Rare earth ions doped aluminosilicate and phosphate double clad optical fibres

D. DOROSZ*

Bialystok University of Technology, 5D Wiejska St., 15-351 Bialystok, Poland

Abstract. The paper presents the result of investigations of aluminosilicate (low silica – 25 mol%) and phosphate optical fibres. The methods of glass preparation and their properties are showed. A set of physical measurements including: DTA, DSC, DL analysis, absorption spectroscopy, visible and infrared absorption edges and thermo-physical properties were determined. The stable glass compositions were doped with rare earth elements. Selected properties of obtained glasses are: high transmission, refractive index 1.53–1.68, high solubility of RE ions (up to 10 wt%). Double-crucible and rod-in-tube drawing techniques were applied to obtain aluminosilicate and phosphate double clad optical fibres doped with neodymium and ytterbium ions. Luminescence spectra of manufactured glasses and fibres are presented.

Key words: rare-earths in glasses, double clad optical fibre, oxide glasses, low silica glass.

1. Introduction

Interest in glass, due to its diverse applications, has been observed from time immemorial. Glass as a material is comparatively cheap, relatively easy to produce as well as use for synthesis in a wide range of compositions. No wonder that modern optoelectronics has chosen glass as a material for its latest applications, e.g. from elements used to build all optical network to more and more complex constructions of optical fibres for fibre lasers. The search for appropriate glass compositions has been focused on obtaining required optical proprieties keeping simultaneously their thermal stability. Good thermal properties of glasses make it possible to process them in such a way as to obtain definite constructions of optical fibres, including fibres doped with high rare-earth (RE) ion concentrations. The isotropic proprieties of glasses permit to achieve a suitable degree of the disordered state around the doped RE ions, which results in the broadening of the luminescence band [1]. This in turn makes it possible to build broadband amplifiers or impulse lasers. The uses of glass for these purposes, apart from suitable optical and thermal proprieties, require elastic matrix to allow for the dissolution of large concentrations of RE ions. If the host material can incorporate a high concentration of the dopant, it will allow to build short, only a few centimetres long amplifiers, indispensable for optical networks or high power lasers. The search for glasses possessing required optical and thermal properties has led to the development of a large number of glass manufacturing formulas. The most promising are: silicates, phosphates, tellurites and fluorites.

Of the most significance for telecommunications uses is the silicate glass used to build EDFA fibre amplifiers. Taking a closer look at fibre lasers above 100 W, it should be noted that the silicate glass has been the only material allowing to achieve such high values. Glasses of high SiO_2 content, due to their strong Si-O-Si covalent bonds, permit only small amounts of RE elements (500 ppm). At higher concentrations we encounter the phenomenon known as clustering i.e. bonding of the active dopant ions. An observable effect of the phenomenon is the phase separation of dopant groups or the occurring of crystalline phase. As a result, we obtain a lower level of luminescence for a higher concentration of the active dopant. The above is caused by energy transfer processes that occur between the dopant ions in the created cluster.

Phosphate glasses make it possible to introduce a large number of RE elements to build a few watt amplifiers using only a few centimetres long fibres [1]. Moreover, phosphate glasses on the contrary to silicate have lower melting and transition temperatures and posses no tendency to crystallisation which is critical during optical fibre drawing [2].

Tellurite and fluorite glasses manifest both good optical properties and low phonon energy, however their industrial applications are limited due to their low thermal stability and relatively difficult and costly synthesis [3].

An alternative for the applications within mid-infrared range (up to 5 μm) may be glasses of low SiO_2 content modified by the elements that either combine with the dopant ions or cause non-bridge oxygen to appear in the rigid silicate structure. Such properties are manifested in particular by: Al_2O_3, P_2O_5, Na_2O i K_2O. It has been known that an addition of Al_2O_3 with an RE ion in about 8:1 ratio to silicate matrix prevent clustering, thus making it possible to introduce higher concentrations of RE elements [3]. However, the SiO_2 content in the glasses used so far is quite high (50–80% mol), which limits the possibilities of effective doping. An alternative for this are glasses of low SiO_2 content (<40% mol) modified by high aluminium oxide contents.

---

*e-mail: domdor@pb.edu.pl

The paper describes method of obtaining low SiO_2 content (25% mol) and phosphate glasses doped with RE elements (0.5–10% wt) as well as their physical and optical properties. The presented compositions of phosphate [4–10] and silicate [11–15] glasses were chosen in order to incorporate into the glass high concentration of rare earth elements without clustering effect. It allows obtaining high luminescence from the short length optical fibres. In the presented paper manufactured silicate and phosphate glasses were used to draw double clad optical fibres.

2. Experiments

As a glass hosts for RE ions doping two different systems based on SiO_2 and P_2O_5 were obtained. The concentrations of the particular components in silica glass were the following: 28 mol% Al_2O_3, 25 mol% SiO_2, 15 mol% PbO, 15 mol% H_3BO_3, 12 mol% Na_2CO_3, 5 mol% K_2CO_3-xNd_2O_3 ($x = 0.5-7.5$ wt%) (28Al-25Si). The second investigated phosphate glass was melted in accordance with composition: $65P_2O_5$-$8Al_2O_3$-$27BaO+ZnO+Na_2O+MgO$ (% mol) (65P-8Al). The glasses used in this work were synthesized by a conventional melting and quenching method. Pure oxide materials (99.99%) were used to prepare glass batches in the investigated system doped by Yb_2O_3 and Nd_2O_3 (99.99%) in the range 0.5–10 wt%. The glasses were melted in covered platinum crucibles, in an electric furnace, at the temperature 1623–1723 K. The melting time was 90 min. The melted mass of glass was poured into a brass mould preheated around the glass transition temperature and annealed in the temperature range 743–903 K depending on the glass composition. The amorphous state was tested by the method of X-ray diffraction on a roentgen meter Seifert – FMP XRD7. The effect of crystallization or phase separation of the active dope was not noticed. The thermal properties of obtained glasses were determined by DTA/DSC measurements. A Perkin Elmer DTA 7 System and Setaram Labsys were used to conduct the thermal characterization. The sample was contained in platinum crucible and heated at a rate of 10 K/min over a temperature range of 323–1273K. The system was purged with nitrogen gas. The glass transition temperature T_g was determined in the inflection point of the DTA/DSC curve. The change of T_g is combine with value of specific heat Δc_p. The ability of glasses to crystallization were determined by the value of crystallization temperature T_c as well as connected with it enthalpy of crystallization ΔH_c. The thermal expansion coefficient was measured by a standard dilatometer. Samples with a size of 5×5×20 mm were prepared and heated from 293–853 K with a heating rate of 5 K/min. The density of the glass was determined by the method of hydrostatic weighing. The light transmission measurement of samples having the form of polished plates 20×10×2 mm was carried out in the range 0.2–1.1 μm on a monochromator OL-750 with HSD-300 Silicon detector and in the range 2.5–25 μm on a spectrophotometer Specord M80 Carl Zeiss Jena. The refractive indexes of obtained glasses were measured by Abbe refractometer RL3. The measurements were carried out in reflected and transmitted light. The spectral absorption coefficient $k(\lambda)$ was evaluated using the relationship:

$$k(\lambda) = \frac{1}{d} \ln \frac{1}{T_r(\lambda)} \tag{1}$$

where: $T_r(\lambda)$ is the spectral transmission through the optical path length, d – thickness of sample.

In the luminescence measurements, glasses and fibres were excited by a system that consisted of: pumping diodes – HLU30FAC400-808P ($\lambda = 808$ nm) HLU25FAC400-940P ($\lambda = 937$ nm) with optical fibre output (400 μm, NA = 0.22) and the laser beam forming system. Luminescence output from glasses and fibres was transmitted by an optical fibre (100 μm) to the spectrometer (Ocean Optics HR4000) – scattering radiation is measured for the typical geometry of fibre laser.

The microhardness of the glasses was determined by the Vicker's method, measuring the diagonal of the indentation of a diamond pyramid at a load of 100g forced into a sample for 5s.

3. Results and discussion

3.1. Aluminosilicate glasses and fibres. Table 1 shows typical ranges of values for the measured properties of the obtained aluminosilicate glasses. Figure 1 presents the dilatometer curve of the 28Al-25Si glass doped with Nd^{3+} (2.5 wt%). The thermal expansion coefficients as well as transition temperatures (T_g) and softening points (Ts) of investigated glasses are given in Table 2. The thermal expansion coefficient of the glasses is about 85×10^{-7} [K^{-1}]. Due to this the obtained glass can be combined with other types of glasses with similar values of that parameter but other refractive index. The above is essential for choosing appropriate optical fibre materials. Another key parameter in the optical fibre manufacturing process is the tendency of the glass to crystallization. If the glass has a crystallization peak, its position should be considerably distant from the drawing temperature. It has been found that even thermally stable glasses ($T_c - T_g = 100$), undergo re-crystallization during the optical fibre manufacturing process [16]. Figure 2 shows a typical DSC curve of the 28Al-25Si glass. The value of the transition temperature of the glass equals to 726 K and the specific heat connected with transition $\Delta c_p = 0.434$ J g^{-1}°C^{-1}. There is a small tendency for crystallization within the temperature range of 884–917 K in the glasses obtained.

Table 1

Properties of glasses

Property	Range of values
Density [g cm^{-3}]	3.8–4.2
Microhardness [GPa]	8.5–9.0
Molar volume [cm^3 mol^{-1}]	24.6–25.8
Refractive index (633 nm)	1.63–1.68
The range of spectral transmission [μm]	0.4–4.5

Table 2
Thermal analysis results

Property	Range of values
DL analysis	
Thermal expansion coefficient α (373–673 K) [10^{-7} K^{-1}]	82–89
Glass transition temperature T_g [K]	711–753
Softening point T_s [K]	773–808
DSC analysis	
Glass transition temperature T_g [K]	718–731
Specific heat Δc_p [J g^{-1} K^{-1}]	0.434–0.621
Crystallization Temperature T_c [K]	884–917
Enthalpy of crystallization ΔH_c [J g^{-1}]	1.74–119.86
Thermal stability parameter ($\Delta T = T_c - T_g$) [K]	166–186
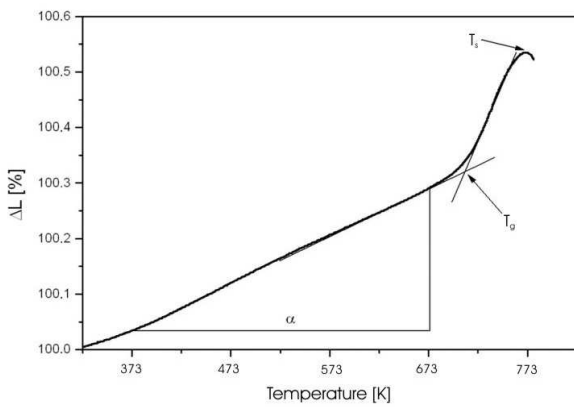
Fig. 1. Thermal expansion coefficient of 28Al-25Si glass
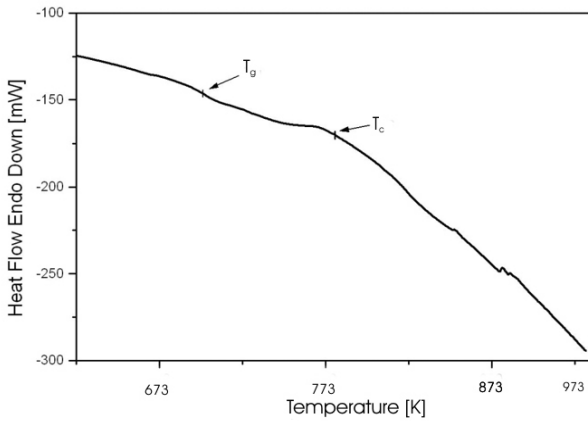
Fig. 2. DSC curve of 28Al-25Si glass

Results of the thermal investigations of aluminosilicate glasses doped with Nd_2O_3 have shown the thermal effects characteristic for typical phase transitions occurring in a glassy material during heating (Fig. 3). Increase of Nd_2O_3 content, introduced into the structure of glasses, causes an increase of the glass transition temperature T_g and also an increase of the specific heat (Δc_p) accompanying the glass transition region (Table 3). The key parameter in the optical fibre

manufacturing process is the tendency of the glass to crystallization. Thermal analysis shows that obtained aluminosilicate glasses doped with Nd_2O_3 are resistant to crystallisation and can be easily used for drawing optical fibres.
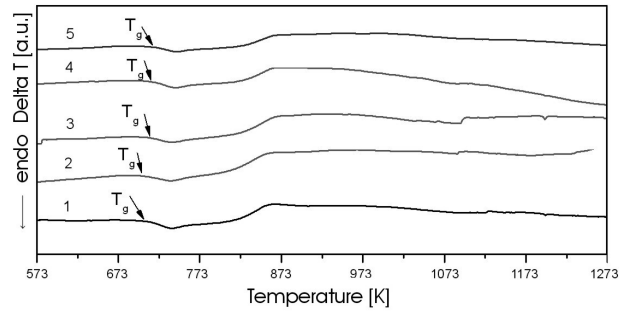

