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Low-phonon RE-doped Glasses for Multicolor Upconversion Luminescence

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ABSTRACT

In this work the spectroscopic properties of two different glass systems co-doped with $Yb^{3+}/Tm^{3+}/Ho^{3+}$ ions: tellurite (TeO_2 - ZnO - Na_2O) and germanate (GeO_2 - Sb_2O_3 - SiO_2) were compared. Multicolour luminescence spectra with three characteristic emission bands at 479 nm (blue), 546 nm (green) and 650 nm (red) have been observed by NIR (λ_{exc}=976nm) to visible energy conversion. Difference between the shape of upconversion (UC) luminescence showed that in fabricated glasses the energy transfer mechanisms between donor (Yb^{3+}) and acceptor (Tm^{3+}/Ho^{3+}) ions strongly depends on phonon vibration of glass-forming elements. Influence of acceptor ions ratio (Tm^{3+}/Ho^{3+}) and molar concentration of donor ions on the chromaticity coordinates (CIE-1931) have been investigated. White colour emission for the chromaticity coordinates equals x = 0.355 and y = 0.327 in germanate glass co-doped with $0.5Yb_2O_3$: $0.1Tm_2O_3$: $0.2Ho_2O_3$ was observed.

Keywords: photonic glasses, upconversion luminescence, RE ions, white emission.

INTRODUCTION

Nowadays, white light emission from materials doped with lanthanides based on upconversion process, which convert near-infrared photons into visible emission via multiphoton absorption processes have been obtained in rare-earth (RE) co-doped systems, such as $Yb^{3+}/Er^{3+}/Tm^{3+}$, $Yb^{3+}/Tm^{3+}/Tb^{3+}$ and $Yb^{3+}/Tm^{3+}/Ho^{3+}$ [1-8]. It should be noted that the efficiency of upconversion process is strongly dependent on the type of the glassy matrix, particularly to phonon energy. If the maximum vibration frequency of the lattice $h\omega_{max}$ is lower, the probability of upconversion is higher. Photonic glasses with low phonon energy such as fluoride [9] and HMO (Heavy Metal Oxide) [10], whose phonon vibrations energy (300-600 cm^{-1}) preclude the occurrence of non-radiative transitions are good candidate to former requirement. Unfortunately, low mechanical and environment resistance make it difficult to use those kinds of glasses in free-space optical applications. These problems can be overcome by using tellurite- or germanate-based glasses.

Tellurite glasses have relatively low phonon energy (750cm^{-1}), and exhibit better environment resistance. Additionally, such glasses are characterized by a high capacity for dissolving rare earth elements. Moreover, the refractive index (n~2) allows to obtain large values of absorption and emission cross-section coefficients, as well as longer lifetime on exited laser levels [11-15]. Other kind of materials which can be useful for the effective conversion of infrared to visible radiation are germanate glasses characterised also by good solubility of lanthanide ions [11, 16-20] and relatively low phonon energies (850 cm^{-1}). It is derived from the reason that high concentration of RE ions (donor and acceptor) ensure efficient optical pump absorption, energy transfer and in result emission from acceptor ions.

In this paper the optical properties of two glass systems: TeO_2 - ZnO - Na_2O and GeO_2 - Sb_2O_3 - SiO_2 co-doped with $Tm^{3+}/Ho^{3+}/Yb^{3+}$ ions were presented. Multicolour emission resulting from up-conversion and energy transfer mechanisms between $Yb^{3+}\rightarrow Tm^{3+}$ and $Yb^{3+}\rightarrow Ho^{3+}$ have been obtained under excitation at 976 nm. According to analysis of luminescence spectra, CIE colour coordinates were calculated.

