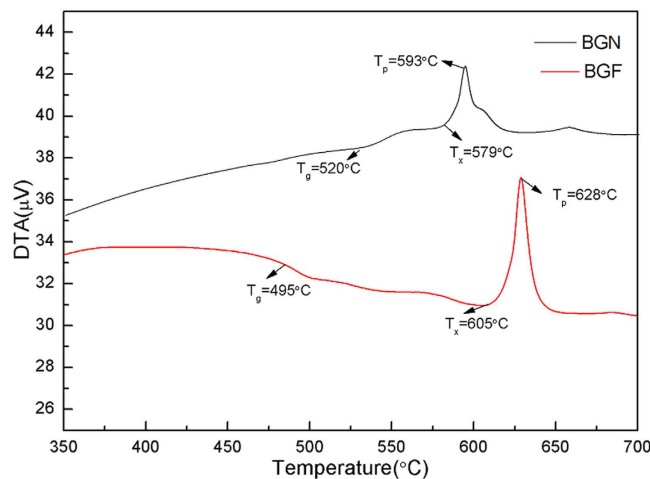


Figure 1. DTA curves of BGN and BGF glasses doped with 1 mol% Tm_2O_3 at the heating rate of 10 K/min.

advantages such as easy preparation process, low melting temperature, large rare-earth solubility²¹, high refractive index (~ 2.1)²⁵ and wide transparency window²⁶, make bismuthate glass particularly promising for fiber amplifiers and infrared fiber lasers.

The OH^- groups may quench ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ emissions of Tm^{3+} ions and reduce emission efficiency⁵. But hydroxyl and the fluorine ions are isoelectronic and their ionic size was similar; hydroxyl ions could easily be removed by fluoride during melting²⁷. Therefore, 1 mol% Tm^{3+} -doped bismuth-germanium-gallate glasses in absence and presence of BaF_2 were studied for $\sim 1.8\ \mu\text{m}$ emission.

Experimental

Molar composition of $36\text{Bi}_2\text{O}_3 - 29\text{GeO}_2 - 25\text{Ga}_2\text{O}_3 - 10\text{Na}_2\text{O} - 1\text{Tm}_2\text{O}_3$ (BGN) and $36\text{Bi}_2\text{O}_3 - 29\text{GeO}_2 - 25\text{Ga}_2\text{O}_3 - 10\text{BaF}_2 - 1\text{Tm}_2\text{O}_3$ (BGF) glasses were fabricated by conventional melting-quenching method in an alumina crucible at $1200\ ^\circ\text{C}$ under oxygen atmosphere respectively. The glass samples were formed by casting molding and finally annealed at $480\ ^\circ\text{C}$ for 3 h to remove thermal strains. Samples were cut and polished to $10 \times 10 \times 2\ \text{mm}^3$ for property measurements.

Differential thermal analysis (DTA) was performed using a SETARAM TAG24 analyser, for characteristic temperatures (the temperature of glass transition T_g , temperature of onset crystallization T_x and temperature of peak crystallization T_p). Density and refractive index of samples was obtained by Archimedes method and spectroscopic ellipsometer method, respectively. The absorption spectrum was recorded using a spectrophotometer (Perkin Elmer Lambda9). The near-infrared emission spectra and luminescence lifetime were measured by FLS920 (Edinburgh instruments Ltd., UK) under 808 nm laser diode pumped. Raman spectra were monitored with a FT Raman spectrophotometer (Nicolet Module). All measurements were carried out at room temperature.

Results and Discussions

Thermal property. Figure 1 shows the DTA curve of the studied glass, and the values of T_g , T_x and T_p in Tm^{3+} -doped BGN and BGF samples are indicated. The difference between the glass transition temperature T_g and the onset crystallization temperature T_x , $\Delta T = T_x - T_g$, has been frequently used as a rough estimate of glass formation ability or glass thermal stability. It can be seen that the values of T_g is decreased from $520\ ^\circ\text{C}$ to $495\ ^\circ\text{C}$ as the Na_2O is replaced by BaF_2 in BGF glass. However, it is still higher than of fluoride²⁸, tellurite²⁹ glasses, this results show that the glasses have good thermal shock resistance performance under the condition of high power pump. Generally, the ΔT of the glass sample should be higher than $100\ ^\circ\text{C}$ to obtain a better thermal stability and to avoid crystallization during the optical fiber drawing process^{30,31}. After the addition of BaF_2 , the thermal stability (ΔT) of Bi_2O_3 - GeO_2 - Ga_2O_3 glass is increased quite significantly. The value of ΔT for BGF sample is $110\ ^\circ\text{C}$, which is higher than of BGN ($59\ ^\circ\text{C}$), indicating that the BGF sample has better thermal stability against crystallization for $\sim 1.8\ \mu\text{m}$ emission.

