Highly Tm$^{3+}$ doped germanate glass and its single mode fiber for 2.0 μm laser

Xin Wen$^{1,2,3}$, Guowu Tang$^{1,2,3}$, Qi Yang$^{1,2,3}$, Xiaodong Chen$^{1,2,3}$, Qi Qian$^{1,2,3}$, Qinyuan Zhang$^{1,2,3}$ & Zhongmin Yang$^{1,2,3}$

Highly Tm$^{3+}$ doped optical fibers are urgently desirable for 2.0 μm compact single-frequency fiber laser and high-repetition-rate mode-locked fiber laser. Here, we systematically investigated the optical parameters, energy transfer processes and thermal properties of Tm$^{3+}$ doped barium gallo-germanate (BGG) glasses. Highly Tm$^{3+}$ doped BGG glass single mode (SM) fibers were fabricated by the rod-in-tube technique. The Tm$^{3+}$ doping concentration reaches 7.6 × 10$^{20}$ ions/cm$^3$, being the reported highest level in Tm$^{3+}$ doped BGG SM fibers. Using ultra short (1.6 cm) as-drawn highly Tm$^{3+}$ doped BGG SM fiber, a single-frequency fiber laser at 1.95 μm has been demonstrated with a maximum output power of 35 mW when in-band pumped by a home-made 1568 nm fiber laser. Additionally, 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%. The results confirm that the as-drawn highly Tm$^{3+}$ doped BGG SM fibers are promising in applications that require high gain and high power from a short piece of active optical fiber.

Fiber lasers near 2.0 μm region have been a research topic with an increasing emphasis due to the important applications such as eye-safe light detection and ranging (LIDAR), remote sensing, laser surgery, spectroscopy and mid-infrared (mid-IR) frequency generation. Among the rare earth ions, Tm$^{3+}$ and Ho$^{3+}$ are commonly utilized to generate 2.0 μm lasers owing to Tm$^{3+}$: $^3F_4 → ^3H_4$ and Ho$^{3+}$: $^4I_9 → ^4I_8$ transition, respectively. However, due to the lack of an appropriate ground absorption band in commercial laser diode (LD), the development of Ho$^{3+}$ doped fiber lasers are still in initial stages. Tm$^{3+}$ has gained significant attention because of its inherent advantages. It can be directly pumped by commercial 808 nm LD through $^3H_4 → ^3H_4$ transition. Under such pump scheme, quantum efficiency of Tm$^{3+}$ is expected to reach 200% from the cross relaxation energy transfer ($^3H_4 + ^3H_4 → ^3F_4 + ^3F_4$). In addition, the broad emission about 300 nm of Tm$^{3+}$ allows a wide wavelength tuning range and makes it suitable for femtosecond pulse generation.

It is well-known that the Tm$^{3+}$ high doping concentration in fiber enables efficient one-for-two energy transfer by bringing the Tm$^{3+}$ ions closer, and remarkably enhances the slope efficiency and output power of fiber lasers. Moreover, the high Tm$^{3+}$ doping concentration leads to large pump absorption and high gain per unit length of the fiber, which can reduce the required fiber length in fiber lasers and contributes to background loss reduction, nonlinear effect mitigation and narrow emission linewidth. Hence, using heavily Tm$^{3+}$ doped fibers, small-sized short cavity single-frequency fiber lasers with narrow laser linewidth or high-repetition-rate mode-locked fiber lasers with high stability can be built. Additionally, it is possible to scale the output power of 2.0 μm fiber lasers with maintained good spatial mode qualities. Fabricating highly Tm$^{3+}$ doped single-mode (SM) fibers has now been a hot subject in the field of 2.0 μm fiber lasers.

To obtain heavily Tm$^{3+}$ doped fibers, the choice of the host glass is important. A high doping concentration is not achievable in commercially utilized silica glass due to its defined glass structure. The multi-component oxide glasses (e.g., silicate glass, tellurite glass, germanate glass) which allow higher Tm$^{3+}$ solubility triggered great interest. Recently, a silicate glass fiber with high Tm$^{2+}$ doping concentration of 7 wt% (8.35 × 10$^{20}$ ions/cm$^3$) was

1State Key Laboratory of Luminescent Materials and Devices and Institute of Optical Communication Materials, South China University of Technology, Guangzhou 510640, P. R. China. 2Guangdong Engineering Technology Research and Development Center of Special Optical Fiber Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China. 3Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, South China University of Technology, Guangzhou 510640, P. R. China. Correspondence and requests for materials should be addressed to Q.Q. (email: qianqi@scut.edu.cn)
reported\(^9\). However, silicate glasses are not the ideal host glasses for mid-IR lasers since the high phonon energy could lead to fast multiphoton relaxation which decreases the quantum efficiency and also causes thermal damage of the fiber laser. 2.0 μm fiber lasers have also been realized in tellurite glass fibers, but the reported Tm\(_2\)O\(_3\) doping concentration is relatively low, moreover, the low laser damage threshold and brittleness of tellurite glass fibers are still bottlenecks\(^{10}\). Germanate glasses, especially barium gallo-germanate (BGG), offers an ideal alternative, as it combines the attributes of high rare-earth solubility, comparatively low phonon energy, superior IR transparency, high damage threshold and strong mechanical strength\(^{11-13}\). According to the previous researches, the highest Tm\(_2\)O\(_3\) doping concentration in BGG SM glass fibers is only 1 mol%\(^{14}\), thereafter; further effort is greatly needed to put into the fabrication of BGG glass SM fibers with higher Tm\(_2\)O\(_3\) doping concentration.