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EXPERIMENTAL

A two different glasses were prepared from special high purity agents (99.99%). Homogenous sets of glass sample with molar composition (TZN): TeO_2-ZnO-Na_2O and (GSS): GeO_2-Sb_2O_3-SiO_2 were melted at 900°C and 1350°C for 60 min. in a platinum crucible using an electrically heated furnace, respectively. Next a fused glass was poured into brass plate and annealed near to glass transition temperature (T_g) for 12 h. Homogenous and transparent glasses were obtained without visible effect of crystallization. For a better readability, the glass was labelled and the samples studied in this work were presented in Table 1. The optical density of fabricated glass samples were measured in the range of 350 – 1100 nm by using Stellarnet spectrometer with Si detector. The upconverison luminescence spectra in the wavelength range of 400 to 750 nm was measured with Stellarnet spectrometer under 976 nm excitation.

Table1. *Molar Concentration and Ratio of Rare Earth Ions Doped Fabricated Glasses*

Glass label	Molar concentration [mol%]			Tm_2O_3/ Ho_2O_3 ratio
	Yb_2O_3	Tm_2O_3	Ho_2O_3	
TZN_1	0.5	0.25	0.125	2
TZN_2	0.5	0.125	0.25	1/2
GSS_1	0.5	0.1	0.2	1/2
GSS_2	1	0.1	0.2	1/2

RESULTS AND DISSCUSSION

Optical Density of Glasses

Figure1 shows the optical density spectra of tellurite (TZN) and germanate (GSS) glasses co-doped with $Yb^{3+}/Tm^{3+}/Ho^{3+}$ ions. In the range of 350 - 1100 nm five absorption bands of holmium ions originating from $^5I_8 \rightarrow {}^5G_5$, $^5G_6$, $^5F_3$, $^5F_5$, transitions were localized. Other three absorption bands are derived from thulium ions corresponding to transitions from $^3H_6$ state to $^1G_4$ $^3H_4$, $^3F_{2,3}$ states. Characteristic strong and wide absorption band at the wavelength of 978 nm is a result of $^2F_{7/2} \longrightarrow {}^2F_{5/2}$ transition in ytterbium structure. In both glasses the position of maximum absorption bands was similar. Due to different glass-forming elements in the tellurite glasses the absorption edge is slightly red-shifted, which is correlated with structural vibrations of Te-O bonds [11].

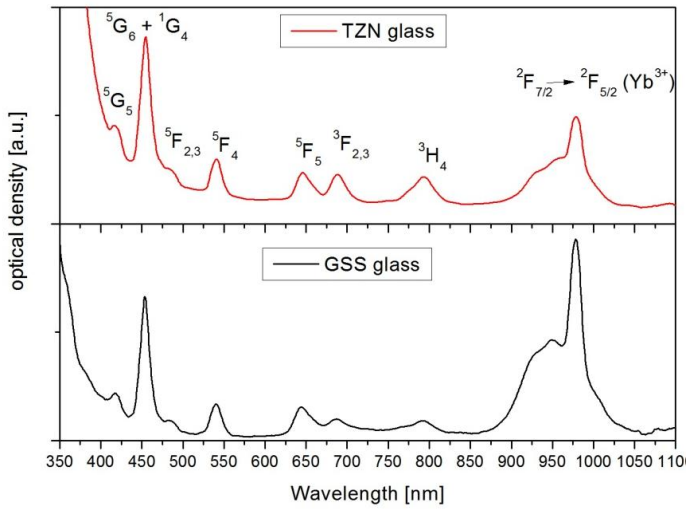

Figure1. *Optical density spectra of fabricated glasses: tellurite (red line) and germanate (black line) co-doped with $Yb^{3+}/Tm^{3+}/Ho^{3+}$ ions.*

In this RE ions systems, Yb^{3+} ions act as a effective sensitizer of excitation energy from IR radiation at the wavelength of 976nm. This phenomenon enables to occurrence of upconversion processes between $Yb^{3+} \rightarrow Tm^{3+}$ and $Yb^{3+} \rightarrow Ho^{3+}$ ions.

