Optical and Acoustical Methods in Science and Technology

Nd^{3+}/Yb^{3+} Doped Phosphate and Antimony Glasses for Optical Fibre Source

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In the article there are presented two different series of glass: fluorophosphate with molar composition: $65P_2O_5$–$8Al_2O_3$–$2BaO$–$5BaF_2$–$6ZnF_2$–$5Na_2O$–$6MgF_2$–$3B_2O_3$ and antimony glasses $40Sb_2O_3$–$3Al_2O_3$–$57SiO_2$ doped with Nd^{3+} and Yb^{3+} ions. Dopant contents influence efficient spatial overlapping of emission level for neodymium and absorption level for ytterbium was analyzed. While exciting the produced glasses with a laser diode ($\lambda = 808$ nm) a broad luminescence spectrum ($\Delta\lambda = 100$ nm) has been obtained in both cases in the vicinity of 1 μm, being the superposition of the following transitions: ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ for Nd^{3+} and ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ for Yb^{3+}. Based on the luminescence measurements the probability of non-radiative energy transfer was described. Because of a small difference in energy (≈ 1190 cm^{-1}) between the laser levels of neodymium and ytterbium the resonant process of energy transfer has been obtained.

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1. Introduction

Research on special optical glasses doped with lanthanide ions have been conducted for several years in order to improve their physicochemical and spectroscopic properties. Nd^{3+} and Yb^{3+} ions are one of the best examined rare-earth elements used in double-clad fibre lasers. Nd^{3+}/Yb^{3+} systems excited with high-energy semiconductor diodes, characterised by radiation emission of approximately 1 μm [1, 2], are applied as compact sources in non-linear microscope technology [3], in image processing with THz frequency [4], or for exciting ultrafast optical amplifiers [5]. More and more often, beside commonly used silicate glasses [6] new multicomponent glasses based on phosphorus [7] or antimony [8] compounds are applied. The ultrahigh spectral transmission (> 98%), a low level of non-linear refractive index and good mechanical stability make phosphate and antimony glasses serious competitors for silicate glasses [9].

High quantum efficiency, long fluorescence lifetime, and strong stimulated emission, which are typical of phosphate glasses are the reasons for using these matrices as active media in ultrafast solid-state lasers [10]. Moreover, Nd^{3+}-doped metaphosphate glasses are excellent materials applied in high-power CW laser systems (of the order of a few kJ) and impulse laser systems (of a few TW) [11]. Introducing a fluoride compound into the oxide glass matrix enables to reduce the bond energy, allowing at the same time to use high concentrations of rare-earth ions [12]. However, an excessive amount of fluoride particles breaks strong P–O–P bonds, which results in reducing the mechanical resistance of fluorophosphate glasses and in the increase of the probability of crystallization.

Sb_2O_3-based oxide glasses characterised by high mechanical and thermal stability are an alternative solution [8]. The low energy of the lattice (≈ 605 cm^{-1}) influences the appearance of non-linear effects, thus deteriorating laser parameters of Nd^{3+}-doped glasses [13]. Combining two glass-forming elements with radically different levels of oscillatory vibrations of covalent bonds brings about the rise in the efficiency of energy transfer between activator ions, minimizing at the same time non-linear effects [14].

The article presents findings of the author's research on material and optical properties of two types of glasses, i.e. fluorophosphate and antimony glasses. Both matrices have been doped with the Nd^{3+}/Yb^{3+} ion system and the mechanism of energy transfer between rare-earth ions has been discussed.

2. Experimental

Two series of glasses co-doped with Nd^{3+}/Yb^{3+} ions were prepared from special high purity agents (99.99%). Homogeneous set of fluorophosphate glass sample with molar composition: $(63.85–x)P_2O_5$–$8Al_2O_3$–$2BaO$–$5BaF_2$–$6ZnF_2$–$5Na_2O$–$6MgF_2$–$3B_2O_3$–$0.15Nd_2O_3$–xYb_2O_3 ($x = 0.15$, 1.5) was melted at 1350 °C for 60 to 90 min in a platinum crucible using an electrically heated furnace. Analogically, the glass system: $(56.85–x)SiO_2$–$3Al_2O_3$–$40Sb_2O_3$–$0.15Nd_2O_3$–xYb_2O_3 ($x = 0.15$, 0.45) was melted at 1600 °C for 1 h. In both cases fused glasses were poured into brass form