In this work, the optical parameters, energy transfer processes and thermal properties of Tm\(^{3+}\) doped BGG glasses were systematically studied. BGG SM fibers with high Tm\(_2\)O\(_3\) doping concentration of 1.8 mol% (7.6 × 10\(^{20}\) ions/cm\(^3\)) were fabricated. An in-band pumped single-frequency fiber laser operating at 1.95 μm has been realized using ultra short (1.6 cm) highly Tm\(^{3+}\) doped BGG SM fiber. Additionally, a multilongitudinal-mode fiber laser with 165 mW laser output and 17% slope efficiency has been achieved in a 10 cm long as-drawn active fiber.

**Experiments and Measurements**

BGG glasses with molar composition of 20BaO-(16.8-\(x\))Ga$_2$O$_3$-60GeO$_2$-3.2(La$_2$O$_3$ + Y$_2$O$_3$)-xTm$_2$O$_3$ (\(x = 0.2, 0.6, 1.0, 1.4, 1.8, 2.2\)), denoted as BGG-\(x\), were prepared by the conventional melting-quenching technique using high purity reagents (99.99% minimum). For each glass, well-mixed raw materials (80 g) were melted at 1350 °C for 30 min in a covered crucible, and then dried O\(_2\) was bubbled into the melt for 30 min to remove the OH

- **Results and Discussions**

**Transmittance and Raman spectrum.** The OH

- **Figure 1.** (a) Transmittance spectrum and (b) Raman spectrum of the core glass.
seen, the absorption cut-off edge is up to 6.5 μm. The broad absorption near 3 μm is corresponding to the stretching vibration of free OH− groups, and the glass absorption coefficient, αOH (cm−1) can be calculated using the following equation (1)16:

$$\alpha_{OH} = \frac{1}{L} \ln \frac{T_0}{T}$$

where L is the thickness of the sample, T is the transmission at 3000 nm, T0 is the transmission at 2600 nm.

The OH− absorption coefficient of core glass is 0.39 cm−1, lower than that of Tm3+ doped lead silicate glass (1.7 cm−1)17, and Tm3+ doped tellurite glass (0.5 cm−1)18.

The Raman technique was utilized to analyze the structure of BGG glass, and the vibrational spectrum of core glass was shown in Fig. 1(b). Two broad bands centered at 519 cm−1 and 845 cm−1 are observed which are assigned to the symmetric bending and stretching mode contributions from Ge–O–Ge or Ga–O–Ga bridging oxygen's vibrations, as well as the asymmetric stretching vibrations of Ge–O or Ga–O structural units, respectively19,20. Meanwhile, it can be found that the largest phonon energy only extends to 845 cm−1, much lower than that of silicate glass (1100 cm−1)21, and lanthanum tungsten tellurite glass (920 cm−1)22. The lower phonon energy, as well as smaller OH− absorption coefficient, could reduce the probability of non-radiative relaxation and thus be very conducive to Tm3+ 1.8 μm luminescence.

Absorption and emission spectra. The BGG glasses with different Tm2O3 doping concentration were completely transparent and homogeneus in appearance. Figure 2 depicts the absorption spectra of these glass samples in the wavelength region of 300–2200 nm. Six characteristic absorption bands located at 1652 nm, 1210 nm, 790 nm, 660 nm and 468 nm, and 356 nm can be ascribed to the typical transitions from 3H6 ground state to excited state 3F4, 3H5, 3H4, 3F2 and 3F3, 1G4 and 1D2 of Tm3+, respectively. The obvious absorption bands around 790 nm and 1652 nm indicate that commercially available AlGaAs LD or a ~1.5 μm fiber laser can be utilized as the pump sources. As can be seen, there is no obvious change in the position of the Tm3+ absorption peaks, but the intensity enhances with the increment of Tm2O3 content. The solubility of rare earth ions can be estimated roughly by the variation of the integral absorption intensities with Tm2O3 content12,23. The inset of Fig. 2 shows variation of integral absorption intensities of 3H6 → 3H4 and 3H6 → 3F4 transitions as a function of Tm2O3 content. It is noted that the good linearity fittings reveal excellent solubility of Tm3+ in the current BGG glass system.