Upconversion luminescence

Figure 2 presents the luminescence spectra of fabricated tellurite and germinate glasses co-doped with $Yb^{3+}/Tm^{3+}/Ho^{3+}$ ions. Introducing into the glassy matrix three different RE elements and adjusting the

ratio of their concentrations we can optimize the shape of UC luminescence bands. Multicolour luminescence spectra with three characteristic emission bands at 479 nm (blue), 546 nm (green) and 650 nm (red) have been observed by NIR (λ_{exc}=976nm) to visible energy conversion. Correct proportion of intensity of each luminescence bands is necessary to obtain a white colour emission. It is worth to note that in fabricated glasses these proportions are quite different. In the case of tellurite glasses the strongest emission band for green colour was observed. Blue and red colour bands were characterized by almost the same intensity for glass TZN_2. For glass labelled as TZN_1 changing the concentration ratio Tm/Ho to 2 the blue emission band strongly decrease.

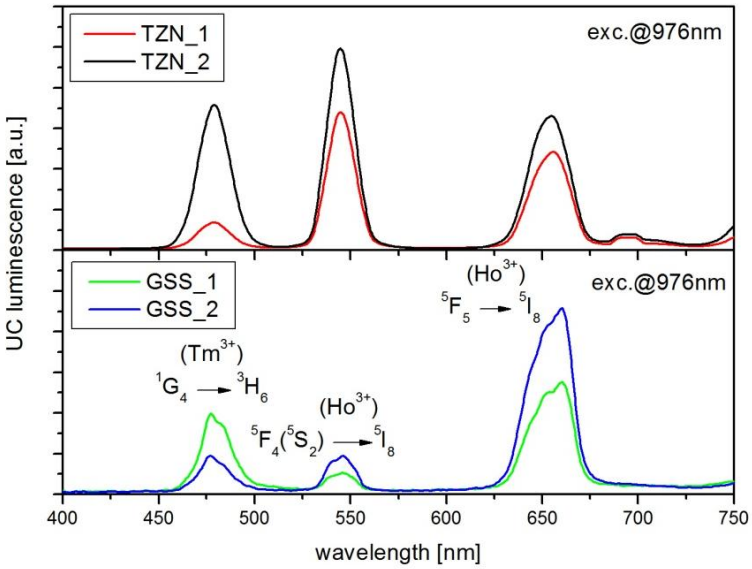

Figure2. *Comparison of up-conversion luminescence spectra of tellurite and germanate glasses co-doped with rare earth ions excited at 976 nm.*

In both germanate glass samples the strongest emission for red colour were observed. In opposite to tellurite glass the green colour band originating from $^5F_4(^5S_2) \rightarrow {}^5I_8$ transition, is characterized by the lowest level of UC luminescence. Increasing of donor ions concentration up to 1mol% Yb_2O_3 leads to strong quenching of blue emission band (GSS_2). Simultaneously, green and red emission bands were enhanced. Different mechanisms of UC processes in fabricated glasses confirmed that transfer of excitation energy between donor (Yb^{3+}) and acceptors (Tm^{3+}, Ho^{3+}) ions dependents on type of glass structure.

CIE Coordinates

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 spectral distribution of luminescence, which was obtained from spectroscopic measurements, colour coordinates were calculated as follows:

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z} \tag{1}$$

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

$$\mathbf{X} = \int_{380}^{780} \mathbf{P}(\boldsymbol{\lambda})\bar{\mathbf{x}}(\boldsymbol{\lambda})\mathbf{d}\,\boldsymbol{\lambda} \quad \mathbf{Y} = \int_{380}^{780} \mathbf{P}(\boldsymbol{\lambda})\bar{\mathbf{y}}(\boldsymbol{\lambda})\mathbf{d}\,\boldsymbol{\lambda} \quad \mathbf{Z} = \int_{380}^{780} \mathbf{P}(\boldsymbol{\lambda})\bar{\mathbf{z}}(\boldsymbol{\lambda})\mathbf{d}\,\boldsymbol{\lambda} \tag{2}$$

Where: λ is a wavelength corresponding to the monochromatic colour of light, and $\bar{\mathbf{x}}(\boldsymbol{\lambda})$, $\bar{\mathbf{y}}(\boldsymbol{\lambda})$ **and** $\bar{\mathbf{z}}(\boldsymbol{\lambda})$ are colour-matching functions. Figure 3 presents obtained tri-chromatic coordinates appropriate for tellurite (TZN_1 and TZN_2) and germanate (GSS_1 and GSS2) glasses co-doped with ytterbium, thulium and holmium ions at different ratio of rare-earths.

