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Nd^{3+}-doped oxyfluoride glass ceramics optical fibre with SrF_2 nanocrystals

MANUELA REBEN[1*], DOMINIK DOROSZ[2], JAN WASYLAK[1],
BOŻENA BURTAN[3], JANUSZ JAGLARZ[3], JOANNA ZONTEK[1]

[1]Faculty of Materials Sciences and Ceramics, AGH – University of Science and Technology, al. Mickiewicza 30, 30-059 Cracow, Poland

[2]Department of Optoelectronics and Lighting Technology, Białystok University of Technology, ul. Wiejska 45, 15-351 Białystok, Poland

[3]Institute of Physics, Cracow University of Technology, ul. Podchorążych 1, 30-084 Cracow, Poland

[*]Corresponding author: manuelar@agh.edu.pl

A neodymium (Nd^{3+}) doped oxyfluoride glass ceramics containing SrF_2, LaF_3 nanocrystals has been presented. Transparent glass ceramics was obtained by heat treating the glass from the SiO_2–Al_2O_3–ZnO–Na_2O–SrF_2 and SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3 system at the first crystallization temperature. Cerammization of glass was studied by DTA/DSC, XRD. It has been found that nanocrystallization of SrF_2 and LaF_3 strongly depends on the ratio between the components and the amount of SrF_2 and LaF_3, respectively. The optical studies of the glasses comprised spectrophotometry (reflectance and transmittance) and spectroscopic ellipsometry. The spectrophotometric measurements yield a number of narrow absorption bands which correspond to characteristic transitions between the ground- and consecutive excited states of rare earth ions. Growth luminescence at typical neodymium wavelength was observed under diode laser (808 nm) excitation in glass ceramics with SrF_2 in comparison to parent glass. The optimization of cerammization process allowed to fabricate the oxyfluoride glass ceramics optical fibre with strong emission originated from Nd^{3+} ions. The influence of the cerammization process on the changes in the refractive index of glass was examined.

Keywords: cerammization, oxyfluoride glass, refractive index of glass, glass ceramics optical fibre.

1. Introduction

In recent years, rare earth (RE) ions doped glass ceramics (GC) have attracted much attention due to their potential application in optical devices such as frequency-conversion materials and solid-state lasers [1–3]. GC with large transparency as their main feature have shown potential optical applications as large telescope mirror blanks, liquid crystal displays, solar concentrator cells, and photonic devices [4–8].

Transparent glass ceramics are two phase materials containing nanocrystallites with sizes less than 30 nm embedded in a glassy matrix. GC are polycrystalline ceramics matrices formed through the controlled nucleation and growth of crystalline phases in the precursor glass. The transparent GC is usually made in two steps: first, the precursor glass is made by normal melt quenching technique, then, a structural phase transition is thermally induced to transform it into a composite material formed by at least one crystalline phase dispersed within the glass matrix [9–11]. The special interest in these materials is due to the fact that thermal treatment causes that fluoride nanocrystals precipitate in the vitreous matrix. Most of the RE ions partition in the fluoride nanocrystalline phase. The thermal treatment improves the mechanical, chemical and optical properties of these materials [1, 12, 13]. Oxyfluoride glass ceramics combine the good optical properties of RE ions in a low phonon energy fluoride host with the easy elaboration, manipulation in air atmosphere and suitability for industrial production of oxide glasses. Therefore, these materials combine various remarkable properties of oxides and fluorides in one material. Thermal, chemical and mechanical properties of GC are characteristics of the aluminosilicate glass, whereas the spec-troscopic properties of the RE ions are typical of low-phonon energy fluoride crystals. Many investigations have been performed into lanthanide ion doped glass ceramics containing $Pb_xCd_{1-x}F_2$, β-PbF_2, LaF_3 nanocrystals [5, 14–17]. Trivalent lanthanide ions could be substituted for the divalent alkaline earth cations, what gave probabilities of preparing lanthanide doped glass ceramics containing alkaline earth metal fluoride MF_2 (M = Mg, Ca, and Sr) nanocrystals [18–26].