Absorption and IR transmittance spectra. Figure 2 shows the absorption spectra of the Tm^{3+} doped BGN and BGF samples under room temperature. All absorption bands belong to transition of Tm^{3+} ions from ground state to higher levels are labeled in Fig. 2. As expected, BGN and BGF samples have similar absorption peaks, and the ${}^3\text{H}_6 - {}^1\text{G}_4$ transition has not appeared, due to the UV cut-off wavelength of bismuthate glasses is redshift. Strong absorption around 790 nm indicates that these glasses can be excited efficiently by 808 nm LD. As shown in Fig. 3, BGF sample shows better IR transmittance than BGN sample. The absorption band ranging from 2700 to $3700\ \text{cm}^{-1}$ is due to stretching vibrations of free OH^- groups. Hydroxyl and the fluorine ions are isoelectronic and their ionic size is similar²⁸, hydroxyl ions can easily be removed by fluoride during melting through the reaction $\text{OH}^- + \text{F}^- \rightarrow \text{HF} + \text{O}^{2-}$. The OH^- absorption coefficient in the glass can be calculated by the IR transmission spectra, which is given by³¹

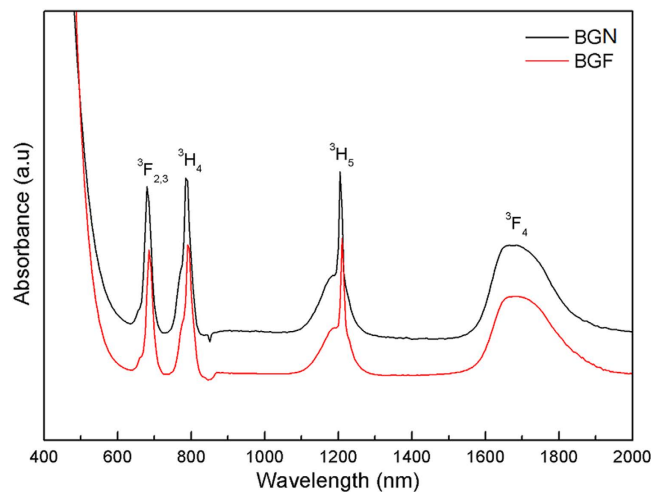


Figure 2. Room temperature absorption spectra in the range from 400 to 2000 nm of the BGN and BGF glass samples doped with 1 mol% of Tm_2O_3 .

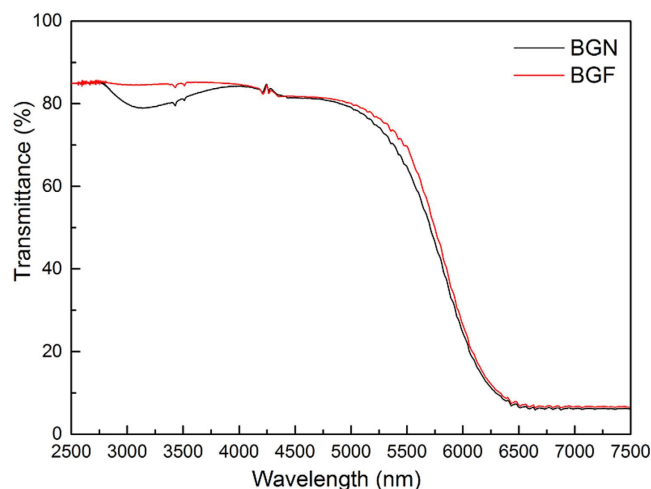


Figure 3. Infrared transmission spectrum of the BGN and BGF glasses doped with 1 mol% of Tm_2O_3 in the range of the absorption bands of water.

$$\alpha_{OH} = 2.303 \log \frac{T_0}{T} / l \quad (1)$$

where l is the thickness of a sample, T_0 and T are the transmission value of maximum and at 3000 cm^{-1} , respectively. The OH^- absorption coefficient of BGN and BGF samples are calculated according to Eq. (1), 0.34 cm^{-1} and 0.05 cm^{-1} , respectively. It is obvious that typical OH^- groups' absorption of BGN sample is much stronger than that of BGF sample at $3 \mu\text{m}$ regions, which is one of the main reasons for the difference between BGN and BGF samples in $\sim 1.8 \mu\text{m}$ emission.

