# $Tm^{3+}$-doped $Ga_2O_3$-$GeO_2$-$Bi_2O_3$-$PbO(PbF_2)$ Glasses for 1.47-$\mu$m Optical Amplifications *

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*We report the spectroscopic properties and thermal stability of $Tm^{3+}$-doped $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–$PbO(PbF_2)$ glasses for 1.47-$\mu$m optical amplifications. Effects of $PbF_2$ doping on the optical properties and thermal stability of $Tm^{3+}$-doped gallate–germanium–bismuth–lead glass are investigated. The measured peak wavelength and full width at half-maximum of the fluorescence are 1465 nm and $\sim$ 120 nm, respectively. Significant enhancement of the 1.47-$\mu$m emission and the lifetime of a $^3H_4$ level with increasing $PbF_2$ doping have been observed. The presence of $GeO_2$ provides two potentials of increasing the thermal stability and shortening the ultraviolet cutoff band of host glasses.*

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With the rapid increase in information traffic, there is an urgent demand for broadband optical amplification beyond the conventional band of 1530–1565 nm developed by erbium-doped fibre amplifiers (EDFA).[1] One of the most promising methods is to expand the window to the S band (1460–1530 nm) by using $Tm^{3+}$-doped fibre amplifiers in order to fully utilize the entire 1.3–1.65 $\mu$m low-loss window of silica-based optical fibre.[1,2] Great effort has been directed to the research of $Tm^{3+}$-doped fluorides due to their low phonon energies.[3−5] However, by considering the rather poor chemical durability of most halide glasses,[1,6,7] the development of more robust oxide glasses with sufficiently low maximum phonon energy is necessary. Heavy metal oxide glasses have attracted a considerable interest in recent years because of their special properties such as low phonon energies and high refractive index.[8,9] The low phonon energy and high refractive index could yield low nonradiative decay rates and high radiative emission rates of rare-earth (RE) energy levels, so that an efficient fibre optics amplifier with a wider gain bandwidth becomes possible.[10] Interest in the $Ga_2O_3$–$Bi_2O_3$–PbO system has been recently renewed as a potential host for S-band fibre-optic amplifiers due to its advantages, such as the good transparency in the mid-infrared (up to $\sim 8\,\mu$m), the lowest phonon energy ($\sim 550\,cm^{-1}$) among oxide glasses, which is comparable to that of fluoride glasses, the high refractive index ($\sim 2.3$), the possibility to incorporate a large amount of RE ions, and the good glass stability and chemical durability.[11−16] However, its low glass transition temperature of 334°C and low thermal stability will lead to crystallization during the fibre drawing process.

In this Letter, we present the development and an experimental investigation on the optical spectroscopic properties and thermal stability of $Tm^{3+}$-doped $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–$PbO(PbF_2)$ glasses for a broad S-band fibre amplifier. In order to improve the optical properties, we partly replace the oxygen with fluorine, specifically replacing PbO with $PbF_2$. The effects of $PbF_2$ doping on the optical spectroscopic properties and thermal stability of $Tm^{3+}$-doped $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–$PbO(PbF_2)$ glass have been investigated.

Gallate–germanium–bismuth–lead glasses with the molar composition of (100-$x$) [$15Ga_2O_3$–$20GeO_2$–$20Bi_2O_3$–(45-$y$)PbO–$y$$PbF_2$]–$x$$Tm_2O_3$ ($x$ = 0.1, 0.2, 0.5 and 0.8, $y$ = 0, 3, 6 and 12) were prepared by using a conventional melt method from powders with reagent-grade chemicals of $Ga_2O_3$, $GeO_2$, $Bi_2O_3$, PbO, $PbF_2$ and $Tm_2O_3$ in a crucible for 15 min at around 950°C, followed by a quenching in air on a stainless-steel plate. To eliminate impurities from the crucible in the melt, a platinum crucible was used. However, glass melted in a platinum crucible can have a more intense colour.[12] Study of the influence of the crucible on the optical properties of glass is in progress. After being annealed, all the samples were polished and cut into the size of $20 \times 10 \times 1\,mm^3$. Glasses with the molar composition of (100-$z$) ($18Ga_2O_3$–$25Bi_2O_3$–$57PbO$)–$z$$GeO_2$ ($z$ = 0, 5, 10 and 20) were also prepared in similar manner for a comparison.

Glass transition and crystallization temperatures were measured on the powders samples using a dif-

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ferential scanning calorimetry (DSC) method on STA 449/C at a heating rate of 10 K/min. The absorption spectra were measured with a PERKIN-ELMER Lambda 900 UV–Visible–NIR spectrophotometer in the range of 450–2000 nm with the resolution of 1 nm. The fluorescence spectra in the range of 1320–1580 nm were obtained with a computer-controlled Triax 320 spectrofluorimeter upon excitation of an 808-nm laser diode (LD). Fluorescence lifetimes were obtained from the first e-folding time of decay curves by using a computer-controlled digitizing oscilloscope.