Figure 3 shows the emission spectra from 1300 to 2200 nm of BGG-x (x = 0.2, 0.6, 1.0, 1.4, 1.8, 2.2) samples upon excitation of an 808 nm LD. As can be seen, the 1470 nm emission from 3H4→3F4 transition is only observed in BGG-0.2 and BGG-0.6 samples. With increment of Tm2O3 content, the 1470 nm emission becomes negligible, and the 1.8 μm emission from 3F4→3H6 transition strengthens gradually. This phenomenon can be accounted for shorting the distance between Tm3+ ions which increases the cross-relaxation energy transfer (3H6 + 3H6→3F4 + 3F4) probability before it attains the maximum value at 1.8 mol% Tm2O3. The result that the 1.8 μm emission intensity decreases with further addition of Tm2O3 content may be explained by the enhanced energy transfer rate from 3F4 to OH− or impurities. The inset of Fig. 3 shows the lifetime of Tm3+:3F4 level in the core glass. It was measured to be 0.7 ms, which is larger than that in 1.44 wt% Tm2O3 silica fiber (420 μs)24 and 1.46 wt% Tm2O3 silicate fiber (460 μs)25. The higher lifetime is favorable for population accumulation so as to achieve lasers.
It should be noted that the optimal Tm$_2$O$_3$ doping concentration in the current BGG system reaches 1.8 mol \% (equal to 5.1 wt\% of Tm$_2$O$_3$ and Tm$^{3+}$: $7.6 \times 10^{20}$ ions/cm$^3$), which is remarkably higher than that of tellurite glass (Tm$^{3+}$: $3.76 \times 10^{20}$ ions/cm$^3$)\textsuperscript{25} and lead silicate glass (1 mol\%)\textsuperscript{17}, comparable to that of other germanate glass (5 wt\%)\textsuperscript{26}, just a little lower than the reported highest Tm$^{3+}$ doping concentration ($8.35 \times 10^{20}$ ions/cm$^3$) from silicate glass\textsuperscript{27}. This highly Tm$^{3+}$ doped BGG glass will be promising for some special applications such as 2.0 $\mu$m single-frequency fiber lasers and high-repetition-rate mode-locked fiber lasers.

Cross sections and gain properties. In order to further estimate the spectroscopic properties of 1.8 $\mu$m emission in highly Tm$^{3+}$ doped BGG glass, absorption and emission cross sections are calculated. According to the absorption spectrum, the absorption cross-section ($\sigma_a$) can be calculated by using the Beer-Lambert law\textsuperscript{28}:

$$\sigma_a(\lambda) = \frac{2.303 \log(I_0/I)}{Nl}$$

where $\log(I_0/I)$ is absorptivity from absorption spectrum, $N$ is the Tm$^{3+}$ doping concentration, and $l$ is the sample thickness.

Furthermore, the emission cross section ($\sigma_e$) can be obtained from the fluorescence spectrum by using Fuchtbauer–Ladenburg (FL) equation\textsuperscript{29}:

$$\sigma_e^{FL}(\lambda) = \frac{A_{ij} \lambda^4 I(\lambda)}{8\pi n^2 c \int \lambda^4 I(\lambda) \, d\lambda}$$

where $A_{ij}$ is the spontaneous emission probability of the transition, $I(\lambda)$ is the emission intensity, $c$ is the speed of light, $n$ is the refractive index, and $\lambda$ is the wavelength.

Figure 4(a) shows the calculated absorption and emission cross sections of the core glass. It is found that the maximum values of $\sigma_a$ and $\sigma_e^{FL}$ are $4.7 \times 10^{-21}$ cm$^2$ at 1650 nm and $5.95 \times 10^{-20}$ cm$^2$ at 1875 nm, respectively. The prepared core glass has higher emission cross section than that of Tm$^{3+}$ doped ZBLAN glass ($2.4 \times 10^{-21}$ cm$^2$)\textsuperscript{30} and silicate glass ($3.89 \times 10^{-21}$ cm$^2$)\textsuperscript{31}.

Based on the calculated $\sigma_a(\lambda)$ and $\sigma_e(\lambda)$, it is valuable to compute the wavelength dependence of net gain as a function of population inversion for the upper laser level so as to acquire the gain property quantitatively. Assuming that Tm$^{3+}$ ions are either in the ground state ($^3H_4$) or in the upper laser level ($^3F_4$), the net gain coefficient, $G(\lambda)$, can be expressed by the following equation\textsuperscript{32}:

$$G(\lambda) = N[p\sigma_e(\lambda) - (1 - p)\sigma_a(\lambda)]$$

where $p$ represents the population of the upper laser level, and $N$ stands for the total Tm$^{3+}$ concentration.

