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New Nanoglassceramics Doped with Rare Earth Ions and Their Photonic Applications

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1. Introduction

1.1 Why glassceramics?

Glass-crystalline materials (or glassceramics) are heterophase composite materials, usually consisting of a glassy matrix (glass phase) and micro- or nano-sized dielectric or semiconductor crystals (crystalline phase), or metallic particles distributed in it. Glassceramics are formed by the growth of crystalline phase inside of a glass matrix. The crystal growth can occur as a result of spontaneous thermal crystallization of glass, as in case of heat treatment. For example, there are following typical representatives of the spontaneous crystallization: glasses doped with microcrystals of CdS, CdSe, CdTe, PbS, PbSe (non-linear media) [1-7], glasses doped with semiconductor microcrystals AgBr, AgCl, CuBr, CuCl (photochromic media) [8], glasses doped with dielectric microcrystals $\text{Li}_2\text{O-SiO}_2$ (photoetchable media – FOTURANTM, FOTOFORMTM, PEGTM [9-11]. The crystal growth can occur as a result of photo-thermo-induced crystallization caused by UV photoirradiation and subsequent heat treatment. In this case, UV radiation generates centers of nucleation and the thermal treatment results in the growth of microcrystals in irradiated area of the glass host. Glasses doped with complicated microcrystals of NaF-AgBr (polychromatic glasses [12] and photo-thermo-refractive - PTR glasses [13]) are typical representatives of the photo-thermo-induced crystallization.

1.2 Why nanostructured glassceramics?

One of the major drawbacks of glass ceramic materials is a high light scattering occurring at the boundary of crystalline phase and glass phase. That is why current research in the development of optical glass-crystalline materials is aimed at decreasing of light scattering by means of formation of nanosize (5-30 nm) crystals or nanoparticles in the glass matrix. Only the nanoscale nature of the crystalline phase can significantly reduce the light scattering in heterophase composites (where the extinction coefficient can reach less than 0.01 cm^{-1}) and classify these materials as optical. Fig.1 illustrates transition from millimeter-size crystals to micrometer-size crystals and finally nano-size crystals in the glass host. The transition to the nanoscale crystalline phase not only leads to changes in physical, chemical and optical properties of glassceramics, but is also a cause for fundamentally new and

unique properties. For example, nano-size of crystalline phase results in quantum-size, resonance, and other effects. Such materials can possess unique properties, that can't be realized in traditional materials. Following new materials can be synthesized on the base of nanoglassceramics: plasmonic materials, photonic crystals, meta-materials.

Currently, optical transparent glassceramics are of the great interest for the modern element base of photonics, because they stay at intermediate state between crystalline materials and glasses. These glassceramics combine the best properties of crystals (high emission cross-section, quantum yield of luminescence, mechanical and thermal strength etc.) and glasses (possibilities of pressing and molding, spattering, pulling optical fibers, and carrying out ion exchange to fabricate waveguide structures).

In this paper a new type of glassceramics, namely the nanostructured lead oxifluoride glassceramics, which was developed by the authors have been discussed. In addition some examples of using the novel nanoglassceramics for photonics applications have been outlined.

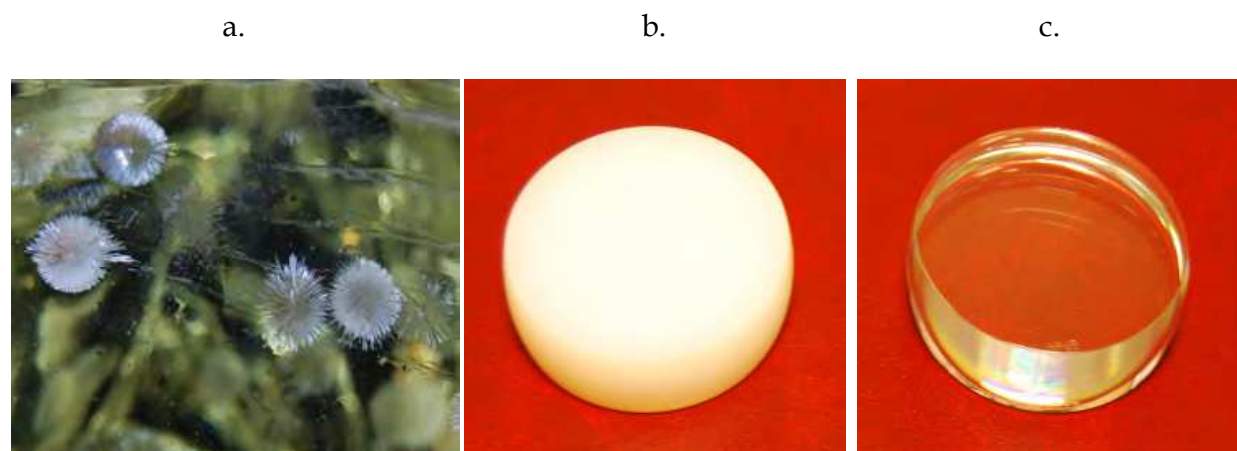


Fig. 1. Transition from millimeter-size crystals (a) to a micrometer-size crystals (b) and to nano-size crystals (c) in the glass host.

2. Structure and properties of nanostructured oxifluoride glassceramics

The story of the oxifluoride glassceramics production technology starts in 1970-es. In [14] was made an attempt to synthesize the oxifluoride glasses, containing Ln_2O_3 (Y, La, Gd, Lu), Yb_2O_3 , PbF_2 , M_nO_m ($M = \text{B, P, Te, Si, Ge}$), activated by Er_2O_3 or Tm_2O_3 . This attempt has resulted in production of the nontransparent glassceramic materials, containing the microcrystals with diameter of about $10\text{ }\mu\text{m}$. The efficiency of luminescence, revealed by these media, was in several times larger than that of the etalon luminophors $\text{LaF}_3 : \text{Yb} : \text{Er}$. Later on, in 1993, there was published the first paper, devoted to synthesis of the transparent glassceramics, containing the cubic fluoride phase, activated by erbium and ytterbium ions [15]. There were for the first time produced the materials, which combine all the advantages of the glass-like aluminosilicate matrix and the optical features of the low-phonon fluoride crystals.

Since recently the transparent fluorine-containing glassceramics matrices, containing the rare-earth ions, included into the fluorite-like nanocrystalline phases, are drawing the

attention do to the series of spectroscopy advantages. It is obvious that from the point of view of laser active media development optimal are the materials, which are characterized by the low-frequency phonon spectrum and by the low content of the OH-groups, because in this case one can reduce the excitation energy losses due to the multi-phonon quenching process. For a long time there was a common opinion that only the fluorine-containing materials (like fluoride glasses and crystals) are optimal for the said problem solution. However, since recently the synthesis of the glassceramics materials like the oxifluoride silicate glasses has become the priority direction of studies [16-24]. Such composite materials combine the optical parameters of the low-phonon fluoride crystals and the good mechanical and chemical features of the silicate glasses. It was also revealed that some of the oxifluoride glass-like materials have a feature of forming the fluoride nanocrystals, doped by the rare-earth ions, during the process of heat treatment of the raw primary glass. Hence such a materials combine all the positive features of the fluoride nanocrystals, which control the optical properties of the rare earth ions, with that of oxide glasses like easy production technology and excellent macroscopy features like chemical and mechanical strength and the high optical quality. It is well known that in the case of production of the optically transparent glassceramics, including those, which are used for optical waveguide fabrication, it is very important to minimize the light losses for absorption and scattering. The Rayleigh scattering by the micro-inhomogeneities with the size about the radiation wavelength is a factor, limiting such materials use. It imposes the strict limitations over the size of the separated crystalline phase. According to the Rayleigh theory for the visible spectral range, the radius of the crystals, dispersed around the glass, has to be not more than 15 nm. The refraction indexes of the crystalline phase and of the amorphous matrix are to differ in not more than 0.1. Later on these limitations were somewhat softened. In [16] on the case of a model it was shown that one can produce the transparent glassceramics with the size of nanocrystals up to 30 nm and with the refraction indexes difference in not more than 0.3.

2.1 The glassy matrix for glassceramics production

The separation of the crystalline phase in a silicate glass is a traditional way of the opalescent glass production. It is well known that insertion of the fluorides into the glass, whose content is similar to the window glass, leads to forming of a large number of microcrystals in the glass volume. It leads to a drastic increase of a light scattering and to the so called opalescence effect. Hence, the fluorine content in a glass leads to intense phase separation; very often the second phase is represented by the introduced fluorides or by their derivatives. This fact has become the basis for the numerous studies, devoted to fabrication and investigation of the silicate nanoglassceramics, based on the fluorite-like nanocrystals like $\text{Ba}(\text{Sr,Ca})\text{F}_2$ or of the hexagonal LaF_3 , activated by small concentration or rare-earth or of transient elements.

The separate group is represented by the glassceramics, fabricated on the basis of the glass-like systems with a big amount of fluorides. One can fill into this type the alkali-less germanate and silicate systems like $\text{GeO}_2\text{-PbO-PbF}_2$, $\text{SiO}_2\text{-PbO-10PbF}_2$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CdF}_2\text{-PbF}_2\text{-ZnF}_2\text{:}(\text{YF}_3)$. In such systems the fluoride concentration can be as high as 60-70 mol.%. The process of crystalline phase formation in this case is not so obvious and needs a more detailed study.

Production of the starting glass and fabrication of the glassceramics on its basis

The glasses of the system of $0.3\text{SiO}_2\text{-}0.15\text{AlO}_{3/2}\text{-}0.29\text{CdF}_2\text{-}0.18\text{PbF}_2\text{-}0.05\text{ZnF}_2\text{-}0.03(\text{Ln,Y})\text{F}_3$ (the content of the glasses is given in molecular percents before synthesis), where $\text{Ln}=\text{La, Pr, Dy, Nd, Tb, Eu, Er, Sm, Tm, Ho}$, have been synthesized. The synthesis was carried out in platinum or corundum crucibles in an air or argon atmosphere, making it possible to produce glasses with a high transparency in a visible spectral range. With the purpose to prevent the spontaneous crystallization, the glass was produced in a gap between two cool glass-carbon plates. Hence the thickness of the produced glass was not more than 2 mm.

Heat treatment with the purpose of evaluation of the crystallization temperature and of the glassceramics production was carried out at the temperature of the crystallization start. It was determined from the thermal curve, measured by means of the differential scanning calorimeter (DSC), see Fig.1. This curve has two separate crystallization peaks, which is the obligatory condition for the transparent glassceramic production. The observed exo-peaks are produced by the bulk (522°C) and by the surface (607°C) crystallizations. The choice of the heat treatment temperature at the start of the first peak makes it possible to prevent completely the surface crystallization, which can lead to the uncontrolled growth of the large crystals. Basing on the DSC data (Fig.2), the specimens of glasses with all contents were exposed to temperature of $480\text{-}500^\circ\text{C}$ for 0.5-10 hours.

In the Fig.2 are shown the thermal curves for the starting specimen (a) and for the glassceramics (b). The elimination of the first exo-peak, which is observed, is an evidence of the complete separation of the volume crystalline phase after heat treatment of the glass during two hours.

Hence on the base of DSC data we have determined the regimes of heat treatment of the starting glass, necessary for the nanocrystalline phase production: temperature 500°C , duration 2 hours.

