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Active optical fibres for application in laser and broadband ASE sources

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Abstract. The article brings into focus the present state of technology employing active fibres doped with rare earth (RE) ions for applications requiring power supply of several dozen watts and broadband ASE sources. Current trends in development of glasses and in construction of active fibres used in fibre sources of radiation within VIS-NIR range are presented. Technological constraints in the doping of fibre core glasses are discussed, with particular consideration of optimal RE concentration for technical applications. Characteristics of glasses are offered, and the glasses are used for manufacturing optical fibres with luminescence within the visible as well as near- and mid-infrared ranges. Also, requirements and luminescence properties concerning glasses co-doped with e.g. Nd^{3+}/Yb^{3+},Tm^{3+}/Ho^{3+} and Yb^{3+}/Tb^{3+} are discussed. Results of research on the impact of technological parameters of glass matrices on luminescence properties of core glasses and optical fibres are quoted. For the doped glasses of which luminescence in a wide spectral range is desired, conditions for their processing into optical fibre systems are mentioned. Additionally, the impact of phonon energy in the glass on producing emission in a specified spectral range is analyzed. Furthermore, the article presents directions of technological studies to solve problems persisting in the phase of glass matrix design, as well as in determining the influence of fibre drawing process on the luminescence properties of core glasses and optical fibres, confirming the differences in luminescence stemming from the drawing process. Finally, some original designs of core glasses and active multicore fibre systems devised for construction of fibre radiation sources are presented.

Key words: active optical fibres, double-clad fibres, RE doped glasses, rare-earth elements.

1. Introduction

In modern optical fibre lasers, several to several dozen kW radiation with a wavelength of ca. 1 μm is generated mainly by means of active doping with ytterbium ions [1, 2], an in rare cases with neodymium or both the kinds of ions. Owing to their simple quantum configuration, ytterbium ions do not exhibit absorption from the excited state, and have low likelihood of concentration quenching related to energy migration. High efficiency of fibre laser achieved in optical fibres using ytterbium ions is a consequence of a wide absorption band from the ground state ($\sim$800 to 1500 nm). From the perspective of pumping effectiveness of laser such media, optical excitation should be conducted with a wavelength within the band of 980 nm, i.e. spectrally close to the generation or amplification band of the considered ytterbium-doped medium. For the same reason, separation of pumping and generation signals may become an important issue in design of high-energy laser systems [3]. Practically, the discussed class of laser systems makes almost exclusive use of silica glass. It can be said that the market of silica fibres doped with RE ions dedicated for multi-kilowatt sources has been dominated by the manufacturers of such systems [4]. However, there remains a wide range of designs and applications of radiation sources with power up to about 100 W (several to several dozen watts sources, classified in the broad VIS-NIR spectral range), for which research on both glass matrix and fibre technologies (including fibres manufactured from glasses other than silicate glass) is still in progress, and optimal configurations of glass matrices and dopants are investigated. Regardless of the technological research, studies focused on increasing excitation efficiency of laser systems and fibre amplifiers are under way. The present article lays particular emphasis on technological research associated with fibres dedicated for the latter class of radiation sources.

Commercially available fibres are taken advantage of as laser sources and radiation amplifiers. The amplifiers are principally used in optical fibre telecommunication, in which silica optical fibres doped with erbium ions serve as signal amplifiers (EDFA), thus allowing all optical transmission [5]. In a similar vein, the laser sources make use of fibres doped with Nd^{3+} [6], Yb^{3+} [1] and Tm^{3+} [7] ions which, due to their absorption bands overlapping with emission spectra of semiconductor excitation diodes, allow to obtain emission with high gain. Practically all currently available solutions are single-mode and have distorted cladding geometry to increase absorption of pumping radiation. Still, despite the advanced technological level of the produced fibres, there exist some serious limitations originating from the laser medium itself, i.e. silica glass. In particular, the strength of Si-O-Si bonds permits silica glass to accept only small quantities of rare earth ions, and above certain levels of concentration (e.g. 1500 ppm Er^{3+}) clusters are formed, which leads to increased interionic interactions. This phenomenon leads to the so-called concentration quenching which lowers the gain level [8]. Another aspect related to the presence of the strong bonds in silica

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glass is an elevated probability of nonradiative decays, being a consequence of high phonon energy equal 1100 cm^{-1}. That is why preparing a matrix for rare earth elements, in the form of glass for optical fibre production, imposes on production engineers far-reaching constraints in comparison to regular processes of glass production. Beyond doubt, the primary goal is to select such glass content which allows absorption and emission of radiation by the chosen rare earth ions. This, however, is not a sufficient condition, as the glass needs to exhibit good thermal stability, making possible such processing into an optical fibre system which does not adversely affect its laser properties. Ultimately, selection of eligible glass-forming elements and careful consideration of synthesis condition leads to materials which doped with lanthanides can become active media in fibre laser systems.

Next issue is associated with effectiveness of active fibre excitation by means of power semiconductor diodes. Absorption of pumping radiation can be bolstered by increasing doping concentration, or by introducing a second doping element from the lanthanide series with the function of a sensitizer. The former solution effects in the occurrence of concentration quenching and optical trapping processes in laser media. Therefore, co-doping with more than one rare earth element seems to be an attractive solution. The introduction of additional ion with strong absorption of radiation opens new possibilities of improving parameters of optical fibres, which has been confirmed by the construction of EYDFA (Erbium-Ytterbium Doped Fibre Amplifier) [9, 10]. In optical fibres co-doped with two rare earth elements in the donor-acceptor configuration, emission of radiation is realised inside the optical fibre, which considerably simplifies laser design, allowing effective excitation of the fibre with semiconductor laser diodes. Among the principal reasons behind the search for new glass materials which can be used to manufacture co-doped fibres is the necessity to ensure optimum conditions of not just emission and absorption, but also of energy transfer between the active dopants. In many of the solutions, an increase of pumping efficiency is achieved, which translates into incremented emission efficiency. Adequate combinations of doping rare earth elements make it possible to take advantage of their absorption and luminescence properties, particularly in such a way that the emitted radiation is a superposition of optical transitions of both the active ions, thus creating broadband sources. What is more, in active optical fibres with specially designed structure it is possible to achieve amplified spontaneous emission in the course of energy transfer between excited states of lanthanides [11–13].