Figure 1 illustrates the DSC curves of $Ga_2O_3$–$Bi_2O_3$–PbO (GBP), $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–PbO (GGBP), and $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–PbO-$PbF_2$ (GGBPF) glasses. 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 quoted as a rough indicator of glass stability against devitrification. It is noted that adding $GeO_2$ increases the thermal stability of gallate–bismuth–lead glasses quite significantly. The value of $\Delta T$ increases from 61 to 129°C, indicating that the sample is more stable against devitrification. The values of $T_g$ and $T_x$ decrease as the $PbF_2$ concentration increases, as shown in Fig. 1. However, no significant change of $\Delta T$ is confirmed. Therefore, the thermal stability in this GGBPF glass system remains almost unaffected by the $PbF_2$ substitution at least below $y = 12$ from the aspect of the difference $\Delta T$.

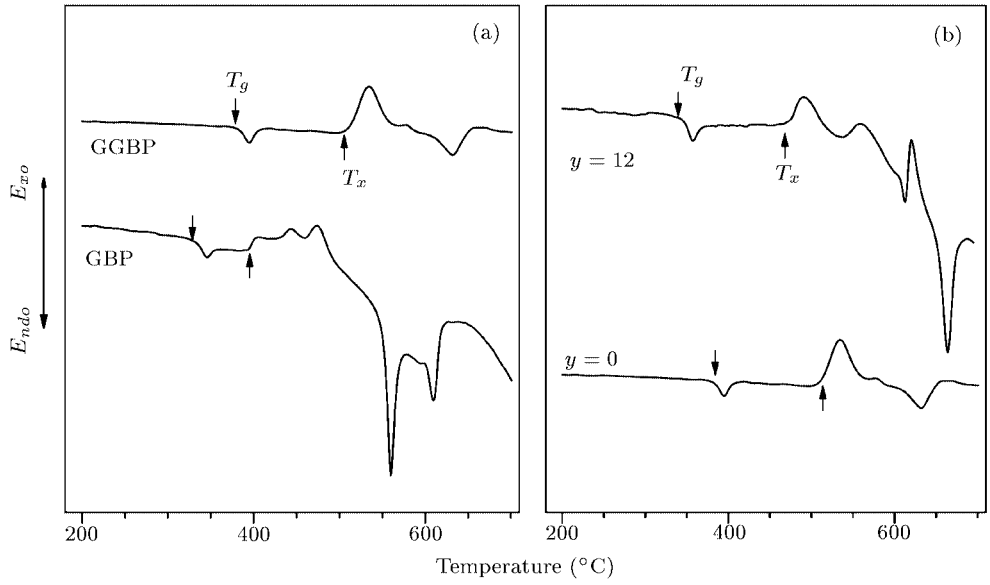



**Fig. 1.** DSC traces of gallate–bismuth–lead glasses (a), and $PbF_2$ modified gallate–germanium–bismuth–lead glasses ($y = 0$ and 12) (b).

Figure 2 shows absorption spectrum of $Tm^{3+}$-doped GGBP glass ($x = 0.2$). The assignments of absorption band indicate the excited level. From the absorption spectral measurements, the Judd–Ofelt[17] intensity parameters, $\Omega_\lambda$, have been computed and the values are $3.08 \times 10^{-20}$, $0.81 \times 10^{-20}$, and $1.24 \times 10^{-20}\,cm^2$ for $\Omega_2$, $\Omega_4$, and $\Omega_6$, respectively. Jorgensen and Reisfeld noted that the $\Omega_2$ parameter of the analysis is indicative of the amount of covalent bonding, where the $\Omega_6$ parameter is related to the rigidity of the host.[18] Generally, the oxide glasses have large $\Omega_2$ and small $\Omega_6$ values, whereas the fluoride glasses have comparable values for all $\Omega_\lambda$. The typical $\Omega_2$ for $Tm^{3+}$ in oxides glasses vary between $4.0 \times 10^{-20}$ and $6.0 \times 10^{-20}\,cm^2$, whereas for fluoride glasses it presents a lower value at around $2.0 \times 10^{-20}\,cm^2$.[5,18,19] It is found that the gallate–germanium–bismuth–lead studied exhibits a low $\Omega_2$ value of about $3.08 \times 10^{-20}\,cm^2$, indicating a more ionic bonding of the $Tm^{3+}$ ions. The inset in Fig. 2(a) illustrates the $GeO_2$ content-dependent transmittances of GBP glasses. It is noted that the UV cutoff of GGBP glasses blue-shifted quite significantly with the adding of $GeO_2$. A similar trend has been observed in $PbF_2$ modified GGBP glasses, as illustrated in the inset of Fig. 2(b). The wavelengths of the UV cutoff are shortened as the $PbF_2$ concentration increases. With extrapolation to zero transmittance at the steepest slope, the cutoff wavelengths for $y = 0$, 3, 6 and 12 are estimated to be 439, 430, 424, and 413 nm, respectively.