2.2 The content of the crystalline phase and its growth kinetics

One has to note that, disregarding a large number of papers, considering the studies of the lead fluoride glassceramics, the chemical content of the nanocrystalline phases is still discussed. In [17] on the base of spectroscopy and X-ray phase data was concluded that the erbium-containing crystalline phase is a solid solution of erbium fluoride in $\beta\text{-PbF}_2$. In [18] there was investigated the separation of the crystalline phase during heat treatment of the glasses $50\text{GeO}_2\text{-}40\text{PbO}\text{-}10\text{PbF}_2$. Their heat treatment has resulted in separation of the fluorite-like phase. Change of the processing temperature from 350 to 395°C has resulted in crystals size growth from 11 to 16 nm. The size of the elementary cell was within the range of $5.82\text{-}5.83\text{ \AA}$, i.e. it was preserved constant within the experimental error limits of $\pm 0.005\text{ \AA}$. It was supposed that the separated crystalline phase is comprised by $\beta\text{-PbF}_2$, doped by ions of Er^{3+} . In a search for confirmation there were synthesized the monocrystals of $\beta\text{-PbF}_2$ with various content of ErF_3 . For the admixture of 20% of ErF_3 the size of the elementary cell was reduced from 5.94 to $5.816\text{ \AA}$. In the oxyfluoride crystals [19] the heat treatment of the glass with the content $32(\text{SiO}_2)\text{-}9(\text{AlO}_{1.5})\text{-}31.5(\text{CdF}_2)\text{-}18.5(\text{PbF}_2)\text{-}5.5(\text{ZnF}_2)\text{:}3.5(\text{ErF}_3)$ has resulted in separation of the crystalline phase with the fluorite structure and cell constant $a=5.72\text{ \AA}$.

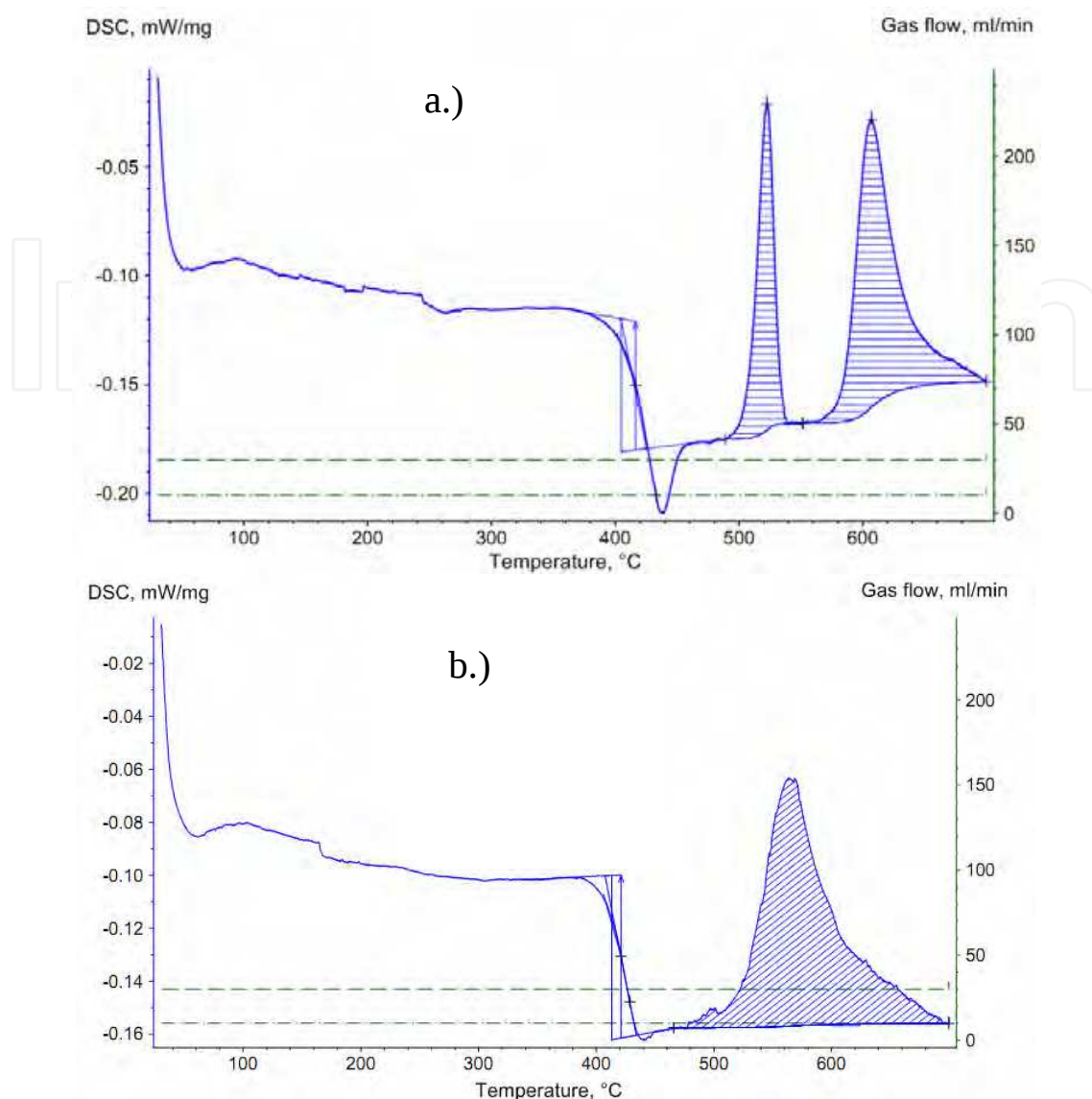


Fig. 2. Thermal curves of the starting glass (a) and of the glass, which was thermally processed for 2 hours (b).

Thus the precipitation of the fluorite-like crystalline phase of β - PbF_2 doped with ErF_3 has been earlier observed in various glass hosts. However the sizes of the elementary cell of the crystalline phase separated in glasses were differ from ones of the solid solution models. In all cases the sizes of elementary cell of the crystalline phase in glass host were much smaller than that observed in the solid solution models or in the crystals of β - PbF_2 doped with ErF_3 . In [20, 21] there was revealed the dependence of the cell constant of the nanocrystals ($a = 5,72 - 5,81 \text{ \AA}$) in the glass of system of $30\text{SiO}_2 - 5\text{ZnF}_2 - (29-x)\text{CdF}_2 - (18+x)\text{PbF}_2 - 7,5\text{Al}_2\text{O}_3 - 3 \text{ErF}_3$ from the ratio of lead and cadmium fluorides concentration. There was made an assumption about formation of the mixed fluoride crystals with partial replacement of Pb^{2+} on Cd^{2+} .

In the present work a complex analysis of the precipitated crystalline phase has been carried out. The precipitation of the crystalline phase during heat treatment of glasses with the content of $30\text{SiO}_2 - 29\text{CdF}_2 - 18\text{PbF}_2 - 5\text{ZnF}_2 - 7,5\text{Al}_2\text{O}_3$, containing the fluorides of yttrium and of the lanthanum group elements, including the case of simultaneous addition of yttrium and

of lanthanum group elements has been studied. The phase content and the cell constants have been determined with the use of XRD analysis. It was found out that thermal procession of the oxyfluoride matrix glass, lacking yttrium or lanthanum group elements, which was carried out for 2-3 hours under the temperature of 480-520°C, did not lead to crystalline phase separation. Only the glasses, containing the yttrium fluoride or lanthanum group fluoride (or their arbitrary concentration) has revealed separation of the crystalline fluorite-like phase (Fig.3).

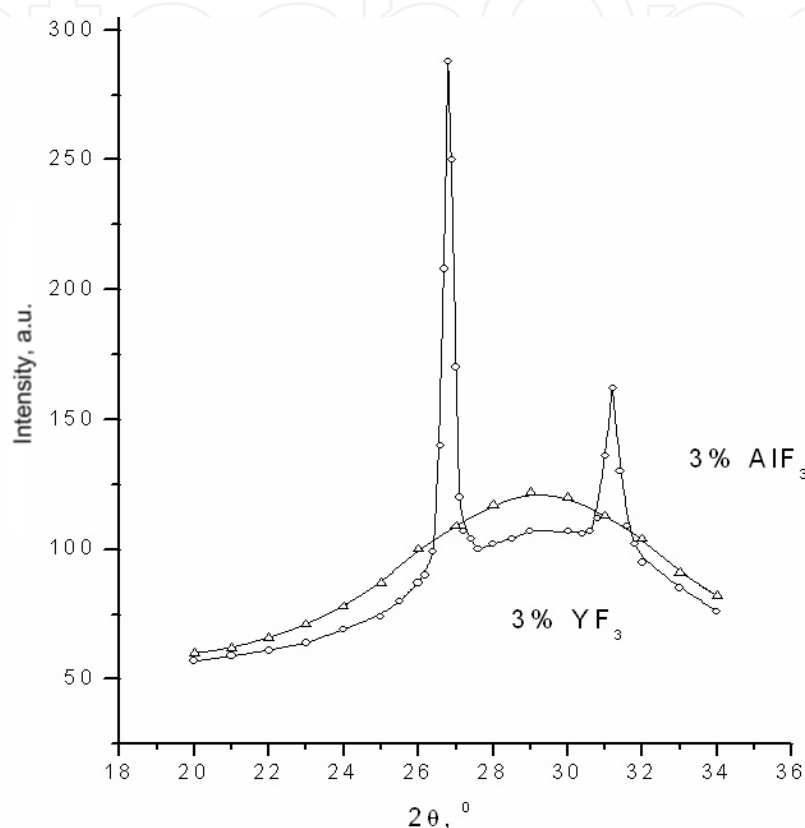


Fig. 3. X-ray diffraction curves for the angle range 2θ from 20 to 35°, 1 – thermally processed glass without YF_3 и lanthanum group fluorides, 2 – thermally processed glass, containing 3% of YF_3 .

The presence of REI (rare-earth ions) in the crystalline phase is also confirmed by the absorption spectrum data. It is obvious, that redistribution of REI between the glass-like and crystalline phases has to result in variation of REI absorption and luminescence spectra. In the Fig.4 are shown as an example the absorption spectra of the starting glass, activated by erbium, and after its thermal processing.

The size of the crystals was evaluated by means of X-ray scattering to small angles. It was determined from the diffraction reflection width with the accuracy $\pm 5\%$. After heat treatment of the glass at $T = 480^\circ\text{C}$ at 2-3 hours the size of the crystals has reached 250-300 Å. In such a regime the phase volume was close to the equilibrium one, i.e. it was not increasing in the case or increasing the heating duration or temperature. The further heat treatment has resulted in crystal size increase, while the integral intensity of diffraction reflection was practically constant. I.e., in this case mainly the re-crystallization processes

took place; it is also indirectly confirmed by the spectroscopy data. In the Fig.5 is shown the kinetics of the crystals growth during heat treatment.

