

White Upconversion in $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ Co-Doped Antimony–Germanate Glasses

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In the paper the spectroscopic properties of antimony–germanate glass co-doped with $\text{Yb}^{3+}/\text{Ho}^{3+}$ has been investigated. Fabricated $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped glass is characterised by the emission of simultaneous multicolour upconversion luminescence. Strong blue ${}^1G_4 \rightarrow {}^3H_6$ (Tm^{3+}), green ${}^5F_4 \rightarrow {}^5I_8$ (Ho^{3+}) and red ${}^5F_5 \rightarrow {}^5I_8$ (Ho^{3+}) upconversion emission bands have been measured under 976 nm excitation at room temperature. Influence of molar ratio of active ions and excitation power on the colour coordinates (CIE-1931) have been investigated.

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1. Introduction

Upconversion luminescence (UC) of glasses doped with rare-earth ions has attracted much attention during the last decade due to its potential applications in solid-state lasers, colour displays, optical data storages, photodynamic therapy, and other photonics devices [1–4]. White light emission from material doped with lanthanides based on frequency upconversion process, which can convert near-infrared photons into visible emission via multiphoton processes, has been obtained by use of RE ions, such as $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$, $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Tb}^{3+}$ and $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped systems [5–11].

It is known that glass hosts should possess relatively low phonon energy which makes it possible to obtain high upconversion luminescence efficiency. The germanate glasses are characterised by phonon energy at 850 cm^{-1} . This value is relatively lower than in silicate (1100 cm^{-1}), phosphate (1200 cm^{-1}) or borate (1400 cm^{-1}) glasses. Thanks to this, conversion of excitation processes are more likely to occur with a lower level of power of the radiation pump. However, compared to a group of low-phonon glasses i.e. tellurium or fluoride glasses, antimony–germanium glasses are characterized by shorter lifetime of higher energy levels. As a result, in a glass co-doped with $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ ions, radiative transition in a band corresponding to a red colour becomes dominant [8, 4].

This paper presents optical properties of new antimony–germanate glasses triply doped with ytterbium, thulium and holmium ions. Based on luminescence measurements of the produced glass, emission of white colour resulting in an upconversion process between Yb^{3+} and Tm^{3+} , Yb^{3+} and Ho^{3+} ions has been

observed. By analysing the resulting emission spectrum, CIE colour coordinates were calculated, considering the impact of molar content ratio of the thulium and holmium ions and the power of the optical pump.

2. Experiment

Glasses with molar compositions of $30\text{GeO}_2\text{--}15\text{Sb}_2\text{O}_3\text{--}55[\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2]\text{--RE}$, where RE: $1\text{Yb}_2\text{O}_3\text{--}(0.1, 0.2)\text{Tm}_2\text{O}_3\text{--}(0.2, 0.5)\text{Ho}_2\text{O}_3$ were prepared using high purity (99.99%) compounds. The all mixed powders were melted at 1500°C for 60 to 90 min in a platinum crucible using an electrically heated furnace. The melted glass was poured into preheated brass plate and annealed at 450°C for 12 h to remove thermal strains. Transparent, homogeneous glasses without crystallization was fabricated. Finally, the glass samples were polished in order to carry out the optical measurements.

TABLE

Molar concentration of fabricated antimony–germanate glass.

Glass label	Molar concentration [mol.%]			$\text{Tm}^{3+}/\text{Ho}^{3+}$ ratio
	Yb_2O_3	Tm_2O_3	Ho_2O_3	
A	1	0.1	0.5	0.2
B	1	0.2	0.5	0.4
C	1	0.1	0.2	0.5
D	1	0.2	0.2	1.0

For a better readability, the glass was labeled and the samples studied in this work were presented in Table. The light transmission of samples was performed in the range of $0.3\text{--}1.1\ \mu\text{m}$ by using Stelarnet GreenWave spectrometer. The upconversion luminescence spectra within the range from 400 to 750 nm were measured at a system equipped with a Stelarnet spectrometer and a pump laser diode ($\lambda_{\text{exc}} = 976\text{ nm}$) with an optical fibre output having the maximum optical power $P = 30\text{ W}$.