2. Experiment

2.1. Samples preparation

The batch was based on the Al_2O_3–ZnO–Na_2O–SrF_2 and SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3 glass systems, with rare earths admixtures of Nd_2O_3. The glass shows relevant high rare earths stability. The following raw materials were used to prepare the batches: silica oxide (SiO_2), strontium fluoride (SrF_2), lanthanum fluoride (LaF_3), sodium oxide (Na_2O), zinc oxide (ZnO), zinc fluoride (ZnF_2) and neodymium oxide (Nd_2O_3). All the chemicals were mixed properly to ensure the homogeneity. Oxyfluoride glass was obtained by melting 50 g batches in platinum crucibles in an electric furnace at the temperature of 1450 °C in air atmosphere. The crucible was

T a b l e 1. Glass compositions (ion concentration of Nd^{3+}: $n_{Nd} = 18.4004\times10^{16}$ cm^{-3}).

	Glass composition [mol%]							
ID	SiO_2	Al_2O_3	ZnF_2	SrF_2	Na_2O	ZnO	NaF	LaF_3
AW	60	10	–	15	–	–	15	–
AW1	55	10	10	–	22	–	–	3
AW2	55	10	10	–	23	–	–	2
AW3	55	10	–	10	15	10	–	–

covered with a platinum plate to avoid vaporization losses. The melt was poured out onto a steel plate which was preheated at 450 °C, forming a layer thickness 2 to 5 mm, then annealed at the temperature of 20 °C below T_g and subsequently polished with commercial media and water free lubricant. The samples could be obtained with good transparency and uniform thickness of 0.2 cm and 2.0 cm diameter. The composition of the investigated glasses is listed in Table 1. The XRD system analysis was used to confirm the glass structure of the samples.

2.2. Methods and procedures

The ability of the obtained glasses to crystallize was determined by DSC measurements conducted on the NETZSCH 5 System operating in heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate 10 °C/min in dry nitrogen atmosphere to the temperature 1100 °C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve; the jump-like changes of the specific heat ΔC_p accompanying the glass transition, enthalpy of crystallization ($\Delta H_{\mathrm{cryst}}$) were calculated using the NETZSCH 5 Thermal Analysis Software Library. The ability of glasses for crystallization was measured by the values of the thermal stability parameter of glasses ($\Delta T = T_{\mathrm{cryst}} - T_g$). Glasses revealing the crystallizations events were selected for further thermal treatment. To obtain glass ceramics, they were subjected to heating for 3 h at the temperature of the maximum crystallization events, respectively. The kind and the size of the formed crystallites were examined by XRD methods. To obtain GC with nanocrystallization of LaF_3 and SrF_2, they were subjected to heating for 30 min at the temperature of the maximum ceramming effect. The kind and the size of the formed crystallites were examined by XRD methods. Glasses were cut into 1.5 mm thick slices and polished to an optical quality. UV–VIS–NIR spectroscopy in transmission was carried out in order to assess the absorption spectra of the rare earth doped glasses. A spectrophotometer Jasco V-630 UV/VIS was used to measure the transmittance and absorption spectra in the range of 190–1100 nm. The spectra of transmittance and absorption of Nd^{3+} doped glasses are shown in Fig. 3. For the determination of the optical indices (*i.e.*, the refractive index n of GC doped with neodymium ions), the investigations by means of the M 2000 spectroscopic ellipsometer (J.A. Woollam Co.) have been done. These measurements have allowed to determine the refractive index in the whole investigated range (190–1700 nm). The ellipsometric angles Ψ and Δ fulfill the fundamental equation of ellipsometry, namely $\tan(\Psi) = |r_p|^2/|r_s|^2\exp(i\Delta)$, where r_p and r_s are complex Fresnel reflection coefficients for p and s polarizations, respectively, and Δ is a phase shift between both polarized waves. Knowledge of Ψ and Δ allow to determine the dispersion of refractive n. The data have been analyzed using Complete EASE 4.1 software. The luminescence of glasses and optical fibre within the range from 500 to 1400 nm were measured at a station equipped with an Acton SP2300i spectrometer and a laser diode (λ_p = 808 nm) with an optical fibre output (diameter 400 μm, NA = 0.22) having the maximum optical power 30 W. The glass from the SiO_2–Al_2O_3–ZnO–Na_2O–SrF_2 system was used for producing optical fibre whose luminescent parameters were then evaluated. The excitation of optical fibre was realized directly by using an aspheric lens setup.

