Up-conversion luminescence in germanate glass and double-clad optical fibre co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$ ions

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In the paper the analysis of up-conversion (UC) luminescence in $0.5\text{Yb}_2\text{O}_3/(0.25-1)\text{Eu}_2\text{O}_3$ (mol.%) co-doped germanate glass and optical fibre has been investigated. Up-conversion emission of bands at 591, 616, 652, 701 nm to which correspond Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively was obtained as a result of cooperative energy transfer between Yb^{3+} and Eu^{3+} ions. The highest up-conversion emission ($\text{Yb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer efficiency $\eta = 24\%$) was obtained in $0.5\text{Yb}_2\text{O}_3/0.75\text{Eu}_2\text{O}_3$ co-doped glass. Comparison of up-conversion and down-conversion luminescence spectra of bulk glass, glass fibre and different length double-clad optical fibre (up to 5 m) showed subtle differences in shape of the spectrum. In comparison to down – conversion emission ($\lambda_{\text{exc}} = 405$ nm) main UC luminescence band is red-shifted by 2 nm and is characterized by 5 nm greater full – width half – maximum (FWHM).

Keywords: germanate glass, co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$, optical fibre, up-conversion luminescence.

1. Introduction

Luminescence in a visible spectral range in rare earth's doped glasses and optical fibres have found a wide range of potential photonic applications, such as solid state lighting, fluorescence imaging, display monitors, solid compact lasers and, especially, light sources used in PDT (Photodynamic therapy) [1–5]. Due to activation of photosensitizers and “therapeutic optical window” efficient irradiation light sources in a wavelength range of 600–800 nm are especially desirable [6]. Nowadays, lasers and light emitting diodes are commonly used as PDT light sources. Eu^{3+} – doped optical fibres open new possibilities in construction irradiation light sources for PDT where problem coupling of a light source with an optical fibre was naturally solved. Visible emission in Eu^{3+} doped glasses and optical fibres can be realized in two ways: down-conversion ($\lambda_{\text{exc}} = \text{UV} - 405$ nm) and up-conversion ($\lambda_{\text{exc}} = 976$ nm) in $\text{Yb}^{3+}/\text{Eu}^{3+}$ system [7–9]. Sensitization of Eu^{3+} ions by co-doping with Yb^{3+} ions enables to obtain visible emission under pumping by commercial high power 976 nm laser diodes but only materials with relatively low phonon energies enable an effective conversion of IR to VIS radiation. Among oxide glasses, germanate

glasses owing to their good capacity for dissolving lanthanides, chemical resistance, good mechanical properties, high thermal stability are good candidates for constructing optical fibres. Furthermore, low phonon energy (~ 850 cm^{-1}) results in longer lifetimes of the metastable energy levels, thus germanium-based glasses are suitable for the implementation of up-conversion schemes [10–16]. The up-conversion luminescence processes have been studied in $\text{Yb}^{3+}/\text{Eu}^{3+}$ ions also in glass-ceramics, as well as phosphors but not in germanate glasses and optical fibres [17,18].

In the paper, the effects of optical pumping by a NIR diode-laser on up-conversion luminescence in germano-gallate glasses and double-clad optical fibre co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$ have been investigated. Special attention has been paid to an analysis of difference in luminescence spectra of fabricated different optical structures: bulk glass, glass fibre and double-clad optical fibre.

2. Experiment

The glasses from molar system: $(74.5-x)\text{GeO}_2 - 15\text{Ga}_2\text{O}_3 - 10\text{BaO} - 5\text{Na}_2\text{O} - 0.5\text{Yb}_2\text{O}_3/x\text{Eu}_2\text{O}_3$, where $x = 0; 0.25; 0.5; 0.75; 1$; were melted from spectrally pure (99.99%) raw materials. The homogenized set was placed in a platinum crucible and melted in an electric furnace at the temperature