The article presents material properties and spectroscopic characteristics of active glasses are presented from the viewpoint of optical fibres production. Taking into account co-doping with $\mathrm{Nd}^{3+}/\mathrm{Yb}^{3+}$, $\mathrm{Tm}^{3+}/\mathrm{Ho}^{3+}$ and $\mathrm{Yb}^{3+}/\mathrm{Tb}^{3+}$ ions, several doping configurations are devised, and technological constraints concerning optical fibres forming are expounded. Energy transfer process occurring between the doping ions are explained, and the impact of glass phonon energy on emission in the specified spectral ranges is analyzed. New optical fibre structure is proposed: a multicore construction whose parameters permit its application in compact sensor systems as broadband sources of optical radiation.

2. Results and discussion

2.1. Broadband luminescence at 1μm wavelength in $\mathrm{Nd}^{3+}/\mathrm{Yb}^{3+}$ doped optical fibres. For laser systems with power up to about 100 W, the approach involving co-doping of the medium with $\mathrm{Nd}^{3+}/\mathrm{Yb}^{3+}$ ions seems to be particularly attractive [14–16]. In such a configuration, neodymium ions function as donors, supplying a portion of their excitation energy in the course of $\mathrm{Nd}^{3+} \rightarrow \mathrm{Yb}^{3+}$ resonant energy transfer. Spectral adjustment of the doping ions results in a broad luminescence spectrum, which allows to manufacture fibre lasers working as sources of amplified spontaneous emission (ASE) [17, 18]. Excitation of neodymium ions with 808 nm wavelength leads to the population of $^4F_{3/2}$ energy state, from which the emission in the band of 890 nm proceeds corresponding to the transition of photons to the ground state $^4I_{9/2}$, with simultaneous energy transfer to the excited state $^2F_{5/2}$in Yb^{3+} ions. In this manner, due to a combination of emission transitions, it is viable to achieve a wide luminescence spectrum in the 1 μm region [18]. Figure 1 shows a simplified diagram of energy states transpiring in glasses doped with $\mathrm{Nd}^{3+}/\mathrm{Yb}^{3+}$ ions, highlighting the processes of donor-acceptor energy transfer. Due to a small energy difference ($\sim$ 900 cm^{-1}) between laser levels of neodymium and ytterbium, a quasi-resonant energy exchange can be elicited.

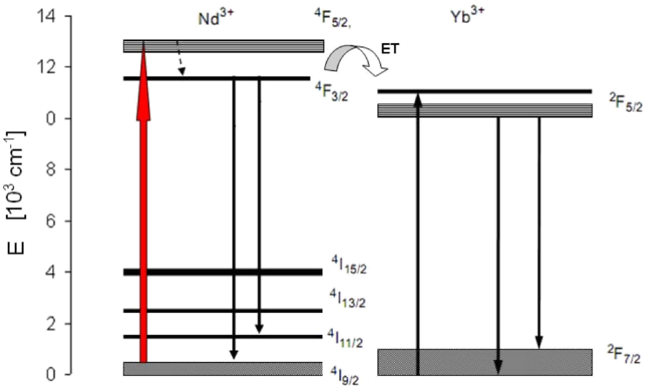

Fig. 1. Simplified energy level diagram with the possible energy transfer mechanism in $\mathrm{Nd}^{3+}/\mathrm{Yb}^{3+}$ codoped glasses

Most frequently, glasses used for construction of fibre lasers are described by such parameters as emission cross section and radiative life time. Alongside the commonly used silica glasses [19], more and more often new multi-component silicate and phosphate glass matrices are encountered [20]. In both cases, the matrices are marked by high phonon energy, and as a consequence exhibit high mechanical strength, as well as decrease probability of radiative transfers which limits laser gain. In the course of numerous syntheses, the authors came up with glass compositions with spectroscopic properties which allowed to accomplish double-clad fibres distinguished by strong emission of radiation in the 1 μm region. Table 1 contains physicochemical and optical parameters of the manufactured glasses. Silicate glasses with SiO_2 – B_2O_3 – PbO – Na_2O – Al_2O_3 composition (denoted as SBP), as well as phosphate glasses with P_2O_5 – Al_2O_3 – BaO – ZnF_2 – Na_2O – MgO composition (denoted as PF) were doped respectively with Nd^{3+} and Yb^{3+} ions. The concentration of rare earth dopants was chosen in a way that ensured the highest efficiency of energy transfer which was being estimated by analyzing absorption and emission cross sections.

Table 1
Material and thermal parameters obtained in manufactured glasses

Parameter	Value	
	SBP	**PF**
Refractive index n (633 nm)	1.64	1.52
Mass density ρ [g/cm^3]	3.85	2.85
Thermal expansion coefficient α_{100}^{400} [10^{-7} 1/K]	90.9	55.3
Dylatometric softennig point T_s [°C]	464	582
Transformation temperature T_g [°C] (DSC)	443	550
Maximum of phonon energy $4h\omega_{\max}$ [cm^{-1}]	1338	1273

On the basis of spectral absorbance measurements, and referring to the modified McCumber relation [21], emission cross sections for neodymium ions and absorption cross sections for ytterbium ions were calculated. Figure 2 demonstrates spatial overlapping of bands which ensued in SBP glasses. Because of the energy difference between energy states $^4F_{3/2}(Nd^{3+})$ and $^2F_{5/2}(Yb^{3+})$ amounting to ca. 900 cm^{-1}, quasi-resonant energy transfer $Nd^{3+} \rightarrow Yb^{3+}$ occurred in the doping pair.