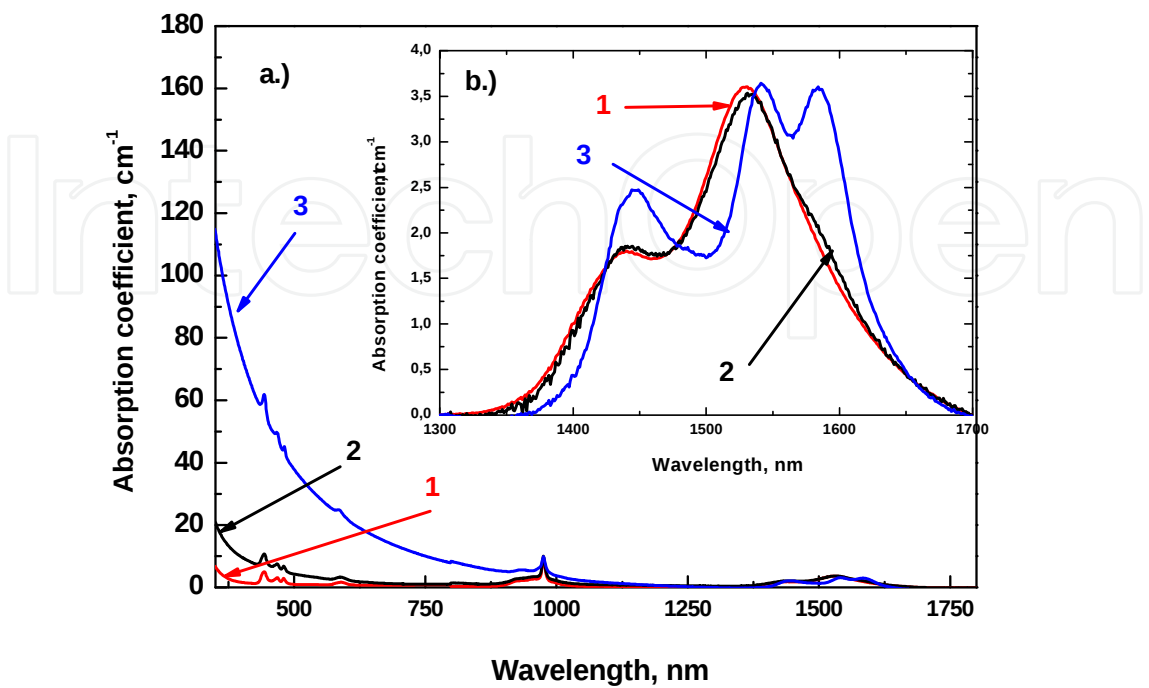


Fig. 4. Attenuation spectra of the (1) initial glass containing 3 mol % PrF₃ and (2, 3) nanoglassceramics obtained after heat treatment at $T = 475^{\circ}\text{C}$ for 4 (2) and (3) 32 h and (b) a fragment of the absorption spectra for the $^3H_4 \rightarrow ^1G_4$ transition (normalized spectra).

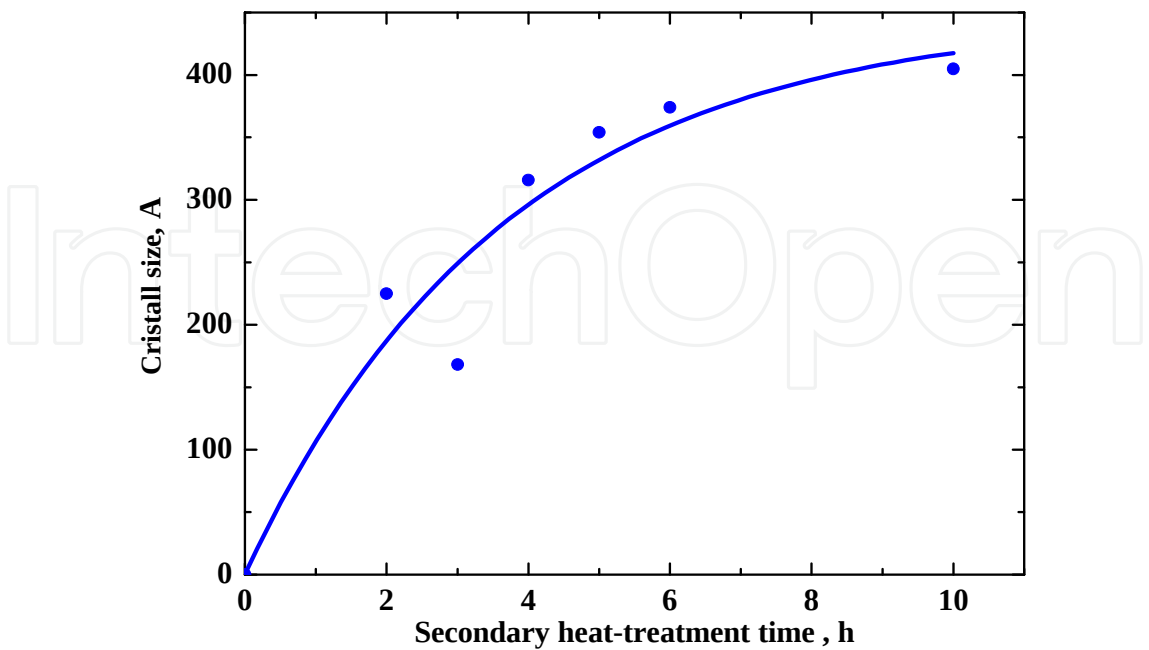
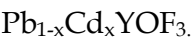


Fig. 5. Dependence of the crystal size on the heat treatment time at $T = 480^{\circ}\text{C}$. ErF_3 concentration is 1.5 mol %.

There was observed the definite correlation between the concentration of the introduced fluorides of the lanthanum group elements and the integral intensity of the fluorite-like phase diffraction reflection. Hence one can conclude that the presence of fluorides of rare-earth elements and of yttrium totally determines the crystalline phase separation, and their concentration in the starting glass completely determines the volume of the extracted phase. One can treat it as an evidence of one and the same stoichiometry of the separated crystalline phases.

All the produced nanocrystalline phases have the fluorite-like structure – cubic, edge-centered, spatial group Fm3m. The lattice constants depend upon the REI radius (Table 1). The size of the elementary cell of the phase, produced by heat treatment of the glasses with YF₃, was equal to 5.74 Å. It differs significantly from the size of the elementary cell of the yttrium oxyfluoride of lead PbYOF₃, which is equal to 5.792 Å. The reduction of the size of the elementary cell of the phase separated in the studied glasses with YF₃ can be explained by presence of Cd. Hence the significant variation of the elementary cell size is connected with the formation of the solid solution



	Lanthanum group element	R, Å	a, Å
1	Pr ³⁺	1	5.83
2	Nd ³⁺	0.99	5.82
3	Sm ³⁺	0.97	5.81
4	Eu ³⁺	0.96	5.8
5	Tb ³⁺	0.89	5.765
6	Dy ³⁺	0.88	5.75
7	Ho ³⁺	0.86	5.735
8	Er ³⁺	0.85	5.725
9	Tm ³⁺	0.84	5.715
10	Yb ³⁺	0.81	5.7
11	Y ³⁺	0.97	5.74

Table 1. Size of the elementary cell of the fluorite-like crystalline phases, separated in the investigated glasses, containing the fluorides of various lanthanum group elements and the ion radiuses of such elements and yttrium, R, according to Goldschmidt.

One the base of the investigations, which were carried out, one can make some conclusions and outline some recommendations for the synthesis of the lead oxifluoride glassceramics with the required spectral and luminescence properties:

- the presence of the fluorides of rare-earth elements and yttrium results in the precipitation of the crystalline phase in glass host, and the volume fraction of the precipitated nanocrystals is completely determined by their concentration in the starting glass;
- heat treatment of the starting glasses at 480-500°C for 2-3 hours results in the growth of crystalline phase in size of 250-300 Å. For such regimes of heat treatment the volume

- fraction of the crystalline phase approaches equilibrium, i.e. it does not change after consequent heat treatment or its temperature increase;
- the crystalline phase, precipitated in the starting glass doped with YF_3 , is the modified yttrium oxyfluoride of lead ($\text{Pb}_{1-x}\text{Cd}_x\text{YOF}_3$). The crystalline phases, precipitated in glass, which contains fluorides of various lanthanum group elements or such fluorides together with yttrium fluoride, are lanthanum or yttrium-lanthanum oxyfluorides of lead like $\text{Pb}_{1-x}\text{Cd}_x\text{Y}_y\text{Ln}_{1-y}\text{OF}_3$. The crystalline phase has a fluorite-like structure (cubic, edge-centered, spatial group $\text{Fm}\bar{3}\text{m}$). The value of “x” may be different for various elements of lanthanum group;
 - the synthesis of the mixed yttrium and lanthanum group element nanocrystal can provide different required concentrations of RE ions in the crystal like $\text{Pb}_{1-x}\text{Cd}_x\text{Y}_y\text{Ln}_{1-y}\text{OF}$. It can be achieved by simple variation of the raw material content.

2.3 The luminescence and spectral properties of the lead oxyfluoride nanoglassceramics

The conclusions of the Section 2.2 are confirmed by the luminescence and spectral studies. If the rare earth ion environment has changed - for instance, when it has moved to the crystalline phase - the energy gaps between its levels and manifolds change due to changing of the electric and magnetic field tension around the ion. These changes, obviously, are to reveal themselves in the shape and position of the absorption and luminescence spectra, and are also to modify the radiation probabilities.

In the novel lead oxyfluoride nanoglassceramics the rare earth ion shifts from the glass-like phase to a fluoride crystal one, i.e. its environment changes drastically. Let us consider these changes on the example of the europium, erbium and neodymium ions.

In the Fig.6 is shown the modification of the europium ions luminescence after the isothermal heat treatment (480°C) in its dependence upon the time of thermal treatment. The europium ion is traditionally used as the sounding ion for interpretation of its environment modification both in crystals [21] and in glasses [22], because this ion transitions reveal intense and well theoretically explained dependence upon the ligands fields. The analysis was carried out on the basis of modification of three bands in the three-valence europium spectrum, corresponding to the transitions from manifold 5D_0 to 7F_0 (extremely sensitive), 7F_1 (magnetic dipole) and 7F_2 (electric dipole).

The starting glass is characterized by the spectrum, where the most intense line corresponds to the degenerated transition $^5D_0 \rightarrow ^7F_2$. The second intensity is revealed by the transition $^5D_0 \rightarrow ^7F_1$. It is a triplet line, making thus the basement for the conclusion that Eu^{3+} is positioned in the low symmetry environment, usual for the fluoride glass-like media. Heat treatment for 30 minutes results in some decrease of intensity of transition $^5D_0 \rightarrow ^7F_2$ (620 nm) in comparison with $^5D_0 \rightarrow ^7F_1$ (590 nm). Heat treatment for 60 minutes leads to drastic changes. The triplet $^5D_0 \rightarrow ^7F_1$ is replaced by the doublet with the maxima at 16875 and 17150 cm^{-1} . This can be an evidence of improvement of environment symmetry of rare earth ions and of general transfer of europium to a crystalline phase [22]. Treatment for 90 minutes results in yet larger modification of the europium ion luminescence spectrum and reveals the complete transfer of REI to the nanocrystal. The analysis of the “extremely sensitive” transition line confirms the assumptions, which were done earlier. The frequency shift in the

process of the glassceramics formation is practically absent, confirming thus the assumption that the europium ion is in a completely fluoride environment. The half width of the transition ${}^5D_0 \rightarrow {}^7F_0$ is a measure of the rate of inhomogeneity of environment across the ensemble of the activating ions. Hence its reduce in nearly 2 times in comparison with the starting value after treatment for 90 minutes is an evidence of a nearly complete transfer of europium from glass to a crystalline phase. The modification of the ratio of the characteristic bands is also an evidence of a radical re-building of the europium ion environment, accompanied by its symmetry improvement.