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of 1500°C for 30 minutes. The molten glass was poured out onto a brass plate and, then exposed to the process of annealing at 610° for 12 hours. Homogenous and transparent glasses were obtained without visible effect of crystallization. In order to determine spectral properties a series of samples with the dimensions of $6 \times 6 \times 2 \text{ mm}^3$ were prepared. The spectral transmission measurement within the range from 0.3 to 1.1 μm was taken using Stellarnet Green – Wave spectrometer. The glass density was calculated using the method of hydrostatic weighing. The refractive index (@632.8 nm) was determined using a Metricon 2010 refractometer. The characteristic temperatures of the obtained glasses were calculated based on the measurement taken with a SETARAM Labsys thermal analyzer using the DSC method. FTIR spectra were recorded with a Bruker Company Vertex 70v spectrometer. Spectra were collected in the middle infrared regions (MIR) 1400–400 cm^{-1} after 128 scans at 4 cm^{-1} resolution. The luminescence spectra of glasses and optical fibre (end-face pumped) within the range of 300–750 nm were measured at a station equipped with a Stellarnet Green-Wave spectrometer and a pumping laser diode ($\lambda_{\text{exc}} = 405 \text{ nm}$ or $\lambda_{\text{exc}} = 976 \text{ nm}$) with a 0.5 nm resolution. A system PTI QuantaMaster QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (OpotekOpolette 355 LD) was used for luminescence decay measurements. The laser system was equipped with a double 200 mm monochromator, a multi-mode UV-VIS 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 with an accuracy of $\pm 1 \mu\text{s}$. The double-clad optical fibre with off-set of core was fabricated using a modified rod-in-tube technique. Core of the fibre was made by using crucible method. Next, 3 mm diameter hole was mechanically drilled in a lead-silicate glass cylinder – inner cladding (30 mm diameter, $n_{\text{cladding1}} = 1.62$). As an outer cladding was used a borosilicate glass tube ($n_{\text{cladding2}} = 1.51$). Fibre was drawn at a temperature range of 850–920°C. The diameter of the fibre was controlled by monitoring the drawing speed and the feeding of the preform.

3. Results and discussion

3.1. Material and thermal properties

Table 1 presents basic physicochemical and thermal properties of the produced $\text{Yb}^{3+}/\text{Eu}^{3+}$ co-doped germanate glasses.

The fabricated glasses are characterized by high thermal stability which determines their suitability as a material for the construction of optical fibres. A difference $\Delta T = T_x - T_g$ called glass thermal stability factor is determined to be

Table 1. Physical and thermal properties of $75\text{GeO}_2 - 25[\text{GaO} - \text{BaO} - \text{Na}_2\text{O}]$ glass.

Parameter	Value
Refractive index n (@632.8 nm)	1.688
Mass density ρ (g/cm^3)	4.4
Transformation temperature T_g ($^{\circ}\text{C}$) (DSC)	600
Crystallization temperature T_x ($^{\circ}\text{C}$) (DSC)	810
Maximum of phonon energy $\hbar\omega_{\text{max}}$ (cm^{-1})	805

210°C. Moreover, relatively low phonon energy (805 cm^{-1}) enables to effective IR to VIS conversion.

3.2. Up-conversion luminescence and analysis of cooperative energy transfer

Figure 1 presents up-conversion emission spectra of fabricated germanate glasses co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$ ions under excitation by the diode laser with $\lambda_{\text{exc}} = 976 \text{ nm}$ and the optical pump power $P_{\text{exc}} = 1 \text{ W}$. The concentration of Yb_2O_3 was fixed at 0.5 mol%.

The measured up-conversion spectra consist of emission bands at 591, 616, 652 and 701 nm, which correspond to Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively. In fabricated glasses the local symmetry of the RE ion site parameter R defined as the intensity ratio of $I_{616\text{nm}}/I_{591\text{nm}}$ is c.a 3 which indicates that the Eu^{3+} ion site has no inversion centre [19,20]. The maximum intensity of up-conversion luminescence was obtained with the concentration ratio of $0.5\text{Yb}_2\text{O}_3/0.75\text{Eu}_2\text{O}_3$. Above 1.25 mol% of RE the intensity of up-conversion luminescence of all emission bands decreases due to concentration quenching. The possible up-conversion emission mechanism in a germanate glass co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$ is presented in Fig. 1 (inset). Population of Eu^{3+} excited levels is realized in the course of known phenomenon cooperative energy transfer from pair Yb^{3+} ions [19] accordingly to following relation:

It should be noted that emission at 531 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition wasn't observed in the manufactured glass. Figure 2 shows the luminescence decays from the $^2\text{F}_{5/2}$ state of Yb^{3+} ions excited under 976 nm. Luminescence decay analysis clearly indicates that the measured lifetime starts to reduce from 984 μs (0.5% Yb_2O_3) up to 712 μs (0.5% Yb_2O_3 / 1% Eu_2O_3). Decay curve given in semi-logarithmic scale is linear, which proofs single-exponential decay behaviour.