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and annealed near to glass transition temperature (T_g) for 12 h to remove thermal strains. Homogeneous and transparent glasses were obtained without visible effect of crystallization. The glass density, ρ, was calculated using the method of hydrostatic weighing. The refractive indices of the samples at 633 nm were recorded on a Metricon 2010 by means of a prism coupling method. The light transmission of fabricated samples with 10 mm diameter and 3 mm thickness was performed in the range of 0.4–1.1 μm by using Acton Spectra Pro 2300i monochromator with InGaAs detector. The characteristic temperatures of the obtained glasses were calculated based on the measurement taken with a SETARAM Labsys thermal analyzer using the differential scanning calorimetry (DSC) method. The luminescence spectrum within the range from 800 to 1400 nm was measured at a station equipped with an Acton Spectra Pro 2300i spectrometer and a laser diode (λ_p = 808 nm) with an optical fibre output having the maximum optical power P = 31 W. The produced glasses have been analysed as far as the impact of the matrix type on the energy transfer process between Nd^{3+} ions of the donor and Yb^{3+} ions of the acceptor is concerned.

3. Results and discussion

Table compares physicochemical parameters of the produced glasses doped with Nd^{3+} and Yb^{3+} ions, silicate glasses [15] and high silica glass (HSG) [16]. Light transmission in the visual spectrum and in the near-infrared region is at the level of 96%, which has a significant influence on the pumping efficiency and the energy transfer between active dopants.

TABLE

The physicochemical parameters of glasses doped with Nd^{3+} and Yb^{3+}.

Glass	n_d	ρ [g/cm^3]	$\bar{M}$ [g/mol]	$N_{Yb} + N_{Tm}$ [10^{20} ions/cm^3]	R [Å]	T_g [°C]
fluorophosphate	1.529	2.86	131.65	4.32	8.20	500
antimony	1.699	3.59	155.82	1.66	11.29	527
silicate [15]	1.615	3.85	109.13	2.38	10.02	448
HSG [16]	1.462	1.98	61.71	0.72	14.91	–

Moreover, the main advantage of the formed glasses is their high thermal stability determined by DSC measurement. The obtained fluorophosphate and antimony glasses are characterised by good mechanical and chemical properties. Due to the application of fluoride compounds fluorophosphate glasses enable to use high concentrations of activator ions ($\approx 4 \times 10^{20}$ ions/cm^3) without a visible effect of demixing and crystallization. While comparing the produced antimony glasses to silicate glasses [12, 15] it has been observed that due to the low phonon energy (≈ 605 cm^{-1}) their matrix is characterised by a low level of oscillatory vibrations in Sb–O–Sb bonds [13], which brings about the rise in the energy transfer efficiency between ions even when the concentration of activators is lower (Table).

3.1. Absorption coefficient

Based on spectral transmission the absorption coefficient spectrum of the obtained glass doped with Nd^{3+} and Yb^{3+} ions (Fig. 1) has been calculated. Introducing two different activators to the matrix at the same time leads to complication of the energy structure and division of the pumping radiation quantum by means of energy transfer between the donor and the acceptor. It has been observed that fluorophosphate glass due to a high molar concentration of Yb_2O_3, is characterised by a strong absorption of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition at the wavelength of $\lambda = 978$ nm. Absorption bands resulting from the complex structure of neodymium corresponding to the following transitions: $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^4F_{5/2}$, $^2H_9$, $^4F_{3/2}$ are similar for both glasses.

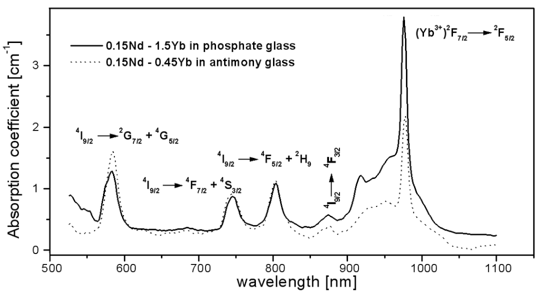

Fig. 1. Absorption coefficient spectra for Nd^{3+}/Yb^{3+} co-doped fluorophosphate (solid line) and antimony (dotted line) glasses.