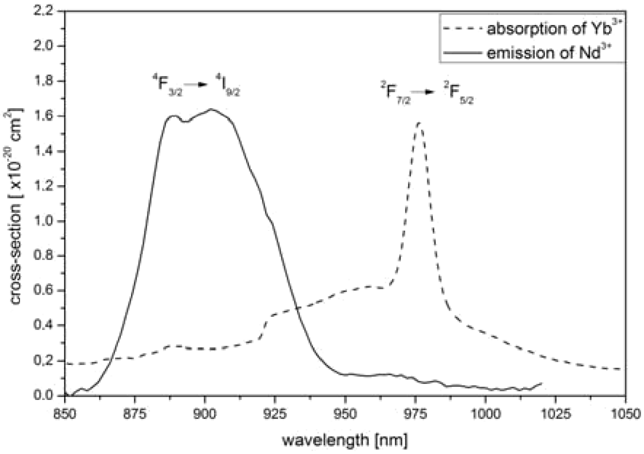

Fig. 2. Overlap the emission cross-section of Nd^{3+} and absorption cross-section of Yb^{3+} for silicate glasses (SPB) doped with 0.15%mol Nd_2O_3 : 0.45%mol Yb_2O_3

Subsequent optimization of donor (Nd^{3+}) and acceptor (Yb^{3+}) ions molar composition enabled to designate glasses with the most efficient spatial adjustment between the neodymium ions emission band and ytterbium ions absorption band, creating at the same time a luminescence band three-times wider than in the case of glass doped with neodymium only (Fig. 3). The most advantageous ratio of dopants in SPB glass was $0.15Nd_2O_3 : 0.45Yb_2O_3$, whereas in fluorophosphates glass it was $0.15Nd_2O_3 : 1.5Yb_2O_3$. Also, it is worthy of note that increasing the concentration of Yb^{3+} in the described glass matrices caused reduction of the emission level at the three characteristic for Nd^{3+} ions wavelengths of ca. 900, 1060 and 1350 nm, and simultaneous increase of the emission from the metastable states in Yb^{3+}, which implied an effective energy transfer $Nd^{3+} \rightarrow Yb^{3+}$. In both of these cases, full width at half maximum (FWHM) of the luminescence band reached 100 nm. Employing Dexter-Förster [22, 23] semi-empirical model, maximum efficiency of energy transfer was calculated; for silicate glasses, its value was equal $\eta_{ET} = 61\%$, while for fluorophosphates glasses $\eta_{ET} = 65\%$.

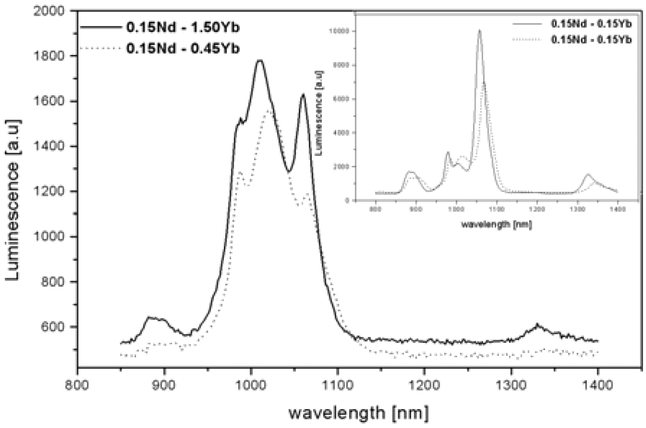

Fig. 3. Luminescence spectra of fluorophosphates (solid line) and antimony glasses (dotted line) co-doped with Nd^{3+}/Yb^{3+} ions excited by 808 nm LD. The inset compares the luminescence intensities between fluorophosphates (solid line) and antimony glasses (dotted line) co-doped with $0.15\%molNd_2O_3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

The devised glass compositions constituted the basis for production of multicore double-clad optical fibres [24, 25]. Obviously, in fibres of this kind, the amount of doping rare earth ions is higher than in single-core fibres which makes it possible to reduce length of the fibre necessary to absorb pumping radiation. Consequently active multicore fibres are characterized by increase in the number of absorption centres which makes the possibility for higher energy generation. Basic parameters of the manufactured 5-core fibre (Fig. 4) were as follows: internal cladding diameter (300 μm), core diameter (10 μm), $NA_{cladding} = 0.58$, $NA_{cores} = 0.1$.

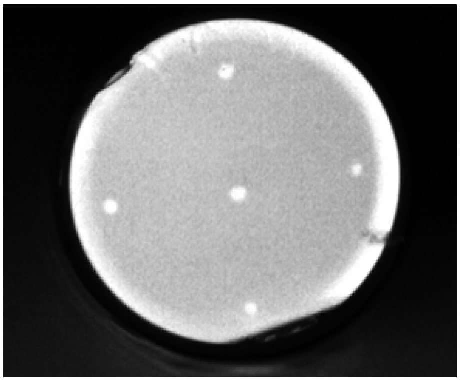

Fig. 4. Cross-section of fabricated multicore fibre

In effect of optical excitation at 808 nm, in the Nd^{3+}/Yb^{3+} co-doped fibre amplified spontaneous emission at a wavelength within 1 μm band was observed. It resulted from the energy transfer between neodymium and ytterbium ions. Figure 5 presents the measured emission spectra for the fibres with lengths respectively of 10, 50, 100, 450, and 950 mm, and compares them with the emission spectrum of core glass doped in the proportion 0.15mol% Nd_2O_3 : 0.45mol% Yb_2O_3.

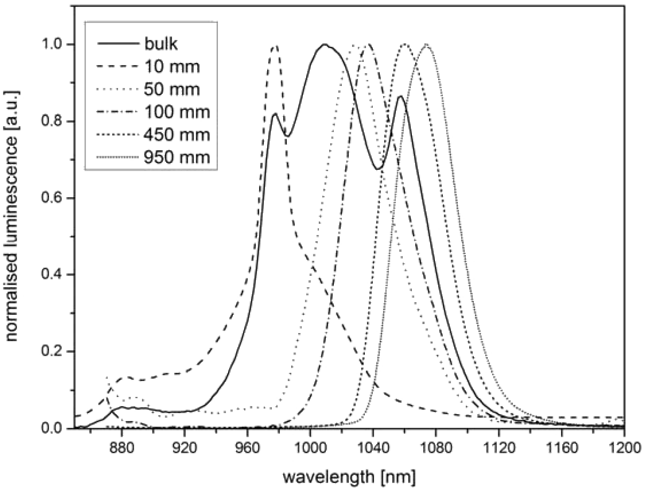

Fig. 5. The emission spectra of 0.15%mol Nd_2O_3:0.45%mol Yb_2O_3 codoped silicate fibre and bulk glass excited with 808 nm laser source. The spectra have been normalized with respect to the peak at ~ 1.0 μm

Analysis of the recorded spectra demonstrated that the highest intensity of luminescence corresponds with $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition in the energy levels configuration of ytterbium ions, which was confirmed by the luminescence curve of a 10 mm fibre. In this configuration, the donor Nd^{3+} ion transfers almost all of its excitation energy to the laser level of Yb^{3+} ions throughout effective quasi-resonant energy transfer $Nd^{3+}\rightarrow Yb^{3+}$. This is substantiated by the fact that the luminescence maximum of a 10 mm fibre at a wavelength in the 980 nm band (red line) overlaps with the luminescence band of the glass sample (black line). Additionally, the position of maximum ASE value is strongly dependent on the length of the fibre. This phenomenon is related to the reabsorption of the generated ASE signal proceeding in the function of fibre length, and as such can be observed in ions characterized by three-level laser energy system.

