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Analysis of Nd^{3+}/Yb^{3+} ions energy transfer in oxyfluoride silicate glass for optical fibre ASE source

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Abstract

The paper presents optimisation of Nd^{3+}/Yb^{3+} ratio to enhance the emission bandwidth at 1 µm. Analysis of the energy transfer scheme between Nd^{3+} and Yb^{3+} ions incorporated in oxyfluoride glass was performed. The highest efficiency (60 %) was measured for the equal values of absorption cross-section (Yb^{3+}) and emission cross-section (Nd^{3+}). The emission spectrum with 100 nm bandwidth of the Nd^{3+}/Yb^{3+} co-doped glass samples under excitation at 808 nm was determined. The fabricated glass with the highest efficiency of energy transfer $Nd^{3+} \rightarrow Yb^{3+}$ was used as a core in helical core double clad optical fibre.
Keywords: Double clad optical fibre, Oxyfluoride silicate glass, Optical properties, Energy transfer, Nd^{3+} ions, Yb^{3+} ions

ANALIZA PRZEKAZYWANIA ENERGII POMIĘDZY JONAMI Nd^{3+} I Yb^{3+} W SZKLE TLENOFLUORKOWYM KRZEMIANOWYM DLA ŚWIATŁOWODOWEGO ŹRÓDŁA ASE

Artykuł przedstawia optymalizację stosunku Nd^{3+}/Yb^{3+} w celu zwiększenia szerokości pasma przy 1 µm. Przeprowadzono analizę schematu przekazywania energii pomiędzy jonami Nd^{3+} i Yb^{3+} wprowadzonymi do szkła tlenofluorkowego. Największą efektywność (60 %) zmierzono w przypadku równych wartości przekrojów czynnych na absorpcję (Yb^{3+}) i emisję (Nd^{3+}). Określono widmo emisyjne o szerokości pasma 100 nm w przypadku próbek szkła współdomieszkowanego jonami Nd^{3+} i Yb^{3+} wzbudzanych przy 808 nm. Wytworzone szkło o najwyższej efektywności przekazywania energii $Nd^{3+} \rightarrow Yb^{3+}$ wykorzystano jako rdzeń w światłowodzie typu *double-clad* o rdzeniu spiralnym.
Słowa kluczowe: światłowód *duble-clad*, tlenofluorkowe szkło krzemianowe, właściwości optyczne, przekazywanie energii, jony Nd^{3+}, jony Yb^{3+}

1. Introduction

Optical glasses double-doped with trivalent lanthanide ions find broad application in optoelectronics. Initially, systems based on Nd^{3+} and Yb^{3+} ions were used to improve the efficiency of solar cells [1]. Due to its strong absorption at the wavelength of 580 nm corresponding with the following transition: $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2,}$ the neodymium ion operates as an efficient absorber of solar radiation. The effect of non-radiative energy transfer occurring between $Nd^{3+} \rightarrow Yb^{3+}$ ions leads to emission of radiation from the $^2F_{5/2}$ level of ytterbium. Adjusting the energy gap of solar cells (9182 cm^{-1}) to the energy difference between Stark levels of ytterbium ions ensures high efficiency of solar energy absorption [2].

In addition, because of their high quantum efficiency, Yb^{3+} ions are applied in up-conversion systems for inducing the fluorescence line of elements such as: Er^{3+}, Tm^{3+}, Tb^{3+} [3-5]. In order to increase the pumping efficiency of the systems mentioned above, Nd^{3+} ions are used as the third component, which are characterised by a high value of emission cross-section and a strong absorption band of approx. 800 nm [7].

The $^2I_{9/2} \rightarrow {}^4F_{5/2}$ transition enables to use laser diodes emitting radiation with the wavelength of λ_p = 808 nm as excitation sources. In this case ytterbium serves as an agent in the energy exchange between interacting dopant ions [8,9].

