Silica-based oxyfluoride glass and glass-ceramic doped with Tm^{3+} and Yb^{3+} -VUV-VIS-NIR spectroscopy and optical thermometry

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Abstract

Optical, structural and morphological properties of $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped NaYF_4 -based nano-glass-ceramic and a precursor glass have been investigated. The controlled heat-treatment of multicomponent oxyfluoride glass at 640 °C for 2h was used to obtain crystalline precipitations. The differences in optical characteristics have been discussed analysing spectra recorded within wide VUV–VIS–NIR spectral range and considering relaxation dynamic of involved excited states. Optical spectra and luminescence decay curves were measured as a function of temperature in the range of 295–725 K. Based on up-converted emission spectra excited at 975 nm, temperature sensing properties of glass-ceramic were verified. The fluorescence intensity ratio between the up-converted emission bands located at around 795 nm ($\text{Tm}^{3+}:^3\text{H}_4\text{-}^3\text{H}_6$) and 695 nm ($\text{Tm}^{3+}:^3\text{F}_{3,2}\text{-}^3\text{H}_6$) was studied. The maximum relative temperature sensitivity was determined to be 0.35% K^{-1} at 445 K.

Keywords: oxyfluorotellurite glass, (Tm^{3+} , Yb^{3+}) upconversion, temperature sensor

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Introduction

Oxyfluoride glasses and glass – ceramics combine advantages of both oxide and fluoride materials revealing high stability and low phonon energies, respectively [1-2]. Rare-earth – doped oxyfluoride materials are characterized frequently by effective luminescence, high transparency and efficient upconversion processes [3-5]. Incorporation of optically active ions into nanocrystalline fluoride precipitations is attractive method to enhance luminescence efficiency of the optical materials [6-7]. Especially, NaYF₄ nanoparticles containing lanthanide ions were studied due to excellent luminescent qualities [8-10]. A. de Pablos-Martín et. al assumed that NaYF₄ crystallization in silica-based oxyfluoride glasses is realized by diffusion-controlled crystallization mechanism with a constant number of nuclei. It was observed that incorporation of RE ions into oxyfluoride glass is relevant for nucleation effect [11]. The crystalline fraction increases and the activation energy for nucleation and crystallization decreases when lanthanide dopant concentration is higher. Cubic and hexagonal forms were recognized for NaYF₄ [12]. In cubic system Na⁺ and Y³⁺ randomly occupy the cationic crystallographic sites while three different local positions were found for Y³⁺ and Na⁺ ions in hexagonal form. No hexagonal polymorph crystallization was observed during study of glass-ceramics doping with various rare earth ions and consequently the luminescent ions were located into cubic NaYF₄ form [13]. One of the most efficient energy transfer optical system is combination of Tm³⁺ and Yb³⁺ ions [14-15]. Nowadays, ceramics and glasses containing thulium and ytterbium admixtures are investigated as effective infrared solid-state lasers and photo-conversion materials [16]. Conversion of near infrared (NIR) excitation into visible light in luminescent materials co-doped with Tm³⁺ and Yb³⁺ may be applied in optical thermometers as well [17-18]. Temperature measurement is realized by determination of fluorescence intensity ratio (FIR) between luminescent excited states which are thermally coupled levels. Among others Yb/Tm: YF₃ nanoparticles embedded into transparent glass ceramic was

investigated as potential optical temperature sensor and high relative sensitivity of 1.84% per K was found for this optical system [19]. It can be noticed that our paper deals with spectroscopic properties of Tm,Yb co-doped silica-based oxyfluoride glass and glass-ceramic containing NaYF₄ nanoparticles. Additionally, we investigate the excitation and emission spectra in VUV (vacuum ultraviolet) spectral range and effect of temperature on near infrared (NIR) ytterbium and thulium luminescence is studied as well. The maximal relative sensitivity of potential optical sensor is compared with the aforementioned system. Moreover, Wei Xu et. al. revealed that the Tm³⁺/Yb³⁺ co-doped oxyfluoride glass ceramic is a very promising candidate for accurate optical temperature sensors with much high sensitivity [20]. Quite recently, visible to near-infrared persistent luminescence from Sr₂SnO₄:Tm³⁺ was studied as well [21].

