

Tm³⁺/Ho³⁺ co-doped germanate glass and double-clad optical fiber for broadband emission and lasing above 2 μm

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Abstract: In this paper, a 2 µm broadband emission under 796 nm laser diode excitation in low phonon energy GeO₂-Ga₂O₃-BaO glass system is co-doped with 0.7Tm₂O₃/(0.07-0.7)Ho₂O₃ (mol%). The widest emission band (where the Tm³⁺ \rightarrow Ho³⁺ energy transfer efficiency is 63%) was obtained for 0.7Tm₂O₃/0.15Ho₂O₃ co-doped glass from which a double-clad optical fiber was realized and investigated. Optimization of Tm³⁺/Ho³⁺ concentration enabled the acquisition of broadband amplified spontaneous emission (ASE) in double-clad optical fiber with a full width at half maximum (FWHM): 377 nm and 662 nm for 3 dB and 10 dB bandwidth, respectively. ASE spectrum is a result of the superposition of (Tm³⁺: ³H₄ \rightarrow H³F₄) 1.45 µm, (Tm³⁺: ³F₄ \rightarrow ³H₆) 1.8 µm and (Ho³⁺:⁵I₇ \rightarrow ⁵I₈) 2 µm emission bands. Hence, highly rare-earth co-doped germanate glass is characterized by a remarkably broader ASE spectrum than silica and tellurite fibers showed promising lasing properties for their further application in tunable and dual wavelength lasers.

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1. Introduction

Optical fiber lasers and broadband amplified spontaneous emission sources (ASE) operating in the 2 µm region (also called the eye-safe spectral region) have attracted much interest owing to numerous fields of application such as, optical component testing, remote sensing, atmosphere pollution monitoring, and medical applications including laser surgery [1-9]. Among lanthanides the energy level transitions Tm^{3+} : ${}^{3}F_{4} \rightarrow {}^{3}H_{6}$ and Ho^{3+} : ${}^{5}I_{7} \rightarrow {}^{5}I_{8}$ are responsible for the emission in the $2 \mu m$ region [10,11]. Both transitions operate in the 3-level quantum scheme, and the luminescence spectrum emitted from these transitions is relatively broad. It should be also noted that holmium is characterized by a higher emission crosssection, a broader emission band and longer fluorescence lifetime, which makes it more suitable for the generation of a 2 μ m laser or broadband ASE radiation [12]. Recently, the ASE or lasing at 2 µm have been presented in silicate, fluorophosphate, tellurite, antimony and germanate fibers [13–18]. A key factor in co-doped optical fibers where a donor-acceptor energy transfer takes place is phonon energy of a core glass host. It is known that the probability of non-radiative transition is proportional to the phonon energy of glass. High thermal stability, good mechanical properties, and solubility of rare-earths are not less important in terms of optical fiber technology. Among oxide glasses, germanium based glasses meet these requirements and thus they are good candidates for drawing the optical fibers. The amorphous system in BaO-Ga₂O₂-GeO₂ chemical composition referred as BGG glass is known as a window for high energy laser HEL systems [19]. The BGG glass possesses interesting photo-physical properties, relatively high thermal stability necessary to

fabricate optical fibers and it seems to be an excellent host to incorporate rare earths playing a role of optically active ions. A special attention has been paid to rare earth doped barium gallo-germanate glasses and their promising near-infrared luminescence applications [20–24]. In particular, our recent studies indicate that barium gallo-germanate glass singly doped with Ho^{3+} ions may be a good candidate for near-infrared laser sources operated at 2 µm [24]. However, direct pumping of Ho³⁺ singly doped glasses or the optical fibers is rather inefficient due to small ${}^{5}I_{8} \rightarrow {}^{5}I_{5}$ and ${}^{5}I_{8} \rightarrow {}^{5}I_{6}$ absorption cross-sections. With the rapid development of AlGaAs laser diodes (LD), the diode-pumped Tm³⁺/Ho³⁺ glass system has been proposed alternatively as a promising way to achieve efficient near-infrared radiation at $2 \mu m$ [25,26]. In most cases, these phenomena were limited mainly to Tm³⁺/Ho³⁺ co-doped oxide silica-based glasses and optical fibers [25]. However, the nonradiative decay is very competitive and reduces the quantum efficiency for the silica-based glasses with their phonon energies extending nearly to 1100 cm⁻¹. For that reason, low-phonon Tm³⁺/Ho³⁺ co-doped tellurite-based glasses have been proposed recently as a good alternative for the near-infrared fiber technology [26–28]. These aspects for the $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped BGG glasses have not been examined yet. Moreover, it should be also noticed that luminescent properties of the germanate glass system doped with Er³⁺, Pr³⁺, Ho³⁺, Tm³⁺ were systematically examined in the broad spectral range from the visible range up to $3 \mu m [29-35]$. Due to their relatively low phonon energy the rare-earth co-doped germanate glasses have been studied in terms of obtaining visible emission through an upconversion process [36,37].