Based on performed calculations for the tellurite glass doped with $0.5Yb_2O_3$: $0.25Tm_2O_3$: $0.125Ho_2O_3$ (TZN_1) calculated tri-chromatic coordinates are as follows: x = 0.333 and y = 0.534 and are located in green region. Changing of molar ratio between Tm^{3+} and Ho^{3+} ($0.125Tm_2O_3$: $0.25Ho_2O_3$ (TZN_2)) tri-chromatic coordinates equals: x = 0.270 and y = 0.435 and the colour point was shifted to the

centre of CIE diagram, but is still green. In case of germanate glass samples labelled as GSS_1 the chromaticity coordinates are x = 0.355 and y = 0.327 and they are the most closely similar to the coordinates of white light of the illuminate C (x_C = 0.310 i y_C = 0.316). Increasing of Yb_2O_3 concentration up to 1mol% leads to shift of chromaticity coordinates to red region of CIE diagram. Based on the results it was concluded that changing of acceptor ions ratio (Tm^{3+}/Ho^{3+}) and molar concentration of donor ions in fabricated glasses enables to practical realization of white light generation from energy transfer with upconversion between ytterbium, thulium and holmium ions.

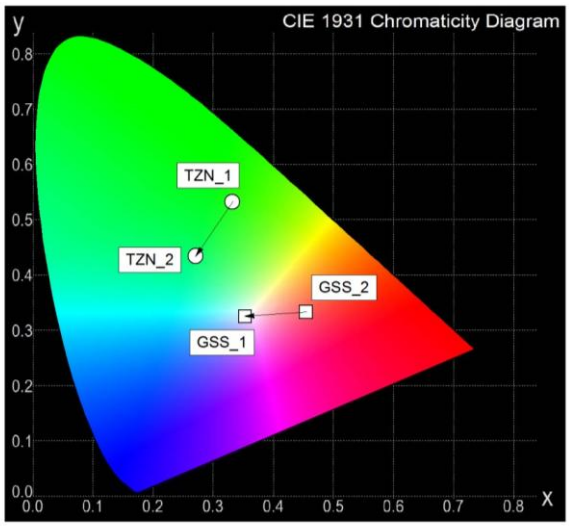

Figure3. *CIE (x, y) chromacity diagram of fabricated tellurite and germinate glasses.*

CONCLUSION

In the article two different glasses: tellurite (TeO_2-ZnO-N_2O) and germanate (GeO_2-Sb_2O_3-SiO_2) co-doped with $Yb^{3+}/Tm^{3+}/Ho^{3+}$ ions were synthesized by melt-quenching technique. As a results of near infrared excitation at 976 nm multicolour emission bands were measured at the wavelengths of 479 nm, 545nm and 650nm corresponding to transitions $^1G_4 \rightarrow {}^3H_6$ (Tm^{3+}), $^5F_4(^5S_2) \rightarrow {}^5I_8$ and $^5F_5 \rightarrow {}^5I_8(Ho^{3+})$, respectively. Analysing the results of spectroscopic measurements it was shown that it is possible to obtain white luminescence spectrum formed as a result of the spatial composing of emission bands with different wavelengths. Different mechanism of UC processes observed in fabricated glasses confirmed that transfer of excitation energy between donor (Yb^{3+}) and acceptors (Tm^{3+}, Ho^{3+}) ions dependents on type of glass structure. In tellurite glass the strongest emission of UC luminescence at green band was observed when in germanate glass the maximum upconversion signal have been observed at red colour. Furthermore, in accordance with calculations of CIE coordinates, the germanate glass co-doped with the molar system $0.5Yb_2O_3$: $0.1Tm_2O_3$: $0.2Ho_2O_3$, is characterized by emission of white light and tri-chromatic coordinates were x = 0.355 and y = 0.327. The results of experiment indicate that the fabricated photonic glasses are promising materials for white light generators.

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