Judd-Ofelt analysis. According to absorption spectra (Fig. 1), Judd-Ofelt (J-O) theory has been applied to determine the important spectroscopic and laser parameters of Tm^{3+} ion. In this paper, J-O intensity parameters Ω_t ($t = 2, 4, \text{ and } 6$) are calculated and radiative transitions within $4f^n$ configuration of Tm^{3+} is analyzed, the value of them list in Table 1. The value Ω_2 of BGF are lower than those of BGN, however, they are still much larger than that of silicate³¹, tellurite³², fluoride³³ and germanate³⁴ glasses. As known Ω_2 is related with the covalency between rare earth ions and ligands anions and reflects the asymmetry of local environment at Tm^{3+} site in the glass hosts. Large Ω_2 means stronger covalency between the rare-earth ions and ligand anions, while the Ω_6 has a relation with the overlap integrals of $4f$ and $5d$ orbits²⁶. Large value of Ω_6 exhibits the large value of emission bandwidth and spontaneous radiative probability of rare earth³¹. Values of Ω_4 and Ω_6 also provide some information on the rigidity and viscosity of hosts.

Glass	$\Omega_2 (\times 10^{-20} \text{cm}^2)$	$\Omega_4 (\times 10^{-20} \text{cm}^2)$	$\Omega_6 (\times 10^{-20} \text{cm}^2)$	Reference
BGN	6.26	0.24	1.6	This work
BGF	5.15	1.01	1.25	
silicate	3.40	0.46	0.66	16
Tellurite	3.20	2.01	1.83	29
Fluorophosphate	3.01	2.56	1.54	32
Germanate	3.93	1.1	1.1	35

Table 1. Judd-Ofelt intensity parameters in BGN and BGF samples.

Transition	λ (nm)	A_{rad} (s^{-1})	BGN sample				BGF sample			
			$\sum A$ (s^{-1})	β (%)	τ (ms)	A_{rad} (s^{-1})	$\sum A$ (s^{-1})	β (%)	τ (ms)	
${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$	1847	454.48	454.48	100	2.20	406.38	406.38	100.00	2.46	
${}^3\text{H}_5 \rightarrow {}^3\text{F}_4$	3563	27.5	609.08	4.53	1.64	21.45	507.51	4.23	1.97	
$\rightarrow {}^3\text{H}_6$	1216	581.51		95.47		486.07		95.77		
${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$	2428	10.81	3679.83	0.29	0.27	26.49	2894.29	0.92	0.35	
$\rightarrow {}^3\text{F}_4$	1444	283.61		7.71		235.88		8.15		
$\rightarrow {}^3\text{H}_6$	810	3385.40		92.00		2631.92		90.93		
${}^3\text{F}_3 \rightarrow {}^3\text{H}_4$	5200	7.05	4938.24	0.14	0.20	7.00	4302.28	0.16	0.23	
$\rightarrow {}^3\text{H}_5$	1655	832.61		16.86		685.69		15.94		
$\rightarrow {}^3\text{F}_4$	1310	184.22		3.73		133.42		3.10		
$\rightarrow {}^3\text{H}_6$	701	3914.36		79.27		3476.17		80.80		
${}^3\text{F}_2 \rightarrow {}^3\text{F}_3$	20449	0.01	2155.96	0.00	0.46	0.01	1639.24	0.00	0.61	
$\rightarrow {}^3\text{H}_4$	4145	41.78		1.94		33.83		2.06		
$\rightarrow {}^3\text{H}_5$	1531	370.17		17.17		347.88		21.22		
$\rightarrow {}^3\text{F}_4$	10722	2.09		0.10		1.63		0.10		
$\rightarrow {}^3\text{H}_6$	678	1741.92		80.80		1255.88		76.61		
${}^1\text{G}_4 \rightarrow {}^3\text{F}_2$	1632	20.61	5445.72	0.38	0.18	24.28	4493.39	0.54	0.22	
$\rightarrow {}^3\text{F}_3$	1511	118.63		2.18		97.46		2.17		
$\rightarrow {}^3\text{H}_4$	1171	714.61		13.12		533.45		11.87		
$\rightarrow {}^3\text{H}_5$	790	1946.18		35.74		1434.64		31.93		
$\rightarrow {}^3\text{F}_4$	647	383.41		7.04		318.74		7.09		
$\rightarrow {}^3\text{H}_6$	479	2262.29		41.54		2084.82		46.40		
${}^1\text{D}_2 \rightarrow {}^1\text{G}_4$	1538	432.58	71946.23	0.60	0.01	374.52	62466.60	0.60	0.02	
$\rightarrow {}^3\text{F}_2$	792	1258.84		1.75		1569.68		2.51		
$\rightarrow {}^3\text{F}_3$	762	3113.90		4.33		2523.72		4.04		
$\rightarrow {}^3\text{H}_4$	665	5208.87		7.24		3930.55		6.29		
$\rightarrow {}^3\text{H}_5$	522	244.90		0.34		188.45		0.30		
$\rightarrow {}^3\text{F}_4$	455	55623.17		77.31		43031.91		68.89		
$\rightarrow {}^3\text{H}_6$	365	6063.96		8.43		10847.76		17.37		
${}^1\text{I}_6 \rightarrow {}^1\text{D}_2$	1424	0.00	25009.80	0.00	0.04	0.00	26885.62	0.00	0.04	
$\rightarrow {}^1\text{G}_4$	739	3182.74		12.73		3497.78		13.01		
$\rightarrow {}^3\text{F}_2$	509	2202.92		8.81		1707.47		6.35		
$\rightarrow {}^3\text{F}_3$	497	55.70		0.22		49.53		0.18		
$\rightarrow {}^3\text{H}_4$	453	3851.15		15.40		4264.61		15.86		
$\rightarrow {}^3\text{H}_5$	382	150.15		0.60		125.55		0.47		
$\rightarrow {}^3\text{F}_4$	345	14686.53		58.72		15939.71		59.29		
$\rightarrow {}^3\text{H}_6$	291	880.60		3.52		1300.96		4.84		