This paper examined the effects of 796 nm pumping by the diode-laser and the $Tm^{3+} \rightarrow Ho^{3+}$ energy transfer process to achieve the broadband emission at 2 µm and lasing in the manufactured germanate glasses and double-clad optical fiber. Double-clad germanate core optical fibers co-doped with Tm^{3+}/Ho^{3+} and an analysis of their luminescent properties have not yet been presented and discussed. In literature, only singly doped Ho^{3+} [17] and Tm^{3+} [21] germanate optical fibers emitting in the 2 µm spectral range have been presented.

Novelty of this paper is the optimization of $\text{Tm}^{3+}/\text{Ho}^{3+}$ content in silica free GGB glass in order to obtain broadband emission at 2 µm and its application as core glass in a double-clad optical fiber. Besides, it's worth to note that our elaborated optical fiber showed a broader ASE spectrum than known silica fibers and promising lasing properties for its further application in tunable and dual wavelength lasers.

2. Experimental

The germanium based glasses were prepared according to the following molar compositions: (1-x)60GeO₂-15Ga₂O₃-10BaO-15Na₂O-0.7Tm₂O₃-xHo₂O₃ (x = 0, 0.07, 0.15, 0.35, 0.7%) by melting and quenching method. The homogenized in glove box set (pure materials 99.99%) was melted in a platinum crucible in an electric vacuum furnace in $T = 1500^{\circ}C$ for 30 minutes. The molten glass was poured out onto a stainless plate and then annealed in air atmosphere at 610°C for 12 h. Luminescence measurements in the range of 1100 – 2300 nm were carried out using Acton 2300i monochromator equipped with PbS detector in lock-in detection setup and a high power LIMO laser diode ($\lambda_p = 796$ nm, P_{opt} = 1-30W). ASE spectrum of the optical fiber has been measured by AQ6375 optical spectrum analyzer. Luminescence decay measurements were performed using a system PTI QuantaMaster QM40 coupled with a tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (OpotekOpolette 355 LD). The laser system was equipped with a double 200 monochromator, a multimode UV-VIS photomultiplier tube (PMT) (R928) and Hamamatsu H10330B-75 detectors controlled by a computer. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope. Double-clad optical fibers were manufactured using the modified rod-in-tube technique. The fabricated germanate glass rod was located in drilled internal cladding and structure was placed in a glass tube. Finally, the double-clad optical fiber was drawn from 10 cm length prefom in the temperature range of 890-930°C and coated with low index acrylate.

3. Results and discussion

3.1 Properties of the germanate core glass

Table 1 presents basic physico-chemical properties of the Tm^{3+}/Ho^{3+} co-doped germanate glasses.

Parameter	Value
Refractive index n (633nm)	1.73
Mass density ρ [g/cm ³]	4.4
Transformation temperature T_g [°C] (DSC)	570
Crystallization temperature T _x [°C] (DSC)	780
Thermal stability factor $\Delta T = T_x - T_g[^{\circ}C]$	210
Phonon Energy [cm ⁻¹]	790
OH content [ppm]	74

Table 1. Physical and thermal properties of manufactured germanate glass.