For the manufactured fibres it was noted that ASE signal was amplified when passing through the fibre to the point where the pumping signal was still present. At the distance from the head of the fibre where pumping signal no longer prevailed, and over the remaining section to the end of the fibre, ASE signal was partially reabsorbed as a result of the wide absorption band of ytterbium ions. The maximum of absorption band corresponded to 976 nm. Therefore, fractions of ASE signal with shorter wavelengths were absorbed to a greater extent. Among the immediate ramifications of this fact are redshifting of the emission spectrum, as well as reduction of FWHM proportionally to the length of the fibre (Fig. 5). The conducted observation of changes in the position of emission maximum in the band of ca. 1 μm, and of full width at half maximum (FWHM) in relation to the fibre length (Fig. 6) indicated that in comparison to the luminescence of glass, in the manufactured fibre over the segment of 1000 mm redshifting of luminescence band maximum took place ($\lambda_e = 1074$ nm), along with the narrowing of full width at half maximum ($\Delta\lambda_{FWHM} = 45$ nm).

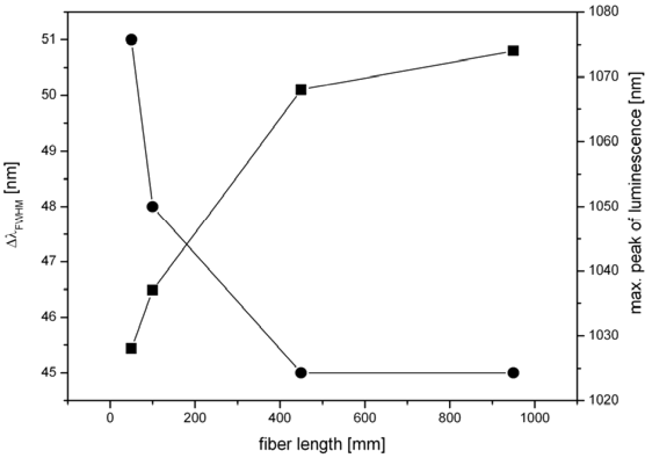

Fig. 6. The maximum emission at 1 μm and $\Delta\lambda_{FWHM}$ as a function of fibre length

2.2. 2μm infrared emission of Tm^{3+}/Ho^{3+} doped optical fibre. Laser sources which generate radiation with a wavelength in the 2 μm band have a wide range of applications in many scientific disciplines, such as e.g. microsurgery or remote sensing of the atmosphere in DIAL systems [26, 27]. Achieving emission in the 2 μm region is made viable by the application of Ho^{3+} ions, in which $^5I_7\rightarrow{}^5I_8$ radiative transition is marked by a wide emission band, high emission cross section, and relatively long radiative lifetime [27]. However, a serious problem related to the optical pumping of Ho^{3+} ions is posed by the fact than none of their absorption bands overlaps with the emission spectra of the commonly encountered power semiconductor diodes. For this reason, suitable sensitizers in the form of Tm^{3+} ions need to be introduced, in order to transfer the absorbed excitation energy and pave the way for the emission of radiation with a wavelength in the 2 μm band corresponding with $^5I_7\rightarrow{}^5I_8$ (Ho^{3+}) transition.

The diagram (Fig. 7) presents fundamental mechanisms of energy transfer occurring as a result of interaction between the active medium and radiation at the wavelength in the band of 795 nm, corresponding with $^3H_6\rightarrow{}^3H_4$ transition.

Laser level $^3F_4(Tm^{3+})$ is populated as an effect of depopulation of the $^3H_4$ multiplet in the course of $^3H_4\rightarrow{}^3H_5\rightarrow{}^3F_4$ multi-phonon relaxation (dotted line) and cross-relaxation (CR). Ions gathered on this level in effect of transmission to the ground state $^3H_6(Tm^{3+})$ can emit an energy quantum in the form of photon emission in the band of 1810 nm, as well as transfer a portion of their energy to the holmium ions in the process of quasi-resonant energy transfer (ET). Following $^3F_4(Tm^{3+}) \rightarrow {}^5I_7$ (Ho^{3+}) transition, population of the $^5I_7$ level increases and a band of spontaneous emission appears at the wavelength within the band of 2010 nm.

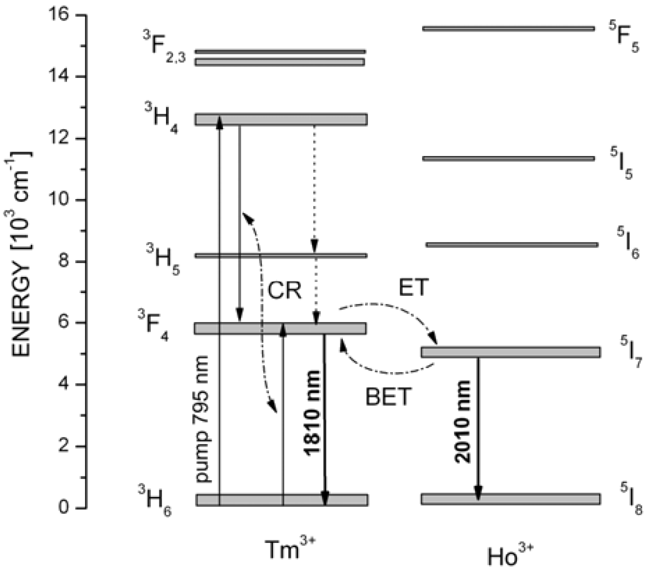

Fig. 7. Mechanisms of the energy transfer between Tm^{3+} and Ho^{3+} in antimony-silicate glasses

Maximizing emission efficiency in the mid-infrared range originating from the transfer of energy between Tm^{3+} and Ho^{3+} ions is closely associated with the type of used glass matrix. Thermal constraints concerning working conditions for laser action, arising mainly from the processes of non-radiative relaxation, necessitate experimental research on glasses in which lower – in comparison to silicate glasses – lattice vibration energy facilitates minimization of losses and increase in efficiency of $Tm^{3+} \rightarrow Ho^{3+}$ energy transfer [28]. At present, the search continues for new glasses which would provide high efficiency of energy transfer, i.e. the parameter determining their potential application. One of the available solutions includes arranging the matrix composition in such a way so as to come up with extremely different phonon vibration frequencies. Here, for instance, antimony-borate [29], antimony-phosphate [30], or antimony-silicate [31, 32] glasses can be mentioned. The combination of glasses with diametrically different energy of phonons effects in a greater separation of optically active centers, noticeably widening the band of spontaneous emission [33].