Fig. 3. DTA curves of aluminosilicate (28Al-25Si) glasses No 1, 2, 3, 4, 5

Table 3
Thermal DTA characteristics of aluminosilicate glasses doped with Nd_2O_3

Glass No	Nd_2O_3 [wt%]	T_g [K]	Δc_p [Jg$^{-1 \circ}$K^{-1}]
1	1% Nd_2O_3	442	0.612
2	1.5% Nd_2O_3	443	0.690
3	2% Nd_2O_3	447	0.670
4	2.5% Nd_2O_3	449	0.896
5	3% Nd_2O_3	452	0.672

The glasses are characterized by a high thermal stability manifested by the difference between the crystallization and transition temperatures. The samples kept at room temperatures showed no deterioration of their optical parameters, which demonstrates low hygroscopicity of the glass. Another property of the obtained glasses is their microhardness, which is high. The property is critical for the strength of the optical fibre made from those glasses.

The infrared spectrum of the investigated glasses has the transmission range of the order of 80% (3.7 μm) and 50% (4 μm). The transmission spectra of the glass doped with Nd^{3+} ions in the range 0.5–7.5 wt% were made. The strongest absorption bands in the transmission curve of the glass doped with Nd_2O_3 (3 wt%) are found at the following wavelength: 515, 525, 585, 805 and 880 nm. However, as the neodymium content increases, the absorption bands also increase. For the sake of the used pump wavelength (808 nm), the important absorption band is placed at about 805 nm. Using the transition band-band for this value, it is possible to determine the distance of the neodymium energy level (^{2}H$_{9/2}$, ^{4}F$_{5/2}$), which are excited from the ground state ^{4}I$_{9/2}$. Following quick non-radiative relaxation at the excitation level, the electrons take a metastable state ^{4}F$_{3/2}$, that enables luminescence at the following wavelength: 900 nm (^{4}F$_{3/2} \rightarrow ^4$I$_{9/2}$), 1060 nm (^{4}F$_{3/2} \rightarrow ^4$I$_{11/2}$) and 1300 nm (^{4}F$_{3/2} \rightarrow ^4$I$_{13/2}$). The strongest absorption band occurs, however, at 585 nm, which is related to the ESA phenomenon that is disadvantageous due to the energy balance.

To determine the absorption coefficient spectra $k(\lambda)$ formula (1) is used. To determine the energy levels each of the absorption bands is described using Paschen notation [3]. Fig-

ure 4 shows the determined absorption coefficient spectra of the glass activated with Nd^{3+} ions. The absorption spectra of the glass doped with neodymium indicate a complex of the energy structure. Some bands are described by more that one notation which indicates that in glass matrix with neodymium there is a considerable multiple mixing.

The refractive indexes were determined using Abbey method. Figure 5 shows the refractive index (633 nm) for the increasing concentration of Nd^{3+} dopant. The increase of the glass refraction index caused by the active dopant makes it possible to use the same or similar host glass composition for the optical fibre cladding. Such a system allows precise control of the cladding refraction index in order to ensure single mode fibre operation. Moreover, the similarity of both core and cladding glass compositions on account of practically no mechanical stress, ensures high quality of the optical fibre especially required for fibre lasers.

the transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$ and indicates a possibility of pumping the obtained glasses with a laser diode 980 nm. Figure 6 shows absorption coefficient spectra of the glass activated with Yb^{3+} ions. The absorption spectra of the glass doped with ytterbium is quite simple and has two absorption bands. In this case, close to the energy state $^2F_{5/2}$ there is another band at about 910 nm $^2F(3)_{5/2}$. This band results from the interactions with the local matrix field and causes Stark multiple broadening $^2F_{5/2}$ [3]. In ytterbium structure of energy levels there are usually two transitions from the state $^2F_{5/2}$ to $^2F_{7/2}$. These two multiples are separated from each other by energy E=10500 cm^{-1} and gives a simple system of energy levels. Namely the luminescence is observed at the wavelength of about 975 nm and 1020 nm. In silicate glasses ytterbium keeps very good stability with temperature change during the excitation, this makes it so successful in the optical fibre lasers.
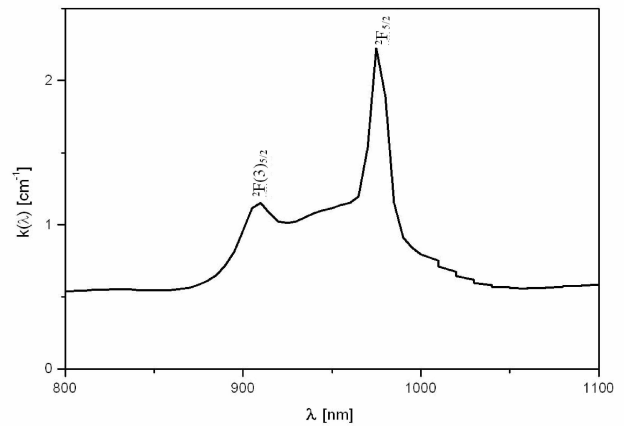

Fig. 4. Spectral absorption coefficient k(λ) of Nd^{3+} (3 wt%) glass

Fig. 6. Spectral absorption coefficient k(λ) of Yb^{3+} (2 wt%) glass
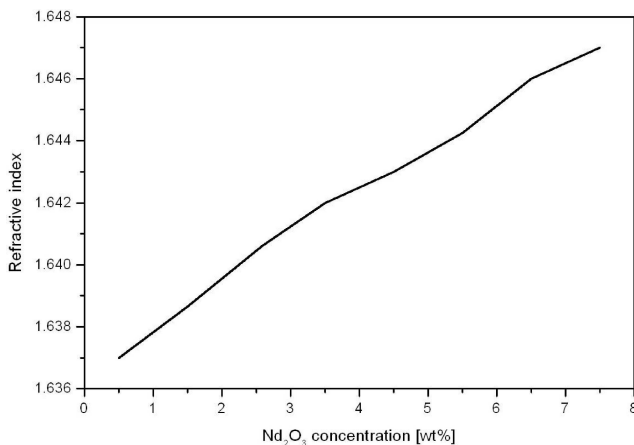
Fig. 5. Refractive index vs. Nd_2O_3 concentration