Structural and thermal properties of presented glass host were studied by authors previously [18]. It should be emphasized that thermal stability factor ΔT defined as T_x -T_g is quite high (210°C) among low-phonon glasses. Another key parameter in construction Tm^{3+}/Ho^{3+} co-doped optical fibers is phonon energy of core glass. Fabricated germanate glass is characterized by reduced (with reference to silica glass) maximum phonon energy, which results from asymmetric stretching motions of GeO₄ tetrahedron containing bridging Ge–O–Ge and non-bridging Ge–O⁻ oxygens [18]. Figure 1 shows the 2 µm emission spectra of Tm^{3+} doped and Tm^{3+}/Ho^{3+} co-doped germanate glasses doped with various concentrations of Ho³⁺ ions excited at 796 nm. Based on our results the maximum acceptable concentration of RE (without quenching and clustering) in glass (sum of Tm^{3+} and Ho^{3+}) is 1.4 mol%. From one side the concentration above 0.7 Tm₂O₃ results in concentration quenching of luminescence. Other co-doped systems (e.g. 1 Tm₂O₃ /0.7 Ho₂O₃) showed decrease of emission intensity of Tm³⁺ and Ho³⁺ ions. Three characteristic sub-bands with peaks at 1800 nm, 1960 and 2060 nm correspond to transitions from $\text{Tm}^{3+:3}F_4$ and $\text{Ho}^{3+:5}I_7$ levels, respectively. The multiple band profiles of the holmium luminescence spectra are mainly resulted of the Stark splitting of Ho³⁺: ${}^{5}I_{7}$ level.



Fig. 1. Luminescence spectra of the germanate glass (a), simplified energy diagram with energy transfer mechanism (b) in germanate co-doped with Tm^{3+}/Ho^{3+} under 796 nm excitation.

It is noticed that increasing of Ho₂O₃ content above 0.15 mol. % leads to strong decreasing of luminescence at 1800 nm - Fig. 1(a), which confirms effective $Tm^{3+} \rightarrow Ho^{3+}$ energy transfer (ET). Luminescence at 2 µm was obtained in the way of the quasi-resonant non-radiative (Tm^{3+}) ${}^{3}F_{4}\rightarrow{}^{3}H_{6}$, (Ho^{3+}) ${}^{5}I_{8}\rightarrow{}^{5}I_{7}$ energy transfer - Fig. 1(b). As a result of effective ${}^{3}F_{4}$ (Tm^{3+}) and ${}^{5}I_{7}$ (Ho^{3+}) multiplet coupling, the highest level of luminescence and FWHM was achieved in the glass co-doped with 0.7Tm₂O₃/0.15Ho₂O₃ (mol. %). Analysis of luminescence decay measurements in glass samples doped with Tm^{3+} and co-doped with Tm^{3+} /Ho³⁺ presented in Fig. 2(a) enables to calculate the efficiency of $Tm^{3+} \rightarrow Ho^{3+}$ energy transfer according to the equation:

$$\eta = 1 - \tau_{Tm}^{Tm-Ho} / \tau_{Tm} \tag{1}$$

where: τ_{Tm}^{Tm-Ho} is the lifetime of Tm³⁺:³F₄ in the presence of Ho³⁺, τ_{Tm} is the lifetime of Tm³⁺:³F₄ in singly Tm³⁺ -doped glass. The lifetime of Tm³⁺:³F₄ (singly doped glass) is characterized by single-exponential behaviour for samples doped with 0.7Tm³⁺, 0.7Tm³⁺/0.07Ho³⁺ and double-exponential for samples with higher content of co-dopants (0.7Tm³⁺/(0.15-0.7)Ho³⁺). It can be result of Ho³⁺ \rightarrow Tm³⁺ back energy transfer.



Fig. 2. Luminescence decay curves from Tm^{3+} : ${}^{3}\text{F}_{4}$, Ho^{3+} : ${}^{5}\text{I}_{7}$ level (inset) (a), fifetime of ${}^{3}\text{F}_{4}$ state of Tm^{3+} and energy transfer efficiency as a function of Ho^{3+} content (b), ($\lambda_{\text{exc}} = 796$ nm).