The purpose of this paper was to obtain the Tm³⁺,Yb³⁺ co-doped oxyfluoride glass and glass ceramic and to gain the knowledge on their structural, morphological and spectroscopic properties. Ability of the materials under study to conversion of VUV excitation into visible emission was studied. Thulium upconversion luminescence achieved upon NIR excitation was examined as well. The especial attention was directed to the dependence of thulium and ytterbium emission on temperature in range of 295-725 K. Eventually, the potential application of glass-ceramic system for temperature sensor was verified.

2. Experimental

The high purity (4N) anhydrous SiO_2 , Al_2O_3 , Na_2CO_3 , NaF , YF_3 , TmF_3 and YbF_3 reagents were used to obtain the glass sample with the batch composition in mol%: 40SiO_2 - $25\text{Al}_2\text{O}_3$ - $18\text{Na}_2\text{CO}_3$ - 7NaF - 6YF_3 - 1TmF_3 - 3YbF_3 . The starting reagents were thoroughly mixed and put into a cylindrical corundum crucible in a dry box. The batch of 20 g was introduced into a resistant furnace at 1470°C and melted for 1.5 h in ambient atmosphere. The melt was quenched in a brass mould. The obtained glass was thermally treated at 640°C for 2h in order to activate controlled precipitation of the NaYF_4 or $\text{NaY}_{1-x-y}\text{Tm}_x\text{Yb}_y\text{F}_4$ crystalline phases. The X-ray diffraction spectra were measured with a STOE Powder Diffraction System (Ni-filtered CuK radiation) in the range of $2\theta = 5$ – 80° . The TEM experiments were performed with a Philips Transmission Electron Microscope CM-20 Super Twin. The analysis of sample was made by Hitachi 3400N scanning electron microscope with an energy dispersive spectroscopy (EDS) system. Part of emission and excitation spectra in the VUV region were recorded utilizing a facility available at SUPERLUMI station at HASYLAB in the Deutsches Electron Synchrotron (DESY, Hamburg). Spectra in the range of 100–300 nm were measured using the primary 2 m McPherson monochromator and PMT (Hamamatsu R6358P) detector at secondary ARC monochromator. VUV excitation spectra were corrected for the incident photon flux according to the reference sample of NaSal and emission spectra at the SUPERLUMI station were recorded with a CCD camera (Princeton Instruments, Inc.). The remaining emission spectra were recorded using Argon laser (457 nm), AlGaAs (803 nm) and InGaAs (975 nm) diode lasers as excitation sources. The signal was dispersed by a Optron DongWoo monochromator with 750 mm focal length and detected by a Hamamatsu R-955 photomultiplier, a InGaAs or a PbS detector depending on spectral region. Luminescence decay curves were recorded employing an experimental set-up consisting of a tuneable optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser, a double grating monochromator with a 1000

mm focal length, the detectors operating in the visible and NIR as well as a Tektronix MDO 4054B-3 Mixed Domain Oscilloscope. For high - temperature measurements, the sample was placed into a chamber furnace. The temperature of sample was detected by a copper constant thermocouple and controlled by a proportional-integral-derivative (PID) Omron E5CK controller.