The transmission spectra of the glass doped with Yb^{3+} ions in the range 0.5–7.5 wt% were determined. However, as the ytterbium content increases, the absorption bands also increase. In the case of ytterbium the strongest absorption bands in the transmission curve are found at wavelength 910 and 975 nm. A strong absorption at 975 nm corresponds to

The refractive indexes for glasses with various concentrations of Yb^{3+} and slight changes of PbO were determined. The increase of the core glass refraction index is caused by the co-dopants makes it possible to use the same host glass composition for the optical fibre cladding. Such a system allows precise control of the cladding refraction index in order to ensure single mode fibre operation. Moreover, the similarity of both core and cladding glass compositions on account of practically no mechanical stress, ensures high quality of the optical fibre especially required for fibre lasers.

The luminescence emission spectra of glasses (28Al-25Si) doped with Nd_2O_3 1 wt% and 2 wt% is shown in Fig. 7. The obtained aluminosilicate glasses emit light at 870 nm and 1064 nm that corresponds to $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition respectively. It means that we have three-level laser scheme which is usually unparalleled in silica glasses. Possibly, it is the result of the presence of Al_2O_3 in a significant amount. In order to explain that phenomenon the further structure investigations are needed. The lifetime of the $^4F_{3/2}$ state is approximately 250 μs and constant of dopant concentration up to 2.5 wt% Nd_2O_3.
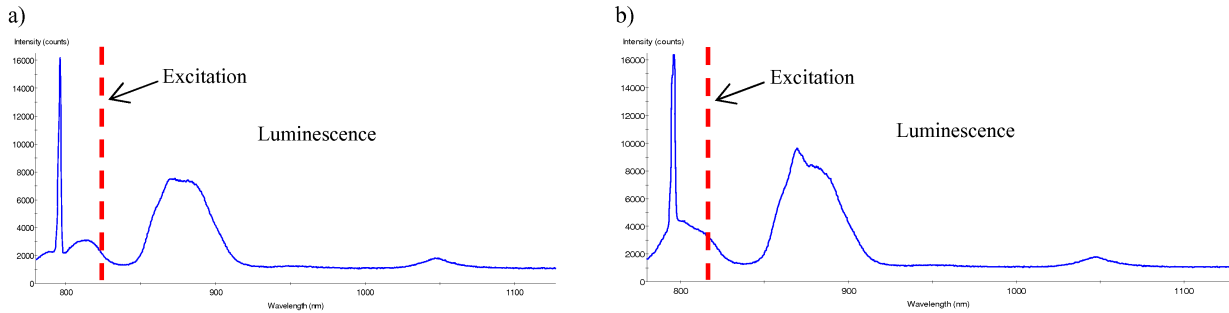
Fig. 7. Measured luminescence emission spectra of silicate glasses (28Al-25Si) doped with Nd_2O_3 1.5 wt% (a) and 2 wt% (b). Diode laser emission spectrum is marked by dashed line

Aluminosilicate glasses presented in the paper were used to draw a double clad optical fibre doped with Nd_2O_3 (1.5 wt%). Glasses with the following refractive indexes: $n_{core} = 1.64$, $n_{1clad} = 1.636$ and $n_{2clad} = 1.52$ were used for the core and claddings. The numerical aperture of the obtained fibre amounts to $NA_{core/n1} = 0.12$ and $NA_{n1/n2} = 0.61$. The diameters of the obtained double clad fibre are the following: $d_{core} = 35$ μm, $d_{1clad} = 145$ μm and $d_{2clad} = 150$ μm (Fig. 8). Luminescence spectrum of that fibre is shown in Fig. 9. Surprisingly, after drawing process we discover both luminescence bands at 870 nm and 1010 nm. It implies that after re-melting the structure configuration of the glasses is changed. However, we notice that repeated melting of earlier synthesized glasses in a separated crucible fail to generate luminescence at 1010 nm. It may result from the usage of the crucible method for fibre drawing. In crucible method the temperature of the system is raised to achieve 10^4 dPas of glass viscosity. It may cause diffusion processes between liquid core and cladding glasses, which, in turn, cause RE structure change. However, this phenomenon needs to be investigated in detail.

Rod-in-tube method drawing technique was used to fabricate double clad optical active fibres with D- profile inner cladding. The numerical aperture of the obtained fibre amounts to $NA_{core/n1} = 0.27$ and $NA_{n1/n2} = 0.58$. The diameters of the obtained double clad fibre are the following: $d_{core} = 40$ μm, $d_{1clad} = 340$ μm and $d_{2clad} = 360$ μm

(Fig. 10). Significant diameter of inner cladding and numerical aperture $(NA)_1$ facilitate effective coupling pump laser diode with fibre.

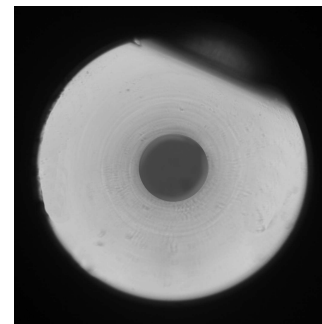Fig. 8. Double clad optical fibre doped with Nd_2O_3 (1.5% wt)

The luminescence spectra of manufactured optical fibres under excitation of 808 nm laser diode are shown in Fig. 11. In the emission spectra of obtained optical fibres strong band at 1015 nm were identified. This band is assigned to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition [13].