The luminescence decay of the $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped glasses was fitted by the sum of two exponential decay components from:

$$I(t) = A_1 exp\left(-\frac{t}{\tau_1}\right) + A_2 exp\left(-\frac{t}{\tau_2}\right)$$
(2)

where τ_1 and τ_2 were short- and long-decay components, respectively. Parameters A₁ and A₂ were fitting constants. According to Eq. (2), the average lifetime $<\tau>$ was given by:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{3}$$

According to Eq. (3), the average lifetimes of ${}^{3}F_{4}$ energy level of Tm³⁺ in the fabricated germanate glasses were calculated.

Dependence of Tm^{3+} : ${}^{3}\text{F}_{4}$ lifetime and the energy transfer efficiency with holmium concentration is presented in Fig. 2(b). The ${}^{3}\text{F}_{4}$ lifetime of Tm^{3+} is reduced from 516 µs (0.7Tm₂O₃) to 97 µs in the presence of Ho³⁺ (0.7Tm₂O₃/0.7Ho₂O₃) and the efficiency of Tm³⁺ \rightarrow Ho³⁺ energy transfer increases with increasing Ho³⁺ concentration because the

distance between the interacting lanthanide ions is reduced. As a result of calculations, maximum efficiency of energy transfer (ET) $(\text{Tm}^{3+} \rightarrow \text{Ho}^{3+})$ was determined to be 83% (Fig. 2(b). However, the highest value FWHM of emission band was obtained for glass co-doped with $0.7\text{Tm}_2\text{O}_3/0.15\text{Ho}_2\text{O}_3$ (ET efficiency = 63%). Further investigation of this glass sample indicates that the lifetime of Ho^{3+} :⁵I₇ level based on decay curve measurement (the inset of Fig. 3) at 796 nm (excitation) and 2030 nm (emission) is close to 2.17 ms.

3.2 Double - clad optical fiber

The double-clad optical fiber with core co-doped with $0.7Tm_2O_3/0.15Ho_2O_3$ system was fabricated using a modified rod-in-tube technique. The inner and outer cladding glasses composition were as follows:

$$44SiO_{2} - 8Al_{2}O_{3} - 15B_{2}O_{3} - 16PbO - 12Na_{2}O - 5K_{2}O(\text{inner cladding}, n = 1.62)$$

$$69SiO_2 - 4Al_2O_3 - 13Na_2O - 5CaO - 3K_2O - 3MgO - 2BaO - 1B_2O_3$$
 (outer cladding, n = 1.51)

Glasses have been selected in terms of similar value of thermal expansion coefficient and adequate refractive indices. Basic parameters of the manufactured optical fiber was as follows: outer cladding diameter = $260 \mu m$, inner cladding diameter = $235 \mu m$, core diameter = $18 \mu m$. The index profile of the drawn fiber was measured with a fiber index profiler IFA-100 (Interfiber Analysis, LLC) and is shown in Fig. 3. The inset shows a 2D index profile from which 1D curves in x- and y-direction were taken and plotted in the diagram. The measured values for core NA is approx. 0.51 and for the cladding NA = 0.49 both showing a distinct gradient.



Fig. 3. Measured refractive index profile of the double-clad fiber.

Absorption of pump radiation (796 nm) measured by cutback method was 790 dB/m, while background attenuation at 1360 nm was 7 dB/m. Figure 4 presents ASE spectrum of 50 cm length optical fiber under "one end" 796 nm laser diode excitation. The obtained broadband emission is a result of the superposition of bands related to the $Tm^{3+}.^{3}H_{4} \rightarrow H^{3}F_{4}$, $Tm^{3+}.^{3}F_{4} \rightarrow ^{3}H_{6}$ and $Ho^{3+}.^{5}I_{7} \rightarrow I^{5}I_{8}$. transitions.



Fig. 4. ASE spectra of double-clad germanate optical fiber co-doped with $0.7Tm_2O_3/0.15Ho_2O_3$, photo of fiber (inset).