3. Results and discussion

3.1. Thermal properties

AW glass composition, which is characterized by the greatest amount of strontium fluoride, crystallized spontaneously during casting. Therefore, the glass with a lower content of SrF_2 whose amount was reduced by introducing zinc oxide (ZnO) was designed (Tab. 1). Zinc oxide increases the viscosity at low temperatures, and thus reduces the tendency to crystallization in the temperature of glass formation [25]. The glasses with LaF_3 content above 4% mol crystallized during casting. Therefore in case of glass AW1, AW2 zinc fluoride (ZnF_2) was introduced, which slightly increases the melt viscosity without reducing the length of the lens technology in their formation.

The glasses from the Al_2O_3–ZnO–Na_2O–SrF_2 and SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3 systems, with rare earth admixtures of Nd_2O_3 during heating demonstrated, besides the thermal effect characteristic of typical phase transitions occurring in a glassy material, an additional exothermal effect near the T_g temperature connected with SrF_2 and LaF_3 crystallization. The analysis of DSC curves indicates that the presence of a well visible effect of the glassy state transformation in the examined glasses is closely connected with the cerammization effect (Fig. 1). The appearance of exothermal events in the high temperature range are also connected with SrF_2 and LaF_3 crystallization, but the heat treatment of the glass in the maximum of the temperature causes microcrystals formation. In case of glass AW1 containing LaF_3 glass transition temperature T_g of glassy state is reduced (517 °C) compared with the glass AW3 containing SrF_2 (T_g = 547 °C). At the same time the reduction of the specific heat (ΔC_p)

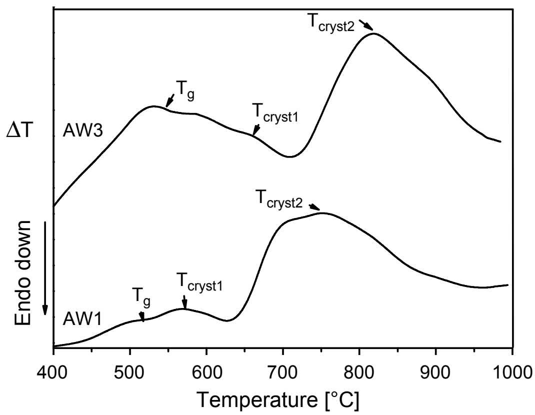


Fig. 1. DSC curves of AW3 and AW1 glasses doped with Nd^{3+} ions.

T a b l e 2. Thermal characteristic of oxyfluoride glass.

ID	T_g [°C]	ΔC_p [$Jg^{-1}C^{-1}$]	$T_{beg.cryst1}$ [°C]	$T_{max.cryst1}$ [°C]	ΔH_{cryst1} [Jg^{-1}]	ΔT [°C]	Crystalline phases
AW3	547	0.170	635	661	2.16	88	SrF2
AW1	501	0.108	563	598	2.24	97	LaF3

accompanying the glass transition region is observed, which may be an evidence of increased flexibility of the glass network (Table 2). Simultaneously, the temperature of the maximum effect of the cerammization of glass AW1 is shifted towards lower temperatures and the enthalpy ΔH of this process slightly increases (Tab. 2). This is an evidence of a decreasing ability of the glass AW1 for cerammization, manifested by increasing value of the index of thermal stability of the glass ΔT (Tab. 2). Thus, the glass AW3 with the greatest cerammization ability was selected for optical fibre production.

XRD measurements for the glass AW3 from the Al_2O_3–ZnO–Na_2O–SrF_2 system obtained by heat treating at its first crystallization effect temperature showed that

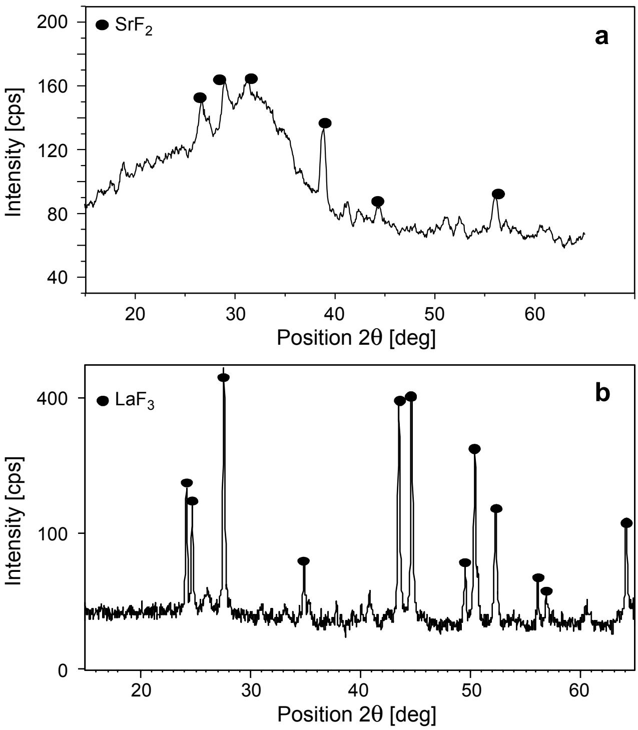


Fig. 2. XRD patterns of glasses after the heat treatment: glass AW3 635 °C/30 min (**a**), glass AW1 563 °C/30 min (**b**).