The possibility of manufacturing optical fibres from the obtained aluminosilicate glasses was also confirmed by producing of double core optical fibre containing 2 wt% Yb_2O_3 by means of the crucible method. For the cores and cladding were used glasses with the refractive indexes: $n_1 = 1.649$ and $n_2 = 1.637$ [17].
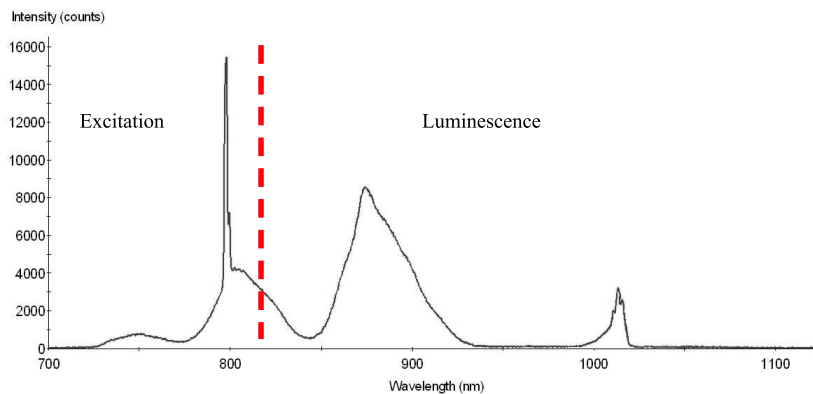

Fig. 9. Luminescence spectrum of the fibre doped with Nd_2O_3 (1.5 wt%). Pumping diode laser emission spectrum is marked by dashed line
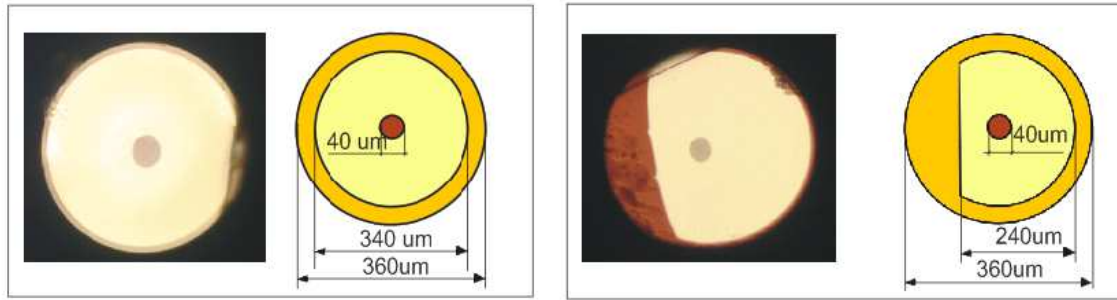
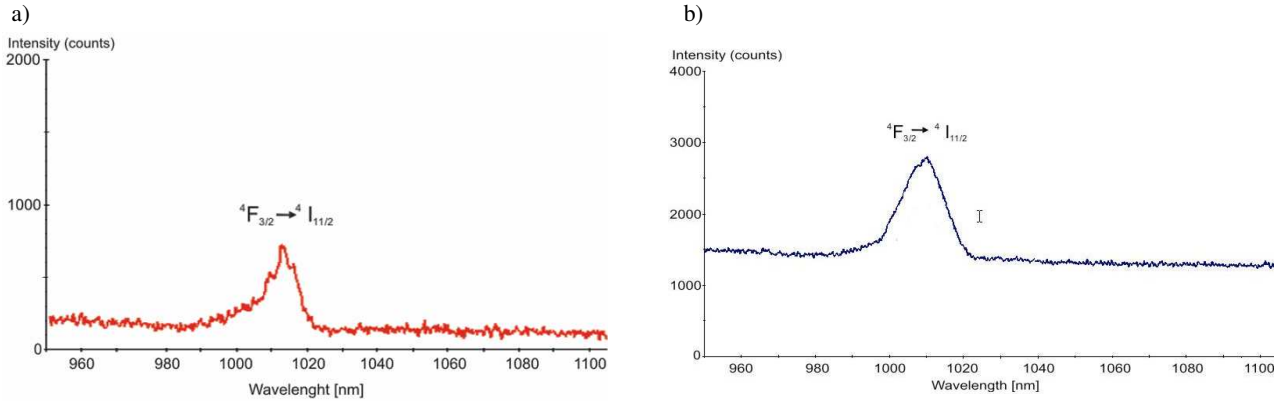Fig. 10. Geometrical dimensions of obtained double clad optical fibers

a)

b)

Fig. 11. Luminescence spectra of obtained phosphate double clad optical fibers. (a) circular, (b) D – profile

3.2. Phosphate glasses and fibres. Figure 12 shows the transmission of phosphate glass host ($65P_2O_5 - 8Al_2O_3 - 27BaO + ZnO + Na_2O + MgO$ % mol) within the range from 400 to 1100 nm. The measurement was carried out for polished glass plate with thickness of 3.6 mm without taking into account of Fresnel reflection.
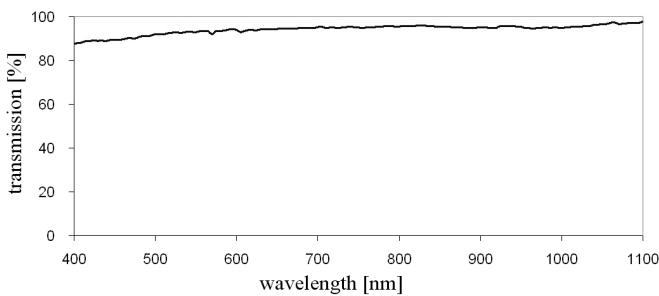
Fig. 12. Transmission spectra of 65P-8Al glass

Table 4 shows typical ranges of values for the measured properties of the obtained glasses from the P_2O_5-Al_2O_3-BaO-ZnO-Na_2O-MgO (% mol) system. The values of density and molar volumes values are connected with molar mass of atoms forming glass and phosphorus ion as the main network builder.

The refractive index increases with increase of the polarizability and decrease of the molar volume [18]. The incorporation of 3-valued RE^{3+} ions into phosphorus glass increases the polarizability of glass matrix which in consequence results in higher glass refractive index (Fig. 13).