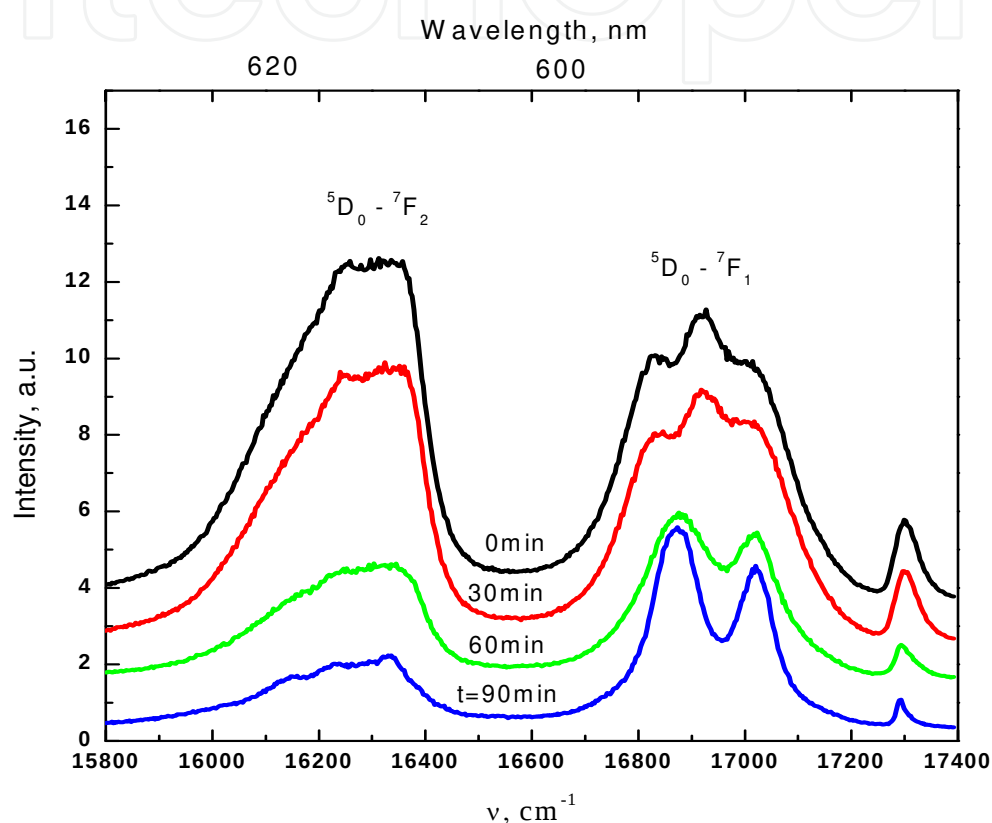


Fig. 6. Luminescence spectra of the glass, activated by 3 mol.% of EuF_3 before and after isothermal heat treatment ($T=480\text{ }^\circ\text{C}$)

Similar modifications are observed in the absorption (Fig.7,a) and luminescence (Fig.7,b) of erbium ions. One can see that the heat treatment results in a strong deformation of the erbium ion absorption and luminescence contours. Transition from glass to nanoglassceramics definitely reveals the Stark structure of erbium, which is usual for the crystalline media. Such a behavior of the absorption and luminescence contours is an evidence of modification of the activation ion environment during transfer from glass phase to a crystalline one.

In addition the rare earth ion transfer to a crystalline phase results in modification of the radiation probabilities from different levels. It reveals itself in intensity growth of some bands in the luminescence spectrum and in reduces of some other bands. Let us consider this effect on the example of the glassceramics, activated by erbium (Fig.8).

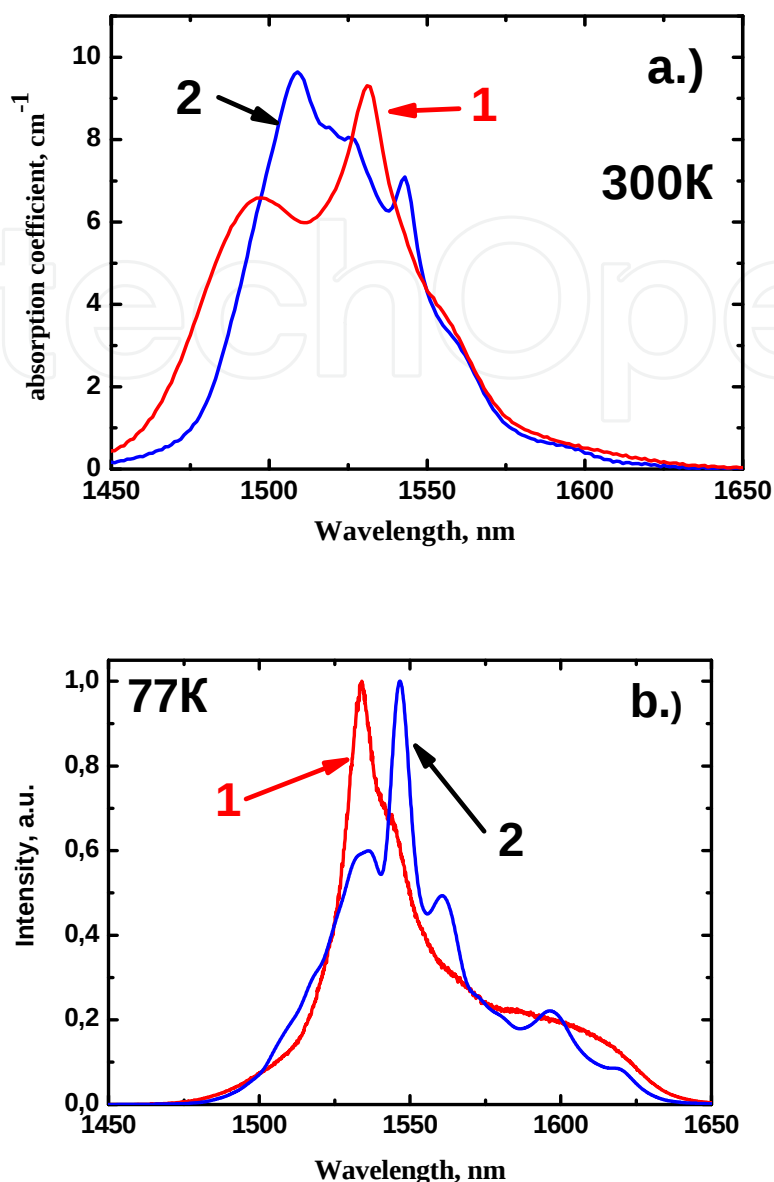


Fig. 7. Absorption (a) and luminescence (b) spectra for the transition $4I_{15/2} \rightarrow 4I_{13/2}$ in the glass, containing 0.4 mol.% of ErF_3 (curve 1) and of nanoglassceramics, obtained after heat treatment (curve 2).

One can see that after the heat treatment the relative intensities of luminescence transitions have changed. For instance, the intensities of transitions with the maxima at 478, 530 and 540 nm have reduced in comparison with 660 nm, while a new transitions in an UV band (365 nm) have arose. In addition, the intensity of the transition in a blue range (405 nm) has grown up. The arise of additional bands became possible due to increase of probability of radiative transitions from these levels.

The heat treatment results in a significant modification of the spectral and luminescence features of the rare earth ions. The spectral and luminescence studies provide the independent confirmation of the X-ray phase analysis conclusion that the rare earth ions shift to the crystalline phase.

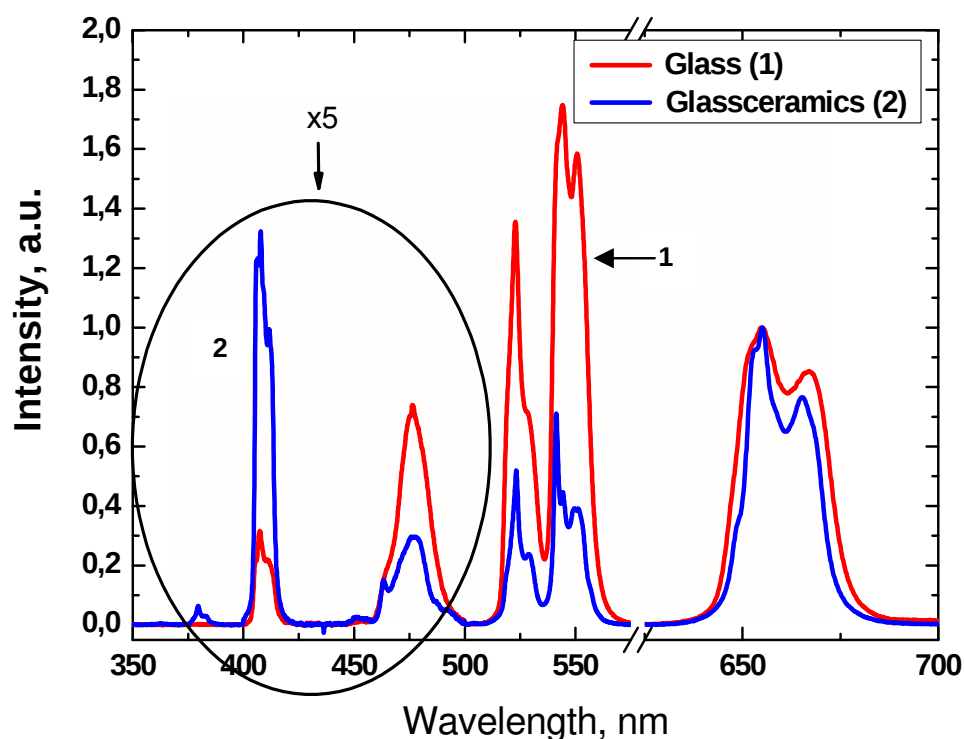


Fig. 8. Luminescence spectra of the (1) initial glass containing 0,2 mol % ErF_3 and (2) nanoglassceramics samples obtained over 10 hours at heat treatment. The spectra are normalized at peak of 660 nm

3. Application of new lead-oxifluoride nanoglassceramics for lasers and amplifiers

Various laser media are used for various types and applications of lasers and optical amplifiers. During the design the luminescence and spectral properties of the medium are chosen so as to provide the best fit to the solved problem. One has also to mention that the use of some rare earth ions imposes its own limitations over the medium use. For instance, the praseodymium ion practically does not luminescence in the oxygen glasses, and that is why the oxide-less fluoride glasses like ZBLAN are used in a praseodymium amplifiers. One has also to mention that the important feature of laser medium is its applicability for design of either super compact mini- or micro-chip lasers or amplifiers, when one has to increase the activator concentration, or of the extended fiber-optical lasers or amplifiers with the length of several meters. Hence the definite requirements are imposed onto the laser material. For instance, the material (glass, glassceramics etc.) has to be possible to accept a high concentration of the activator, while the factors, leading to the luminescence quenching (the presence of OH-groups or the nonlinear up-conversion) are to be minimized. In other case of fiber-optical lasers and amplifiers the material is to be possible to be used as the pre-form for the activated fiber production. The lead fluoride nanoglassceramics, activated by the rare earth ions, which was developed, can be used as an active medium for the miniature lasers or for the fiber-optical lasers and amplifiers. Let us discuss the laser features of the lead-fluoride nanoglassceramics on an erbium ion example and let us compare it with the other well known glass analogs.

Erbium ion activated glasses are widely used for creation of the mini-microchip and fiber lasers, emitting at 1.5 and 3 μm . The lasers and amplifiers at 1.5 μm are used for data transfer via fiber-optical communication lines and also in range finders, because their radiation falls into the so-called third window of the fused silica transparency and to the eye-safe spectral range. In the telecommunication tasks a very important feature of the fiber-optical amplifying medium is the width of its amplification spectrum, because the wider amplification range makes it possible to fill into and to provide simultaneous amplification of the big number of spectral channels. Unfortunately, disregarding a very good technology (from the point of view of fiber production), optical and luminescence spectral features of the erbium doped silicate and phosphate glasses, the halfwidth of their amplification spectrum is not large. It is equal to $\Delta\lambda=20\text{-}30\text{ nm}$, thus limiting significantly the number of spectral channels in the amplifier. The fluoride glasses ZBLAN, doped by erbium, have a wide amplification spectrum of $\Delta\lambda=50\text{-}80\text{ nm}$. However, they meet some problems and limitations – first of all from the point of view of the fluoride fiber production and exploitation. One can overcome the said disadvantages and limitations in a new lead-fluoride nanoglassceramics, where erbium is in the crystalline fluoride phase and the glass matrix contains oxygen.