3 Results and Discussion

3.1 XRD Analysis

The XRD patterns of precursor glass and glass – ceramic sample with 1% of Tm^{3+} and 3 % of Yb^{3+} are shown in Figure 1. It follows from these patterns that no diffraction peaks appear in the X-ray diffractogram of the as-melted sample and in results the amorphous state of this sample is confirmed. Contrary, intense diffraction peaks are discerned in patterns of glass - ceramic that was annealed for 2 hours at the temperature of 640 °C. After heat treatment the crystalline phase has been formed in glass system and the sodium orthofluoride NaYF_4 crystallites have been identified. It is worth to mention that the resulting glass-ceramic has been transparent. It is known that the NaYF_4 fluoride occurs in two polymorphous forms; cubic - α - NaYF_4 and hexagonal – β - $\text{Na}_{1.5}\text{Y}_{1.5}\text{F}_6$. The first of these belongs to fluorite structure (space group Fm-3m , $Z = 4$) with unit cell parameter of $a = 5\,470\text{ \AA}$, in which Y^{3+} and Na^+ ions are randomly distributed in the cationic sublattice. The structure of second one is characterized by two types of Y^{3+} sites and is related to the P63/m space group with the following cell parameters: $a = 5\,6022\text{ \AA}$, $b = 5\,6022\text{ \AA}$, $c = 3\,3295\text{ \AA}$. The Fm-3m and P63/m NaYF_4 crystal structures are presented in upper part of Fig. 1. It was postulated that in a metastable glass system crystallization of the cubic NaYF_4 form as kinetic product is preferred but at higher temperatures, the transformation to the hexagonal form may take place [13]. We used the XRD pattern of both forms to recognize the crystalline phase in the samples studied and undoubtedly the pure cubic NaYF_4 crystallites have been identified in the glass-ceramic sample. The crystallization of hexagonal phase wasn't detected in the X-ray diffractogram. The mean crystallite size was estimated to be 18 nm utilizing the Scherrer's formula. It can be assumed that the $\text{NaY}_{1-x-y}\text{Tm}_x\text{Yb}_y\text{F}_4$ lattice parameter should be gently lower than $a = 5\,470\text{ \AA}$ determined for undoped NaYF_4 owing to the difference of ionic radii; the Tm^{3+} ionic radii (0.88

Å; CN=6) and Yb³⁺ ionic radii (0.87 Å; CN=6) in fluorine coordination is lower than the Y³⁺ one (0.90 Å; CN=6).

3.2 TEM Characterization

The transmission electron microscope (TEM) analysis allowed the examination of sample morphology and growing nanocrystals in our glass-ceramic system. The Fig. 2a presents bright field TEM image of the glass-ceramic sample (1%Tm, 3%Yb) acquired at 640 °C during 2h heating. It may be seen that our glass-ceramic sample contains numerous well - defined crystalline species. Consequently, TEM image shows the spherical in shape and closely monodisperse nanoparticles embedded into amorphous glass phase. The mean crystal size was found to be 15 nm and it is similar to that estimated during XRD analysis. The Fig. 2b,c display high resolution TEM images revealing more details of nanocrystals ingrained in the glassy host. High resolution electron image (Fig. 2c) and the FFT image of the ordered area (Fig. 2d) confirm the crystalline character of the precipitates. The electron diffraction pattern taking from the crystalline object implies presence of the cubic NaYF₄ nanocrystals. It follows from these findings that electron diffraction examination confirms XRD study pointing growth of cubic NaYF₄ sodium orthofluoride structure.

3.3 Optical study

VUV excitation

Because of development of the new and effective light sources, the processes related to conversion of VUV radiation into visible emission in glass and glass-ceramic systems can be