The research carried out by the authors yielded new antimony-silicate glasses with $SiO_2 – Al_2O_3 – Sb_2O_3$, composition which were doped with Tm^{3+} and Ho^{3+} ions to secure emission in the range 1.7–2.2 μm. To the authors' best knowledge, thus far there have been no accounts of emission in the mid-infrared range for antimony-silicate fibres. Results of the measurements concerning material and thermal properties of the manufactured antimony-silicate glasses are offered in Table 2. High refractive index is proper to these glasses, and as a consequence, high emission cross section is achieved.

Table 2
Material and thermal parameters obtained in manufactured silicate glasses

Parameter	Value
Refractive index n (633 nm)	1.71
Mass density ρ [g/cm^3]	3.3
Thermal coefficient [10^{-7} 1/K]	55.1
Softening point T_s [°C]	429
Transformation temperature T_g [°C] (DSC)	451
Maximum of phonon energy $h_{\max}$ [cm^{-1}]	1186

In the examined case of doping simultaneously with Tm^{3+} and Ho^{3+} ions, the probability and efficiency of donor-acceptor energy transfer is dependent on the spectral adjustment between absorption and emission cross sections and on the distance separating the interacting ions. Because of a small difference in energy between multiplets $^3F_4$ (Tm^{3+}) and $^5I_7(Ho^{3+})$, amounting to 400 cm^{-1} only, quasi-resonant $Tm^{3+} \rightarrow Ho^{3+}$ energy transfer could be discerned in the produced glasses. Figure 8 shows spectral overlapping of emission cross section of thulium and absorption cross section of holmium in the glass doped with 1 mol% Tm_2O_3 : 0.75 mol% Ho_2O_3.

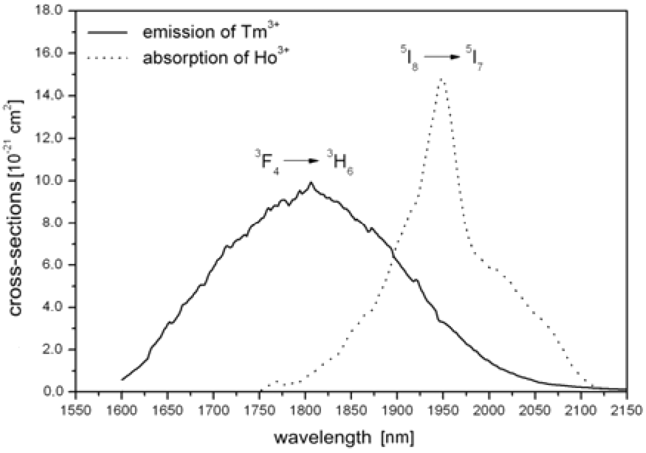

Fig. 8. The emission cross-section of Tm^{3+} ion and the absorption cross-section of Ho^{3+} ion doped antimony-silicate glass

According to Dexter-Förster semi-empirical model, in the considered glasses maximum energy efficiency reached about 90%.

Optimization of the thulium and holmium concentration ratio in the glasses allowed for efficient transfer of energy between the ions $(Tm^{3+} \rightarrow Ho^{3+})$, with simultaneous reduction of energy up-conversion phenomena. The procured luminescence band was a superposition of emission transitions in the configurations of Tm^{3+} $(^3F_4 \rightarrow {}^3H_6)$ and Ho^{3+} $(^5I_7 \rightarrow {}^5I_8)$ (Fig. 9). Carefully regulated increase in the molar content of the acceptor ions (Ho^{3+}) extends control over intensity of luminescence bands originating from the both elements. On the basis of the luminescence measurements, the glass doped in the proportion of 1mol% Tm_2O_3 : 0.75mol% Ho_2O_3 was selected as material the most suitable for the core of a double-clad optical fibre. Figure 10 features the cross section of the manufactured optical fibre. Basic parameters of the fibre with offset core are: optical fibre diameter (380 μm), internal cladding diameter (350 μm), core diameter (20 μm), NA$_{core}$ (0.32), offset (100 μm).

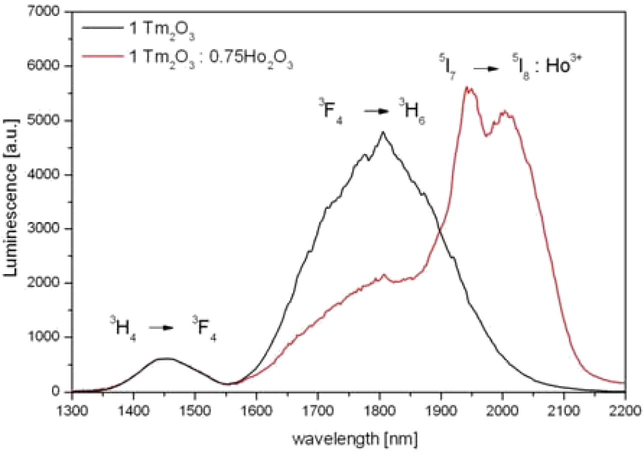

Fig. 9. Comparison of the luminescence spectra of singly Tm^{3+} doped and Tm^{3+}/Ho^{3+} co-doped antimony-silicate glass samples under 795nm LD excitation

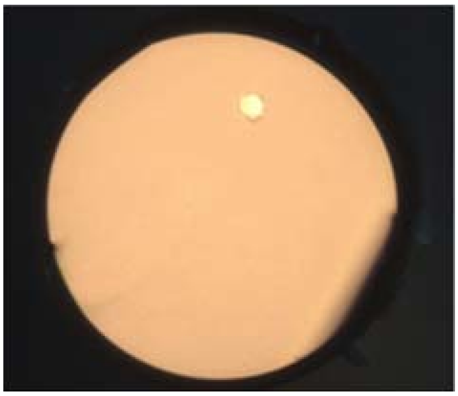

Fig. 10. Cross-section of fabricated fibre

Figure 11 presents a normalized comparison of spontaneous emission spectra for optical fibres of different lengths with the spectrum of core glass co-doped with the combination of 1 mol% Tm$_2$O$_3$: 0.75 mol% Ho$_2$O$_3$. Optical trapping of holmium ions related to the distance of the interaction and to energy confinement in the fibre effects in the narrowing and shifting of the band maximum towards longer wavelengths. Moreover, the reabsorption of radiation occurring at a wavelength within the band of 1950 nm, corresponding with the maximum absorption of $^5I_8 \rightarrow {}^5I_7$(Ho^{3+}) transition, eliminated the characteristic saddle shape appearing in the luminescence spectrum of the glass doped with Ho^{3+} ions.