For instance, Fig.9 illustrates the spectra of erbium ions luminescence in a novel lead-fluoride nanoglassceramics and in the commercially available silicate glass.

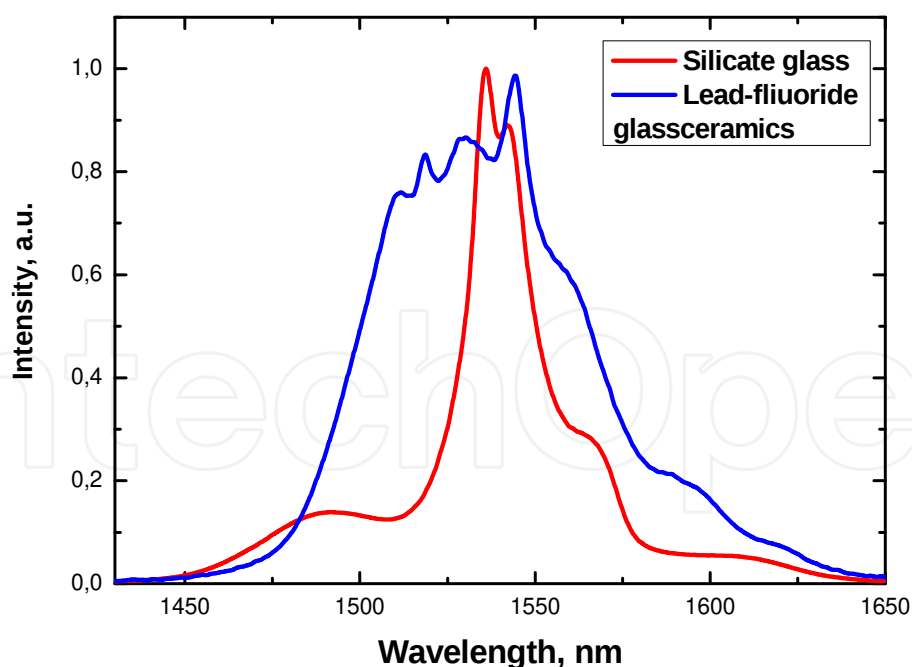


Fig. 9. Luminescence spectra of erbium ions in silicate glass and lead-oxifluoride nanoglassceramics.

One can see that for the nanoglassceramics the spectrum halfwidth is equal to $\Delta\lambda = 66$ nm, while that for the silicate glass it is equal to $\Delta\lambda = 20$ nm. One has also to note that the new nanoglassceramics reveal the high (>80%) quantum yield of luminescence for the transition $^4I_{13/2} \rightarrow ^4I_{15/2}$.

In the Fig.10 are shown the amplification cross-sections for the new nanoglassceramics in comparison with the starting glass (before treatment) and with the commercially available silicate glass.

One can see that the transfer from the starting glass to the nanoglassceramics by heat treatment results in increase of the amplification range from 48 to 64 nm. It is accompanied by the increase of the maximal amplification gain for the same pumping level. For instance, for the starting glass for the pumping level 70% the gain is equal to $g = 0,35$ cm⁻¹, while for the glassceramics it is equal to $g = 0,42$ cm⁻¹. One can also see that the amplification spectrum for the commercial silicate glass is much worsens than that of both of the untreated fluorine-containing glass and of the nanoglassceramics on its basis.

Let us briefly consider the medium for lasers, emitting at 3 μ m, which are used first of all in medicine. Today the oxygen-less crystals like LiYF₄ or garnet crystals like YAG are used as the matrices for erbium ions. However, it is impossible to fabricate the optical fiber and fiber-optical amplifier on the base of these crystals. Hence the search of new media and realization of fiber-optical lasers, emitting at 3 μ m, are today a very important task. The new lead-oxyfluoride nanoglassceramics, activated by erbium, can become an interest object from the point of view of realization of a fiber three-micron lasers.

In the Fig.11 is shown the luminescence spectrum of the erbium activated nanoglassceramics for the transition $^4I_{11/2} \rightarrow ^4I_{13/2}$.

One can see from the Fig.11 that the heat treatment leads to broadening of the luminescence spectrum. It, for instance, makes it possible to tune the laser wavelength within the range 3-3.15 μ m. The life time for transition of the $^4I_{11/2} \rightarrow ^4I_{13/2}$ is a very important parameter for lasers operated at 3 μ m. The life time for new nanoglassceramics achieves 5 ms. In comparison, for crystal of Er:YAG (that very often used as a laser media at 3 μ m) the life time decay achieves 1 ms. Thus, the new nanoglassceramics is a very attractive candidate for 3 μ m-fiber lasers.

Hence a novel lead-fluoride nanoglassceramics, activated by erbium, reveals the luminescence spectral and laser features, which are not worse than that of the well-known commercial glasses, and exceeds them for such parameters, as the amplification spectrum width and the lifetime of the metastable manifold. At the same time the structure and the content of the nanoglassceramics makes it possible to subject it to a traditional technology the optical fiber production. So one can treat the novel lead-fluoride nanoglassceramics, activated by erbium, is the prospective medium for fiber-optical lasers and amplifiers.

4. Application of new lead-oxifluoride nanoglassceramics for thermal sensors

The chapter demonstrates application of the new nanoglassceramics for luminescent fiber thermal sensors. Also the characteristics of the sensors are compared with traditional ones.

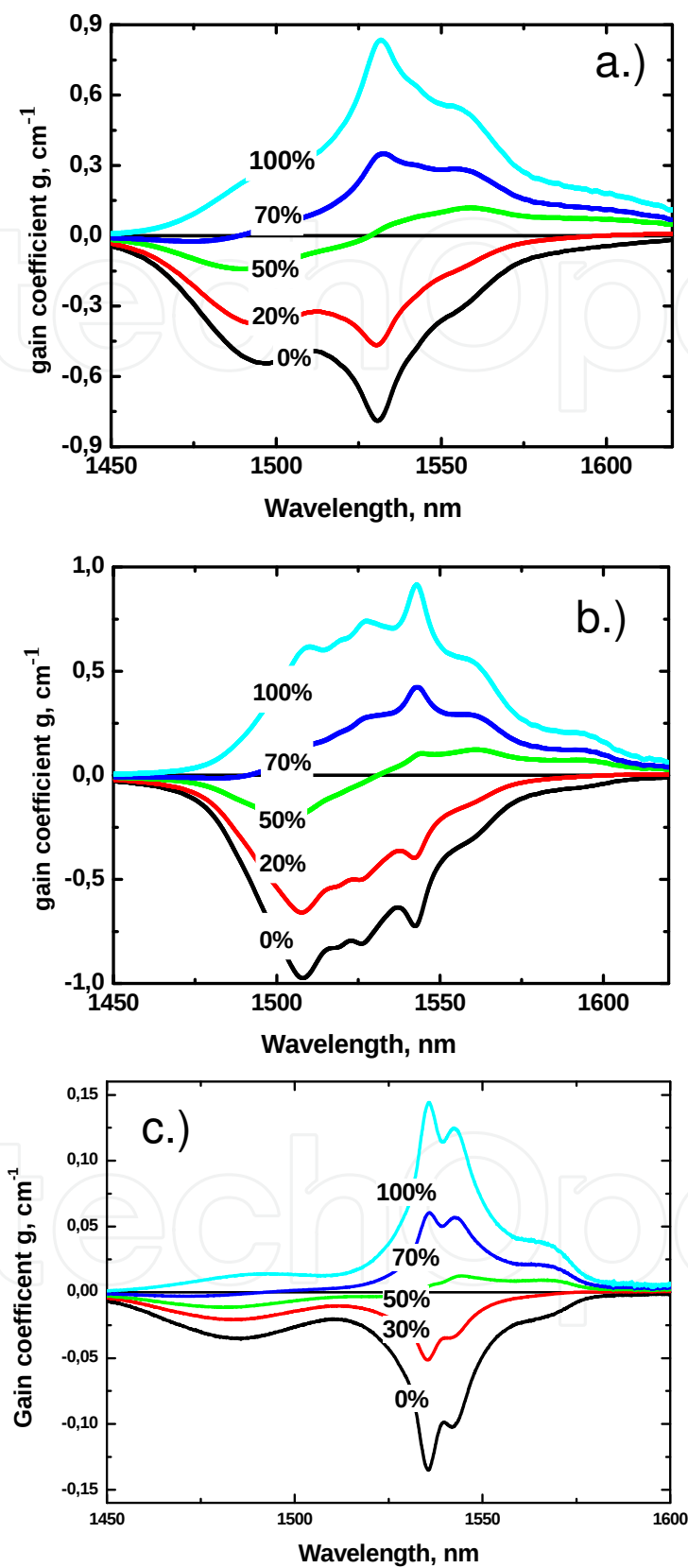


Fig. 10. Gain/loss spectra of initial glass (a), glassceramics (b) and commercial silicate glass (c), doped with erbium, for various pumping ratio N_2/N_{Er} . Pump wavelength 980 nm.

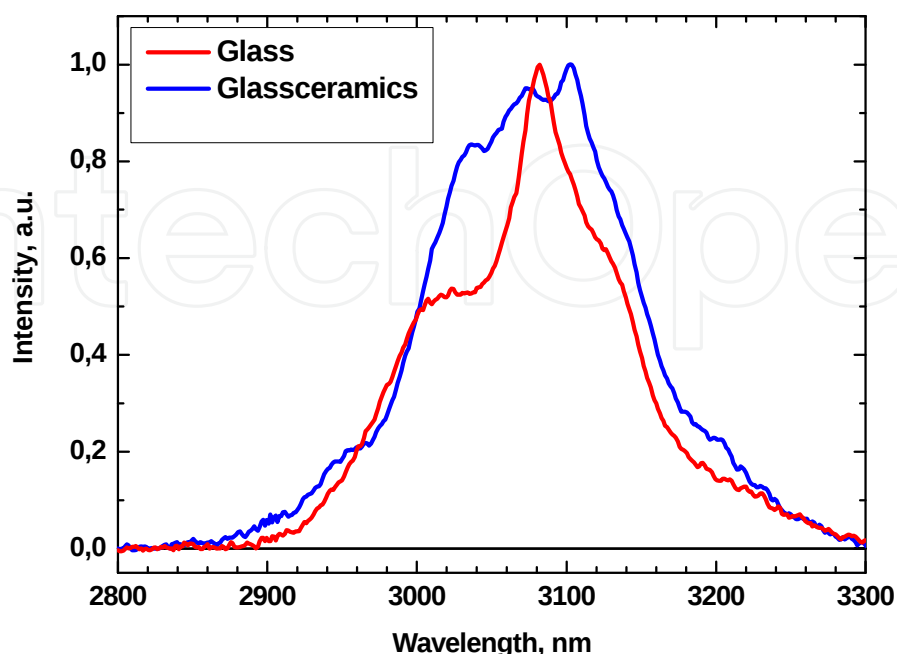


Fig. 11. Luminescence spectrum of the erbium ion in the starting glass and the glassceramics.

In today industry the most widely used (~ 60% of the overall measurements) are the temperature measurements. Wide range of measured temperatures, a big variety of measurement conditions and the requirements to the measuring devices, provide, on one hand, the big variety of the temperature measurement tools, but on the other hand require the development of the novel types of sensors and primary converters, which meet the constantly growing requirements to the accuracy, response and noise protection.