The calculated gain coefficient of core glass with $p$ ranging from 0 to 1 with the step of 0.1 is shown in Fig. 4(b). It is found that the gain becomes positive when $p$ is more than 0.1, indicating that a low pumping threshold will be required for 2.0 $\mu$m laser operation in the highly Tm$^{3+}$ doped BGG optical fibers. In addition, the maximum gain coefficient reaches 4.53 cm$^{-1}$ around 1875 nm due to the high Tm$^{3+}$ doping concentration. It is three times than that of Tm$^{3+}$ doped silicate glass ($1.5$ cm$^{-1}$)\textsuperscript{21}, showing promising applications of building compact and efficient 2.0 $\mu$m fiber lasers.

Energy transfer microparameters. To gain better understanding about the energy transfer processes, the energy-level diagram obtained from the absorption spectra of Tm$^{3+}$ doped BGG glass is demonstrated in

Figure 3. Emission spectra of BGG-x (x = 0.2, 0.6, 1.0, 1.4, 1.8, 2.2) samples upon excitation of 808 nm LD. The inset of Fig. 3 shows fluorescence decay curve of 1.8 $\mu$m emission in the core glass.
Fig. 5. The cross-relaxation transfer process (CR, $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{F}_4 + ^3\text{F}_4$), energy migration into $^3\text{H}_4$ level (EM1, $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{H}_6 + ^3\text{H}_4$), energy migration into $^3\text{F}_4$ level (EM2, $^3\text{F}_4 + ^3\text{H}_6 \rightarrow ^3\text{H}_6 + ^3\text{F}_4$), and energy transfer (ET) from $\text{Tm}^{3+}$ to $\text{OH}^-$ are indicated. The extended integral method is widely used to analyze energy transfer processes between the donor and acceptor. Concerning a dipole–dipole interaction, the microscopic energy transfer probability between donor (D) and acceptor (A) ions can be expressed as follows:

$$W_{D \rightarrow A} = \frac{C_{D \rightarrow A}}{R^6}$$

where $R$ is the distance between the donor and the acceptor, $C_{D \rightarrow A}$ is the transfer constant defined as:

$$C_{D \rightarrow A} = \frac{g \cdot \omega_0}{\pi \cdot \hbar}$$

where $g$ represents the critical radius of the interaction and $\tau_D$ stands for the intrinsic lifetime at the donor excited level. When phonons participate in the considered process, the transfer constant can be obtained by the following equation:

$$C_{D \rightarrow A} = \frac{g \cdot \omega_0}{\pi \cdot \hbar} \sum_{m=0}^{\infty} e^{-\frac{(2n+1)\hbar}{\omega_0}} \frac{S_0 S_m^{\text{em}}}{m!} \int \sigma_{\text{em}}^D (\lambda; m) \sigma_{\text{abs}}^A (\lambda) d\lambda$$

where $c$ is the light speed, $n$ is the refractive index of the glass, $\omega_0$ and $\omega_0'$ are the degeneracies of the lower and upper levels of the donor, respectively, $\hbar \omega_0$ is the maximum phonon energy, $\bar{n} = 1/(e^{\hbar \omega_0/\kappa T} - 1)$ is the average occupancy of the phonon mode at temperature $T$, $S_0$ is the Huang–Rhys factor (0.31 for Tm (ref. 35)), $m$ is the number of the phonons that participate in the energy transfer, and $\lambda_m^{\text{em}} = 1/(1/\lambda - m \hbar \omega_0)$ is the wavelength with $m$ phonon creation.

According to equation (6) and equation (7), the energy migration rate between $^3\text{H}_4$ energy levels (EM1: $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{H}_6 + ^3\text{H}_4$) and cross-relaxation (CR: $^3\text{H}_4 + ^3\text{H}_6 \rightarrow ^3\text{F}_4 + ^3\text{F}_4$) rate in BGG-0.6 sample are analyzed.
as listed in Table 1. It is found that the transfer constant for energy migration process (CD–D) is evidently larger than that for cross-relaxation process (CD–A). Hence, the condition for applying the hopping model to calculate the energy transfer rate \( W_{ET} \) is fulfilled. The macroscopic CR probability, \( W_{ET} \), can be expressed by the product of transfer constants:

\[
W_{ET} = \frac{C_{D,A} \cdot C_{D,D} \cdot N_{D}}{C_{C,A} - C_{C,D} \cdot N_{D}}
\]

where \( N_{D} \) is the concentration of donors, and in this case the donor is Tm\(^{3+}\). According to equation (8), the \( W_{ET} \) for BGG-0.6 is calculated to \( 1799 \times 10^{-20} \) cm\(^3\)/s, which is far larger than that of Tm\(^{3+}\) doped silicate glasses (\( 103.4 \times 10^{-20} \) cm\(^3\)/s). The results suggest that favorable cross-relaxation can be realized in the Tm\(^{3+}\) doped BGG glasses.