The narrowing and redshifting of the emission at a wavelength within the band of 2.1 μm corresponding with $^5I_7 \rightarrow {}^5I_8$ transition in the energy-level structure of the holmium ion ensues as a consequence of emission transitions from the same Stark sub-level of the $^5I_7$ multiplet to a higher Stark sublevels of $^5I_8$ multiplet. Participation of the remaining luminescence bands at a wavelength of 1.46 μm and 1.81 μm, originating from the transitions $^3H_4 \rightarrow {}^3F_4$, $^3F_4 \rightarrow {}^3H_6$ in the structure of Tm^{3+}, is negligible in the fibre when compared to the active glass. Thus, as a result of effective energy transfer Tm$^{3+} \rightarrow$Ho^{3+} in the manufactured fibre, narrow and strong bands of amplified spontaneous emission (ASE) are created. In comparison to the luminescence of the glass, in the produced fibre, over the length of 100 mm, the luminescence maximum is achieved at a wavelength within the band $\lambda_e = 2108$ nm, while the full width at half maximum $\Delta\lambda_{FWHM} = 63$ nm (Fig. 12).

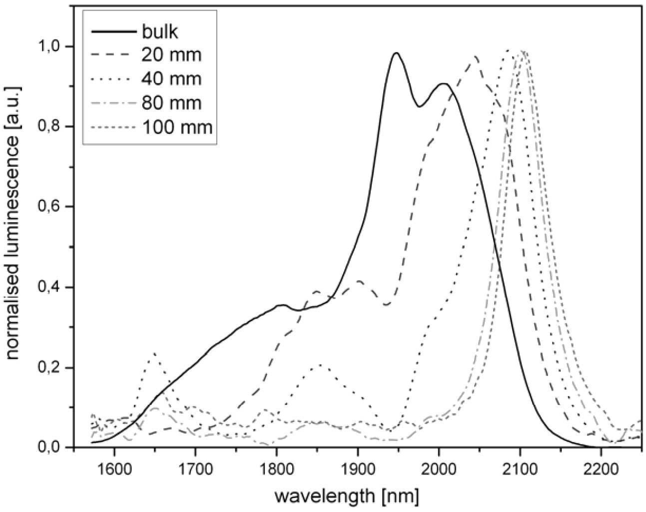

Fig. 11. The emission spectra of 1%mol Tm$_2$O$_3$:0.75%mol Ho$_2$O$_3$ co-doped antimony-silicate fibre and bulk glass excited with 795 nm laser source. The spectra have been normalized with respect to the peak at $\sim$ 2.0 μm

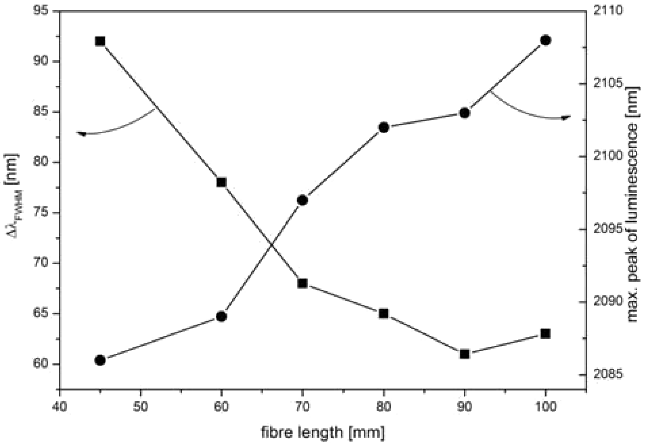

Fig. 12. The maximum emission at 2 μm and $\Delta\lambda_{FWHM}$ as a function of fibre length

2.3. Luminescence in the visible spectral range. Rapid development of fibre sensors encourages the quest for new and efficient sources of radiation in the visible spectrum which would be noticeable for their high stability of emission and compactness [34, 35]. Allocating several lanthanide ions in a single matrix offers a possibility of producing luminescence by means of transitions which are difficult to realize through direct optical pumping. Moreover, in the case of co-doped materials such processes may often transpire as e.g.

energy transfers which lead to the appearance of emission bands at wavelengths shorter than pumping wavelength (up-conversion) [36–38]. The parameters of donor-acceptor energy transfer are heavily dependent on the type of used matrix, and in particular on the energy of phonon vibration. Specifically, the lower the maximum frequency $h\omega_{\max}$ of lattice vibrations, the higher the probability of excitation energy conversion [39]. The most numerous group of glass materials which meet the above condition (i.e. have low phonon energy) are tellurite glasses [40]. There are many publications dedicated to co-doping of tellurite glasses with Yb^{3+}/Er^{3+}, Yb^{3+}/Tm^{3+}, Yb^{3+}/Ho^{3+} ions, as well as describing the usage of these glasses for production of optical fibres with up-conversion luminescence [39, 41, 42]. It has to be mentioned, however, that high content of TeO_2 as the glass-forming element considerably decreases spectral transmission (~75%), and shifts the shortwave boundary towards longer wavelengths, at the same time narrowing the transmission range. What is more, maximum photon energy of 780 cm^{-1} along with high refractive index $n \sim 2$ increase the likelihood of non-linear phenomena [43]. Keeping that in mind, an excellent alternative for tellurite glasses are germanium-based glasses [44]. Due to their high spectral transmission and low phonon energy (900 cm^{-1}), they facilitate effective conversion of excitation energy. Besides, their decent mechanical properties accompanied by high stability expedite the process of fibre structures forming.

