Green upconversion emission in tellurite optical fibre codoped with Yb^{3+}/Er^{3+}

M. Kochanowicz, W. Mazerski, J. Żmojda, K. Czajkowski, D. Dorosz

Bialystok University of Technology, Wiejska Street 45, 15 – 351 Bialystok

Received February 09, 2013; accepted March 22, 2013; published March 31, 2013

Abstract—In the paper the spectroscopic properties of Yb^{3+}/Er^{3+} codoped tellurite glass have been investigated. Upconversion luminescence at 525 nm, 546 nm, 651 nm corresponding to the Er^{3+}: $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions, respectively was obtained as a result of energy transfer between Yb^{3+} and Er^{3+} ions. The developed tellurite glass characterized by the highest intensity of upconversion luminescence (0.5mol% Yb_2O_3/0.1mol% Er_2O_3) was used as a core of optical fiber. The amplified spontaneous emission in the fabricated optical fiber resulting from the optical transition in the structure of erbium was observed.

Upconversion luminescence of glasses doped with rare-earth ions have attracted much attention during the last decade due to their potential applications in solid-state lasers, colour displays, optical data storages, medical diagnostics, optical sensors [1-4]. Upconverting glass host should be characterized by relatively low phonon energy which makes it possible to obtain high upconversion luminescence efficiency. Tellurite glasses, thanks to perfect solubility of rare earth elements as well as low phonon energy (~780 cm^{-1}) enable an effective conversion of IR radiation to VIS radiation and make a perfect alternative to fluoride as well as to HMO glasses [5]. Furthermore, their excellent mechanical properties as well as high thermal stability make it possible to form them into optical fibers. The article presents the results of the optimization of acceptor concentration in Yb^{3+}/Er^{3+} codoped glass from TeO_2 – GeO_2 – PbO – PbF_2– BaO – Nb_2O_5 – LaF_3 system in order to obtain the highest intensity of green upconversion emission. The core of optical fiber was made of glass characterized by the highest green upconversion and comparative analysis of luminescent properties of bulk glass and optical fiber was conducted.

The glass system: TeO_2 – GeO_2 – PbO – PbF_2– BaO – Nb_2O_5 – LaF_3 codoped with Yb^{3+}/Er^{3+} ions was melted from spectrally pure (99.99%) raw materials. The homogenized set was placed in a platinum crucible and melted in an electric furnace in a temperature of 900°C for 30 minutes in an argon atmosphere. The molten glass was poured out onto a brass plate and then exposed to the process of annealing in a temperature approximate to the transformation temperature for 12 hours. Homogenous and transparent glasses were obtained without any visible effect of crystallization. In order to determine the spectroscopic properties a series of samples with the dimensions of 10 x 10 x 2 mm^3 was prepared. The glass density was calculated using the method of hydrostatic weighing. The refractive index (633nm) was determined using a Metricon 2010 refractometer. The characteristic temperatures of the obtained glasses were calculated on the basis of measurements taken with a SETARAM Labsys thermal analyzer using the DSC method. Absorption spectra of rare earth ions doped samples were determined using an Acton Spectra Pro 2300i monochromator in a spectral range of 350÷1700 nm. The tellurite optical fiber was manufactured by using a modified for the purpose, double - crucible technique [6]. Luminescence spectra in a range of 450÷750 nm were measured by using a Stelarnet GreenWave spectrometer and a high power laser diode (λ_p = 976 nm) as a pump source.

The parameters of tellurium-based glasses codoped with Yb^{3+}/Er^{3+} are presented in Table 1. Tellurite glasses are characterised by a high coefficient of light refraction (2.07), which is the cause of a high value of the emission cross-section. Furthermore, the complex composition of the obtained tellurite glasses made it possible to introduce significant amounts of rare earth elements to the matrix.

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

Parameter	*Value*
Refractive index n (633nm)	2.074
Mass density ρ [g/cm^3]	6.21
Thermal expansion coefficient α_{100}^{400} [10^{-7} 1/K]	108.9
Dilatometric softening point T_s [°C]	364
Transformation temperature T_g [°C] (DSC)	345
Maximum of phonon energy $h\omega_{maax}$ [cm^{-1}]	790

Based on transmission spectra measurement the absorption coefficient spectrum of the obtained tellurite glass codoped with Er^{3+}/Yb^{3+} ions (Fig. 1) was calculated. The absorption bands resulting from the complex structure of erbium corresponding to the following transitions: $^4I_{15/2} \rightarrow {}^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2,}$ $^4I_{13/2.}$

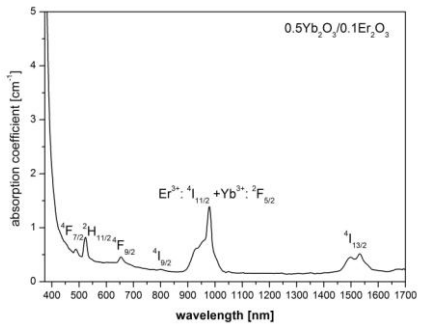

Fig. 1. Absorption spectra of fabricated tellurite glass codoped with 0.5mol% Yb_2O_3/0.1mol% Er_2O_3.