According to equation (8), the macroscopic CR probability \( W_{ET} \) is directly proportional to the Tm\(^{3+}\) doping concentration, which has also been proven in the previous experiment. Accordingly, the emission intensity at 1.8 \( \mu \)m should increase with Tm\(_2\)O\(_3\) doping content. However, the emission results in Fig. 3 do not show this tendency, this result can be attributed to the concentration quenching phenomenon. Although Tm\(^{3+}\) shows excellent solubility in the current BGG glass, it is of great importance to select suitable Tm\(_2\)O\(_3\) doping concentration to achieve optimal 1.8 \( \mu \)m emission.

**Thermal properties and refractive index.** Except excellent emission property, thermal stability is also a critical property for laser glasses, particularly for high rare earth doped glasses since they are easier to result in occurrence of crystallization during the fiber drawing reheating processes. The glass transition temperature (\( T_g \)), onset crystallization peak temperature (\( T_x \)), and the top crystallization temperature (\( T_p \)) of the core and cladding glasses can be determined from the DSC curves, as shown in Fig. 6. The criterion, \( \Delta T = T_p - T_g \), is frequently used as an important parameter to evaluate glass thermal stability. The larger the value of \( \Delta T \) is, the better anti-crystallization ability gets. The \( \Delta T \) of core and cladding glasses are 187 \(^\circ\)C and 168 \(^\circ\)C, respectively, which are far larger than that of fluorogermanate glass (144 \(^\circ\)C), tellurite glass (102 \(^\circ\)C) and fluorophosphate glass (87 \(^\circ\)C). The large values indicate that BGG core and cladding glasses can possess a lower crystal nucleation and growth rate during the reheating process, which makes it possible to obtain crystal-free glass fibers. Furthermore, it should be noted that the \( T_g \) value of the glasses reaches 685 \(^\circ\)C, suggesting that BGG glass possesses high ability against thermal damage.

The coefficients of thermal expansion (CTE) value of core and cladding glasses were also measured in the 30–700 \(^\circ\)C, and the values were 6.3 \( \times \) 10\(^{-6}\)/\(^\circ\)C and 6.8 \( \times \) 10\(^{-6}\)/\(^\circ\)C, respectively. The refractive indices of core and cladding glasses at 1533 nm are 1.735 and 1.730, respectively. It can be seen that characteristic temperatures, the CTE values and the refractive indices of core and cladding glasses are well-matched and suitable for fiber fabrication.
Fiber laser performances. Table 2 summarizes some important basic parameters of the core and cladding glasses. It is noted that the Tm$^{3+}$ doping concentration reaches $7.6 \times 10^{20}$ ions/cm$^3$, being the reported highest level in Tm$^{3+}$ doped BGG fibers to our best knowledge. The fiber preform was designed for the requirement of SM optical fibers. Continuous highly Tm$^{3+}$ doped BGG glass fibers were successfully fabricated in-house with cladding diameter of 125 μm and core diameter of 9.2 μm by the typical rod-in-tube technique. The numerical apertures (N.A.) of the BGG glass fiber is 0.132. The propagation loss of the as-drawn Tm$^{3+}$ BGG glass fibers at 1310 nm was measured to be 0.095 dB/cm by the cutback method, which is lower than that of tellurium germanate glass (0.15 dB/cm)$^{42}$, but little larger than that of Tm$^{3+}$ doped lead silicate glass fiber (0.07 dB/cm)$^{17}$. The large fiber loss may be attributed to the impurities which were brought into the glass during the melting process.

As is well known, when the normalized frequency $V$ of a fiber is less than or equal to 2.405, only the fundamental mode (LP$_{01}$) can be propagated in the active fiber and the single-mode operation can occur. The $V$ of a fiber is given as:

$$V = \frac{2\pi a}{\lambda} \sqrt{n_1^2 - n_2^2}$$

where $\lambda$ is the wavelength, $a$ is the radius of the fiber, $n_1$ and $n_2$ are refractive index of core and cladding glass, respectively. Assuming that $V$ is equal to 2.405, the cut-off wavelength ($\lambda_c$) for the as-drawn fiber is calculated to be 1.59 μm, suggesting that once the operation wavelength is larger than 1.59 μm, the condition for single-mode operation is satisfied. The wavelength of the Tm$^{3+}$ fiber laser is usually around 1.8 μm, giving a result of $V < 2.405$ which indicates that the highly Tm$^{3+}$ doped germanate fiber can be single-mode operated.

Figure 7 shows schematic diagram of the experimental set-up for highly Tm$^{3+}$ doped BGG fiber laser. The inset of Fig. 7 shows the photomicrograph of highly Tm$^{3+}$ doped BGG fiber.