Based on luminescence decay measurements for $^2\text{F}_{5/2}$ state of Yb^{3+} ions in glass samples without and with Eu^{3+}

Fig. 1. Up-conversion luminescence spectra of Yb³⁺/Eu³⁺ co-doped germanate glasses ($\lambda_{exc} = 976$ nm).

ions, the Yb³⁺ → Eu³⁺ energy transfer efficiency was determined. Dependence of ²F_{5/2} (Yb³⁺) lifetime and the energy transfer efficiency with europium concentration is presented in Table 2. Efficiency of the Yb³⁺ → Eu³⁺ energy transfer can be calculated according to the equation

$$\eta = 1 - \frac{\tau_{Yb-Eu}}{\tau_{Yb}}, \quad (2)$$

where: τ_{Yb-Eu} , τ_{Yb} – lifetime of ²F_{5/2} state in Yb³⁺/Eu³⁺ co-doped and Yb³⁺ – singly doped sample, respectively. Efficiency of cooperative Yb³⁺ → Eu³⁺ energy transfer increases with increasing Eu³⁺ concentration up to $\eta = 27\%$ for 1% Eu₂O₃, while maximum UC intensity due to concentration quenching was obtained in 0.5 Yb₂O₃/0.75 Eu₂O₃ co-doped glass.

Table 2. Lifetime of Yb³⁺: ²F_{5/2} level and ET efficiency in glasses co-doped with 0.5Yb₂O₃/(0–1)Eu₂O₃.

Content of Eu ₂ O ₃	Lifetime Yb ³⁺ : ² F _{5/2} (μs)	ET efficiency (%)
0	984	0
0.25	953	3.15
0.5	869	11.67
0.75	744	24.39
1	712	27.64

3.3. Double clad optical fibre co-doped with 0.5Yb₂O₃/0.75Eu₂O₃

Basic parameters of the produced optical fibre were as follows: outer cladding diameter = 300 μm, core diameter = 20 μm, core – offset = 70 μm, $NA_{cladding} = 0.58$, $NA_{core} = 0.44$. Measured by the cutback method ASE signal attenuation at 616 nm is 2.18 dB/m (Fig. 4 – inset) and it is lower

Fig. 2. Luminescence decay curves of Yb³⁺: ²F_{5/2} level in glasses co-doped with, 0.5Yb₂O₃/(0, 0.75)Eu₂O₃.

Fig. 3. Comparison of the luminescence spectra of bulk glass (further fibre core) and DC optical fibre (length of 0.1–5 m) co-doped with 0.5 $\text{Yb}_2\text{O}_3/0.75 \text{Eu}_2\text{O}_3$ [mol%]. (Inset) Cross – section of the end face of the optical fibre.

than in a tellurite and fluoro-germanate optical fibre [21,22]. Due to helical modes of pump radiation offset of the core from the centre of the fibre enables to improve efficiency of optical pumping of the double-clad optical fibre [23]. In the standard double – clad optical fibre a large amount of pump energy do not interact with the core. The possible solutions of that problem concern shaping of cladding or placing the active core with offset. Figure 3 shows normalized up-conversion luminescence spectra and cross-section of the end face of the fabricated bulk glass (further fibre core) and double-clad optical fibre co-doped with 0.5 $\text{Yb}_2\text{O}_3/0.75 \text{Eu}_2\text{O}_3$.

While analysing UC emission of different length of DC optical fibre with bulk glass (further core) significant differences were not observed. $I_{616\text{nm}}/I_{591\text{nm}}$ luminescence intensity ratio (Fig. 4) remains nearly unchanged. In comparison to $\text{Yb}^{3+}/\text{Ho}^{3+}$ or $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped optical fibres where reabsorption of ASE (amplified spontaneous emission) signal affecting the shape of emission spectra takes place, in a produced $\text{Yb}^{3+}/\text{Eu}^{3+}$ – co-doped DC fibre this phenomenon does not occur [22,24]. However, in a glass fibre (0.1m length) UC emission at 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) becomes dominant ($I_{616\text{nm}}/I_{591\text{nm}} = 4.17$).