A wide absorption band around 980 nm Yb^{3+}/Er^{3+} codoped glasses resulting from spectral overlap between Yb^{3+} emission ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) and Er^{3+} absorption ($^4I_{15/2} \rightarrow {}^4I_{11/2}$).

Figure 2 presents the emission spectra of tellurite glasses codoped with Yb^{3+}/Er^{3+} ions. As a result of exciting glasses with the 976 nm wavelength radiation, three anti-Stokes emission bands: 525 nm, 546 nm, 651 nm corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) transitions, respectively (Fig. 2), were measured. The concentration of Yb_2O_3 (0.5mol%) on the one hand results from maximization of the sensitization process and, on the other hand, it is limited by clustering.

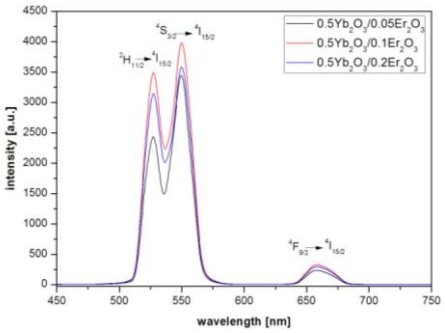

Fig. 2. Upconversion luminescence spectrum of Yb^{3+}/Er^{3+} codoped tellurite glasses.

The analysis of emission intensity as a function of Er_2O_3 molar concentration has shown that the maximum of upconversion luminescence was obtained in the glass codoped with 0.5mol% Yb_2O_3/0.1mol% Er_2O_3 (TeGe_05Y01E). The fall in the emission intensity of glass codoped with 0.5mol% Yb_2O_3/0.2mol% Er_2O_3 results from concentration quenching. The energy level scheme with mechanisms of upconversion emission from Er^{3+} ion in the presence of Yb^{3+} under 976nm excitation is shown in Fig. 3. The population of Er^{3+} metastable levels occurs mainly as a result of resonance energy transfer $Yb^{3+} \rightarrow Er^{3+}$. Green emission resulting from energy transfer and upconversion processes takes place according to the following scheme:

(ET) $^2F_{5/2}(Yb^{3+})+{}^4I_{15/2}(Er^{3+})\rightarrow{}^2F_{7/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+})$, (GSA) $^4I1_{5/2}(Er^{3+})$ + photon$\rightarrow{}^4I_{11/2}(Er^{3+})$.
(CR) $^4I_{11/2}(Er^{3+})+{}^4I_{11/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})+{}^4F_{7/2}(Er^{3+})$, (ESA) $^4I_{11/2}(Er^{3+})$ + photon$\rightarrow{}^4F_{7/2}(Er^{3+})$ $^2F_{5/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+})+{}^4F_{7/2}(Er^{3+})$.

In the next step, the nonradiative relaxation $^4F_{7/2} \rightarrow {}^2H_{11/2}$, $^4S_{3/2}$ and emission at 525 nm ($^2H_{11/2}\rightarrow{}^4I_{15/2}$), 546nm ($^4S_{3/2}\rightarrow{}^4I_{15/2}$), 651 nm ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) takes place.

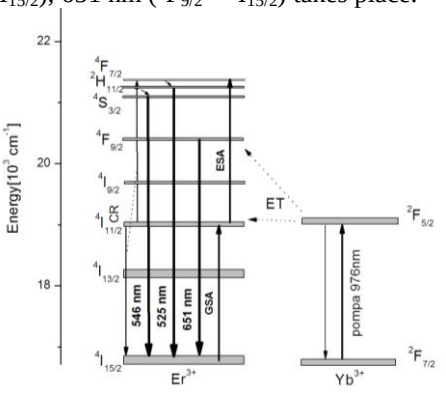

Fig. 3. Simplified diagram of energy level Yb^{3+}/Er^{3+} with energy transfer mechanism.

The efficiency of the above upconversion process depends on the lifetime of excited levels Er^{3+}, concentration of active dopant influencing the multiphonon relaxation and cross - relaxation.

Figure 4 presents the cross-section of the fabricated tellurite optical fiber codoped with 0.5mol% Yb_2O_3/ 0.1mol% Er_2O_3.