Finally, broadband emission (FHWM = 377 nm - 3 dB and FWHM = 662 nm - 10 dB) is wider than presented in silica fiber co-doped with Tm^{3+}/Ho^{3+} fabricated by MCVD and solution doping method, where bandwidth achieved at the level of -10 dB was 645 nm [38]. Broadband ASE was also reported in Tm^{3+} -doped and Tm^{3+}/Ho^{3+} -co-doped tungsten double clad tellurite fibers [16,39]. However, it should be noted that in these cases ASE spectra with the maximum bandwidth (FWHM) 140 nm and 210 nm were achieved in fibers doped with Tm^{3+} and co-doped with Tm^{3+}/Ho^{3+} , respectively.

3.3 Fiber laser experiments

For the evaluation of laser properties of the double – clad fiber, we have realized a Fabry-Perot fiber laser setup shown in Fig. 5. Pump light from a 790 nm fiber-coupled laser diode is coupled via two lenses of same focal length into the cladding of the $\text{Tm}^{3+}/\text{Ho}^{3+}$ -doped fiber. The resonator is formed by a straight cleave at the front side of the fiber and a butt-coupled dichroitic mirror highly reflecting in the range of 1900...2100nm and transmitting the pump wavelength at the back side of the fiber. A similar mirror is used for out-coupling of the laser signal on power meter 1. The second power meter allows measuring the residual pump light, which is not absorbed within the laser fiber. To enhance pump absorption of the circular pump cladding we have coiled the fiber in "kidney shape". We have characterized 4 different fiber lengths and found out that laser efficiency is highest for 0.5 m length. In this case, the slope efficiency presented in Fig. 6 is about 4.7% with respect to the absorbed pump power.



Fig. 5. Fabry-Perot setup for laser characterization of double-clad fibers with different fiber lengths.



Fig. 6. Laser characteristics for different fiber lengths and slope efficiency reaching 4.7% at 2070nm wavelength (inset with laser output spectrum).

The output spectrum is measured with a Yokogawa AQ6375 optical spectrum analyzer with a resolution of 0.1nm at the position of power meter 1. The laser emission is shown in inset of Fig. 6 and ranges from 2061 to 2075nm. The obtained performance of our BGG Tm^{3+}/Ho^{3+} fiber laser ($\eta = 4.7\%$, $P_{max} = 140$ mW) is at level of Tm^{3+} -doped BGG ($\eta = 5.5\%$ $P_{max} = 35$ mW) [40]. In work [27] authors have obtained efficiency c.a. $\eta = 1.5\%$ and $P_{max} = 35$ mW in Tm^{3+}/Ho^{3+} doped tungsten tellurite single mode fiber laser. Tungsten tellurite fiber laser co-doped with Nd^{3+}/Ho^{3+} presented in [41] was characterized by efficiency $\eta = 11.2\%$ and $P_{max} = 12$ mW. While parameters of lanthanum tungsten germanium tellurite fiber laser co-doped with Tm^{3+}/Ho^{3+} presented in work [42] are as follows $\eta = 31.9\%$, $P_{max} = 900$ mW. Main factors influencing the laser performance are phonon energy of glass host, efficiency of donor-acceptor energy transfer, and losses of the optical fiber (OH content and quality of the core/cladding surface).

4. Summary

In conclusion, the optimization of $\text{Tm}^{3+}/\text{Ho}^{3+}$ co-dopants in low phonon germanate core glass enabled to fabricate a double-clad optical fiber emitting broadband ASE with -10dB bandwidth of 662 nm. The ASE spectrum is a result of direct excitation of thulium ions, resonant energy transfer to holmium with 63% efficiency and superposition of (Tm^{3+}) 1.45 µm, (Tm^{3+}) 1.8 µm and (Ho^{3+}) 2 µm emission bands, which are broader compared to silica fibers. Moreover, a high co-doping level of the developed fiber was achieved with 0.7Tm₂O₃/0.15Ho₂O₃ (mol. %) without emission quenching or phase separation which shortens the required optical fiber length due to high pump absorption (790 dB/m). We could demonstrate lasing at 2070nm with a slope efficiency of 4.7% and 145 mW output power resulting from an efficient Tm³⁺ \rightarrow Ho³⁺ energy transfer.

To summarize, the cladding pumped Tm^{3+}/Ho^{3+} -co-doped double–clad germanate optical fiber is therefore a very appropriate source for the production of novel dual-wavelength and tunable laser operating in the 2 µm spectral region.

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