In this case all pump power is absorbed in a glass fibre structure at a short length, thus transition corresponding to

the highest luminescence band branching ratio starts to be promoted during propagation along the fibre. Figure 5 enables detailed comparison of the down-conversion ($\lambda_{\text{exc}} = 405 \text{ nm}$) and up-conversion ($\lambda_{\text{exc}} = 976 \text{ nm}$) luminescence obtained in the fabricated DC optical fibre co-doped with 0.5 $\text{Yb}_2\text{O}_3/0.75 \text{Eu}_2\text{O}_3$. Up-conversion emission band at 616 nm is slightly red-shifted by 2 nm and FWHM is 5 nm greater (FWHM = 18 nm) than in the same optical fibre Eu^{3+} ions directly excited by 405 nm. Moreover, when visible emission is realized in course of UC process the $I_{616\text{nm}}/I_{591\text{nm}}$ intensity ratio is smaller and equals 3.4 while for $\lambda_{\text{exc}} = 405\text{nm}$ is 4.2. Moreover, in case of $\lambda_{\text{exc}} = 405\text{nm}$ the $I_{616\text{nm}}/I_{701\text{nm}}$ intensity ratio is smaller. Calculated tri-chromatic coordinates (Fig. 5 inset) shows subtle differences in CIE 1931 triangle.

4. Conclusions

In the article thermally stable ($\Delta T = 210^\circ\text{C}$) and low phonon energy (805 cm^{-1}) germanate glass co-doped with $\text{Yb}^{3+}/\text{Eu}^{3+}$ ions were synthesized and used as the core of a double-clad optical fibre. The optimal concentration of rare-earths is 0.5 $\text{Yb}_2\text{O}_3/0.75 \text{Eu}_2\text{O}_3$ (mol.%), which has shown the highest up-conversion emission intensity at 616 nm

Fig. 4. Comparison of the up-conversion luminescence spectra of bulk glass (further fibre core), glass fibre and double-clad optical fibre (length 0.1 m) co-doped with 0.5Yb₂O₃/0.75Eu₂O₃ [mol%] ($\lambda_{\text{exc}} = 976$ nm), ASE attenuation in DC optical fibre (inset).

Fig. 5. Comparison of the luminescence spectra of double-clad optical fibre (length 1 m) co-doped with 0.5Yb₂O₃/0.75Eu₂O₃ pumped by 405 nm and 976 nm, CIE (x, y) chromaticity diagram – the colour coordinates of the luminescence (inset).

($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and 591 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) obtained as a $\text{Yb}^{3+} \rightarrow \text{Eu}^{3+}$ cooperative energy transfer. Calculated on the basis of the analysis of the $\text{Yb}^{3+}:^2\text{F}_{5/2}$ level energy the maximum transfer efficiency is up to 27.6% for 0.5 $\text{Yb}_2\text{O}_3/1$ Eu_2O_3 . Comparison of UC luminescence of bulk glass and different length of optical fibre (up to 5 m) showed no significant differences in shape of the spectrum. However, in a glass fibre (0.1 m length) UC emission at 616 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition becomes dominant. Comparative analysis of the down-conversion ($\lambda_{\text{exc}} = 405$ nm) and up-conversion ($\lambda_{\text{exc}} = 976$ nm) luminescence obtained in the fabricated DC optical fibre co-doped with 0.5 $\text{Yb}_2\text{O}_3/0.75$ Eu_2O_3 showed subtle differences in shape of emission spectra. In relation to down – conversion emission $\lambda_{\text{exc}} = 405$ nm main UC luminescence band is red-shifted by 2 nm and is characterized by 5 nm greater FWHM. The main advantage of UC mechanism in obtaining visible emission is possibility of pumping $\text{Yb}^{3+}/\text{Eu}^{3+}$ co-doped glasses and optical fibres by low cost, high power InGaAs laser diodes. However, it should be noted that $\text{Yb}^{3+} \rightarrow \text{Eu}^{3+}$ cooperative energy transfer is less efficient than other energy transfer mechanisms (e.g., up-conversion energy transfer) and requires low phonon glass host. To summarize, the obtained results show applicability of the produced germanate double-clad optical fibre co-doped with 0.5 $\text{Yb}_2\text{O}_3/0.75\text{Eu}_2\text{O}_3$ in a construction of up-conversion superfluorescent optical fibre sources of radiation operating in the visible spectrum.

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