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

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In the paper the analysis of up-conversion (UC) luminescence in 0.5Yb$_2$O$_3$/(0.25–1)Eu$_2$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$^{3+}$: $^5$D$_0$/$^7$F$_1$, $^5$D$_0$/$^7$F$_2$, $^5$D$_0$/$^7$F$_3$, $^5$D$_0$/$^7$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 (Yb$^{3+}$ → Eu$^{3+}$ energy transfer efficiency $\eta = 24\%$) was obtained in 0.5Yb$_2$O$_3$/0.75Eu$_2$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 Yb$^{3+}$/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 Yb$^{3+}$/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 Yb$^{3+}$/ 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 Yb$^{3+}$/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)GeO$_2$ – 15Ga$_2$O$_3$ – 10BaO –5Na$_2$O – 0.5Yb$_2$O$_3$ /xEu$_2$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...
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°C for 12 hours. Homogeneous 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 × 6 × 2 mm³ 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) 1400–4000 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 (λexc = 405 nm or λexc = 976 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 multimode 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 ±1 μs. The double-clad optical fibre with off-set of core was fabricated using a modified rod-in-tube technique. Core of the fibre and inner cladding (30 mm diameter, ncladding = 1.62). As an outer cladding was used a borosilicate glass tube (ncladding2 = 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 Yb³⁺/Eu³⁺ co-doped germanate glasses.

| Parameter | Value |
|-----------|-------|
| Refractive index n (@632.8 nm) | 1.688 |
| Mass density ρ (g/cm³) | 4.4 |
| Transformation temperature Tg (°C) (DSC) | 600 |
| Crystallization temperature Tc (°C) (DSC) | 810 |
| Maximum of phonon energy hωmax (cm⁻¹) | 805 |

Table 1. Physical and thermal properties of 75GeO₂ – 25[GeO – BaO – Na₂O] glass.

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 Yb³⁺/Eu³⁺ ions under excitation by the diode laser with λexc = 976 nm and the optical pump power Pexc = 1 W. The concentration of Yb₂O₃ 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 Eu³⁺: 5D0 → 7F1, 5D0 → 7F2, 5D0 → 7F3 and 5D0 → 7F4 transitions, respectively. In fabricated glasses the local symmetry of the RE ion site parameter R defined as the intensity ratio of I₀₁₆₆ₙ₄/I₅₉₁ₙ₄ is c.a.3 which indicates that the Eu³⁺ ion site has no inversion centre [19,20]. The maximum intensity of up-conversion luminescence was obtained with the concentration ratio of 0.5Yb₂O₃/0.75Eu₂O₃. 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 Yb³⁺/Eu³⁺ is presented in Fig. 1 (inset). Population of Eu³⁺ excited levels is realized in the course of known phenomenon cooperative energy transfer from pair Yb³⁺ ions [19] accordingly to following relation:

\[
2\times\text{Yb}^{3+}(2F_{5/2}) + \text{Eu}^{3+}(7F_0) \rightarrow 2\times\text{Yb}^{3+}(2F_{7/2}) + \text{Eu}^{3+}(5D_1) \tag{1}
\]

It should be noted that emission at 531 nm corresponding to 5D₀ → 7F₁ transition wasn’t observed in the manufactured glass. Figure 2 shows the luminescence decays from the 4F₉₂ state of Yb³⁺ ions excited under 976 nm. Luminescence decay analysis clearly indicates that the measured lifetime starts to reduce from 984 μs (0.5% Yb₂O₃) up to 712 μs (0.5% Yb₂O₃/1% Eu₂O₃). Decay curve given in semi-logarithmic scale is linear, which proofs single-exponential decay behaviour.

Based on luminescence decay measurements for 4F₉₂ state of Yb³⁺ ions in glass samples without and with Eu³⁺ ions...
ions, the Yb$^{3+}$ → Eu$^{3+}$ energy transfer efficiency was determined. Dependence of $2F_{5/2}$ (Yb$^{3+}$) lifetime and the energy transfer efficiency with europium concentration is presented in Table 2. Efficiency of the Yb$^{3+}$ → Eu$^{3+}$ energy transfer can be calculated according to the equation

$$\eta = 1 - \frac{\tau_{Yb}^{Yb-Eu}}{\tau_{Yb}}$$

where: $\tau_{Yb}^{Yb-Eu}$, $\tau_{Yb}$ – lifetime of $2F_{5/2}$ state in Yb$^{3+}$/Eu$^{3+}$ co-doped and Yb$^{3+}$ – singly doped sample, respectively. Efficiency of cooperative Yb$^{3+}$ → Eu$^{3+}$ energy transfer increases with increasing Eu$^{3+}$ concentration up to $\eta = 27\%$ for 1% Eu$_2$O$_3$, while maximum UC intensity due to concentration quenching was obtained in 0.5 Yb$_2$O$_3$/0.75 Eu$_2$O$_3$ co-doped glass.