T a b l e 3. Calculated size of crystallites.

ID	Time of the ceramming [min]	Temperature of ceramming [°C]	Size of crystallites [nm]
AW1	30	563	99
AW3	30	635	67

cerammization process was ascribed to the precipitation of SrF_2 crystals (Fig. 2**a**). From the obtained peak width of XRD pattern, the size of SrF_2 nanocrystals in oxyfluoride glass ceramics was calculated to be 67 nm by the Scherrer formula [26] – see Tab. 3. From Figure 2**b** it could be found that the heat treatment of glass AW1 from the SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3 system at the max. of the first crystallization event causes the formation of LaF_3 nanocrystals (99 nm).

3.2. Optical properties

The results of specular transmittance spectra for examined AW1, AW3 glasses Nd^{3+} ions doped have been presented in Figs. 3 and 4. The glass AW1 from the SiO_2–Al_2O_3––ZnF_2–Na_2O–LaF_3 glass system is characterized by slightly higher level of transmittance (89%) in comparison with glass AW3 (84%) from the Al_2O_3–ZnO–Na_2O–SrF_2 glass system. Based on transmission spectra of glasses heat-treated at the maximum of nanocrystallization temperature, it was found that the level of transmission decreases considerably as compared to parent glasses (Figs. 3 and 4). The highest decrease in transmission is observed for GC AW3 (containing the SrF_2 nanocrystals).

The recorded optical absorption spectrum of Nd^{3+}:GC and glass in the wavelength ranges 300–1100 nm are presented in Fig. 5. The glass has revealed seven bands in

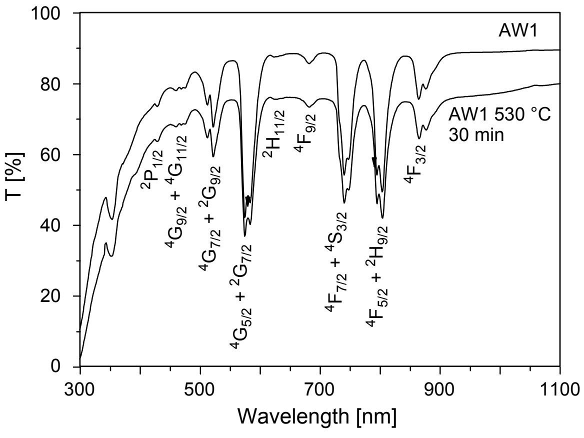
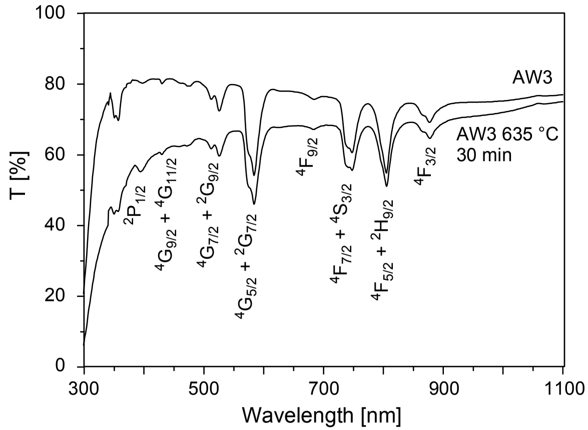
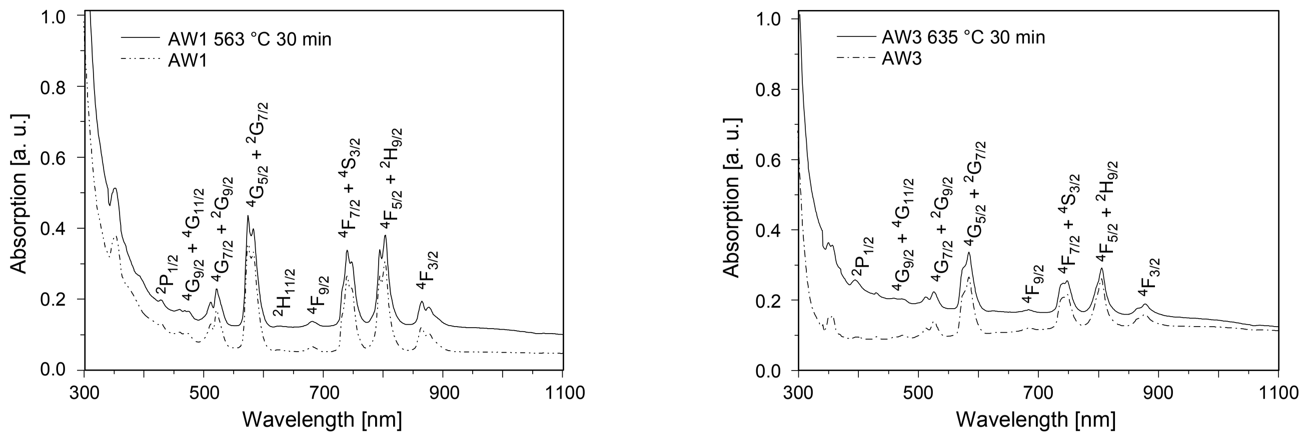