The mechanism of energy transfer occurring in glass matrices is also successfully applied in telecommunications for constructing praseodymium fibre amplifiers (of PDFA type) sensitized with Yb^{3+} ions. Broad and strong absorption band of ytterbium allows to shorten the required fibre length and enables to pump it in a broad spectrum range, thus obtaining high generation efficiency in the second telecommunications window [6, 11].

Transfer of energy between lanthanide ions takes place in a situation when absorption, and then emission, occurs in different optical centres. A theoretical description of this phenomenon is based on the examination of interactions appearing between active centres [6]. In case of the oxygen-fluoride glass double-doped with Nd^{3+}/Yb^{3+} ions (where Nd^{3+} is a donor and $Yb^{3+}$is an acceptor), it is possible to obtain the resonant energy exchange. Inducing neodymium ions with the wavelength of 808 nm leads to rapid population of the $^4F_{3/2}$ metastable state, from which the photon emission at the $^4I_{9/2}$ elementary level is effected, simultaneously inducing ytterbium ions into the $^2F_{5/2}$ laser level. In such a way, as a result of overlapping emission transitions, it is possible to obtain a broad luminescence spectrum in the vicinity of 1 µm.

Introducing fluorine ions to the silicate matrix brings about loosening a rigid glass structure based on strong bonds of oxygen bridges, usually allowing to introduce higher concentrations of rare-earth elements. Moreover, the presence of F^- ions in the glass reduces the distance between Nd^{3+} and Yb^{3+} ions, which results in greater probability of energy transfer [7].

2. Experimental

Glasses with molar compositions of $(36–x–y)SiO_2$-$19PbO$-$9PbF_2$-$8Al_2O_3$–$27(B_2O_3$-Na_2O-$K_2O)$-xNd_2O_3-yYb_2O_3, x = 0.15, y = (0–0.75) were prepared by using high purity (99,99 %) compounds. The all homogenized powders were melted at 1350°C for 90 min. in a platinum crucible using an electrically heated furnace. In order to maintaining repeatability of dimensions of glass sample the melted mass of glass was poured into preheated brass form and annealed at 430°C for 12 h to remove thermal stress. Transparent, homogenous glasses without crystallization was fabricated. Finally, the glass samples were polished in order to carry out the optical measurements. The light transmission of samples (size10x10x3 mm) was performed in the range of 0.4–1.1 μm by using an Acton Spectra Pro 2300i monochromator with the InGaAs detector. Luminescence measurement system consisted of: pumping diode - HLU30FAC400-808P (λ = 808 nm) with optical fibre output (400 μm, NA = 0.22) and the laser beam forming system. Signal was transmitted to the Acton Spectra Pro 2300i monochromator. The efficiency of energy transfer in the fabricated glasses a system was calculated using the Dexter-Forster formula. This method is based on the electrostatic interactions between active dopants (Nd^{3+} - donor and Yb^{3+} - acceptor).

3. Results and discussion

3.1. Absorption coefficient

Fig. 1 presents absorption bands of the glasses co-doped with $0.15Nd^{3+}:0.45Yb^{3+}$ (mol.%). The shape of the absorption band in the glass is described by Gaussian curve. Position of the line maximum corresponds to an average transition energy. Number of observed absorption bands indicates a complex nature of energetic structure. Some of the absorption bands are described with more than one Paschen notation [14]. It can be explained by the fact that multiplet mixing phenomena takes place.

Fabricated glasses doped with Nd^{3+}/Yb^{3+} ions were pumped by AlGaAs laser diodes at 808 nm. Based on absorption coefficient and McCumber theory [12] the absorp-

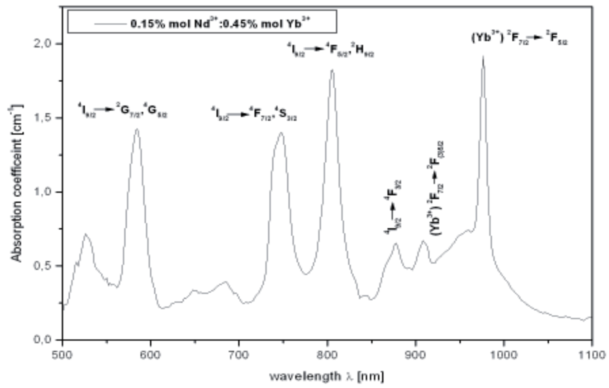

Fig. 1. Absorption spectra of glass doped with $0.15Nd^{3+}:0.45Yb^{3+}$.