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The color coordinates were calculated using the CIE 1931 standard.

3. Results

3.1. Absorption spectra

Absorption coefficient spectrum of the antimony-germanate glass co-doped with 1 mol.% Yb₂O₃:0.2 mol.% Tm₂O₃:0.5 mol.% Ho₂O₃ is shown in Fig. 1. In the range from 300 to 1100 nm, two absorption bands of thulium ions correspond with transitions from the ground state ³H₆ to higher energy states ³H₄, ³F₂ (³F₃). The other following absorption bands (¹D₂, ⁵G₅, ⁵G₆, ⁵F_{2/3}, ⁵S₂ (⁵F₄), ⁵F₅, ⁵I₅) are derived from holmium ions. Strong and wide characteristic absorption band at the wavelength of 978 nm is related to the presence of the ytterbium ions.

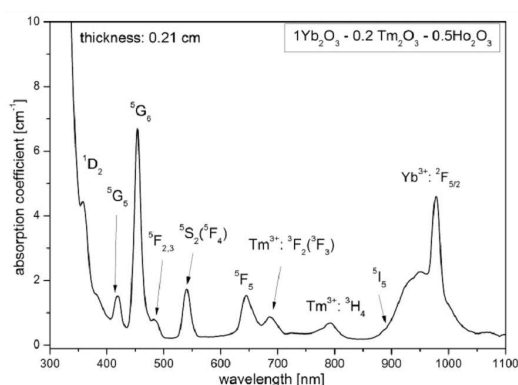


Fig. 1. Absorption spectra of antimony-germanate glass co-doped with 1Yb₂O₃:0.2Tm₂O₃:0.5Ho₂O₃.

Ytterbium ions in co-doped glass act as a donor which transmits an excitation energy to adjacent ions of two acceptors (thulium and holmium) leading to upconversion processes. The proper selection of glass host composition used in the co-doping synthesis assure optical transparency in the range from 350 nm to the near infrared (NIR). This allows to use fabricated glass in fibre structures operating in the range of VIS–NIR.

3.2. Multicolor UC luminescence

Processes of energy transfer between Yb³⁺ and Tm³⁺ [12, 13], Yb³⁺, and Ho³⁺ ions [14] give possibility to obtain white light formed as a result of the spatial composing of emission bands occurring in the structure of thulium and holmium ions. By introducing into the glassy matrix three different rare earth elements and adjusting the ratio of their concentrations, in the luminescence spectra due to radiation excitation with a wavelength of $\lambda_{exc} = 976$ nm, three characteristic emission bands at wavelength of 477 nm (blue), 546 nm (green) and 660 nm (red) have been observed. Figure 2 presents the luminescence spectra of fabricated antimony-germanate glasses triply doped with Yb³⁺,

Tm³⁺ and Ho³⁺ ions. Measured emission was obtained for a four different ratios of acceptors ions (Tm³⁺/Ho³⁺) at constant power of optical pump.

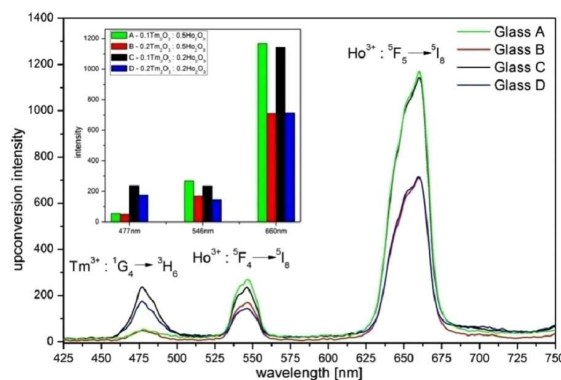


Fig. 2. Upconversion luminescence spectra of antimony-germanate glass triply doped with rare earth ions excited by radiation at 976 nm. Inset — comparison of luminescence spectra of different molar ratio of Tm³⁺/Ho³⁺ ions.