Table 2. The important basic parameters of the core and cladding glasses.

| Glasses | Tm$^{3+}$ concentration (10$^{20}$ ions/cm$^3$) | $T_g$(°C) | $T_p$(°C) | $T_s$(°C) | Refractive index (n) | CTE ($10^{-6}$/°C) | N.A. |
|---------|---------------------------------|----------|----------|----------|-------------------|-----------------|------|
| Core    | 7.6                             | 685      | 872      | 187      | 1.735             | 6.3             | 0.132|
| Cladding| –                               | 687      | 855      | 168      | 1.730             | 6.8             |      |

Figure 7. Schematic diagram of the experimental set-up for highly Tm$^{3+}$ doped BGG fiber laser. The inset of Fig. 7 shows the photomicrograph of highly Tm$^{3+}$ doped BGG fiber.
fiber Fabry-Perot interferometer (FFPI, SA200-18B) with free spectral range (FSR) of 1.5 GHz and resolution of 7.5 MHz. The scanning spectrum over a FSR of the FFPI, shown in the Fig. 8(c), indicates that the laser was operating in single longitudinal mode as we expected.

Additionally, an all-fiber laser performance operating in multilongitudinal-mode has also been achieved in a 10 cm long as-drawn active fiber. The launched pump power was totally absorbed due to the long length of the active glass fiber. It can be seen from the inset of Fig. 8(d) that the fiber laser output is centered at 1950.01 nm, well matches the FBG center. The laser threshold pump power is about 250 mW, and the output laser power rises linearly versus the absorbed pump power, yielding a maximum value of 165 mW and a slope efficiency of 17%, as shown in Fig. 8(d). Much higher output power could be obtained by further increasing the launched pump power, which is beyond the limitation of the handling power of the components in the cavity.

Table 3 summarizes the active fiber length, pumping wavelength, laser threshold, maximum laser output power, and slope efficiency of various fiber lasers.

| Active fiber | Fiber length (cm) | Pumping wavelength (nm) | Laser threshold (mW) | Maximum output power (mW) | Slope efficiency | Reference |
|--------------|------------------|-------------------------|---------------------|--------------------------|-----------------|-----------|
| Silica fiber | ~5.0             | 790                     | 59                  | 1                        | 0.2             | 43        |
| Tellurite fiber | 2.0           | 1590                    | 260                 | 5                        | ~3%             | 44        |
| Siliate fiber | 2.0             | 1575                    | 300                 | ~40                      | 37%             | 45        |
| Germanate fiber | 9.6           | 1568                    | 140                 | 140                      | 7.6%            | 14        |
| BGG fiber    | 10               | 1568                    | 250                 | 165                      | 17%             | This work |
| BGG fiber    | 1.6              | 1568                    | 130                 | 35                       | 5.5%            | This work |

Table 3. Summary of the active fiber length, pumping wavelength, laser threshold, maximum laser output power, and slope efficiency of various fiber lasers.
value of FBGs to match the as-drawn glass fibers, reducing the fiber loss and using efficient 790 nm single-mode laser pump source. The results suggest that the as-drawn highly Tm$^{3+}$ doped BGG SM glass fibers are excellent active medium for 2.0 $\mu$m fiber lasers.

Conclusions

The optical parameters, energy transfer processes and thermal properties of Tm$^{3+}$ doped BGG glasses were analyzed in detail. Highly Tm$^{3+}$ doped BGG glass SM fibers with core diameter of 9.2 $\mu$m and cladding diameter of 125 $\mu$m were designed and fabricated by the rod-in-tube technique. The Tm$_2$O$_3$ doping concentration reaches 1.8 mol % (Tm$^{3+}$: 7.6 $\times$ 10$^{18}$ ions/cm$^3$), which owns the record high Tm$^{3+}$ doping concentration in BGG glass fibers to the best of our knowledge. A single-frequency fiber laser at 1.95 $\mu$m has been demonstrated in a 1.6 cm as-drawn highly Tm$^{3+}$ doped BGG SM fiber with a maximum output power of 35 mW when in-band pumped by a home-made 1568 nm fiber laser. In addition, a multilongitudinal-mode fiber laser has been achieved using a 10 cm long as-drawn active fiber, corresponding to a maximum laser output power of 165 mW and a slope efficiency of 17%. The results confirm that the as-drawn highly Tm$^{3+}$ doped BGG glass SM fiber possesses high pump absorption and high gain per unit length, which make it a promising active medium for compact and efficient 2.0 $\mu$m fiber laser.