Table 4

Properties of glasses from the P_2O_5-Al_2O_3-BaO-ZnO-Na_2O-MgO (% mol) system

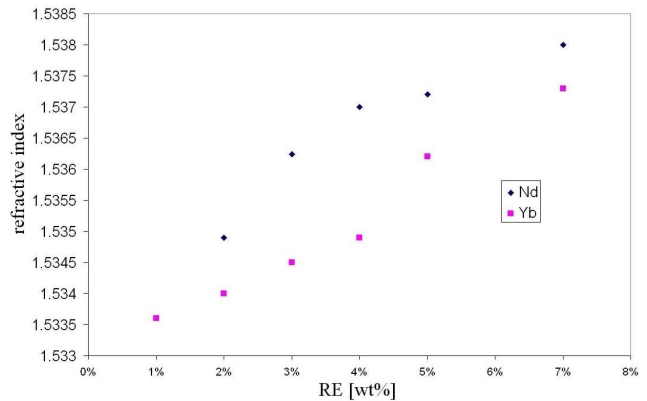| Properties	Range of values
Density [g cm^{-3}]	2.72–2.99
Molar volume [cm^3 mol^{-1}]	42–45
Refractive index (633 nm)	1.52–1.538
The range of spectral transmission [μm]	0.25–2.5
Thermal expansion coefficient (DL) α (373–673 K) [$10^{-7}K^{-1}$]	72–80
Glass transition temperature (DL) T$_g$ [K]	753–773
Softening point (DL) T$_s$ [K]	793–823
Glass transition temperature (DSC) T$_g$ [K]	743–763

Fig. 13. Effect of RE (Nd_2O_3 and Yb_2O_3) doping on the value of refractive index

The presented phosphate glasses allow controlling refractive index which is essential if we have to obtain optical fibre with defined numerical aperture. The refractive index of investigated glassy system can be adjusted by changing Al_2O_3/BaO ratio. When BaO is replaced with Al_2O_3, the number of bridging oxygen's is increased. It is causing decrease of ionic refractivity and in consequence the decrease of refractive index. Figure 14 presents decrease of refractive index from 1.537 to 1.518, when BaO was replaced by Al_2O_3 in the range 8–18% mol.
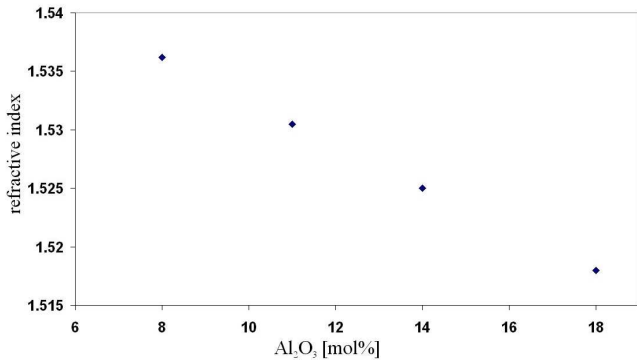
Fig. 14. Effect of Al_2O_3/BaO ratio in P_2O_5-Al_2O_3-BaO-ZnO-Na_2O-MgO (% mol) system on the value of refractive index

The thermal expansion coefficients as well as transition temperatures (T_g) and softening points (T_s) of investigated glasses are showed in Table 4. Figure 15 presents the dilatometer curve of the phosphate glass (65P-8Al) used as a core in optical fibre glass doped with Nd^{3+} (7 wt%).
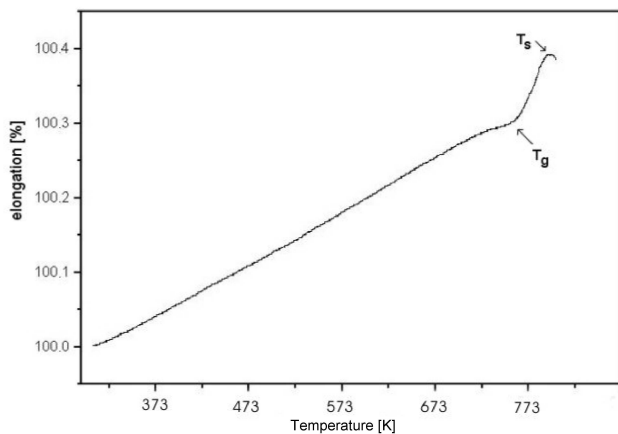

Fig. 15. Dilatometer analysis of glass 65P-8Al

Figure 16 shows DSC curves of the phosphate glass (65P-8Al) doped with Nd_2O_3 and Yb_2O_3 (7 wt%). Glass transition determined from DSC is 485°C and is conforming to dilatometer measurements. Thermal analysis shows that phosphate glasses are resistant to crystallisation and can be easily used for drawing optical fibres.
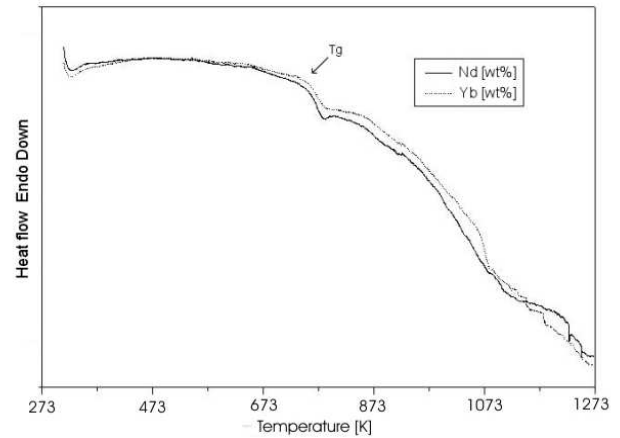

Fig. 16. DSC curves of glass 65P-8Al doped with Nd_2O_3 and Yb_2O_3 (7% wt.)

Figures 17 and 18 show absorption coefficient spectra of the glasses 65P-8Al activated with Nd^{3+} (2–8 wt%) and Yb^{3+} (1–10 wt%) ions.
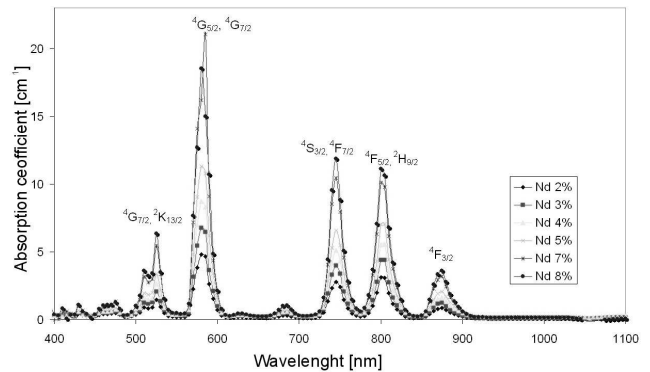

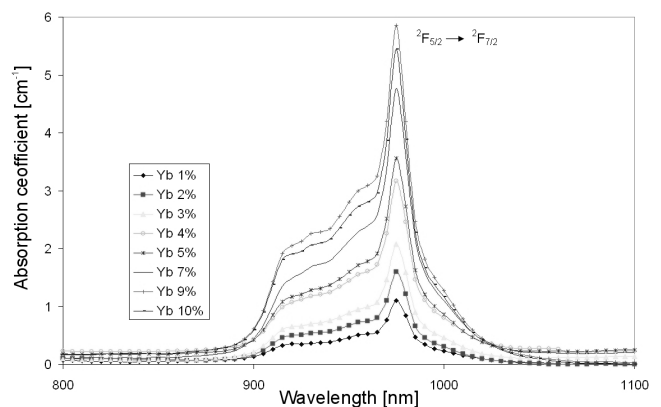Fig. 17. Spectral absorption coefficient $k(\lambda)$ of phosphate glass 65P-8Al doped with Nd_2O_3 (2–8% wt.)