tion cross-section of ytterbium ($\sigma_{abs(Yb)}$) and emission cross-section of neodymium ($\sigma_{em(Nd)}$) were calculated. The integrated absorption cross-section Σ_{abs}, spontaneous radiation probability A_R and radiative life time, τ_d, of neodymium for different Yb^{3+} concentration were analyzed [13]. Table 1 presents the results of calculations.

3.2. Luminescence properties

Matching of the emission cross-section of neodymium and absorption cross-section of ytterbium in co-doped glass enables to obtain wide luminescence spectra at 1 μm. This phenomena is connected with resonance interaction between rare earth ions. The luminescence spectra of the manufactured glasses under excitation of 808 nm laser diode are shown in Figs. 2 and 3.

While analyzing energy level structure of the neodymium and ytterbium, the emission spectra are the superposition of the ${}^4F_{5/2}\rightarrow{}^4I_{9/2}$ (Nd^{3+}) and ${}^2F_{5/2}\rightarrow{}^2F_{7/2}$ (Yb^{3+}) optical transitions [2]. Luminescence spectra bandwidth of the SPF13

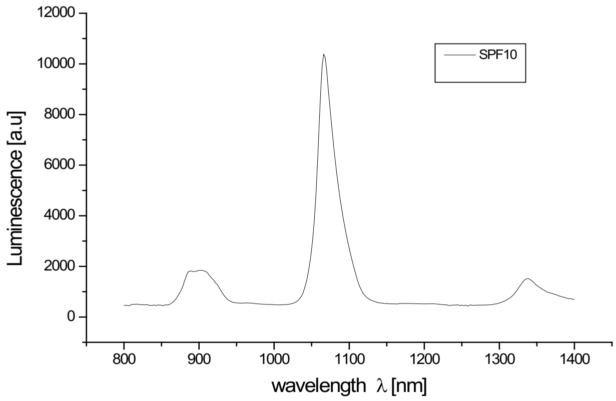

Fig. 2. Luminescence spectra of doped glass with Nd^{3+} (SPF10), λ_p = 808 nm.

Table 1. Spectroscopic properties of Nd^{3+}, Yb^{3+} oxyfluoride silicate glasses doped with different Yb_2O_3 contents.

Glass	N_{Yb} [10^{20} ion/cm^3]	$\sigma_{abs(Yb)}$ [10^{-20} cm^2]	$\sigma_{em(Nd)}$ [10^{-20} cm^2]	$\Sigma_{abs(Nd)}$ [10^4 pm^3]	$A_{R(Nd)}$ [$10^4 s^{-1}$]	$\tau_{d(Nd)}$ [μs]
SPF10	-	-	1.62	3.44	0.68	147
SPF11	0.39	2.77	1.64	3.30	0.94	106
SPF13	1.19	1.61	1.65	3.75	1.07	93
SPF15	2.29	0.52	1.48	6.17	1.77	56

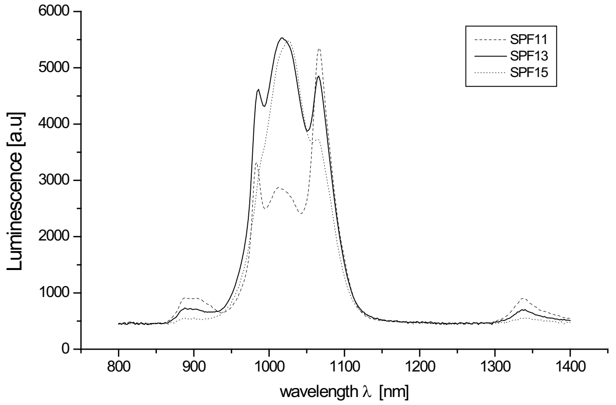

Fig. 3. Luminescence spectra of doped glass with Nd^{3+}/Yb^{3+} (SPF11, SPF13, SPF15) λ_p = 808 nm.