One can separate the big variety of devices for temperature measurement into two big categories – the electrical ones and optical. The optical sensors are used, for instance, for measuring the temperature at the remote object and in the intense electro-magnetic fields. One cannot provide it by means of the electric thermal converters due to high probability of “electric breakdown”.

There exist three main types of the optical temperature sensors: the Fabry-Perot optical fiber interferometers; pyrometers – the contact-less sensors, implementing the radiation from the heated body; and the luminescent ones based on luminescence variation during heating.

The use of color pyrometers is limited by the fact that the body, heated to approximately 400 K, is radiating mainly in the mid-IR spectral range. Due to low sensitivity of majority of sensors in this spectral range, data collection is thus tantalized.

The use of fiber-optical interference sensors, based on the Fabry-Perot interferometer, comprised by the fused silica fiber is limited due to a comparatively high cost and to a complicated design, because the shift of the resonant wavelength is relatively small and

requires the precise measurements. In addition, the interferometer quality degrades with time, especially under the high temperature action.

The luminescent sensors are the most prospective ones, because they combine the simple design and high accuracy ($\pm 0,05$ K). The majority of such sensors are based upon the following principles:

- the temperature shift of the luminescence band maximum across the spectrum;
- the temperature re-distribution of the energy across the excited levels, leading to redistribution of radiation intensity in the neighboring luminescence bands with temperature;
- changes in the luminescence quenching with temperature.

These effects are observed for the rare earth ions like erbium, neodymium, and dysprosium, and for transition metals like chromium, which are contained in the crystalline or glass-like state.

The sensors on the base of temperature shift of the luminescence band maximum across spectrum have not very high accuracy of temperature measurement (± 5 K), in addition, they have rather large inertia (several seconds). Hence today they are not widely used and were replaced by the sensors of other kinds.

The advantage of the sensors on the base of temperature redistribution of energy across the excited levels is their high accuracy of temperature measurement up to ± 0.05 K. Such an accuracy is achieved by the use of optical materials with the low phonon (<900 cm⁻¹) spectrum like fluozirconate or telluride glasses. It increases the intensity of radiation of the temperature-tied levels due to the up-conversion filling of the upper excited manifolds and thus characterized by high radiative probabilities.

The disadvantage of such devices is their small temperature range $T = 7-500$ K. For instance, the fluoride glasses like ZBLAN have a low temperature of softening and melting, while the telluride glasses reveal the high tendency to crystallization with the temperature growth. One can also treat as a disadvantage the high refraction index ($n > 2.0$), which tantalizes significantly the connection with the standard fused silica fiber ($n = 1.47$). In addition, these materials have high cost due to the use of the oxygen-less atmosphere (as in the case of the fluoride glasses) or to the toxic nature of raw materials (in the case of telluride glasses), which require some protection measures during the synthesis.

The advantage of the temperature sensors, based on the variation of the luminescence quenching time with temperature is their small inertia. So one can measure the temperature for the short period of time (several ms) and in the wide spectral range ($T = 77-1000$ K). The sensors have simple design and low cost. Disadvantage of such sensors is a low accuracy of temperature measurement ($> \pm 1$ K). Such sensors employ the crystals of YAG:Cr or YAG:Dy as an active medium. The use of crystalline media provides additional complexity to the design, because such sensors are to combine the optical fibers for delivery of the exciting radiation and for collection of the registered signal, and of the active crystal, used as a sensitive element.

In such a design the thermally sensitive active crystal is connected with an active crystal by gluing. The length of active crystal is limited by the value of several millimeters, and thus its

connection with the optical fiber (glued zone) is usually positioned in the zone of high temperature or of the high temperature gradient. This makes an effect onto the sensors reliability during their exploitation under the high temperatures (more than 200°C). It is impossible to replace such a design by a “purely fiber-optical one”, containing only of the active crystalline fiber, because the technology of fibers production from the said crystals are yet not developed.

The active medium, which is used in such sensors, is to meet the following requirements: the luminescence has to be excited easily; they are to be easily connected with the fused silica fibers; the radiation is to fill into the spectral range, which is convenient for registration etc.

Erbium ions are often used as the luminescence ion, because they has two thermally tied manifolds $^2H_{11/2}$ и $^4S_{3/2}$. The energy gap between these two manifolds is relatively small, and the temperature growth can redistribute the energy between these levels (see Fig.12). One can excite erbium ions via ytterbium ions, which are the efficient sensitizer, and its absorption bands correspond to the spectral range of high power laser diodes (900-1000 nm).

The environment of the erbium ions strongly influences its luminescence properties, and hence the proper choice of the matrix makes it possible to increase the intensity of luminescence from the levels $^2H_{11/2}$ and $^4S_{3/2}$, which will increase the sensitivity of the sensors on this base.

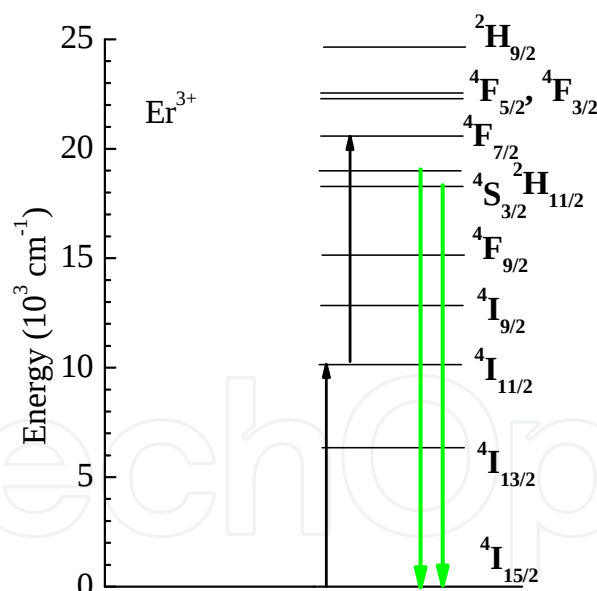


Fig. 12. The scheme of energy transfer from the Er^{3+} ion manifolds

The best intensity of luminescence from these levels is provided by erbium ions, placed in the oxygen-free environment – the fluoride, for instance. In such matrices the quantum yield of luminescence is increased, and the efficiency of up-conversion processes is also increased.

One can treat the glassceramics, which contain in their volume the fluoride nanocrystals – like CaF_2 , PbF_2 etc. – as the prospective media for the luminescent temperature sensors. In present paper it has been shown the possibility to use the transparent glassceramics on the

base of lead-fluoride nanocrystals, containing the rare-earth ions as the active medium for the new generation of the luminescent temperature sensors. In such glassceramics the rare-earth ions playing the role of nucleation centers for the crystalline phase, i.e. they are included into the crystal. In addition, the activated glassceramics can be used for the optical fiber production, solving thus the connection problem. It can be solved, for instance, by the way of welding of the activated and nonactivated fibers, improving thus the sensor stability to fast changes of temperature and to aggressive environment.

Change of the temperature results in changing the population of the erbium manifolds $^2H_{11/2}$ and $^4S_{3/2}$; in other words, takes place re-distribution of the intensity of luminescence bands with maxima at 522 and 547 nm. So, if the luminescence spectra for definite temperatures are known, one can make a conclusion about the object temperature. The temperature growth results in increase of excitation migrations; as a consequence, the number of the radiation-less transitions is growing and grows the probability of luminescence quenching at admixtures. It explains the gradual decrease of radiation intensity at 547 nm and accompanying it increase of intensity at 522 nm (Fig.13).

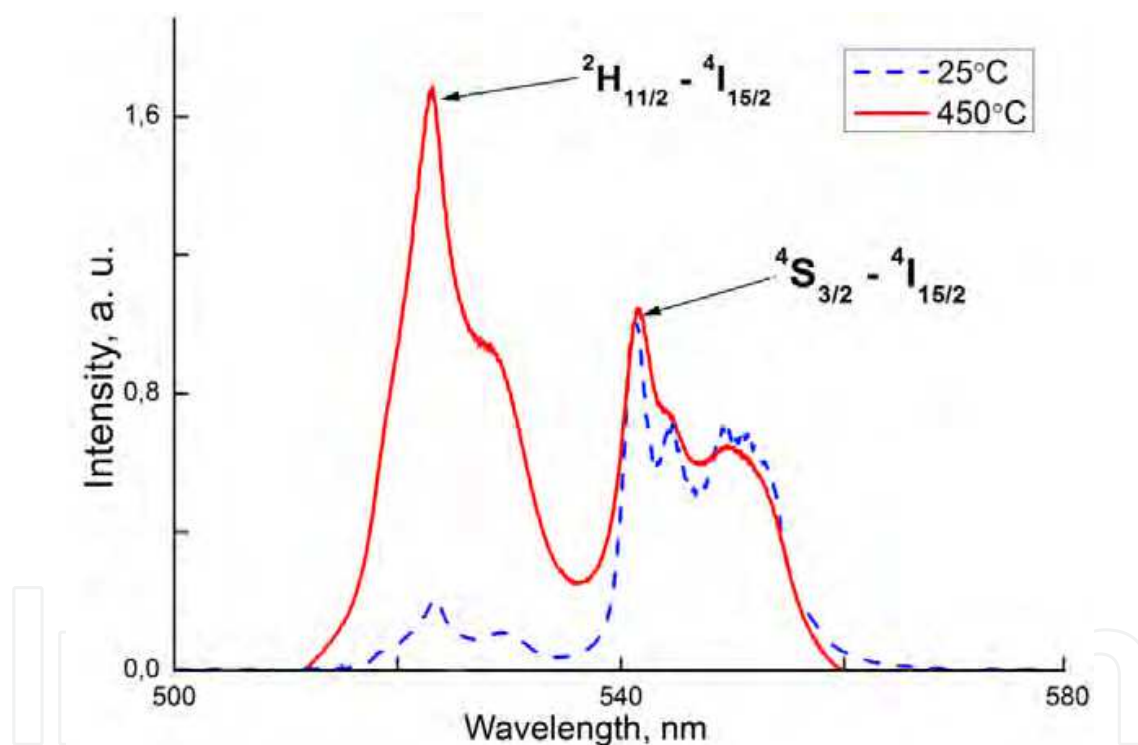


Fig. 13. Temperature dependence of the luminescence spectrum shape of the erbium-doped nanoglassceramics.

In the Fig.14 is shown the evolution of the luminescence spectrum of the erbium activated specimen of lead-fluoride nanoglassceramics with temperature. The shape of the luminescence spectra is explained by the Stark splitting of the erbium manifolds $^4S_{3/2}$ (547 nm) and $^2H_{11/2}$ (522 nm), caused by erbium transfer to the crystalline phase after the secondary heat treatment. If the temperature is increased, the maxima of the peak intensities are shifting one with respect to another, i.e. heating results in thermal redistribution of excitation between the transitions $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^2H_{11/2} \rightarrow ^4I_{15/2}$.