From the standpoint of efficient pumping at wavelength 805 nm of the $^4I_{9/2} \rightarrow {}^4F_{5/2}$ transition it is important to use as the excitation sources the high power semiconductor laser diodes AlGaAs. Almost the same absorption level of the $^4I_{9/2} \to ^4F_{5/2}$ transition in both hosts has allowed for analysis the type of lattice influence on the energy transfer efficiency between $Nd^{3+} \to Yb^{3+}$.

3.2. Analysis of cross-sections for neodymium and ytterbium co-doped glasses

Based on the absorption spectrum the active cross-section to the absorption of ytterbium $\sigma_{abs(Yb)}$ at the wavelength of 975 nm corresponding to the $^2F_{7/2} \to ^2F_{5/2}$ transition has been calculated by means of the following relation [17]:

$$\sigma_{abs}(\lambda) = \frac{2.303\log(1/T(\lambda))}{Nl}, \quad (1)$$

where N — ion concentrations of Nd^{3+} or Yb^{3+}, l — sample thickness.

Using the McCumber method [18] the active cross-section to the emission for the ion of neodymium $\sigma_{em(Nd)}$ at the wavelength of 878 nm has been determined

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda)\exp\left(\frac{\varepsilon - hc\lambda^{-1}}{kT}\right). \quad (2)$$

ε can be calculated by the expression

$$\exp(\varepsilon/kT) = 1.1\exp(E_0/kT), \quad (3)$$

where E_0 — energy gap between the lowest multiplets of $^4F_{3/2}$ and $^4I_{9/2}$ levels.

Figures 2 and 3 show the curve of the active cross-section to the absorption of ytterbium corresponding to the $^2F_{7/2} \to ^2F_{5/2}$ transition and the curve of the active cross-section to the emission of neodymium corresponding to the $^4F_{3/2} \to ^4I_{9/2}$ transition for two types of matrices. A high concentration of ytterbium ions in fluorophosphate glasses doped with 0.15%molNd_2O_3 : 1.5%molYb_2O_3 leads to a good spectral matching of active cross-sections $\sigma_{em(Nd)} \approx \sigma_{abs(Yb)}$, which facilitates obtaining an evenly broad luminescence spectrum. Moreover, because of a small distance between dopant ions (R), the probability of energy transfer between $Nd^{3+} \to Yb^{3+}$ ions is higher.

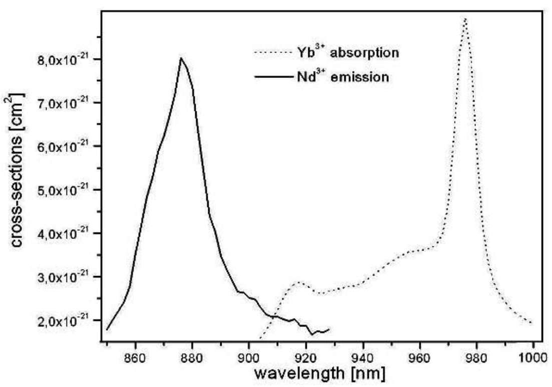

Fig. 2. Overlap of the emission cross-section of Nd^{3+} and absorption cross-section of Yb^{3+} for fluorophosphate glasses doped with 0.15%molNd_2O_3 : 1.5%molYb_2O_3.

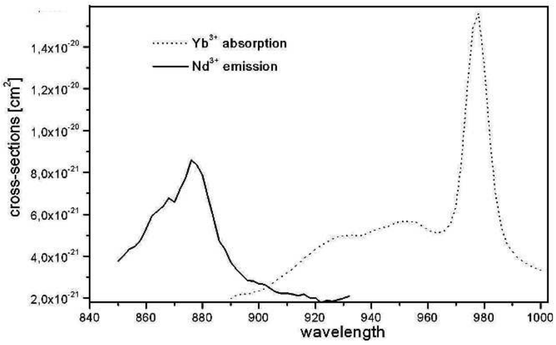

Fig. 3. Overlap of the emission cross-section of Nd^{3+} and absorption cross-section of Yb^{3+} for antimony glasses doped with 0.15%molNd_2O_3 : 0.45%molYb_2O_3.

In case of antimony glasses doped with 0.15%molNd_2O_3 : 0.45%molYb_2O_3 a weak matching between the levels of emission cross-section for neodymium and absorption cross-section for ytterbium has been observed. The molar concentration of ytterbium ions in the antimony matrix, which is three times lower, makes the active cross-section to the absorption of the $^2F_{7/2} \to ^2F_{5/2}$ transition almost twice higher than in case of fluorophosphate glass.