comprehensively investigated. The synchrotron radiation was used to record the emission spectra of Tm, Yb –co-doped oxyfluoride glass and glass ceramic samples. The lower part of Fig. 3 shows the emission spectra excited at 183 nm and recorded within wide spectral range of 300 nm – 820 nm. The high energy part of these spectra consist of most intense emission bands which were assigned to transitions $^1D_2 \rightarrow ^3H_6$ at 356 nm, $^1D_2 \rightarrow ^3F_4$ at 456 nm and $^1G_4 \rightarrow ^3H_6$ at 477 nm. It can be seen that for glass-ceramic sample the intensity of these aforementioned bands is significantly higher in relation to emission lines recorded for an as-melted glass. This effect is especially efficient for $^1D_2 \rightarrow ^3F_4$ transition. At longer wavelengths the weaker thulium emission bands appear and these are related to $^1G_4 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_5$ and $^3H_4 \rightarrow ^3H_6$ transitions peaked at 651 nm, 762 nm and 786 nm, respectively. The intensity of the lower energy luminescence lines of Tm^{3+} measured for glass-ceramic sample is slightly higher in comparison with adequate luminescence of the as-melted glass but it is not as effective as was observed at shorter wavelengths. In fact, the VUV wavelength excites some luminescent levels of thulium in co-doped glass and glass-ceramic samples and it can be inferred from these findings that partial incorporation of optically active ions into ordered fluoride nanocrystals results in increase of luminescence intensity particularly at higher energy.

The upper part of Fig. 3 presents of the excitation spectrum of most intense $^1D_2 \rightarrow ^3F_4$ thulium emission monitored at 450 nm for as-melted glass and glass-ceramic co-doped with 1% Tm^{3+} and 3% Yb^{3+} . It can be seen that for our samples the thulium luminescence is activated as a result of different transitions in VUV-UV spectral range from 300 nm up to 120 nm. The two broad excitation bands may be attributed to inter-configurational $4f^n \rightarrow 4f^{n-1}5d$ transitions of Tm^{3+} . The spin-allowed f-d transition of Tm^{3+} is located at 182 nm while the spin-forbidden transition is centred at 245 nm. Spectral characteristic of these two bands is different for the as-melted glass and glass-ceramic. Actually, for the glass-ceramic sample the maximum of band located at higher energy is clearly shifted towards to shorter wavelengths comparing to the as-

melted glass. Additionally, effective elevation of the excitation band placed at 245 nm can be observed in the glass-ceramic sample. Thulium luminescence in the materials under study is excited as a result of intra-configurational f-f transitions as well and it is evidenced by narrow spectral lines located at 259 nm, 274 nm, 283 and 289 nm. In relation to that the narrow lines are attributed to $^3H_6 \rightarrow ^3P_{2,1,0}$ and $^3H_6 \rightarrow ^1I_6$ Tm^{3+} transitions. In contrast to the as melted glass the band measured for the glass-ceramic from 280 to 297 nm comprises some narrow – line components and eventually all f-f transitions attained for the sample containing $NaYF_4$ nanoparticles are characterized by substantially higher intensity.

VIS and NIR excitation

The luminescence originating in 1G_4 excited state of thulium measured for 1%Tm,3%Yb co-doped glass and glass - ceramic samples was recorded under excitation at 457 nm and is presented in upper part of Fig. 4. The maximum of emission band attributed to $^1G_4 \rightarrow ^3H_4$ transition is located at 791 nm while the emission associated with $^1G_4 \rightarrow ^3F_4$ contains one prominent line peaked at 651 nm. These spectra were normalized to equal intensity of $^1G_4 \rightarrow ^3H_4$ transition in order to show different spectral characteristic of $^1G_4 \rightarrow ^3F_4$ emission bands measured for the glass and glass-ceramic sample. It can be seen that spectral width of the aforementioned emission band is efficiently reduced for sample containing $NaYF_4$ nanoparticles and covers spectral range around 30 nm lower as compared to an analogue emission recorded for the as –melted glass. It is worth noticing that the full width at half maximum of prominent emission line was found to be 24 nm for the glass – ceramic sample and is narrowed to 5 nm in the glass-ceramic sample.