Based on spectroscopic measurements, it was observed that the glass A, in which the ratio of Tm³⁺/Ho³⁺ equal to 0.2 is characterized by strong luminescence within the wavelengths band of 660 nm and 546 nm, corresponding respectively to the ⁵F₅ → ⁵I₈ and ⁵F₄ → ⁵I₈ transitions in the structure of holmium ions. Double increase in the content of thulium ions in the glass B at the concentration of 0.2Tm₂O₃:0.5Ho₂O₃ causes halve reduction in the intensity of the emission band corresponding to the ⁵F₅ → ⁵I₈ (Ho³⁺) transition at almost certain level of the emission at the wavelength of 477 nm (¹G₄ → ³H₆ (Tm³⁺)). Increase of activators concentration for glass B influences on the luminescence quenching. It is associated with higher interaction between two acceptors, which lead to fast exchange of energy between Tm³⁺ → Ho³⁺ at lower metastable levels, thereby limiting the energy transfer processes with upconversion [15].

However, in the glass C decrease of the molar content of Ho³⁺ ions leads to the intensity increasing simultaneously in the band with the wavelength of 477 nm corresponding to the ¹G₄ → ³H₆ transition (Tm³⁺) and in the band at the wavelength of 660 nm corresponding to the ⁵F₅ → ⁵I₈ (Ho³⁺) transition. Ultimately, a selection of equal content of both activators of 0.2 mol.% (glass D) allows reduction of the luminescence intensity at the wavelength of 660 nm with a relatively constant input of the other two emission bands at the wavelengths of 477 nm and 546 nm.

Figure 3 presents the shape of luminescence spectra of the glass doped with a molar composition 1Yb₂O₃:0.2Tm₂O₃:0.2Ho₂O₃ at different power of the optical pump. On the basis of the dependence: $I_{UP} \propto I_{IR}^m$, the relation between luminescence intensity of upconversion I_{UP} as a function of the power of infrared radiation I_{IR} has been defined. The m determines the amount of pho-

tons of the optical pump used in the conversion of excitation process which occurs in a given structure of energy levels of the RE elements.

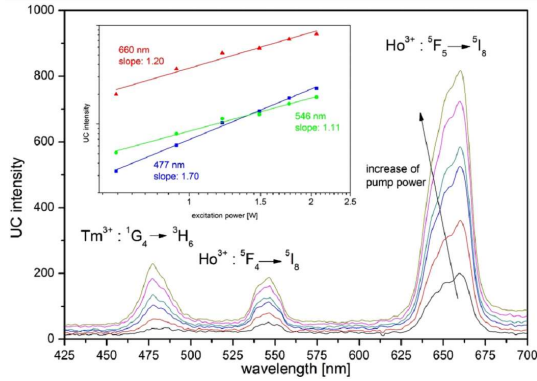


Fig. 3. Upconversion emission spectra of glass sample D under different pump power at the wavelength of 976 nm. Inset — dependence of UC intensity on excitation power.

Dependence of the luminescence intensity of upconversion to the power of the radiation pump is presented within Fig. 3. The fitted slopes for the 477, 546 and 660 nm transitions calculated for the antimony–germanate glass are 1.70, 1.11, and 1.20, respectively. Based on the obtained values it was defined that in both cases $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$ and $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ upconversion mechanism has two-photon nature. However, the higher efficiency of the energy transfer process with upconversion is observed at the ${}^1G_4 \rightarrow {}^3H_6$ transition in the structure of Tm^{3+} ions. In most glasses described in a literature the upconversion mechanism between ytterbium and thulium ions is known and has three-photon nature [15, 16]. However, in produced antimony–germanate glasses besides conversion of excitation also processes of energy transfer between Tm^{3+} and Ho^{3+} ions occur. To better understand phenomena occurring in the produced glass, possible mechanisms of transitions resulting from photon excitation at the wavelength of 976 nm is presented in Fig. 4.