Table 2. Calculated radiative properties in BGN and BGF samples. $\sum A$ is the total spontaneous emission probability of each level, A_{rad} is the spontaneous emission probability of each transition, τ is the calculated radiative lifetime.

As shown in Table 2, spontaneous emission probability (A) for Tm^{3+} can also be calculated by using J-O theory, which is related with the J-O parameters and the refractive-index of host glass. Total spontaneous emission probability ($\sum A$) of Tm^{3+} : ${}^3\text{F}_4$ level in BGN glass (454.8 s^{-1}) is higher than that in BGF glass (406.38 s^{-1}), so is the A_{rad} of transition Tm^{3+} : ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$. High A value in BGN suggests strong emission, especially the $\sim 1.8 \mu\text{m}$ emission. Lower A and Higher τ in BGF are owing to the addition of fluoride could reduce the refractive-index and

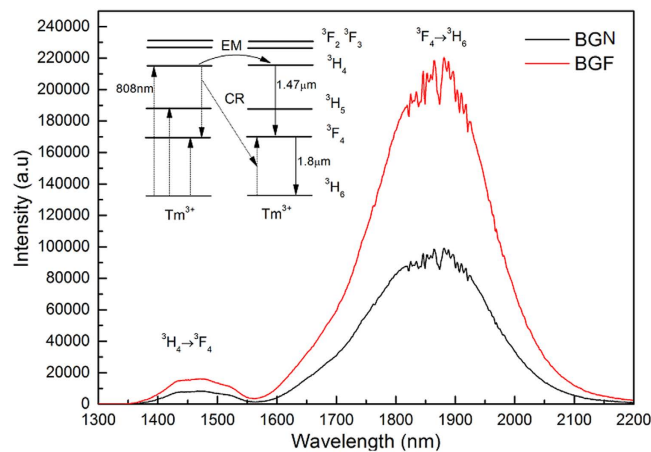


Figure 4. Room temperature $\sim 1.8 \mu\text{m}$ emission spectra obtained by exciting with a cw laser diode at 808 nm for the BGN and BGF glasses doped with 1 mol% of Tm_2O_3 . The inset is the energy level diagram and energy transfer sketch map of Tm^{3+} when pumped at 808 nm.