References

1. Jackson, S. D. Towards high-power mid-infrared emission from a fibre laser. Nat. Photonics 6, 423–431 (2012).
2. Waldb, B. M. Review of Tm and Ho materials; spectroscopy and lasers. Laser. Phys. 19, 855–866 (2009).
3. Wang, Q., Geng, I. J. & Jiang, S. 2-$\mu$m fiber laser sources for sensing. Opt. Eng. 53, 061609 (2014).
4. Peng, Y., Yuan, X., Zhang, J. & Zhang, L. The effect of La$_2$O$_3$ in Tm$^{3+}$-doped germanate–tellurite glasses for 2 $\mu$m emission. Sci. Rep. 4, 03256 (2014).
5. Shah, L. et al. Thulium fiber laser and application development. Proc. of SPIE 9081, 90810H-1–90810H-6 (2014).
6. Wu, J. et al. Efficient thulium-doped 2-$\mu$m germanate glass fiber laser. IEEE Photon. Technol. Lett. 18, 334–336 (2006).
7. Agger, S., Povlsen, J. H. & Varming, P. Single-frequency thulium-doped distributed feedback fiber laser. Opt. Lett. 29, 1503–1505 (2004).
8. Jackson, S. D. Cross relaxation and energy transfer up conversion processes relevant to the functioning of 2 $\mu$m Tm$^{3+}$-doped silica fibre lasers. Opt. Commun. 230, 197–203 (2004).
9. Lee, Y. W., Cho, C. H., Toen, H. W. & Jiang, S. Tm$^{3+}$-doped silica fiber amplifier with gain per unit length of 3.17 dB/cm. Advanced Solid State Lasers. 3, AW3A (2014).
10. Richards, B., Tsang, Y., Binks, L., Drouet, J. & Rha, A. Efficient – 2 $\mu$m Tm$^{3+}$-doped tellurite fiber laser. Opt. Lett. 33, 402–404 (2008).
11. Bayya, S. S., Chin, G. D., Sanghera, J. S. & Aggarwal, I. D. Germanate glass as a window for high energy laser systems. Opt. Express 14, 11687–11693 (2006).
12. Wei, T. et al. Mid-infrared fluorescence, energy transfer process and rate equation analysis in Er$^{3+}$ doped germanate glass. Sci. Rep. 4, 06060 (2014).
13. Xu, R., Tian, Y., Hu, L. & Zhang, J. Enhanced emission of 2.7 $\mu$m pumped by laser diode from Er$^{3+}$/Pr$^{3+}$-codoped germanate glasses. Opt. Lett. 36, 1173–1175 (2011).
14. Wen, X. et al. Tm$^{3+}$-doped barium gallo-germanate glass single-mode fibers for 2.0 $\mu$m laser. Opt. Express 23, 7722–7731 (2015).
15. Fan, X. et al. Spectroscopic properties and quenching mechanism of 2 $\mu$m emission in Ho$^{3+}$ doped germanate glasses and fibers. Opt. Mater. Express 5, 1356–1365 (2015).
16. Wang, R. et al. Heavily erbium-doped low-hydroxyl fluorotellurite glasses for 2.7 $\mu$m laser applications. Opt. Mater. Express 3, 1127–1136 (2013).
17. Liu, X. et al. Realization of 2 $\mu$m laser output in Tm$^{3+}$-doped lead silicate double cladding fiber. Mater. Lett. 125, 12–14 (2014).
18. Li, K. et al. Tm$^{3+}$ and Tm$^{3+}$–Ho$^{3+}$ co-doped tungsten tellurite glass single mode fiber laser. Opt. Express 20, 10115–10121 (2012).
19. Xu, R., Xu, L., Hu, L. & Zhang, J. Structural origin and laser performance of thulium-doped germanate glasses in J. Phys. Chem. A 115, 14163–14167 (2011).
20. Xu, R., Tian, Y., Hu, L. & Zhang, J. Efficient 2 $\mu$m emission and energy transfer mechanism of Ho$^{3+}$ doped barium gallium germanate glass sensitized by Tm$^{3+}$ ions. Appl. Phys. B 108, 597–602 (2012).
21. Li, M., Bai, G., Guo, Y., Hu, L. & Zhang, J. Investigation on Tm$^{3+}$-doped silicate glass for 1.8 $\mu$m emission. J. Lumin. 132, 1830–1835 (2012).
22. Li, K. et al. Energy transfer and 1.8 $\mu$m emission in Tm$^{3+}$/Yb$^{3+}$-codoped lanthanum tungsten tellurite glasses. J. Alloys Compd. 504, 573–578 (2010).
23. Choi, Y. G., Kim, K. H. & Heo, J. Spectroscopic properties of and energy transfer in PbO–Bi$_2$O$_3$–Ga$_2$O$_3$ glass doped with Er$_2$O$_3$. J. Am. Ceram. Soc. 82, 2762–2768 (1999).
24. Waldb, B. M. & Barnes, N. P. Comparison of Tm:ZBLAN and Tm: silica fiber lasers; spectroscopy and tunable pulsed laser operation around 1.9 $\mu$m. Appl. Phys. B 78, 325–333 (2004).
25. Li, K., Zhang, G. & Hu, L. Watt-level –2 $\mu$m laser output in Tm$^{3+}$-doped tungsten tellurite glass double-cladding fiber. Opt. Lett. 35, 4136–4138 (2010).
26. Geng, J., Wu, J. & Jiang, S. Efficient operation of diode-pumped single-frequency thulium-doped fiber lasers near 2 $\mu$m. Opt. Lett. 32, 355–357 (2007).