3.3. Luminescence spectra

While exciting the produced fluorophosphate and antimony glasses with a laser diode (λ = 808 nm), a broad luminescence spectrum in the region of 1 μm has been obtained in both cases, which is the superposition of the $^4F_{3/2} \to ^4I_{11/2}$ transition for Nd^{3+} and $^2F_{5/2} \to ^2F_{7/2}$ for Yb^{3+}. Figure 4 shows the obtained luminescence bands for fluorophosphate glasses doped with 0.15%molNd_2O_3 : 1.5%molYb_2O_3 and antimony glasses doped with 0.15%molNd_2O_3 : 0.45%molYb_2O_3. In order to compare the influence of the type of matrix on the phenomenon of energy transfer the shape of luminescence lines for both glasses doped with 0.15%molNd_2O_3 : 0.15%molYb_2O_3 have been shown in the inset of Fig. 4. As a result of a low content of ytterbium ions the probability of energy transfer is low, and both glasses are characterized by a strong luminescence at the wavelength of 1.06 μm corresponding to the $^4F_{3/2} \to ^4I_{11/2}$ transition in the structure of Nd^{3+}. In addition, a considerably higher luminescence level has been observed for fluorophosphate glasses indicating a high probability of spontaneous emission.

Optimisation of glasses as far as the molar concentration of the donor ions (Nd^{3+}) and the acceptor ions (Yb^{3+}) is concerned leads to efficient spatial overlapping of emission level for neodymium and absorption level for ytterbium, thus facilitating the appearance of three times broader luminescence band than in case of the glass doped with neodymium only [15]. It should be also noted that an increase in the concentration of Yb^{3+} in the obtained matrices results in a decrease of the emission level

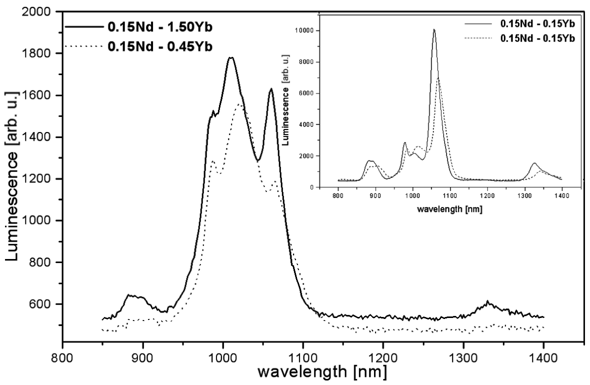

Fig. 4. Luminescence spectra of fluorophosphates (solid line) and antimony glasses (dotted line) co-doped with Nd^{3+}/Yb^{3+} ions excited by 808 nm LD. The inset compares the luminescence intensities between fluorophosphates (solid line) and antimony glasses (dotted line) co-doped with $0.15\%molNd_2O_3 : 0.15\%molYb_2O_3$.

at the three wavelengths characteristic of Nd^{3+}, i.e. approximately 900, 1060 and 1350 nm, and a simultaneous rise in the emission from the metastable levels of Yb^{3+}, which indicates efficient energy transfer between $Nd^{3+} \to Yb^{3+}$. In both cases the half-width of the luminescence band reaches 100 nm.

Based on the absorption and emission bands obtained in the produced glasses a diagram presenting the structure of energy levels has been drawn up on which the processes of energy transfer (ET) between the donor and the acceptor have been marked (Fig. 5). Because of a small difference in energy ($\approx$ 1190 cm^{-1}) between the laser levels of neodymium and ytterbium it is possible to obtain a resonant interaction between the ${}^4F_{3/2}$ excited level for neodymium and the ${}^2F^{5/2}$ level for ytterbium.

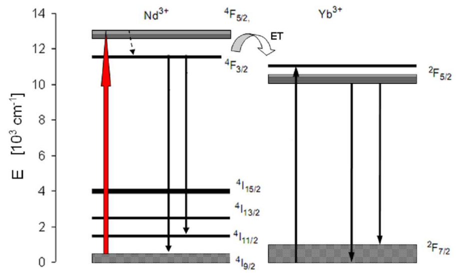

Fig. 5. Simplified energy level diagram with mechanism of energy transfer.