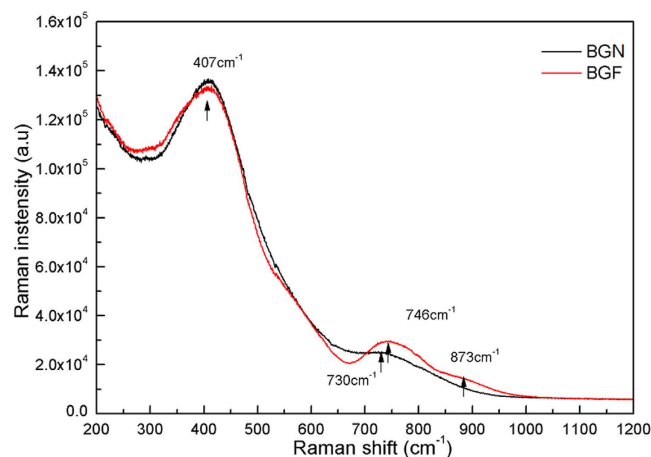


Figure 5. Raman spectra of BGN and BGF host glass samples in the range from 200 to 1200 cm^{-1} .

J-O parameters in bismuthate glass system. Compared with calculated radiative properties in germanate glasses³⁵, BGN and BGF samples have higher A_{rad} value for each transition.

Emission properties. Figure 4 shows the $\sim 1.47 \mu\text{m}$ and $\sim 1.8 \mu\text{m}$ emission spectra in BGN and BGF samples under 808 LD pumped. After the BaF_2 introduced, peak intensity of the $\sim 1.8 \mu\text{m}$ emission in BGF is 2 times higher than that in BGN, while the intensity of $\sim 1.47 \mu\text{m}$ emission is only a little change between two samples. As shown in the insert Fig. 4, the large intensity ratio of $\sim 1800 \text{ nm}$ to $\sim 1470 \text{ nm}$ (I_{1800}/I_{1470}) is related to the cross-relaxation (CR, ${}^3\text{H}_6 + {}^3\text{H}_4 \rightarrow {}^3\text{F}_4 + {}^3\text{F}_4$)³⁶.

With the introduction of BaF_2 , the maximum phonon energy of glass hosts lower accordingly, which can be seen from the measured Raman spectra shown in Fig. 5, the maximum phonon energy of BGN and BGF samples can be presumed about 746 cm^{-1} and 730 cm^{-1} , respectively. The Raman scattering band higher than 700 cm^{-1} is mainly caused by the vibration of the tetrahedron group, the peak bond located in 756 cm^{-1} and 846 cm^{-1} , correspond to the structure unit vibration of Ge-O and Ga-O, respectively³⁴. For BGF sample, lower phonon energy is also a key factor for stronger $\sim 1.8 \mu\text{m}$ emissions.

According to the Fuchtbauer-Ladenburg theory, $\sim 1.8 \mu\text{m}$ emission cross section (σ_{em}) is calculated⁵.

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

where λ is the wavelength, A_{rad} is the spontaneous emission probability calculated by J-O theory, $I(\lambda)$ is the fluorescence intensity, n is the refractive index of the glass, and c is the light speed. It is noted that σ_{em} mainly related to $\sim 1.8 \mu\text{m}$ emission spectrum and radiative transition probability of Tm^{3+} : ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$, which is a normalized line-shape function, respectively. According to Eq. (3), the stimulated emission cross-sections (σ_{em}) of $\sim 1800 \text{ nm}$ calculated are shown in Fig. 6. It can be determined that σ_{em} of BGF sample performs a maximum $7.56 \times 10^{-21} \text{ cm}^2$ at 1865 nm , which is higher than that of BGN sample ($7.01 \times 10^{-21} \text{ cm}^2$, centered at 1865 nm).