27. Lee, Y. W., Ling, H. Y., Lin, Y. H. & Jiang, S. Heavily Tm$^{3+}$-doped silicate fiber with high gain per unit length. Opt. Mater. Express 5, 549–557 (2015).
28. Huang, F. et al. Origin of near to middle infrared luminescence and energy transfer process of Er$^{3+}$/Yb$^{3+}$ co-doped fluorotellurite glasses under different excitations. Sci. Rep. 5, 08233 (2015).
29. Huang, F., Cheng, J., Liu, X., Hu, L. & Chen, D. Ho$^{3+}$/Er$^{3+}$ doped fluoride glass sensitized by Ce$^{3+}$ pumped by 1550 nm LD for efficient 2.0 $\mu$m laser applications. Opt. Express 22, 20924–20935 (2014).
30. Doualan, J. L., Girard, S., Haquin, H., Adam, J. L. & Montagne, J. Spectroscopic properties and laser emission of Tm doped ZBLAN glass at 1.8 $\mu$m. Opt. Mater. 24, 563–574 (2003).
31. Wang, X., Li, K., Yu, C., Chen, D. & Hu, L. Effect of Tm$_2$O$_3$ concentration and hydroxyl content on the emission properties of Tm doped silicate glasses. J. Lumin. 147, 341–345 (2014).
32. Li, R. et al. Mid-infrared emission properties and energy transfer evaluation in Tm$^{3+}$ doped fluorophosphate glasses. J. Lumin. 162, 58–62 (2015).
33. Tarelho, L., Gomes, L. & Ranieri, I. Determination of microscopic parameters for nonresonant energy-transfer processes in rare-earth-doped crystals. Phys. Rev. B 56, 14344 (1997).
34. Wang, X. et al. Compositional dependence of the 1.8 $\mu$m emission properties of Tm$^{3+}$ ions in silicate glass. J. Appl. Phys. 112, 103521 (2012).
35. Gao, S. et al. 2 μm emission properties and non-radiative processes of Tm3+ in germanate glass. J. Appl. Phys. 116, 173108 (2014).
36. De Sousa, D. E. & Nunes, L. A. O. Microscopic and macroscopic parameters of energy transfer between Tm3+ ions in fluoroindogallate glasses. Phys. Rev. B 66, 024207 (2002).
37. Taher, M., Gebavi, H., Taccheo, S., Milanese, D. & Balda, R. Novel calculation for cross-relaxation energy transfer parameter applied on thulium highly-doped tellurite glasses. Proc. of SPIE. 8257, 825707 (2012).
38. Huang, F. et al. 2.7 μm emission of high thermally and chemically durable glasses based on AlF3. Sci. Rep. 4, 03607 (2014).
39. Dietzel, A. Glass structure and glass properties. Glasstech Ber. 22, 41–48 (1968).
40. Yuan, J. et al. Enhanced 2.0 μm emission from Ho3+ bridged by Yb3+ in Nd3+/Yb3+/Ho3+ triply doped tungsten tellurite glasses for a diode-pump 2.0 μm laser. J. Appl. Phys. 114, 133506 (2013).
41. Liao, M., Sun, H., Wen, L., Fang, Y. & Hu, L. Effect of alkali and alkaline earth fluoride introduction on thermal stability and structure of fluorophosphates glasses. Mater. Chem. Phys. 98, 154–158 (2006).
42. Gao, S. et al. Tm3+-doped tellurium germanate glass and its double cladding fiber for 2 μm laser. Mater. Lett. 143, 60–62 (2015).
43. Agger, S., Povlsen, J. H. & Varming, P. Single-frequency thulium-doped distributed-feedback fiber laser. Opt. Lett. 29, 1503–1505 (2004).
44. Li, K. et al. In-band pumping of Tm doped single mode tellurite composite fibers. Proc. of SPIE 8982, 89821M-1–89821M-6 (2014).
45. Geng, J., Wang, Q., Luo, T., Jiang, S. & Amzajerdian, F. Single-frequency narrow-linewidth Tm-doped fiber laser using silicate glass fiber. Opt. Lett. 34, 3493–3495 (2009).

Acknowledgements
This research was supported by China National Funds for Distinguished Young Scientists (61325024) and the China State 863 Hi-tech Program (2013AA031502).

Author Contributions
Z.M.Y., Q.Y.Z. and Q.Q. proposed the project; X.W., G.W.T., Q.Y. and X.D.C. performed all the experiments; X.W. analyzed the results and wrote the main manuscript text; G.W.T. and Q.Q. revised the manuscript; all authors reviewed the manuscript.

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

How to cite this article: Wen, X. et al. Highly Tm3+ doped germanate glass and its single mode fiber for 2.0 μm laser. Sci. Rep. 6, 20344; doi: 10.1038/srep20344 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/