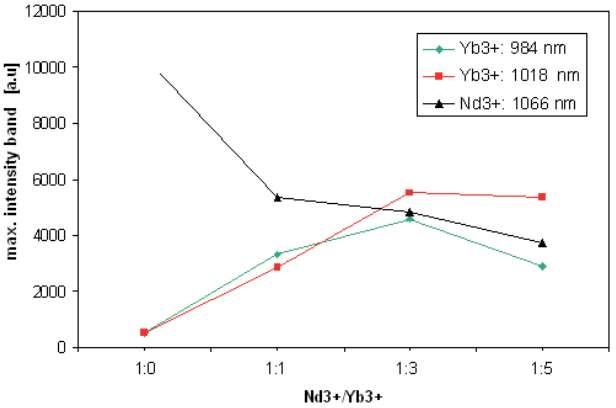

Fig. 4. Dependence of maximum intensity from different ratio of concentrations.

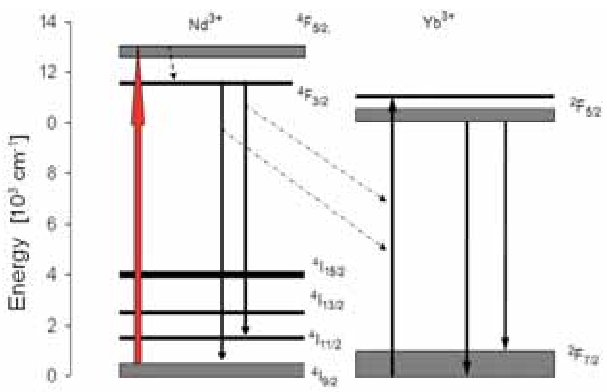

Fig. 5. Simplified energy level diagram with the possible energy transfer mechanism (dotted arrow) in Nd^{3+}/Yb^{3+} co-doped glasses.

($0.15Nd^{3+}:0.45Yb^{3+}$) glass is almost three times wider than of the neodymium singly doped glass.

However, it should be notified that with the increasing of Yb^{3+} ions content the emission level at wavelength: 900 nm, 1060 nm, 1350 nm (Nd^{3+} emission bands) decreases. Simultaneously the emission from Yb^{3+} metastable level increases which indicates effective $Nd^{3+}\rightarrow Yb^{3+}$ (Fig. 3) energy transfer.

Fig. 4 presents the intensity of the emission bands at about 1 μm as a function of dopant concentration ratio. Optimum matching of luminescence emission intensity was attained for glass of 0.15 Nd^{3+}:0.45 Yb^{3+} (mol.%) ratio.

3.3. Energy transfer

On the basis of absorption and emission spectra in Nd^{3+}/Yb^{3+} doped glasses a diagram of energy levels was created (Fig. 5). When exciting Nd^{3+} ions (808 nm) in the Nd^{3+}/Yb^{3+} co-doped glasses, the $^4F_{5/2}$ level is pumped firstly. The 840 cm^{-1} energy mismatch between neodymium $^4F_{3/2}$ (11 086 cm^{-1} from the ground state) and ytterbium $^2F_{5/2}$ (10 246 cm^{-1} from the ground state) levels and the overlap of $^2F_{7/2}\rightarrow{}^2F_{5/2}$ ytterbium absorption and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ neodymium emission cross-sections lead to resonant energy transfer via $^4F_{3/2}$ (Nd^{3+} - donor) to $^2F_{5/2}$ (Yb^{3+} - acceptor) level route. Based on the analysis of emission intensities and Dexter-Forster formula the efficiency and probability of energy transfer between Nd^{3+} and Yb^{3+} ions were calculated.