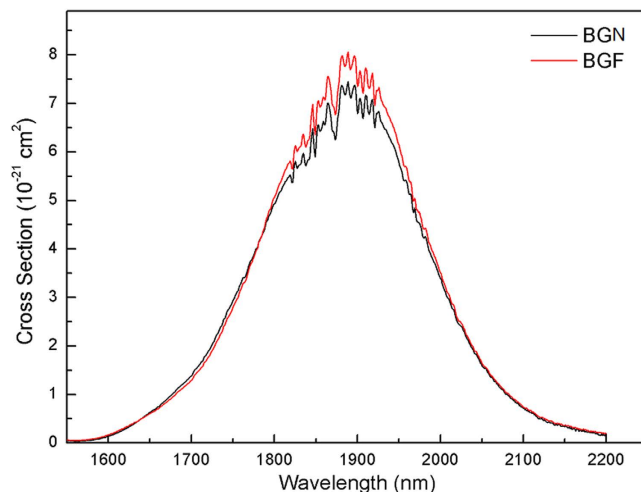


Figure 6. Stimulated emission cross-section of $\text{Tm}^{3+}:\text{}^3\text{F}_4 \rightarrow \text{}^3\text{H}_6$ transition in BGN and BGF glasses doped with 1 mol% Tm_2O_3 .

Glass	$\sigma_{em} (\times 10^{-21} \text{ cm}^2)$	$\tau_{rad} (\text{ms})$	$\sigma_{em} \times \tau_{rad} (\times 10^{-21} \text{ cm}^2 \text{ ms})$	Reference
BGN	7.01	2.25	15.42	This work
BGF	7.56	2.46	18.59	
silicate	3.6	7.91	28.48	28
Tellurite	8.1	1.73	14.00	24
Germanate	7.7	1.77	13.60	37

Table 3. Calculated emission cross-sections σ_{em} , radiative lifetime τ_{rad} , and $\sigma_{em} \times \tau_{rad}$ of $\text{Tm}^{3+}:\text{}^3\text{F}_4 \rightarrow \text{}^3\text{H}_6$ in BGN and BGF samples.

For BGN and BGF samples, the values of the maximum stimulated emission cross-section at the wavelength of 1865 nm, which are larger than that of the fluorophosphate glasses³⁷, silicate glasses^{2,16,31} and germanate glasses³⁸, due to high refractive index, high J-O parameters and good emission, and are beneficial to $\sim 1.8 \mu\text{m}$ laser action of Tm^{3+} ions.

The product of emission cross-section and radiative lifetime $\sigma_{em} \times \tau_{rad}$ is an important parameter for laser materials to obtain high gain. As shown in Table 3, the calculated values $\sigma_{em} \times \tau_{rad}$ of BGN and BGF samples are $15.42 \times 10^{-21} \text{ cm}^2 \text{ ms}$ and $18.59 \times 10^{-21} \text{ cm}^2 \text{ ms}$, respectively, which are lower than silicate glass³¹ $\sigma_{em} \times \tau_{rad} = 28.48 \times 10^{-21} \text{ cm}^2 \text{ ms}$. However, There are still larger than tellurite glass²⁴ $\sigma_{em} \times \tau_{rad} = 14.00 \times 10^{-21} \text{ cm}^2 \text{ ms}$ and germanate glasses³⁸ $\sigma_{em} \times \tau_{rad} = 13.6 \times 10^{-21} \text{ cm}^2 \text{ ms}$.

Cross-relaxation process. Because of the cross-relaxation transfer process ($\text{}^3\text{H}_6 + \text{}^3\text{H}_4 \rightarrow \text{}^3\text{F}_4 + \text{}^3\text{F}_4$) is beneficial for the $\sim 1800 \text{ nm}$ emission⁵. It is necessary to study the cross-relaxation process between Tm^{3+} ions. According to the theory of Dexter and Forster, the cross-relaxation rate can be calculated by the integral overlap of absorption cross-sections and emission cross-sections³³, which belongs to a dipole-dipole interaction. The microscopic transfer probability can be expressed by³⁴

$$W_{D-A} = \frac{C_{D-A}}{R^6} \quad (3)$$

where R is the distance between donor and acceptor, C_{D-A} is the transfer constant defined as follows¹⁵ $C_{D-A} = R_c^6 / \tau_D$, where R_c is the critical radius of the interaction and τ_D is the intrinsic lifetime of the donor-excited level. The transfer constant can be obtained according to Eq. (4) when phonons participate in the process to balance the energy gap⁵.