Fig. 18. Spectral absorption coefficient $k(\lambda)$ of phosphate glass 65P-8Al doped with Yb_2O_3 (1–10% wt.)

Luminescence spectra of phosphate glasses (65P-8Al) doped with Nd_2O_3 7 wt% under excitation of 808 nm laser diode is shown in Fig. 19. The obtained emission bands at 900 nm and 1060 nm correspond to $^4F_{3/2} \rightarrow ^4I_{9/2}$ and

$^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions respectively. It means that three-level laser scheme is predominant in investigated phosphate glasses. Emission spectra of Yb^{3+} ions (9 wt%) in phosphate glass host pumped at 937 nm show us luminescence bands at 980 nm and 1010 nm wavelength. In the investigated glasses $65P_2O_5$-$8Al_2O_3$-$27BaO+ZnO+Na_2O+MgO$ (% mol) we observed very strong emission bands. Further increasing of Nd_2O_3 and Yb_2O_3 concentration over 7 wt% and 9 wt% respectively causes decrease of luminescence. However achieved results show that obtained phosphate glasses posses more open and flexible network than silicate glasses.

Manufactured phosphorus glasses were used to draw a double clad optical fibre doped with Nd_2O_3 (7 wt%). The numerical aperture of the obtained fibres amounts to $NA_{core/n1} = 0.25$ and $NA_{n1/n2} = 0.35$. Two types of double clad fibres were made: round and acentric (offset the core). The cross section of optical fibres and their luminescence spectrum are shown in Figs. 20 and 21. Acentric double clad optical fibre due to offset the core allows to increase pumping efficiency and in consequence its luminescence. Emission spectra of fabricated fibres confirm that fact shoving strongest luminescence band in case of acentric double clad optical fibre.
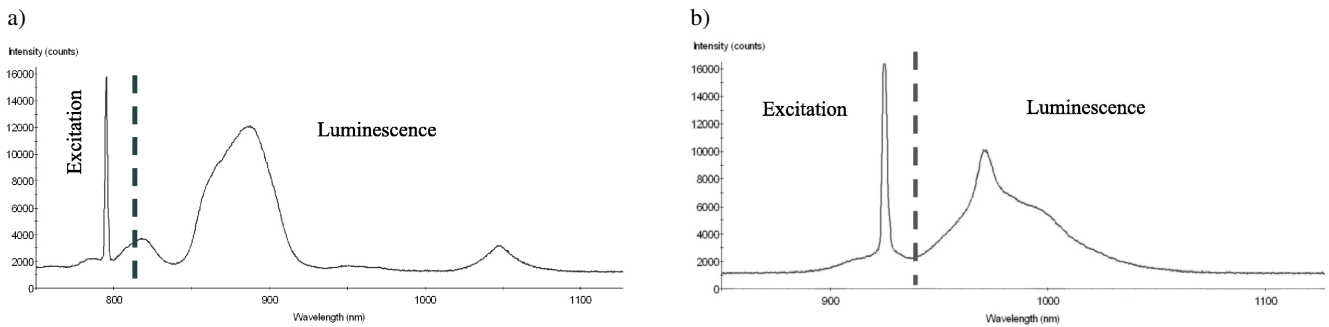

Fig. 19. Measured luminescence emission spectra of glasses doped with Nd_2O_3 (7% wt.) (a) and Yb_2O_3 (9% wt.), (b) Pumping diode lasers emission spectrum are marked by dashed line

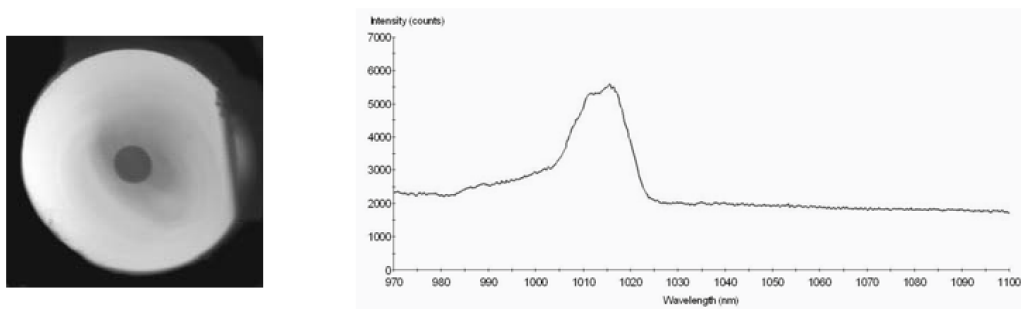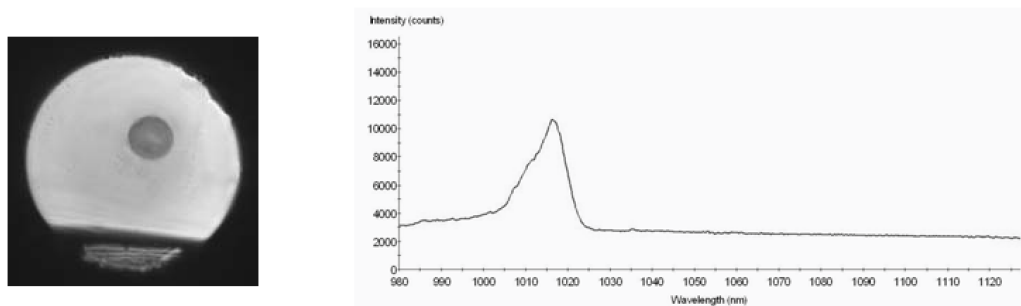Fig. 20. Double clad round optical fibre doped with Nd_2O_3 (7% wt.), Outer diameter – 300 μm, core diameter – 40 μm, NA = 0.25