Table 2. Lifetime of Yb$^{3+}$: $2F_{5/2}$ level and ET efficiency in glasses co-doped with 0.5Yb$_2$O$_3$/(0–1)Eu$_2$O$_3$.

| Content of Eu$_2$O$_3$ | Lifetime Yb$^{3+}$: $2F_{5/2}$ (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 0.5Yb$_2$O$_3$/0.75Eu$_2$O$_3$

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
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 – cladding 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 Yb2O3/0.75 Eu2O3.

While analysing UC emission of different length of DC optical fibre with bulk glass (further core) significant differences were not observed. I616nm/I591nm luminescence intensity ratio (Fig. 4) remains nearly unchanged. In comparison to Yb3+/Ho3+ or Yb3+/Tm3+ co-doped optical fibres where reabsorption of ASE (amplified spontaneous emission) signal affecting the shape of emission spectra takes place, in a produced Yb3+/Eu3+ - co-doped DC fibre this phenomenon does not occur [22,24]. However, in a glass fibre (0.1m length) UC emission at 616 nm (5D0 → 7F2) becomes dominant (I616nm/I591nm = 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 (λexc = 405 nm) and up-conversion (λexc = 976 nm) luminescence obtained in the fabricated DC optical fibre co-doped with 0.5 Yb2O3/0.75 Eu2O3. 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 Eu3+ ions directly excited by 405 nm. Moreover, when visible emission is realized in course of UC process the I616nm/I591nm intensity ratio is smaller and equals 3.4 while for λexc = 405nm is 4.2. Moreover, in case of λexc = 405nm the I616nm/I701nm 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 (ΔT = 210°C) and low phonon energy (805 cm⁻¹) germanate glass co-doped with Yb3+/Eu3+ ions were synthesized and used as the core of a double-clad optical fibre. The optimal concentration of rare-earths is 0.5 Yb2O3/0.75 Eu2O3 (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%] ($\lambda_{exc} = 976$ 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).
Up-conversion luminescence in germanate glass and double-clad optical fibre co-doped with Yb\textsuperscript{3+}/Eu\textsuperscript{3+} ions

(\textsuperscript{5}D\textsubscript{0}→\textsuperscript{7}F\textsubscript{2}) and 591 nm (\textsuperscript{5}D\textsubscript{0}→\textsuperscript{7}F\textsubscript{2}) obtained as a Yb\textsuperscript{3+}→Eu\textsuperscript{3+} cooperative energy transfer. Calculated on the basis of the analysis of the Yb\textsuperscript{3+}:\textsuperscript{2}F\textsubscript{5/2} level energy the maximum transfer efficiency is up to 27.6\% for 0.5 Yb\textsubscript{2}O\textsubscript{3}/1 Eu\textsubscript{2}O\textsubscript{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 \textsuperscript{5}D\textsubscript{0}→\textsuperscript{7}F\textsubscript{2} transition becomes dominant. Comparative analysis of the down-conversion (\(\lambda_{exc} = 405\) nm) and up-conversion (\(\lambda_{exc} = 976\) nm) luminescence obtained in the fabricated DC optical fibre co-doped with 0.5 Yb\textsubscript{2}O\textsubscript{3}/0.75 Eu\textsubscript{2}O\textsubscript{3} showed subtle differences in shape of emission spectra. In relation to down-conversion emission \(\lambda_{exc} = 405\) 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 Yb\textsuperscript{3+}/Eu\textsuperscript{3+} co-doped glasses and optical fibres by low cost, high power InGaAs laser diodes. However, it should be noted that Yb\textsuperscript{3+}→Eu\textsuperscript{3+} cooperative energy transfer is less efficient that other energy transfer mechanisms (e.g., up-conversion energy transfer) and requires low photon glass host. To summarize, the obtained results show applicability of the produced germanate double-clad optical fibre co-doped with 0.5Yb\textsubscript{2}O\textsubscript{3}/0.75Eu\textsubscript{2}O\textsubscript{3} in a construction of up-conversion superfluorescent optical fibre sources of radiation operating in the visible spectrum.

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