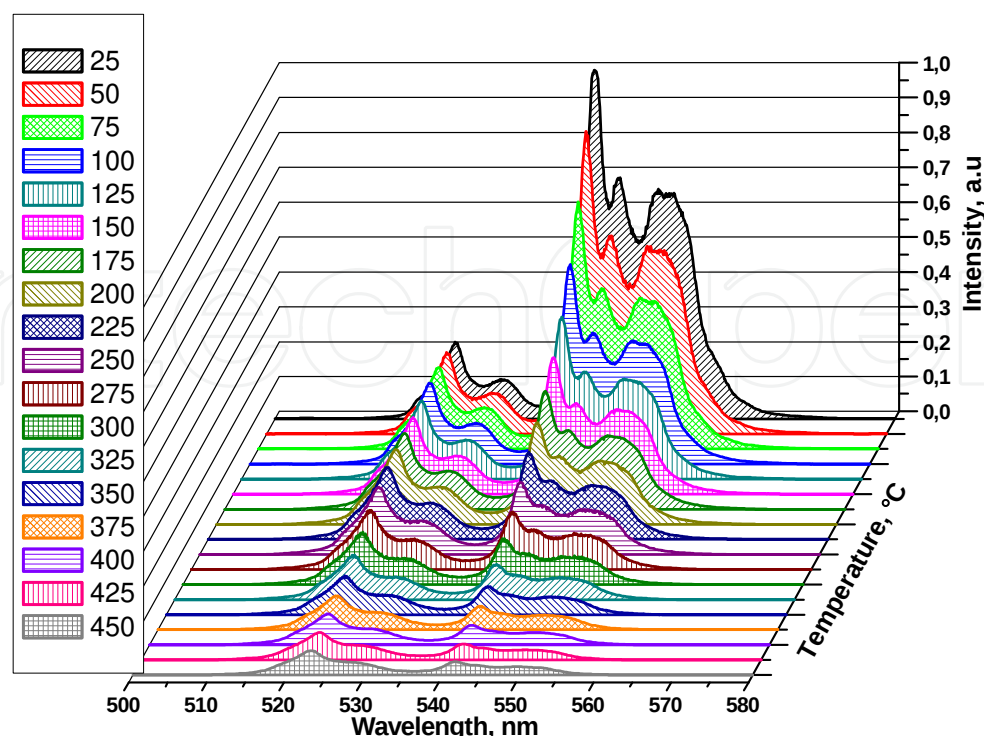


Fig. 14. Evolution of green erbium luminescence from the lead-fluoride nanoglassceramics specimen with temperature.

Let us consider problem of temperature sensitivity of the activated material and hence of the temperature sensor. Speaking of the temperature sensitivity we mean the variation of ratio of luminescence peaks at the selected wavelengths for temperature variation in 1 K. The larger is this variation, the larger is the sensitivity. It more evident from the Fig.15: here the specimen 2 is more sensitive to the temperature variation, than the specimen 1, because $\Delta_2 > \Delta_1$, i.e. the same temperature variation results in larger variation of the signal.

The increase of erbium ions concentration in glass and in nanoglassceramics leads to growth of the luminescence intensity across the overall observed temperature range (Fig.16). The luminescence intensity also grows up across the overall range of measured temperatures with the increase of the time of heat treatment of the erbium activated lead-fluoride nanoglassceramics (Fig.17).

Hence, varying the volume percentage of the crystalline phase by means of variation the time of heat treatment and also of erbium concentration one can control the curve slope, i.e. to control the temperature sensitivity of glassceramics. The dependencies, which were measured, prevent their exponential character across the overall temperature range, i.e. they are predictable and thus they can be used as a graduation curves for temperature evaluation. Hence the knowledge of ratio of the intensities of two erbium transitions makes it possible to determine the material temperature.

The temperature dependencies for the peak ratio for the starting glass and for the glassceramics are the good evidence that the lead-fluoride nanoglassceramics is the most

sensitive to the temperature changes. One can treat this material as the prospective medium to be used in the fiber-optical luminescent temperature sensors. In comparison with known luminescent sensors the temperature sensor, made from the novel lead-oxyfluoride nanoglassceramics, will have a much shorter response time (tens of milliseconds), higher accuracy ($\pm 0.5\text{K}$) and the rather wide range of measured temperatures (77-1000 K).

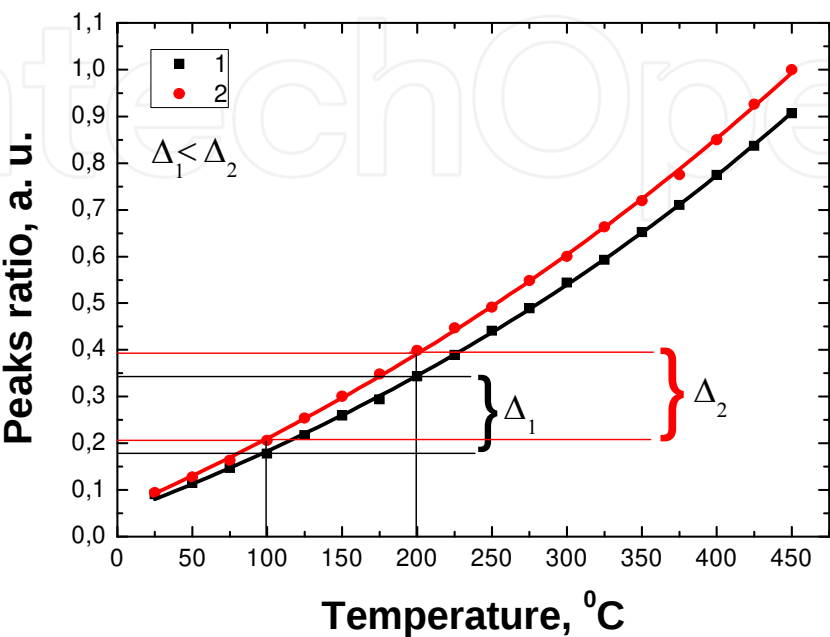


Fig. 15. Determination of the temperature sensitivity of the material.

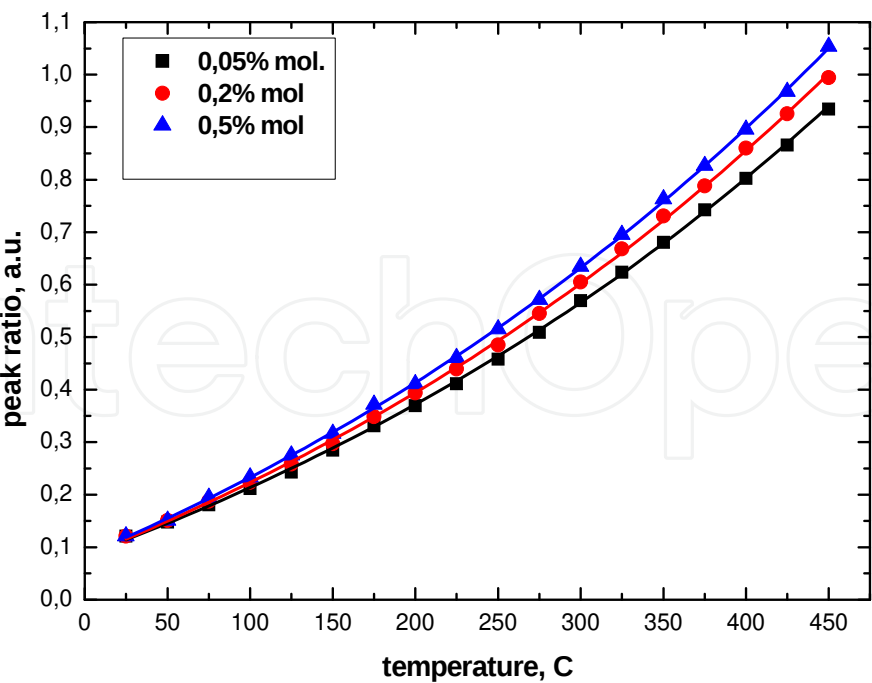


Fig. 16. Temperature dependence of ratio of luminescence peaks in the lead-fluoride nanoglassceramics for various erbium ions concentration and for the same duration of heat treatment ($t = 10\text{ h}$).

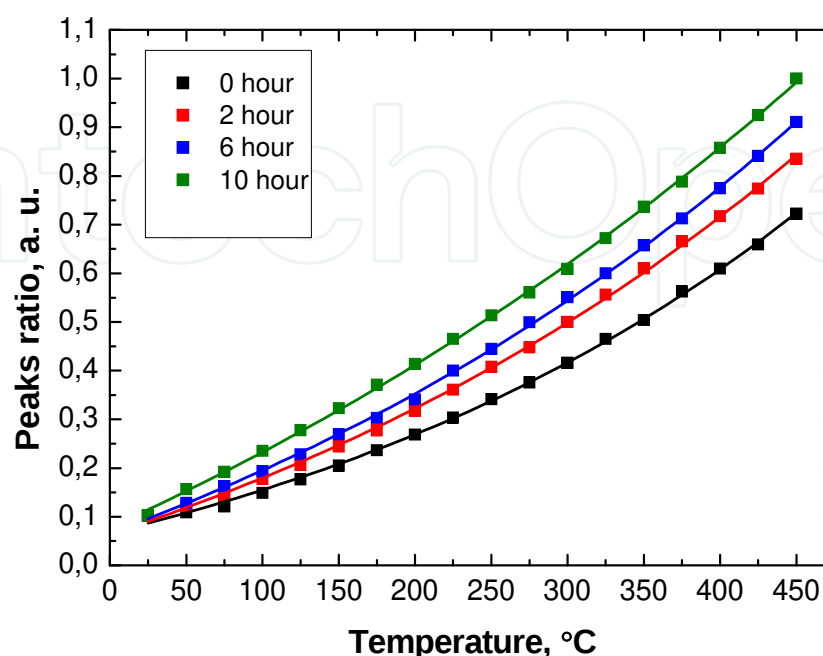


Fig. 17. Temperature dependence of the ratio of erbium luminescence peaks (concentration 0.2 mol %) of the starting glass and of the lead-fluoride nanoglassceramics with the different duration of heat treatment ($t = 2, 6, 10$ h).

5. Application of new lead-oxifluoride nanoglassceramics for luminophors of LEDs

The chapter demonstrates application of the new nanoglassceramics as a luminophor for light emitted diodes (LED). Also, some characteristics of the luminophor are compared with traditional ones.

Today there exist four main approaches to a white light diodes realization:

1. Fabrication of light emitting diodes (LEDs) on the base of ZnSe semiconductor. The structure comprises the blue ZnSe LEDs, “grown up” on the ZnS substratum. In this case the active region of conductor emits the blue light, while the substratum emits yellow. The white light ZnSe LEDs have some advantages. They are working at the voltage 2.7 V and are very stable with respect to static discharges. They can emit the light for the wide range of color temperatures (3500-8500 K). One can thus fabricate the devices with the “warmer” emission. They also have some disadvantages: they have a short lifetime, high electric resistance and still have not found the wide commercial application.
2. RGB mixing of colors. Blue, red and green LEDs are positioned tightly on one and the same matrix. Their radiation is mixed by some optical system – for instance, by a lens. As a result a white light is obtained. The main problem in this case is realization of

green LEDs as well as relatively shorter lifetime of blue diodes. Additional problems arise with technique of mixing the beams, increasing thus the cost of produced LEDs. RGB matrices are widely used in the light-dynamic systems. In addition the large number of LEDs in matrix provides high integral light flow and the high axial light intensity. However, due to the optical system aberrations the light spot has different colors in its center and at the edges. In addition, due to the non-uniform heat sink from the matrix edge and from its center. The LEDs are subjected to different heating. As a result, their color changes due to aging in a different manner and thus the integral color temperature and color are “drifting” during exploitation. Compensation of this unpleasant effect is rather complicated and expensive. The technology of light mixing makes it possible not only to obtain the white light, but also to move across the color diagram by means of changing the current through various LEDs. Special feature of RGB LEDs is the possibility to obtain not only the white light, but also a big variety of light colors with the use of addressing control; one can also obtain various color effects.