Efficiency was determined according to formula [10]:

$$\eta_T = 1 - \frac{I}{I_0} \tag{1}$$

where I and I_0 are the fluorescence intensities in the presence and absence of acceptor, respectively.

The efficiency and probability of energy transfer for emission band at 1.06 μm corresponds to $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition are presented in Table 2.

Table 2. The efficiency and probability of energy transfer for $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition at three different concentrations of Yb^{3+}

Glass	Concentration N_{RE} [mol.%]		Efficient η_T	Probability P_{da} [s^{-1}]
	Nd^{3+}	Yb^{3+}		
SPF11	0.15	0.15	0.48	4500
SPF13	0.15	0.45	0.53	5474
SPF15	0.15	0.75	0.61	8592

Fig. 6 presents probability of the transitions (P_{da}) for donor–acceptor concentration estimated as:

$$P_{da} = \frac{1}{\tau_d}\left(\frac{I_0}{I} - 1\right) \tag{2}$$

where $\tau_d = 1/A_R$ – radiative live time of donor, A_R - spontaneous radiation probability.

When concentration of acceptor (Yb^{3+}) equals 0.75 mol.% then the efficiency of energy transfer between donor and acceptor ions amounts to maximum. However, the increasing of the ytterbium concentration does not lead to an increase

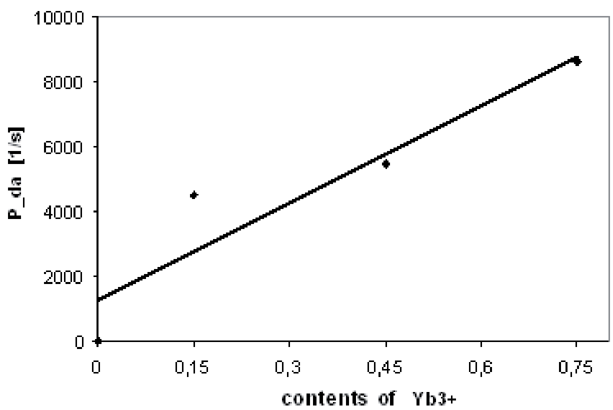

Fig. 6. Energy transfer probability (P_{da}) vs. acceptor contents.

of photon emission from excited energy state $^2F_{5/2}$. It can be explained by the fact of energy migration. In such a case, the donor relaxes transferring its energy resonantly to another donor ion, which can transfer it again to another one and the energy randomly migrates until it is absorbed by the acceptor [2,6]. In the fabricated oxyfluoride silicate glasses, this processes lead to quenching the luminescence bands at 1030 nm Yb^{3+} ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1060 nm Nd^{3+} ($^2F_{3/2} \rightarrow {}^2F_{7/2}$).

4. Conclusions

The article presents findings of the research in the mechanism of energy transfer between neodymium and ytterbium ions in the manufactured oxide-fluoride silicate matrix. As a result of the conducted research, thermally stable oxide-fluoride glasses with low SiO_2 content (< 36 mol.%) doped with Nd^{3+} and Yb^{3+} ions were obtained. Introducing fluorine ions to the silicate matrix reduces the phonon energy, thus facilitating effective transfer of energy between lanthanide ions. In consequence of matching the values of the $\sigma_{em(Nd)}$ level and the $\sigma_{abs(Yb)}$ level in the glass doped with $0.15Nd^{3+}:0.45Yb^{3+}$ a broad ($\Delta\lambda$ = 100 nm) luminescence band in the vicinity of 1 μm was obtained, which was the result of overlapping emission transitions: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ in ytterbium and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ in neodymium. Its half-intensity width is almost three times larger than in case of the glass doped with neodymium ions. In the examined glasses a process of luminescence reduction was observed as a result of excitation diffusion, which occurred while exceeding 1 mol.% of the activators. The percentage efficiency of energy transfer amounts to 60 %, when calculated according to the Dexter-Forster model for the glass doped with $0.15Nd^{3+}:0.75\ \%Yb^{3+}$.

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