Electrostatic interactions between ions described in the work of Forster and Dexter [19, 20] can be determined by energy transfer rate [2]:

$$W_{\mathrm{DA}}^{dd} = \frac{3\hbar c^2 Q_{\mathrm{A}} Q_{\mathrm{D}}}{4\pi^3 n^2 R^6} \int \frac{f_{\mathrm{D}}(E) f_{\mathrm{A}}(E)}{E^4} \mathrm{d}E\,, \qquad (4)$$

where $R = (3/4\pi N)^{1/3-}$ is the average distance between donor and acceptor, N — the total concentration of absorbing centres, Q_{A} (Q_{D}) — the area under the acceptor (donor) absorption lineshape function, n — the refractive index and E — the photon energy. f_{D} and f_{A} are the normalized donor emission and acceptor absorption spectra, respectively. A detailed theoretical description of the accompanying phenomenon of energy exchange between the ions Nd^{3+} and Yb^{3+} is contained in the authors' previous work [15].

4. Conclusions

As a result of the conducted research a thermally stable fluorophosphate and antimony glasses doped with Nd^{3+} and Yb^{3+} have been produced. The high transparency ranging from 400 to 1100 nm obtained by applying spectrally pure compounds (> 99.99%) facilitates high excitation efficiency of the formed glasses with a high-power laser diode. Thanks to lowering the phonon energy of phosphate glasses by introducing fluoride compounds into the matrix a high ($\approx 4 \times 10^{20}$ ions/cm^3) concentration of the activator ions has been obtained without the crystallization effect. The low level of oscillatory vibrations in Sb–O–Sb bonds appearing in antimony glasses induced the increase in the efficiency of energy transfer between rare-earth ions, in comparison to silicate and fluorophosphate glasses. As a result of the analysis of the active cross-sections conducted from the perspective of energy transfer efficiency between the donor and the acceptor, it has been noted that with three times lower molar concentration of ytterbium ions in the antimony matrix doped with $0.15\%molNd_2O_3 : 0.45\%molYb_2O_3$, the active cross-section to the absorption of the ${}^2F_{7/2} \to {}^2F_{5/2}$ transition is almost twice greater than in case of the fluorophosphate glass doped with $0.15\%molNd_2O_3 : 0.15\%molYb_2O_3$.

As a result of the best matching of Nd^{3+} emission level and Yb^{3+} absorption level in fluorophosphate glasses it is possible to obtain a broad luminescence spectrum, which is a composition of emission transitions from metastable levels of neodymium and ytterbium ions in the region of 1 μm. In addition, the rise in concentration of rare-earth ions increases the probability of energy transfer between the donor and the acceptor. Despite the lack of spatial matching, antimony glasses doped with $0.15\%molNd_2O_3 : 0.45\%molYb_2O_3$ display high efficiency of energy transfer between dopant ions, indicating a low level of multiphonon relaxation.

While exciting the produced glasses with a laser diode (λ = 808 nm) a broad luminescence spectrum ($\Delta\lambda$ = 100 nm) has been obtained in both cases in the vicinity of 1 μm, being the superposition of the following transitions: ${}^4F_{3/2} \to {}^4I_{11/2}$ for Nd^{3+} and ${}^2F_{5/2} \to {}^2F_{7/2}$ for Yb^{3+}. Because of a small difference in energy ($\approx$ 1190 cm^{-1}) between the laser levels of neodymium and ytterbium the resonant process of energy transfer has been obtained.

Optimisation of glasses as far as the molar concentration of the donor ions (Nd^{3+}) and the acceptor ions (Yb^{3+}) is concerned leads to efficient spatial overlapping of emission levels for neodymium and absorption levels for ytterbium, thus facilitating the appearance of three times broader luminescence band than in case of the glass doped with neodymium only [15, 18]. The obtained fluorophosphates matrix doped with the Nd^{3+}/Yb^{3+} ion system is characterised by a high spontaneous emission of the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition corresponding to the wavelength of 1064 nm, therefore it can be successfully applied in high-power lasers and ASE sources. The high efficiency of energy transfer and the low level of lattice vibrations obtained in antimony glasses doped with 0.15%molNd_2O_3 : 0.45%molYb_2O_3 determine their application in up conversion systems [19–21] or the Raman lasers. It follows from the conducted analyses that the produced glasses described above can be used for constructing active optical fibres.

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