Fig. 3. Spectra transmittance of oxyfluoride AW1 parent glass and the glass after the heat treatment at 563 °C for 30 min.



◀ Fig. 4. Spectra transmittance of oxyfluoride AW3 parent glass and the glass after the heat treatment at 635 °C for 30 min.



▲ Fig. 5. Visible absorption spectra of Nd^{3+} of oxyfluoride glass and GC.

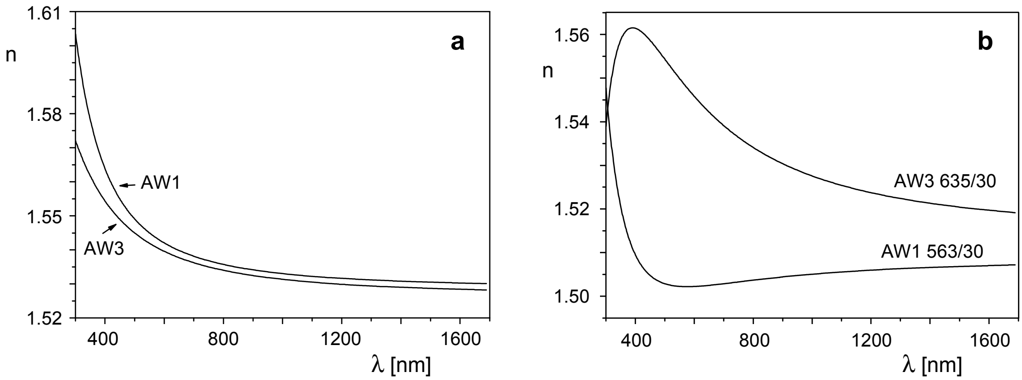


Fig. 6. Dispersion of $n(\lambda)$ of glass (**a**) and oxyfluoride glass ceramic (**b**).

UV–VIS regions from ground state $^4I_{9/2}$ to various excited states of Nd^{3+} ions: $^4F_{3/2}$, $^4F_{5/2} + {}^2H_{9/2}$, $^4F_{7/2} + {}^4S_{3/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2} + {}^2G_{7/2}$ and $^4G_{7/2} + {}^2G_{9/2}$, $^4G_{9/2} + {}^4G_{11/2}$, $^2P_{1/2}$.

The spectral dependence of the refraction n obtained from the fitting procedure for examined glasses and GC is shown in Fig. 6.

In the region of weak absorption (above 300 nm), the Cauchy model of the refractive index dispersion was applied, being expressed by formula:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where A, B and C are fitting parameters.

As can be noticed over the light wavelength $\lambda = 450$ nm, the extinction coefficient is negligibly small and absorption disappears.