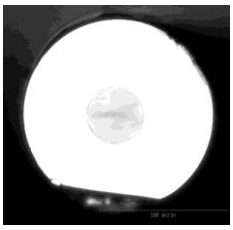

Fig. 4. Cross-section of the fabricated tellurite optical fiber codoped with 0.5mol% Yb_2O_3/ 0.1mol% Er_2O_3.

Table 2. Parameters of the fabricated tellurite optical fiber codoped with 0.5mol% Yb_2O_3/ 0.1mol% Er_2O_3.

Parameter	Value
Cladding diameter [μm]	165
Core diameter [μm]	45
Numerical aperture *NA*	0.56

The relatively high value of numerical aperture NA = 0.56 (Table 2) allows efficient coupling of pump radiation with produced optical fiber.

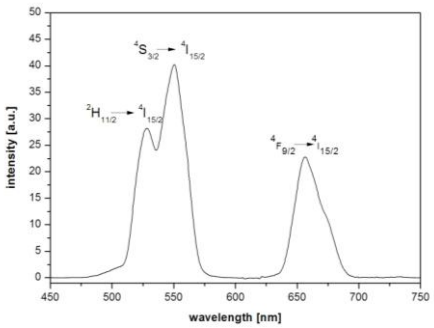

Fig. 5. The luminescence spectra of fabricated tellurite optical fibre codoped with Er^{3+} 0.5mol% Yb_2O_3/ 0.1mol% Er_2O_3 under 976nm LD excitation.

Similarly as in the bulk glass, the luminescence spectra of the produced tellurite optical fiber (λ_p=976nm) consist of three anti-stokes emission bands: 529nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$), 550nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and 656nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) as shown in Fig. 5. However, the ratio of intensity emission 545nm/525nm in the optical fiber is higher than in the case of TeGe_05Y01E bulk glass. Decreasing emission intensity of bulk glass at 545nm and simultaneous increasing emission intensity at 525nm is caused by the thermal population of $^2H_{11/2}$ level. The bulk glass sample is warming up during the pumping process. Moreover, measured emission bands shift towards a longer wavelength of 4nm (550nm and 656nm) as a function of the fiber length. This phenomenon is related to the reabsorption of ASE signal resulting from the Er^{3+}: $^5I_{15/2} \rightarrow {}^2H_{11/2}$, $^5I_{15/2} \rightarrow {}^4F_{9/2}$ transition, which was confirmed in the course of an experiment with different fiber lengths. Besides, the red/green intensity ratio is much larger in the optical fiber. A similar phenomenon has been presented in the literature [1]. However, an in-depth explanation requires further investigation.

In the present article the spectroscopic properties of tellurite glass and optical fiber codoped with Yb^{3+}/Er^{3+} ions were investigated. As a result of optimized acceptor concentration, the best efficiency of energy transfer $Yb^{3+} \rightarrow Er^{3+}$ was obtained for molar composition 0.5mol% Yb_2O_3/0.1mol% Er_2O_3. Fabricated tellurite glass characterized by highest intensity of upconversion luminescence (0.5mol% Yb_2O_3/0.1mol% Er_2O_3) was used as a core of optical fiber. The spectroscopic properties of the fabricated tellurite optical fiber (λ_p = 976nm) were significantly different from the bulk glass. Emission bands of the produced optical fiber shift towards the longer wavelength of 4 nm (550nm and 656nm) as a function of fiber length. This phenomenon is related to the reabsorption of ASE signal resulting from the Er^{3+}: $^5I_{15/2} \rightarrow {}^2H_{11/2}$, $^5I_{15/2} \rightarrow {}^4F_{9/2}$ transition and enables the optimization of the emission spectra of optical fiber. Upconversion amplified spontaneous emission (UASE) in the produced tellurite optical fiber codoped with 0.5mol% Yb_2O_3/0.1mol% Er_2O_3 indicates viable numerous applications of the developed optical fiber in biophotonics.

This work was supported by MNiSW project No. MB/WE/1/2012.

References

[1] J. Zhang, S. Dai, G. Wang, L. Zhang, H. Sun, L. Hu., Phys. Lett. A **345**, 409 (2005).
[2] D. Lande, S.S. Orlov, A. Akella, L. Hesselink, R.R. Neurgaonkar, Opt. Lett. **22**(22), 1722 (1997).
[3] T. Yamashita, Y. Ohishi, Proc. SPIE **6389**, 638912 (2006).
[4] Y.H. Li, G.Y. Hong, Y.M. Zhang, Y.M. Yu, J. Alloys Compd. **456**, 247 (2008).
[5] J.S. Wang, E.M. Vogel, E. Snitzer, Opt. Mater. **3**, 187 (1994).
[6] J. Dorosz, Ceramics **86** (2005).