The fluorescence spectra relative to the $Tm^{3+}$:$^3H_4 \rightarrow {}^3F_4$ transition in the wavelength ranging 1320–1580 nm under 808 nm excitation at room temperature are shown in Fig. 3. The measured peak wavelength and full width at half maximum (FWHM) of the fluorescence, which is defined as the wavelength difference between the two $x$ values at the

half-maximum of the peak of the measured fluorescence, are 1465 nm and $\sim$ 120 nm, respectively. The shape and the width of the band are similar to those observed in fluoride glasses, which was successful used for preparing a $Tm^{3+}$-doped fluoride fibre amplifier operating at 1.47 $\mu$m.[1] The energy gap between the emission level $^3H_4$ and next lower-lying level $^3H_5$ is around 4300 $cm^{-1}$, therefore the multiphonon relaxation becomes the dominant relaxation process if $Tm^{3+}$ ions are doped in a high phonon energy host such as silicate and phosphate glasses. These phenomena make it difficult to form the population inversion between the $^3H_4$ and $^3F_4$ levels. Thus, the $Tm^{3+}$: $^3H_4 \rightarrow {}^3F_4$ transition could not be observed in both silicate and phosphate glasses due to their high phonon energies generally. The dependence of the 1.47-$\mu$m luminescence intensity upon the $PbF_2$ content has also been investigated and the results are also presented in Fig. 3. It is noted that the 1.47-$\mu$m emission intensity of GGBPF ($y = 12$) is over two times higher than that of GGBPF ($y = 0$). Clearly, an enhanced 1.47-$\mu$m emission with increasing $PbF_2$ doping has been obtained, which might be due to the increase of the $4f - 4f$ probability transition caused by the modification of the refractive index of the glass with $PbF_2$ introduction.

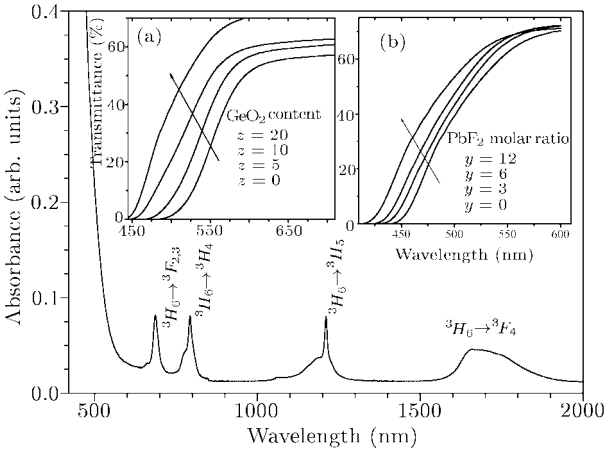



**Fig. 2.** Absorption spectrum of $Tm^{3+}$-codoped GGBP glasses ($x = 0.2$). The assignments of absorption band indicate the excited level. Inset shows the $GeO_2$ content-dependent transmittance of GBP (a) and the $PbF_2$ concentration-dependent transmittance of GGBPF (b).

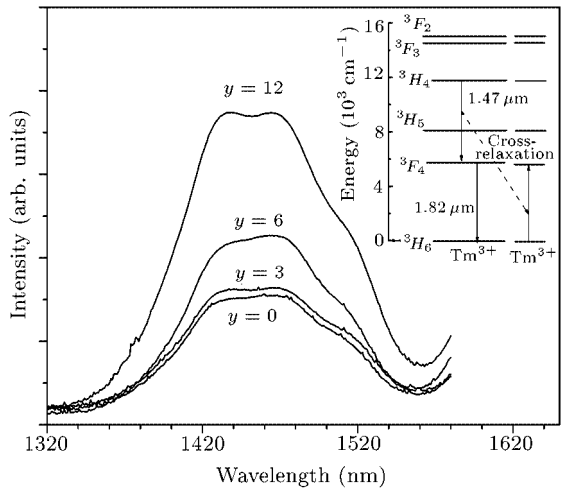



**Fig. 3.** Fluorescence spectra of $Tm^{3+}$-codoped GGBPF glasses ($x = 0.2$) in the wavelength ranging 1320–1580 nm under 808 nm excitation. Inset shows partial schematic energy level diagram of $Tm^{3+}$ ions. One of the cross relaxation process among $Tm^{3+}$ ions is also shown: $^3H_4$, $^3H_6 \rightarrow {}^3F_4$, $^3F_4$.