On the basis of the spectral dependence of the refraction n of the glass AW1, AW3, it was found that the glass AW1 containing fluorine introduced by the lanthanum fluoride is characterized by larger values of the refractive index in the whole investigated range, as compared to the glass AW3 where fluorine is introduced by the strontium fluoride (Fig. 6**a**). The value of the refractive index of the glass AW1 at a wavelength of 600 nm was 1.5418, and 1.5393 for the glass AW3. The ellipsometric examinations proved that the cerammization process has a considerable influence on the changes of the refractive index of the investigated glass (Fig. 6**b**). In the case of glasses heat treated at cerammization temperature an increase of the refractive index of the glass AW3 compared to the glass AW1 is observed (AW3 – $n_{600\ \mathrm{nm}} = 1.5457$ when AW1 – $n_{600\ \mathrm{nm}} = 1.5022$). The reduction of the n value of the glass AW1 heat-treated at the cerammization temperature may be explained by a larger concentration of fluorine compared to the glass AW3.

The conducted thermal analysis of the glass from the SiO_2–Al_2O_3–ZnO–Na_2O–SrF_2 system enabled to determine the conditions of optical fibre manufacturing. The essential parameters during fibre fabricating were temperature and heating time in the following zones in order to obtain SrF_2 nanocrystals in the core. The modified rod-in-tube drawing method was applied to fabricate optical fibre. The luminescence spectra of the parent glass and GC under excitation of 808 nm laser diode is shown in Fig. 7. Luminescence spectra of the oxyfluoride glasses containing SrF_2 as melted and after thermal treatment were measured under the excitation of a 808 nm laser diode. Obtained emission bands at 895 nm, 1056 nm and 1329 nm correspond to the following optical transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{15/2}$ in neodymium. Glass after the thermal treatment is characterized by higher level of luminescence. It is usually explained by the fact that Nd^{3+} ions partially are incorporated in crystalline phase which posses lower phonon energies compared to non-crystallized glassy matrix. Figure 8 shows the luminescence spectrum obtained as a result of exciting optical fibre with the pump (808 nm) power radiation amounted to P_{opt} = 2 W. The introduction of the radiation was realised directly into the optical fibre face.

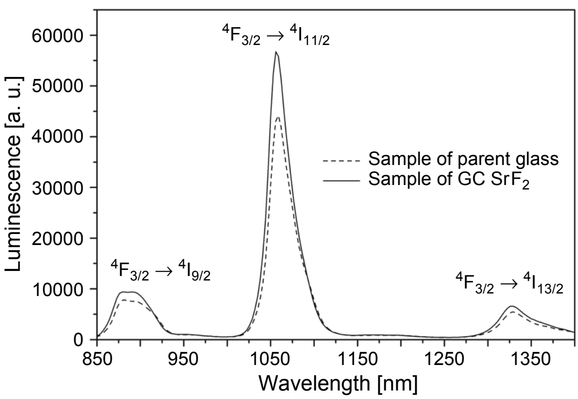


Fig. 7. Luminescence spectra of glass AW3 doped with Nd^{3+} ions.

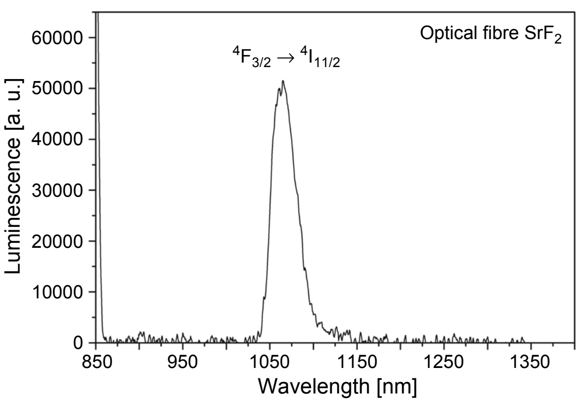


Fig. 8. Luminescence spectra of optical fibre (SiO_2–Al_2O_3–ZnO–Na_2O–SrF_2) doped with Nd^{3+} ions.

While comparing it to the glass luminescence spectrum, only one emission peak was observed at the wavelength of 1066 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$). Additionally, the maximum of emission is shifted to longer wavelength. This is significant from the point of view of laser applications for the transition at about 1060 nm and it can be explained by an amplified spontaneous emission phenomenon.