$$C_{D-A} = \frac{6cg_{low}^D}{(2\pi)^4 n^2 g_{low}^D} \sum_0^\infty e^{-(2\bar{n}+1)S_0} \frac{S_0^m}{m!} (\bar{n}+1)^m \int \sigma_{emis}^D(\lambda_m^+) \sigma_{abs}^A(\lambda) d\lambda \quad (4)$$

where c is the light speed, n is the refractive index, g_{low}^D/g_{up}^D is the degeneracy of the lower and upper levels of the donor, respectively, $\bar{n} = (1/e^{\hbar\omega_0/KT} - 1)$ is the average occupancy of the phonon mode at temperature T , $\hbar\omega_0$ is the maximum phonon energy, m is the number of phonons that participate in the energy transfer, S_0 is Huang-Rhys factor (0.31 for Tm^{3+})⁵, and $\lambda_m^+ = (1/\lambda - m\hbar\omega_0)$ is the wavelength with m phonon creation. The calculated energy migration (EM, $\text{}^3\text{H}_4 + \text{}^3\text{H}_6 \rightarrow \text{}^3\text{H}_6 + \text{}^3\text{H}_4$) and cross relaxation (CR, $\text{}^3\text{H}_6 + \text{}^3\text{H}_4 \rightarrow \text{}^3\text{F}_4 + \text{}^3\text{F}_4$) processes in BG

Glass	EM		CR		W_{ET} (10^{-20} cm ³ /s)
	M% phonons	C_{D-D} (10^{-40} cm ⁶ /s)	M% phonons	C_{D-A} (10^{-40} cm ⁶ /s)	
BGN	0, 1	35.4	0, 1, 2	16.0	938
	99.99, 0.01		12.78, 83.99, 3.23		
BGF	0, 1	37.8	0, 1, 2	18.6	1020
	99.99, 0.01		16.07, 79.37, 4.56		

Table 4. Energy transfer parameters of the energy migration and cross-relaxation processes in BGN and BGF samples.

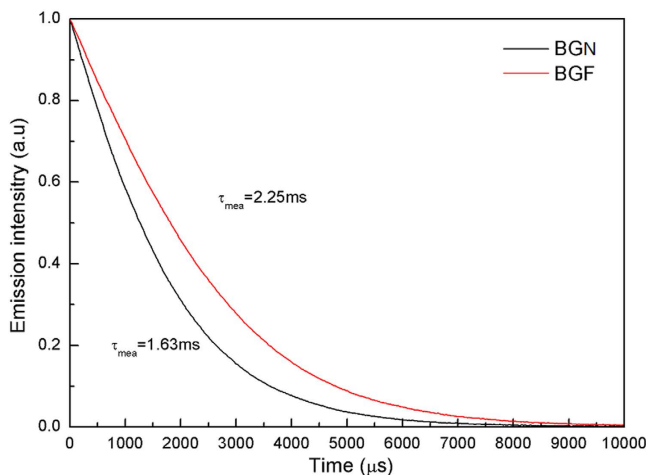


Figure 7. Luminescence decay curves of the 3F_4 level of the Tm^{3+} ions obtained exciting resonantly the ${}^3H_6 \rightarrow {}^3H_4$ absorption transition at 808 nm and monitoring the $Tm^{3+} {}^3F_4 \rightarrow {}^3H_6$ emission at 1865 nm in BGN and BGF glasses doped with 1 mol% Tm_2O_3 .

and BGF are listed in Table 4. Because of the transfer condition of C_{D-D} is much larger than C_{D-A} , the hopping model is fulfilled in both BGN and BGF. to evaluate the energy transfer rate W_{ET} ³⁹,

$$W_{ET} = 13(C_{D-D})^{1/2}/(C_{D-A})^{1/2}n_D \quad (5)$$

where n_D is the concentration of donor. According to Eq. (5), W_{ET} is calculated to be 938 cm³/s and 1020 cm³/s in BGN and BGF, respectively.

Fluorescence lifetime. The fluorescence decays of the $Tm^{3+} {}^3F_4$ level at room temperature is shown in Fig. 7. It can be seen that the measured lifetime τ_{mea} in BGN and BGF are 1.63 ms and 2.25 ms, respectively. The quantum efficiency (η) of the ${}^3F_4 \rightarrow {}^3H_6$ emission can be calculated by