Within the scope of the presented research, the authors synthesized new glasses with GeO_2 – GaO – BaO composition, and doped them simultaneously with ytterbium and terbium ions. In the glasses doped with Yb^{3+}/Tb^{3+} ions, during optical pumping with radiation at a wavelength of 976 nm, a cooperative energy transfer from a coupled pair of Yb^{3+} ions to Tb^{3+} ion occurred, effecting in emission of radiation in the visible spectrum corresponding to the transitions from multiplets $^5D_3$/$^5G_6 \rightarrow {}^7F_J$ (J = 6, 5, 4) and $^5D_4 \rightarrow {}^7F_J$ $(J = 6, 5, 4, 3)$ [45, 46].

Table 3 contains physicochemical properties of the considered germanate glasses. The parameter which determines eligibility of glass for optical fibre production is its thermal stability calculated according to the difference $\Delta T = T_x - T_g$. In the discussed case, the difference amounted to 197°C.

Table 3
Material and thermal parameters obtained in germanate glasses

Parameter	Value
Refractive index n (633 nm)	1.68
Mass density ρ [g/cm^3]	4.4
Transformation temperature T_g [°C] (DSC)	618
Crystallisation temperature T_x [°C] (DSC)	815

As for the up-conversion spectrum observed in the manufactured glasses, it comprised seven emission bands resulting from quantum transitions in the structure of terbium. Figure 13 shows the emission band of the germanium glasses doped respectively with 0.7 mol%Yb_2O_3/(0.07 – 0.7) mol%Tb_2O_3 obtained as a result of excitation with radiation wavelength $\lambda_{exc} = 976$ nm and power $P = 2$ W. The peak luminescence intensity, corresponding to $^5D_4 \rightarrow {}^7F_5$ transition, was obtained at a wavelength in the band of 543 nm.

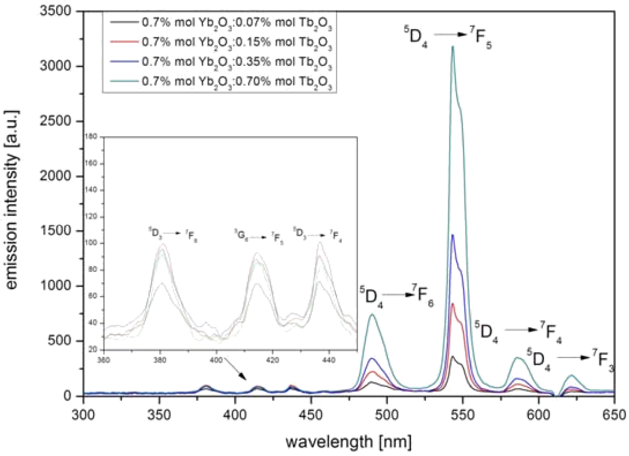

Fig. 13. Up-conversion emission spectra of the Yb^{3+}/Tb^{3+} germanate glasses under 976 nm LD excitation

Relying on the spectral measurements, a diagram illustrating energy states of the Yb^{3+}/Tb^{3+} configuration in the germanium glass was created where the key mechanisms of quantum transitions were presented (Fig. 14). Due to the energy difference ΔE between the laser level $^2F_{5/2}$ of ytterbium and the excited multiplet $^5D_4$ of terbium equal ca. 9350 cm^{-1}, energy transfer proceeds in a cooperative manner from coupled pairs of Yb^{3+} ions. Population of the excited state is an immediate result of $Yb^{3+} \rightarrow Tb^{3+}$ energy transfer. Next, as a consequence of radiative relaxation to lower energy levels of terbium, emission bands can be observed at wavelengths of 489, 543, 586 and 621 nm which correspond to $^5D_4 \rightarrow {}^7F_J$ $(J = 6, 5, 4, 3)$ transitions. As for multiplets $^5D_3$ and $^5G_6$, they are populated through the absorption of pumping photon energy, from the state $^5D_4 \rightarrow {}^5D_1$. Multiphonon relaxation transition $^5D_1 \rightarrow {}^5D_3$ follows, leading to the final population of the coupled multiplets $^5D_3$ and $^5G_6$ which suffices to register emission with wavelength of 381, 415 and 435 nm respectively.

Luminescence level in the glasses co-doped with Yb^{3+}/Tb^{3+} ions is particularly dependent on the concentration of terbium. Efficiency of cooperative transfer is higher when the molar content ratio of donor (Yb^{3+}) and acceptor (Tb^{3+}) equals 1. However, phenomena such as clustering of lanthanides and migration of energy between $Yb^{3+} \leftrightarrow Yb^{3+}$ pairs impose a limit on the concentration of dopants [47]. The relationship between luminescence intensity and pumping power in the analyzed germanium glass allows to investigate the mechanisms of up-conversion. Specifically, the relation between up-conversion emission intensity I_{UP} and pump intensity I_{IR} is determined by the condition:

$$I_{UP} \propto I_{IR}^{n}, \tag{1}$$

where n is the number of photons absorbed in the infrared to the number of photons emitted in the visible spectrum. Increase in the pump radiation intensity rises the number of absorbed photons to the Yb^{3+} laser level, and according to condition (1), emission intensity in the visible spectrum increases. In practice, slope of up-conversion emission intensity I_{UP} is lower than I_{IR}^n, because with increasing pumping power the saturation effect sets in, and competitions for population of intermediary excited states occur between linear processes and up-conversion phenomenon [48].

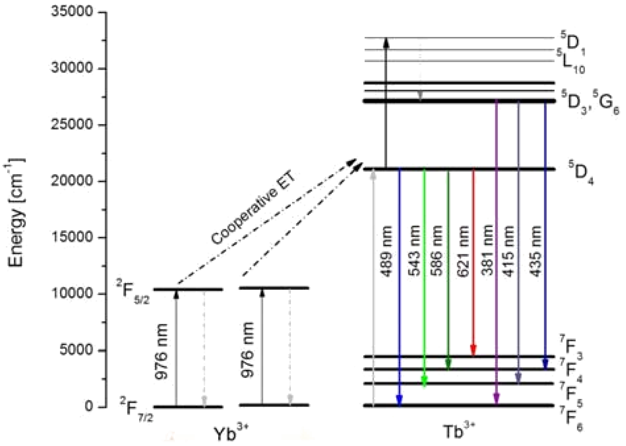

Fig. 14. Simplified energy level diagram of Tb^{3+}/Yb^{3+} ion and possible up-conversion luminescence mechanisms

Intensity of emission bands in the function of pumping power $\lambda_{exc} = 976$ nm is presented in a logarithmic scale in Fig. 15. Slope coefficients of the lines representing luminescence bands at 381, 415, 435 nm equal respectively 2.39, 2.50 and 2.25 which indicates the presence of a three-photon process of excitation conversion, presented on the energy diagram (Fig. 14). In the case of emission bands of 489, 543, 586 and 621 nm, the slope values are less than 2, implicating a two-photon process. Admittedly, emission bands ensued in result of a three-photon process are distinguished by several times lower emission intensity. Even so, in each of the analyzed glasses doped with 0.7 mol% Yb_2O_3/(0.07–0.7)mol% Tb_2O_3 the process did take place, confirming the viability of using germanate glasses for production of optical fibres characterized by up-conversion luminescence.