3. One can deposit three luminophors, emitting red, green and blue light, onto the UV LED surface. Such a LED has a disadvantage – a technology problems with deposition of luminophor layers, as well as luminophor degradation under the UV radiation action. The phosphor-converted LEDs are much cheaper than the RGB LED matrices (per light flow unit) and provide the good white light. Other disadvantages of this type are: (i) the low light efficiency (less than that of RGB matrices) due to light conversion in the luminophor layer; (ii) the problems with homogeneity of luminophores deposition in technology process, and (iii) the degradation of luminophors with time.
4. One can use the yellow-green, green and red luminophors, deposited onto the blue LED. As a result, two or three radiations are mixed, providing the white or nearly white light. Today most usually are used InGaN based blue LEDs with luminophor, comprised by the nanopowder of yttrium-aluminum garnet, activated by cerium, emitting in a yellow-green spectral range. The luminophor – the powder of YAG:Ce³⁺, deposited onto the diode surface, is covered by the protective polymer. The advantages of the polymer medium are the simple technology and the low cost. However, the polymer technology has its own limitation in the case of white LEDs. The polymer has low thermal conductivity, and thus the high-power diodes with the structure “YAG:Ce³⁺-powder luminophor plus polymer coating” meet the heat sink problems. In addition, the polymers degrade during the long-term thermal and light action.. Hence in the case of high power white LEDs there exists the problem of replacement of the unstable polymer matrices by stronger ones.

The blue LEDs with YAG:Ce³⁺ powder as luminophor emit the so-called “cold” white light, because their radiation does not cover the overall visible range. This “cold” white light is not always comfortable for eyes, and this is the second disadvantage of such material as luminophor type. One can shift the color temperature range towards the “warm” white light by means of introducing the additional red band into the radiation spectrum. Thus one has to add to the LED of the “cold” white light – InGaN, emitting with the spectral maximum at 450 nm, accompanied by the yellow-green YAG:Ce³⁺ luminophor with the spectral maximum at 570 nm – some new component, introducing into the spectrum the red component with the maximum at 600-650 nm. The most prospective for this task are, for

instance, the materials with the europium ion admixture. However, this type of LEDs has a significant disadvantage – the rather narrow bands of absorption by cerium ions in the nanocrystals of the yttrium-aluminum garnet. In the case of mass production there exists the variation of the luminescence band maximum due to the technology reasons. In this case is possible only partial overlapping or even mismatch of the bands of LED emission and cerium absorption, providing the significant influence onto the white LED emission intensity.

One can use this problem by use of other luminophor activators – for instance, terbium ions with the emission band maximum at 550 nm and ions of three-valence europium, which introduces into the blue LED emission the red component. As a result, the mixing of blue, green and red light takes place; such an approach is similar to RGB technology.

In present work we have tried to solve the mentioned problems by means of the novel lead-oxyfluoride nanoglassceramics, activated europium and terbium.

In the Fig.18 are shown the luminescence spectra of the lead-oxyfluoride nanoglassceramics, activated by three valence europium ions with various concentration under the excitation by the commercial blue LED with the additional YAG:Ce³⁺ luminophor. In this case the nanoglassceramics plays the role of the additional luminophor.

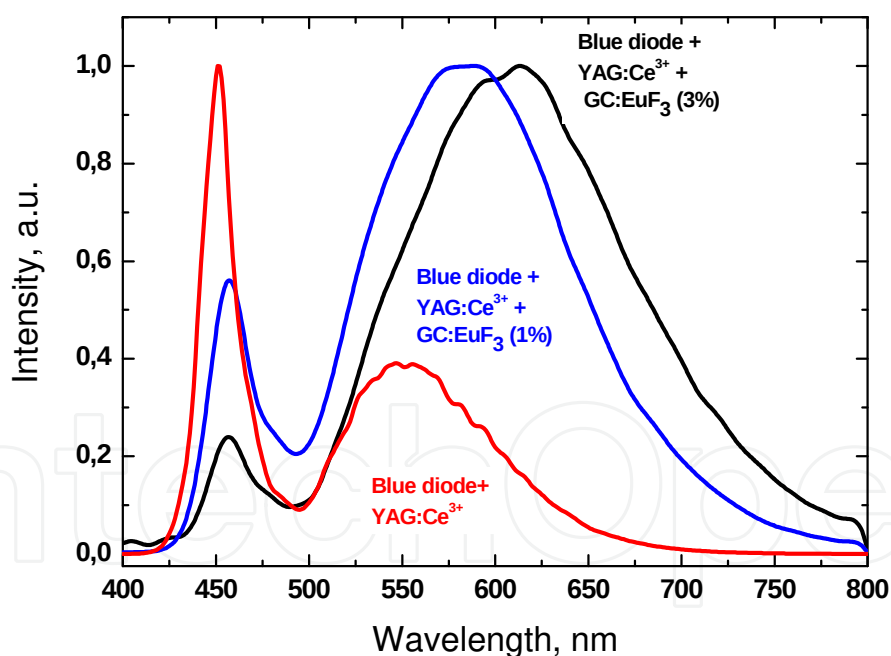


Fig. 18. Luminescence of Ce³⁺ in YAG powder and joint luminescence of Eu³⁺ ions with different concentrations in the glassceramics (GC) and of Ce³⁺ ions in YAG powder under excitation by the commercial blue diode.

The use of europium ions results in arises of the additional bands in the red spectral range. As a result there is observed the wide integral band of Ce³⁺ and Eu³⁺ luminescence with the maximum at ~580 nm. The increase of Eu³⁺ concentration leads to additional shift

of the integral luminescence band maximum to 620 nm. Hence the color temperature is shifting towards higher values (6500 K), i.e. to transfer from the “cold” white light to a “warm” one.

The use of lead oxyfluoride nanoglassceramics, activated by other ions, for instance by terbium ions (green luminescence) and europium ions (red luminescence) makes it possible to use only one luminophore and to prevent the problems, caused by the use of polymer coating and of cerium ions, which have the narrow absorption bands (Fig.19).

The luminescence spectrum now reveals the peaks, produced by luminescence of the Tb^{3+} ions with the maximum at the wavelength 546 nm (transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$) and of the Eu^{3+} ions with the maximums at 595, 615 and 700 nm (corresponding transitions $^5\text{D}_0 \rightarrow ^7\text{F}_0$; $^5\text{D}_0 \rightarrow ^7\text{F}_2$; $^5\text{D}_0 \rightarrow ^7\text{F}_4$). In a combination with the blue LED without $\text{YAG}:\text{Ce}^{3+}$ luminophor these peaks provide the “warm” white light. One has to note specially that the nanoglassceramics, activated by europium and terbium, reveal high thermal and optical strength, and their use as a single luminophor makes it possible to solve the heat sink problems, usual for the high power LEDs. So one can treat the novel oxyfluoride nanoglassceramics, activated by the rare earth ions, as the prospective medium to be used as the luminophor in the high power white light LEDs.

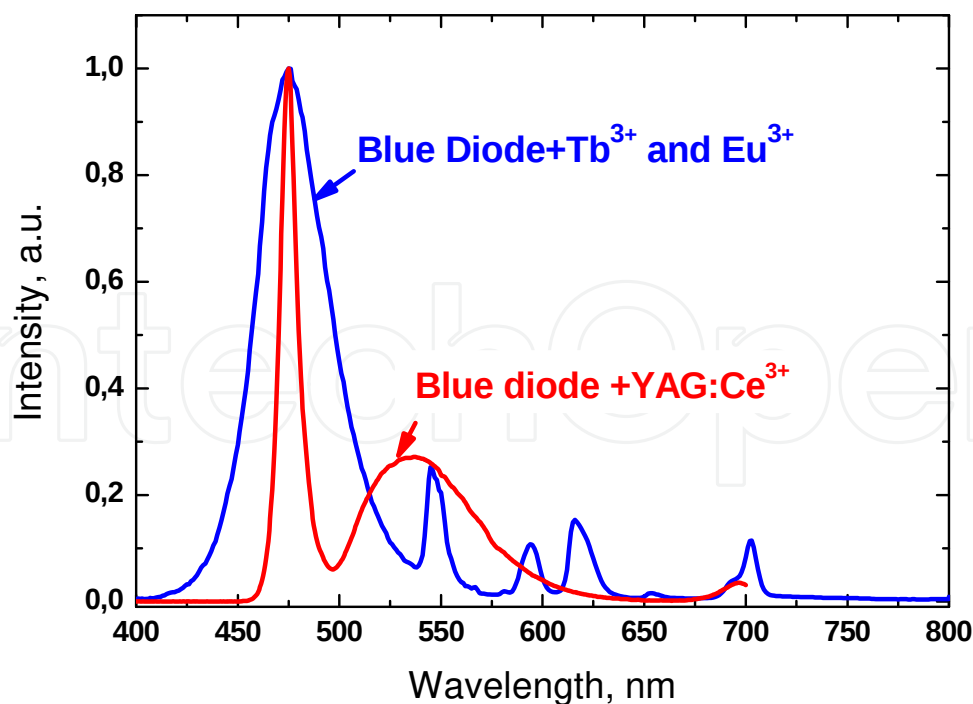


Fig. 19. Luminescence of the nanoglassceramics (GC), activated ions of Tb^{3+} and Eu^{3+} and of the $\text{YAG}:\text{Ce}^{3+}$ powder, excited by the commercial blue diode.

6. Conclusion

Today the novel optical materials are determining the progress in photonics. In this paper it has been shown that one of prospective directions in the field of optical material science for photonics is the development of the nanostructurized glassceramic materials. One example of realization of a novel optical material - the transparent lead-oxyfluoride nanoglassceramics, doped with the rare-earth ions - has been presented. It was shown that due to spontaneous crystallization in a glass are growing the new crystalline phases - the yttrium-oxyfluoride of lead, the lanthanide oxyfluoride of lead and yttrium-lanthanide oxyfluoride of lead. The size of crystalline phase is 15-40 nm, providing thus transparency of nanoglassceramics in a visible and near-IR spectral ranges and thus putting it into the class of optical materials. One can also treat the novel optical nanoglassceramics as a multi-functional material, because it can be used in various fields of photonics. Several examples of the novel material applications in photonics have been demonstrated. Moreover, the features of the novel material with the known analogs have been compared. For instance, it was shown that the novel material can compete with traditional materials in production of fiber-optical lasers and amplifiers, working at 1.5 and 3 μm . It was shown that the novel material can be successfully used for the temperature sensors, including fiber-optical ones. It has been also demonstrated that the novel material can be successfully used as a luminophor for white light LEDs.

7. References

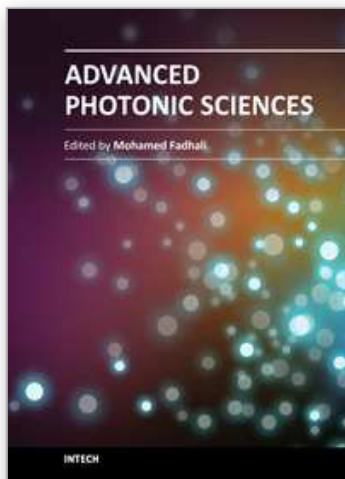
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The new emerging field of photonics has significantly attracted the interest of many societies, professionals and researchers around the world. The great importance of this field is due to its applicability and possible utilization in almost all scientific and industrial areas. This book presents some advanced research topics in photonics. It consists of 16 chapters organized into three sections: Integrated Photonics, Photonic Materials and Photonic Applications. It can be said that this book is a good contribution for paving the way for further innovations in photonic technology. The chapters have been written and reviewed by well-experienced researchers in their fields. In their contributions they demonstrated the most profound knowledge and expertise for interested individuals in this expanding field. The book will be a good reference for experienced professionals, academics and researchers as well as young researchers only starting their carrier in this field.

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