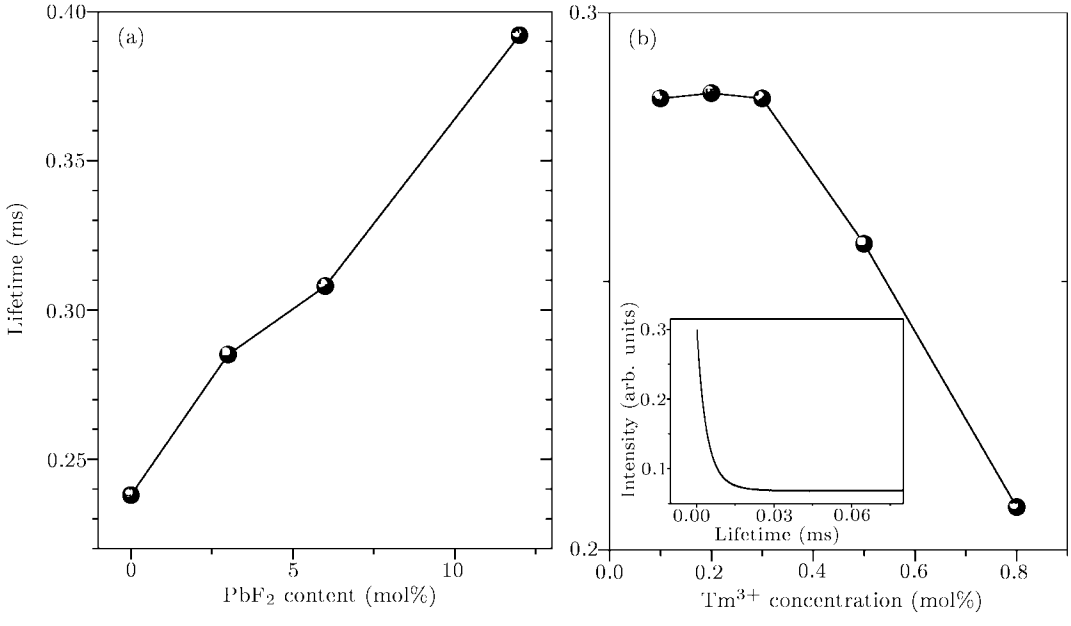



**Fig. 4.** The dependence of the measured lifetime of $Tm^{3+}$-doped GGBPF ($x = 0.2$) upon the $PbF_2$ concentration (a), and $Tm^{3+}$ content ($y = 3$) (b). Inset in (b) shows the decay trace of the $Tm^{3+}$: $^3H_4$ level.

The dependence of the measured lifetimes upon the $PbF_2$ content and $Tm^{3+}$ concentration has been shown in Fig. 4. It has clearly been seen that the lifetimes have increased almost linearly from 0.238 to 0.392 ms with an increase of $PbF_2$ concentration up to 12 mol%, as shown in Fig. 4(a). Figure 4(b) shows lifetimes of the $Tm^{3+}$: $^3H_4$ level varying with the $Tm^{3+}$ concentration. It is noted that the measured lifetimes for $x = 0.1$ is 0.284 ms, and that for $x = 0.8$ is 0.208 ms. A decrease of the lifetimes has been observed when $Tm_2O_3$ content exceeded 0.3 mol%, due to cross relaxation via the $^3H_4$, $^3H_6 \rightarrow {}^3F_4$, $^3F_4$ route as shown in the inset of Fig. 3. It is suggested that the energy transfer rapidly depopulates the $^3H_4$ level especially when $Tm^{3+}$ ion concentration is above a certain limit. To overcome this difficulty, concentration of $Tm^{3+}$ should be kept below a certain limit.

Based on their 1.47-$\mu$m radiative emission performance as are discussed and explained in the respective figures of the present work, we conclude these $Tm^{3+}$-doped $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–$PbO(PbF_2)$ glasses could be suggested as promising and quite useful optical systems towards the development of 1.47-$\mu$m laser and optical amplifier glass materials.

In summary, the spectroscopic properties and the thermal stability of $Tm^{3+}$-doped $Ga_2O_3$–$GeO_2$–$Bi_2O_3$–$PbO(PbF_2)$ glasses have been investigated for S-band optical amplifications. The presence of $GeO_2$ provides two potentials: increasing the thermal stability and shortening the UV cutoff band of host glasses. The measured peak wavelength and FWHM of the fluorescent are 1465 nm and $\sim$ 120 nm, respectively, upon $Tm^{3+}$-doped GGBPF under the excitation of the 808-nm LD. Significant enhancement of the 1.47-$\mu$m emission and the lifetime of $^3H_4$ level with increasing $PbF_2$ doping have been observed.

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