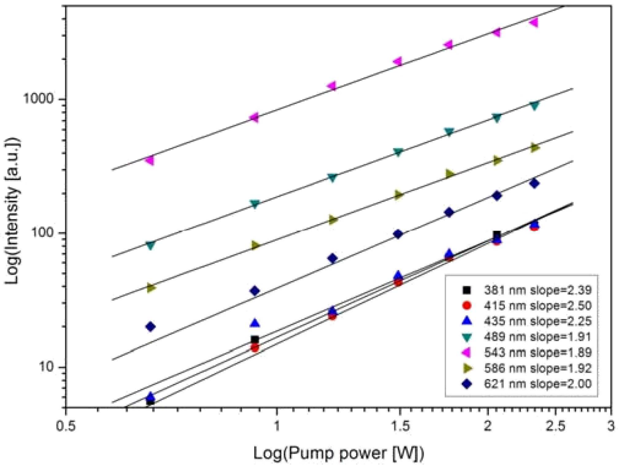

Fig. 15. Dependence of up-conversion emission intensity of 0.7Yb^{3+}/0.7Tb^{3+}- co-doped germanate glass on excitation power (λ_p=980 nm)

3. Conclusions

The research results concerning influence of lanthanide ion concentration on the form of emission spectrum in the produced glasses and optical fibres, as presented in the extent of the article, helped to explain quantum processes that involved transfer of energy between the selected rare earth elements. In fact, careful choice of rare earth element composition and concentration lays foundations for practical realization of broadband emission sources in which the emission spectrum arises from donor-acceptor ionic interactions.

In the course of the conducted experiments, the authors synthesized compound glasses which, after doping with Nd^{3+}/Yb^{3+}, Tm^{3+}/Ho^{3+} and Yb^{3+}/Tb^{3+} ions, emitted radiation originating from energy transfer in the bands of 1 μm, 2 μm and 0.54 μm. Taking into account material specifications along with spectroscopic analyses, selected glasses were used for production of active cores in double-clad optical fibres.

An innovative construction of multi-core optical fibres from silicate and phosphate glasses was proposed, opening new possibilities in the area of compact radiation sources design. Placing several cores in a single clad allowed to reduce the length of a fibre necessary to absorb pumping radiation. As a consequence of excitation with $\lambda_p = 808$ nm wavelength radiation, in the produced fibre doped simultaneously with Nd^{3+}/Yb^{3+} amplified spontaneous emission (ASE) in the band of 1 μm ensued owing to the energy transfer between neodymium and ytterbium ions. Also, it was observed that above 50 mm fibre length, ASE signal generated at the head, when passing through the fibre, was only amplified to the point where pumping signal allowing to induce spontaneous emission was still present. At distances from the head where the pump signal was nonexistent, partial reabsorption of ASE signal took place as a corollary of a wide absorption band of the present ytterbium ions.

In the case of glasses with $SiO_2 - Al_2O_3 - Sb_2O_3$ composition co-doped with Tm^{3+} and Ho^{3+} ions, because of the energy difference between multiplets $^3F_4$ (Tm^{3+}) and $^5I_7$(Ho^{3+}) amounting to ca. 400 cm^{-1}, quasi-resonant effective energy transfer Tm^{3+}→Ho^{3+} was observed. In the subsequently manufactured optical fibres, in the course of effective non-radiative energy transfer Tm^{3+}→ Ho^{3+}, causing a strong narrow band of amplified spontaneous emission (ASE) to appear. During measurements it was noted that inside the active medium, process of optical trapping in holmium ions transpired, prompting the shift of the luminescence maximum towards longer wavelengths, as well as the narrowing of the full width at half maximum. The effect of optical trapping was directly linked to the length of the segment over which the optical pump interacted with active core of the considered fibre, as well as to the concentration of Ho^{3+} ions. In comparison to luminescence of the glasses, in the produced fibre, over the length of 100 mm, maximum luminescence was achieved at the wavelength within the band $\lambda_e = 2108$ nm, while full width at half maximum at $\Delta\lambda_{FWHM} = 63$ nm.

Investigating the phenomena of energy transfer between RE ions located in a common glass medium, the authors developed also germanium glasses doped with Yb^{3+}/Tb^{3+}. During measurements of luminescence, carried out by subjecting the analyzed samples to radiation at a wavelength of 976 nm, luminescence bands in the visible spectrum originating from radiative transitions in energy levels configuration of the terbium ion were discerned. The strongest emission was achieved for a wavelength in the band of 0.54 μm which corresponded to $^5D_4 \rightarrow {}^7F_5$ transition. Due to the energy difference ΔE between laser level $^2F_{5/2}$ of the ytterbium ion and excited multiplet $^5D_4$ in terbium equal ca. 9350 cm^{-1}, the transfer of energy proceeded cooperatively from a coupled pair of Yb^{3+} ions. Further analysis concerning influence of the used dopants on the efficiency of energy transfer attested to the fact that the level of luminescence in glasses co-doped with Yb^{3+}/Tb^{3+} ions was heavily reliant on the concentration of terbium ions; in particular, the level was higher when the molar content ratio of donor (Yb^{3+}) to acceptor (Tb^{3+}) ions was equal to 1.

All in all, the presented wide scope of research on technology of glass production and on design of optical fibres co-doped with RE ions opens the way for practical realization of fibre sources of radiation with power of several to several dozen watts, classified in the broad VIS-NIR spectral range. To this end, concentration of used dopants needs to be optimized with particular consideration of their interdependencies, and material properties of the media employed for production of co-doped optical fibres must be acknowledged.

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