$$\eta = \frac{\tau_{mea}}{\tau_{rad}} \quad (6)$$

where τ_{mea} is the measured fluorescence lifetime and τ_{rad} is calculated with the Judd–Ofelt formalism. According to Eq. (6), the values of quantum efficiency for BGN and BGF are 74.09% and 91.46%, respectively, which are higher than silicate glass (13%)³¹, germanate glass (55.52%)⁵, and lower than 70TeO₂-20ZnO-10ZnF₂ glass (164%)⁴⁰. The larger radiative lifetime (τ_{mea}) of $Tm^{3+} {}^3F_4$ state is benefit for $\sim 1.8 \mu m$ laser action. It can be seen that the measured lifetime is shorter than the calculated lifetime, due to nonradiative quenching³¹. The nonradiative decay caused from several mechanisms, such as energy transfer between the Tm^{3+} ions, multiphonon decay²⁹, quenching by impurities (OH^-), etc. The total rate of the ${}^3F_4 \rightarrow {}^3H_6$ transition can be evaluated by^{41,42}:

$$\frac{1}{\tau_{mea}} = \frac{1}{\tau_{cal}} + W_{NR} = \frac{1}{\tau_{cal}} + W_{MPR} + W_{OH^{-1}} + W_{ET} \quad (7)$$

where $1/\tau_{cal}$ is the spontaneous radiative probability A_{rad} , W_{MPR} is the nonradiative multiphonon relaxation rate, $W_{OH^{-1}}$ is the nonradiative transition probability due to the energy transfer to OH^- impurities and W_{ET} represents an additional nonradiative loss mechanism due to the energy transfer between the RE ions. In this study, the concentrations of Tm^{3+} ions for BGN and BGF are the same, this third process can be neglected.

The multiphonon relaxation W_{MPR} can be expressed⁴³:

$$W_{MPR} = W_0 \exp \left(-\frac{1}{\hbar\omega_{max}} \left(\ln \frac{p}{g-1} \right) \Delta E \right) \quad (8)$$

where W_0 is an experimentally determined parameter which is independent of the particular RE ion. ΔE is the energy gap between the 3F_4 and 3H_6 levels. g is the electron-phonon coupling strength parameter, and $\hbar\omega_{max}$ is the highest phonon energy obtained from Raman spectra and $p = \Delta E/\hbar\omega_{max}$. Multiphonon decay depends on the number of phonons required to bridge the energy gap to the next lower lying manifold. The higher the $\hbar\omega_{max}$ is, the larger the multiphonon relaxation is.

W_{OH^-} is proportional to the concentration of Tm^{3+} ions and the measured absorption coefficient of OH^- groups^{42,44}. For BGF sample, after BaF_2 introduced, the α_{OH^-} shows a significantly decrease, W_{OH^-} is expected to decrease which results in a reduced nonradiative transition rate. Thus the lifetime is much longer while the quantum efficiency is higher in BGF. Generally, the relatively longer radiation lifetime is beneficial to reduce the laser oscillation threshold⁴⁵.

Conclusion

In conclusion, we reported on $\sim 1.8\mu m$ emission in Tm^{3+} -doped Bi_2O_3 - GeO_2 - Ga_2O_3 glasses in absence and presence of BaF_2 . The addition of BaF_2 not only influences the network of glass, but also effectively reduces the content of hydroxyls and maximum phonon energy. For BGF sample, it shows a better thermal stability, and a stronger $\sim 1.8\mu m$ emission than that in BGN sample. It is also found that BGF glass possesses relatively large $\sim 1.8\mu m$ emission cross-section σ_{em} ($7.56 \times 10^{-21} cm^2$), measured fluorescence lifetime τ_{mea} (2.25 ms) and figure of merit gain $\sigma_{em} \times \tau_{rad}$ ($14.69 \times 10^{-21} cm^2 ms$) corresponding to the $Tm^{3+}: {}^3F_4 \rightarrow {}^3H_6$ transition. Our results suggest that introduced the BaF_2 into the glass network structure, which paves a way to enhance the $\sim 1.8\mu m$ emission properties and improve the fluorescence lifetime of $Tm^{3+}: {}^3F_4$ in Tm^{3+} doped bismuthate glass.

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Acknowledgements

This work is financially supported by National Natural Science Foundation of China (No. 51502022).

Author Contributions

K.H., P.Z. and Y.G. and designed the experiments wrote the main manuscript text, F.Y. and D.Z. checked up. S.W. performed the experimental measurement. All authors reviewed the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Han, K. *et al.* Optical characterization of Tm³⁺ doped Bi₂O₃-GeO₂-Ga₂O₃ glasses in absence and presence of BaF₂. *Sci. Rep.* **6**, 31207; doi: 10.1038/srep31207 (2016).



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