4. Conclusions

Stable glasses could be prepared in a relatively large compositions domain of the Al_2O_3–ZnO–Na_2O–SrF_2 and SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3 systems. Unfortunately, the effect of crystallization of SrF_2 and LaF_3 as the only nanocrystalline phases, which is indispensable from an optoelectronics point of view, is strongly dependent on the proportions between the components. Basing on DSC studies, it can be stated that glass from the Al_2O_3–ZnO–Na_2O–SrF_2 system is characterized by the lower value of thermal stability parameter as compared to glass from the SiO_2–Al_2O_3–ZnF_2–Na_2O–LaF_3, thus the cerammization ability is greater. The process of thermal treatment of glasses in the range of the cerammization events results in obtaining the SrF_2 and LaF_3 phases with the crystallites size lower than 100 nm. Obtained material shows the absorption edge of at 300 nm wavelength with good transparency in visible and near infrared spectra. Basing on transmission spectra of glasses heat-treated at the maximum of nanocrystallization temperature, it was found that the level of transmission decreases considerably as compared to parent glasses. The ellipsometric studies proved that the cerammization process has a considerable influence on changes in the refractive index of the investigated glass. Appropriately chosen parameters of fibre drawing allowed the optical fibre formation. Basing on the luminescence spectra, one can conclude that the glass after the thermal treatment is characterized by higher level of luminescence, what is caused by Nd^{3+} ions incorporation onto SrF_2 nanocrystallites. The optical fibre excited spectrum suggests the start of amplified spontaneous emission.

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References

[1] GONÇALVES M.C., SANTOS L.F., ALMEIDA R.M., *Rare-earth-doped transparent glass ceramics*, Comptes Rendus Chimie **5**(12), 2002, pp. 845–854.

[2] HATEFI Y., SHAHTAHMASEBI N., MOGHIMI A., ATTARAN E., *Frequency-conversion properties of Eu^{3+} doped chlorophosphate glass ceramics containing $CaCl_2$ nanocrystals*, Journal of Luminescence **131**(1), 2011, pp. 114–118.

[3] HATEFI Y., ANBAZ K., MOGHIMI A., MADDAH B., *Up and down frequency-conversion properties of Eu^{3+} doped lead fluorophosphate nanoglass ceramics*, International Journal of Optics and Photonics **4**, 2010, pp. 57–61.

[4] DEJNEKA M.J., *The luminescence and structure of novel transparent oxyfluoride glass-ceramics*, Journal of Non-Crystalline Solids **239**(1–3), 1998, pp. 149–155