Fig. 21. Double clad acentric optical fibre doped with Nd_2O_3 (7% wt.), Outer diameter – 300 μm, core diameter – 40 μm, NA = 0.25 Double clad acentric optical fibre doped with Nd_2O_3 (7% wt.), Outer diameter – 300 μm, core diameter – 40 μm, NA = 0.25

4. Conclusions

Aluminosilicate glasses with low SiO_2 content may be doped with a large amount of Nd_2O_3 (0.5–7.5 wt%) and causing neither the crystallization effect nor dopant phase separation. Aluminosilicate glasses posses very good mechanical and optical properties (transmission 0.4–4.5, luminescence at 870 nm). Thermal analysis shows that obtained glasses doped with Nd_2O_3 are resistant to crystallisation and can be easily used for drawing optical fibres. Double clad optical fibre doped with Nd_2O_3 (1.5 wt%) was made using the crucible method. Luminescence emission from the fibre at 870 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$) and 1064 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) was presented.

Rod-in-tube method drawing technique was used to fabricate double clad optical active fibres with circular and D- profile inner cladding. In results of 808 nm laser diode pumping the luminescence spectra of optical fibres were observed. This emission band at 1015 nm corresponds to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ optical transition.

Manufactured double clad optical fibres enables good coupling with pump laser diodes and high efficiency of pumping active core and can be applied to build fibre laser. It has shown that the D- profile optical fibre has higher level of luminescence than circular double clad optical fibre.

The synthesis method and properties of phosphorus glasses from the system P_2O_5-Al_2O_3-BaO-ZnO-Na_2O-MgO were presented. These glasses posses very good optical properties, great thermal stability (no tendency to crystallisation) and can accept high concentration of rare earth ions Nd^{3+} (7% wt.) and Yb^{3+} (9% wt.). Round and acentric double clad optical fibres doped with Nd_2O_3 (7 wt%) were fabricated. Strong luminescence emission from the fibres at 1015 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) was presented.

REFERENCES

[1] B.C. Hwang, S. Jiang, T. Luo, K. Seneschal, G. Sorbello, M. Morrell, F. Smektala, S. Honkanan, J. Lucas, and N. Peyghambarian, "Performance of high-concentration Er^{3+}-doped phosphate fiber amplifiers", *IEEE Photon. Tech. Lett.* 13, 197–199 (2001).

[2] M.J. Dejneka, "The luminescence and structure of novel transparent oxyfluoride glass-ceramics", *J. Non-Crystalline Solids* 239, 149–155 (1998).

[3] M.J.F. Digonnet, *Rare-Earth-Doped Fiber Lasers and Amplifiers*, Marcel Dekker, New York, 2002.

[4] K. Seneschal, F. Smektala, B. Bureau, M. Floch, S. Jiang, T. Luo, J. Lucas, and N. Peyghambarian, "Properties and structure of high erbium doped phosphate glass for short optical fibers amplifiers", *Materials Research Bulletin* 40, 1433–1442 (2005).

[5] E.T.Y. Lee and E.R.M. Taylor, "Optical and thermal properties of binary calcium phosphate and barium phosphate glasses", *Optical Materials* 28, 200–206 (2006).

[6] P.A. Bingham, R.J. Hand, and S.D. Forder, "Doping of iron phosphate glasses with Al_2O_3, SiO_2 or B_2O_3 for improved thermal stability", *Materials Research Bulletin* 41, 1622–1630, (2006).

[7] P.Y. Shih, "Thermal, chemical and structural characteristics of erbium-doped sodium phosphate glasses", *Materials Chemistry and Physics* 84, 151–156 (2004).

[8] Byung Hae Jung, Duk Nam Kim, and Hyung-Sun Kim, "Properties and structure of (50-x)BaO-xZnO-50P_2O_5 glasses", *J. Non-Crystalline Solids* 351, 356–3360 (2005).

[9] F.F. Sene, J.R. Martinelli, and L. Gomes, "Optical and structural characterization of rare earth doped niobium phosphate glasses", *J. Non-Crystalline Solids* 348, 63–71 (2004).

[10] L. Koudelka, P. Mosner, M. Zeyer, and C. Jager, "Structure and properties of mixed sodium-lead borophosphate glasses", *J. Non-Crystalline Solids* 351, 1039–1045 (2005).

[11] P. Glas and D. Fisher, "Cladding pumped large – mode – area Nd doped holey fiber laser", *Optical Society of America. OCIS codes (060.2280) Fiber design, (140.3510) Lasers, Fiber*, (2002).

[12] J. Nilsson, W.A. Clarkson, R. Selvas, J.K. Sahu, P.W. Turner, S.-U. Alam, and A.B. Grudinin, "High-power wavelength-tunable cladding-pumped rare-earth-doped silica fiber lasers", *Optical Fiber Technology* 10, 5–30 (2004).

[13] Y.Qiao, N. Da, D. Chen, Q.Zhou, J. Qiu, and T.Akai, "Spectroscopic properties of neodymium doped high silica glass and aluminum codoping effects on the enhancement of fluorescence emission", *Appl. Phys.* B87, 717–722 (2007).

[14] P. Leproux, D. Valerie, P. Roy, D. Pagnoux, F. Mortessagne, and O. Legrand, "Experimental study op pump power absorption along rare – earth – doped double clad optical fibres", *Optics Communications* 218, 4–6 (2003).

[15] Y.C Ratnakaram, A. Vijaya Kumar, D. Thirupathi Naidu, R.P.S Chakradhar, and K.P. Ramesh, "Optical absorption and luminescence properties of Nd in mixed alkaliborate glasses", *J. Luminescence* 110, 65–77 (2004).

[16] J. Dorosz, "Optical fibre technology", *Ceramics* 86, (2005).

[17] I.V. Kityk, J. Wasylak, D. Dorosz, J. Kucharski, and A. Brenier, "New Nd-doped heavy oxide metal glasses for NIR light emission", *Materials Letters* 49, 272–276 (2001).

[18] S. Jiang, T. Luo, B.C. Hwang, F. Smektala, K. Seneschal, J. Lucas, and N. Peyghambarian, "Er^{3+}-doped phosphate glasses for fiber amplifiers with high gain per unit length", *J. Non. Cryst. Solids* 263–264, 363–368 (2000).