In the first step the ytterbium ions absorb the pump energy, which then is transferred to the adjacent acceptors in the non-radiative decay assisted by phonons: $\text{Yb}^{3+} ({}^2F_{5/2}) \rightarrow \text{Tm}^{3+} ({}^3H_5) \rightarrow \text{Tm}^{3+} ({}^3F_4)$ and $\text{Yb}^{3+} ({}^2F_{5/2}) \rightarrow \text{Ho}^{3+} ({}^5I_6) \rightarrow \text{Ho}^{3+} ({}^5I_7)$. Due to the fact that the energy difference between the 5I_6 energy levels of holmium ions and ${}^2F_{5/2}$ (Yb^{3+}) is lower than in the 3H_5 (Tm^{3+}) level, the efficiency of the $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer is greater which in turn leads to the rapid population of the 5F_5 level and to the emission at the wavelength of 660 nm. A small energy difference between 5F_5 (Ho^{3+}) and ${}^3F_{2,3}$ (Tm^{3+}) levels allows the transition of the portion of ions accumulated in the quasi-resonant $\text{Ho}^{3+} \rightarrow \text{Tm}^{3+}$ energy transfer and fast multi-phonon relaxation to the 3H_4 (Tm^{3+}) level. Subsequently, as a result of the absorption of another photon

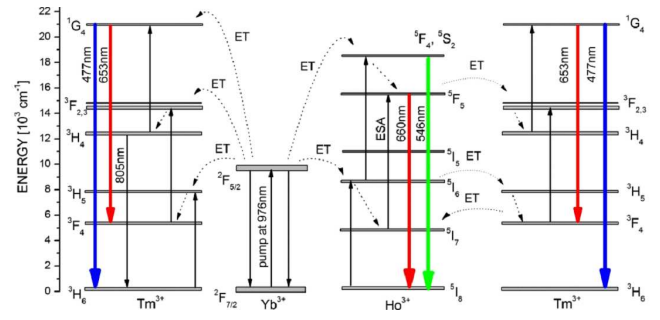


Fig. 4. Energy level diagram of Yb^{3+} , Tm^{3+} , and Ho^{3+} ions with possible upconversion energy transfers in antimony–germanate glass under 976 nm laser excitation.

of the pump the energy transfer occurs with upconversion and ions are transferred to the 1G_4 level from which relax by photon transition at the wavelengths of 477 nm and 653 nm. As a result, populating the $(\text{Tm}^{3+}){}^1G_4$ level occurs in the two-photon process in accordance with the scheme: $\text{Yb}^{3+} ({}^2F_{5/2}) \rightarrow \text{Ho}^{3+} ({}^5I_6) \rightarrow \text{Tm}^{3+} ({}^3H_4) \rightarrow \text{Tm}^{3+} ({}^1G_4)$. Furthermore, high total concentration of lanthanide ions ($\approx 3.6 \times 10^{20}$ ion/cm³) which was obtained in the glass increases the probability of the energy exchange between thulium and holmium ions.

3.3. Color coordinate analysis of upconversion luminescence

In order to determine the chromatic coordinates of the glass doped with Yb^{3+} , Tm^{3+} , and Ho^{3+} ions at various concentrations and pump power, CIE 1931 colour model was used. Based on the spectra distribution of luminescence, which was obtained from spectroscopic measurements, colour coordinates were calculated as followed:

$$x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z},$$

$$z = \frac{Z}{X + Y + Z}, \quad (1)$$

where X , Y , and Z are the three tristimulus values. They can be determined from the spectrum power distribution $P(\lambda)$ described for each component as follows:

$$X = \int_{380}^{780} P(\lambda) \bar{x}(\lambda) d\lambda, \quad Y = \int_{380}^{780} P(\lambda) \bar{y}(\lambda) d\lambda,$$

$$Z = \int_{380}^{780} P(\lambda) \bar{z}(\lambda) d\lambda, \quad (2)$$

where λ is a wavelength corresponding to the monochromatic colour of light, and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are colour-matching functions. Figure 5a presents obtained tri-chromatic coordinates appropriate for antimony–germanium glasses co-doped with ytterbium, thulium, and holmium ions at different ratio of Tm^{3+} to Ho^{3+} . Based on performed calculations for the glass doped with a molar composition: $1\text{Yb}_2\text{O}_3:0.2\text{Tm}_2\text{O}_3:0.2\text{Ho}_2\text{O}_3$ calculated tri-chromatic coordinates are as follows: $x =$

0.4075 and $y = 0.3522$ and are the most closely similar to the coordinates of white light of the illuminate C ($x_C = 0.310$ and $y_C = 0.316$).

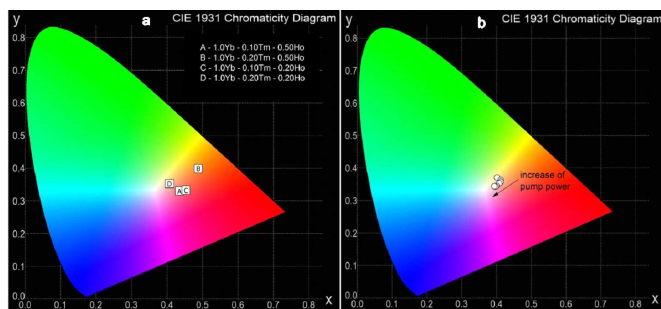


Fig. 5. CIE (x, y) chromacity diagram indicating the color coordinates of the multicolor upconversion emission of the $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ ions co-doped antimony-germanate glass (a). Color tunability of the sample of glass D (b).

In addition, by exciting glass with different optical pump power the effect of light colour tuning which is resulting from several upconversion processes that have occurred. A power increase leads to shifts of colour components towards the centre of the CIE 1931 triangle (Fig. 5b). When the value $P = 2$ W, tri-chromatic coordinates were, respectively, $x = 0.3934$ and $y = 0.3433$. Based on the results it was concluded that in fabricated glasses a practical realization of tuneable white light source is possible, based on energy transfer processes with upconversion between ytterbium, thulium, and holmium ions.

4. Conclusions

In the research the thermally stable antimony-germanium glasses co-doped with $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ ions were synthesized and characterized. By introducing into the glassy matrix simultaneously three activator ions luminescence spectrum consisting three emission bands at the wavelengths of 477 nm (blue), 546 nm (green), and 660 nm (red), respectively, was obtained as a result of optical pumping ($\lambda_{\text{exc}} = 976$ nm). Analysing the results of spectroscopic measurements it was shown that it is possible to obtain luminescence spectrum formed as a result of the spatial composing of emission bands with different wavelengths. The slopes resulting from linear composition of emission transitions at the wavelengths of 477, 546, and 660 nm, were, respectively, 1.70, 1.11, and 1.20. It was determined that in both cases of the $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$ and $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfers, the upconversion mechanism has two-photon nature. Furthermore,

in accordance with calculations for the glass doped with the molar system $1\text{Yb}_2\text{O}_3:0.2\text{Tm}_2\text{O}_3:0.2\text{Ho}_2\text{O}_3$, characterized by the emission of white light, tri-chromatic coordinates were calculated: $x = 0.4075$ and $y = 0.3522$.

In obtained glasses a practical realisation of tuneable source of white emission using energy transfer processes with upconversion between ytterbium, thulium, and holmium ions is possible. Furthermore, the antimony-germanium glass can be used in fibre structures operating in the range of VIS–NIR.

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