[5] LAVIN V., IPARRAGUIRRE I., AZKARGORTA J., MENDIOROZ A., GONZALEZ-PLATAS J., BALDA R., FERNANDEZ J., *Stimulated and upconverted emissions of Nd^{3+} in a transparent oxyfluoride glass-ceramic*, Optical Materials **25**(2), 2004, pp. 201–208.
[6] GOUVEIA-NETO A.S., DA COSTA E.B., BUENO L.A., RIBEIRO S.J.L., *Upconversion luminescence in transparent glass ceramics containing β-PbF_2 nanocrystals doped with erbium*, Journal of Alloys and Compounds **375**(1–2), 2004, pp. 224–228.
[7] LAHOZ F., MARTIN I.R., RODRIGUEZ-MENDOZA U.R., IPARRAGUIRRE I., AZKARGORTA J., MENDIOROZ A., BALDA R., FERNANDEZ J., LAVIN V., *Rare earths in nanocrystalline glass-ceramics*, Optical Materials **27**(11), 2005, pp. 1762–1770
[8] PISARSKA J., RYBA-ROMANOWSKI W., DOMINIAK-DZIK G., GORYCZKA T., PISARSKI W.A., *Nd-doped oxyfluoroborate glasses and glass-ceramics for NIR laser applications*, Journal of Alloys and Compounds **451**(1–2), 2008, pp. 223–225.
[9] YUNLONG YU, DAQIN CHEN, EN MA, YUANSHENG WANG, ZHONGJIAN HU, *Spectroscopic properties of Nd^{3+} doped transparent oxyfluoride glass ceramics*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **67**(3–4), 2007, pp. 709–713.
[10] JAGLARZ J., REBEN M., *The influence of nanocrystallization process on thermal and optical parameter in oxyfluoride glasses*, Optica Applicata **40**(2), 2010, pp. 439–447.
[11] REBEN M., WACŁAWSKA I., PALUSZKIEWICZ C., ŚRODA M., *Thermal and structural studies of nanocrystallization of oxyfluoride glasses*, Journal of Thermal Analysis and Calorimetry **88**(1), 2007, pp. 285–289.
[12] YUHU WANG, JUNICHI OHWAKI, *New transparent vitroceramics codoped with Er^{3+} and Yb^{3+} for efficient frequency upconversion*, Applied Physics Letters **63**(24), 1993, pp. 3268–3270.
[13] LAVIN V., LAHOZ F., MARTIN I.R., RODRIGUEZ-MENDOZA U.R., CACERES J.M., *Infrared-to-visible photon avalanche upconversion dynamics in Ho^{3+}-doped fluorozirconate glasses at room temperature*, Optical Materials **27**(11), 2005, pp. 1754–1761.
[14] TIKHOMIROV V.K., SEDDON A.B., FERRARI M., MONTAGNA M., SANTOS L.F., ALMEIDA R.M., *On a qualitative model for the incorporation of fluoride nano-crystals within an oxide glass network in oxy-fluoride glass-ceramics*, Journal of Non-Crystalline Solids **337**(2), 2004, pp. 191–195.
[15] LI FENG, JING WANG, QIANG TANG, LIFANG LIANG, HONGBIN LIANG, QIANG SU, *Optical properties of Ho^{3+}-doped novel oxyfluoride glasses*, Journal of Luminescence **124**(2), 2007, pp. 187–194.
[16] KAWAMOTO Y., KANNO R., QIU J., *Upconversion luminescence of Er^{3+} in transparent SiO_2–PbF_2–ErF_3 glass ceramics*, Journal of Materials Science **33**(1), 1998, pp. 63–67.
[17] LAKSHMINARAYANA G., JIANRONG QIU, *Photoluminescence of Pr^{3+}, Sm^{3+} and Dy^{3+}: SiO_2–Al_2O_3–LiF–GdF_3 glass ceramics and Sm^{3+}, Dy^{3+}: GeO_2–B_2O_3–ZnO–LaF_3 glasses*, Physica B: Condensed Matter **404**(8–11), 2009, pp. 1169–1180.
[18] XVSHENG QIAO, XIANPING FAN, JIN WANG, MINQUAN WANG, *Luminescence behavior of Er^{3+} ions in glass-ceramics containing CaF_2 nanocrystals*, Journal of Non-Crystalline Solids **351**(5), 2005, pp. 357–363
[19] XVSHENG QIAO, XIANPING FAN, MINQUAN WANG, *Luminescence behavior of Er^{3+} in glass ceramics containing BaF_2 nanocrystals*, Scripta Materialia **55**(3), 2006 , pp. 211–214.
[20] ZHONGCHAO DUAN, JUNJIE ZHANG, DONGBING HE, HONGTAO SUN, LILI HU, *Effect of CdF_2 addition on thermal stability and upconversion luminescence properties in Tm^{3+}–Yb^{3+} codoped oxyfluoride silicate glasses*, Materials Chemistry and Physics **100**(2–3), 2006, pp. 400–403.
[21] XVSHENG QIAO, XIANPING FAN, MINQUAN WANG, XIANGHUA ZHANG, *Spectroscopic properties of Er^{3+}–Yb^{3+} co-doped glass ceramics containing BaF_2 nanocrystals*, Journal of Non-Crystalline Solids **354**(28), 2008, pp. 3273–3277.
[22] LIHUI HUANG, GUANSHI QIN, YUSUKE ARAI, RAJAN JOSE, TAKENOBU SUZUKI, YASUTAKE OHISHI, TATSUYA YAMASHITA, YUSUKE AKIMOTO, *Crystallization kinetics and spectroscopic investigations on Tb^{3+} and Yb^{3+} codoped glass ceramics containing CaF_2 nanocrystals*, Journal of Applied Physics **102**(9), 2007, article 093506.

[23] MURAKAMI T., TANABE S., *Preparation and 1.3 μm emission of Pr^{3+} doped transparent nano-glass ceramics containing SrF_2*, Journal of the Ceramic Society of Japan **115**(1346), 2007, pp. 605–607.
[24] XVSHENG QIAO, XIANPING FAN, MINQUAN WANG, XIANGHUA ZHANG, *Spectroscopic properties of Er^{3+} and Yb^{3+} co-doped glass ceramics containing SrF_2 nanocrystals*, Journal of Physics D: Applied Physics **42**(5), 2009, article 055103.
[25] REBEN M., *The thermal study of oxyfluoride glass with strontium fluoride*, Journal of Non-Crystalline Solids **357**(14), 2011, pp. 2653–2657.
[26] TANABE S., HAYASHI H., HANADA T., ONODERA N., *Fluorescence properties of Er^{3+} ions in glass ceramics containing LaF_3 nanocrystals* , Optical Materials **19**(3), 2002, pp. 343–349.

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