The excitation at 808 nm into the $^3H_6 \rightarrow ^3H_4$ absorption band of Tm^{3+} in materials under study leads to the NIR emission of Yb^{3+} ions. The comparison of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission

bands is shown in lower part of Fig. 4. The ytterbium emission is a result of phonon assisted Tm – Yb energy transfer and consequently luminescence within wide 940 – 1120 nm spectral range is observed. In the case of glass-ceramic sample numerous ytterbium ions may enter the Y^{3+} sites into ordered orthofluoride nanoparticles and as a consequence the spectral characteristic of NIR Yb^{3+} emission is distinct from that attained for the as-melted glass. Actually, in our glass-ceramic $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ spectrum, the additional intense emission lines appear at 978 nm. At longer wavelengths the difference in the discussed Yb^{3+} emission spectra is less spectacular but it can be perceived that a component at 1061 nm disappears for the glass ceramic sample. In contrast to $^1\text{G}_4 \rightarrow ^3\text{F}_4$ thulium transition, the difference in FWHM (full width half maximum) of $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ytterbium emission band is rather ineffective i.e. it is reduced as little as 15 % comparing to adequate spectrum of as-melted glass.

Impact of temperature on the effectiveness of ytterbium emission in the spectral region of potential optical amplification around 1.05 μm may be discerned on upper part of Fig. 5. It can be seen that effect of the temperature on the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ Yb^{3+} emission band in glass-ceramic sample is inefficient up to $T=500$ K. On the other hand above this temperature integrated intensity of ytterbium emission is substantially reduced and at $T= 675$ K barely 38 % Yb^{3+} luminescence acquired at 295 K occurs. Furthermore, the spectral shape of investigated ytterbium emission is rather unchanged within 295 – 625 K temperature range. These findings point that growth of our sample temperature causes a weak lowering of ytterbium emission up to 200 °C above room temperature.

The lower part of Fig. 5 reveals emission spectra attributed to $^3\text{F}_4 \rightarrow ^3\text{H}_6$ potential laser transition of Tm^{3+} in glass – ceramic sample measured in temperature range of 295 – 675 K. The InGaAs diode laser emitting $\lambda = 975$ nm was used as an excitation source. Inset shows the temperature dependence of integrated luminescence intensity in the temperature region of 295 – 675 K. Inherent structural disorder of the material under study where thulium ions are

distributed both in amorphous phase and into NaYF₄ nanoparticles brings about significant inhomogeneous broadening of $^3F_4 \rightarrow ^3H_6$ spectral bands. As result of that thulium emission bands are poorly resolved with an explicit maximum at 1774 nm. The effect of temperature on the NIR thulium emission is especially effective above 475 K and at T=625 K the luminescence intensity is decreased more than 40 % in relation to a spectrum measured at room temperature. Particularly relevant for efficiency of optical amplification in this spectral region is the long-wavelength wing of the considered emission bands owing to expected optical losses related to re-absorption phenomena. In can be seen on Fig. 5 that up to T=625 K the long-wavelength part of $^3F_4 \rightarrow ^3H_6$ thulium emission bands is weakly affected by temperature. Actually, we observe insufficient increase of FWHM below 15 nm for emission bands measured at higher temperature. It can be concluded from these findings that the emission from first excited state of Tm³⁺ in our sample will maintain high efficiency needed for numerous applications even in the presence of an adverse heat generation during pumping processes.

Upconversion phenomena and temperature sensitivity

Figure 6 presents survey up-converted emission spectra in the visible region for the as-melted glass and glass-ceramic containing 1% of TmF₃ and 3% of YbF₃ excited at 975 nm. Prominent emission band located around 800 nm is related to the $^3H_4 \rightarrow ^3H_6$ transition and substantially weaker blue luminescence placed at 476 nm is assigned to $^1G_4 \rightarrow ^3H_6$ one. The observed up-converted Tm³⁺ emission is a result of processes involving consecutive steps of a nonradiative energy transfer from ytterbium to thulium. In first step the excitation energy is non-resonantly transferred from $^2F_{5/2}$ excited state to the 3H_5 level of Tm³⁺ while a part of this transition is released to the host as phonons. Second step involves multiphonon relaxation to the 3F_4 first excited state of thulium from which a transition to the 3F_2 level is result of a second NIR photon

of ytterbium transitions. The 3H_4 Tm^{3+} excited state is fed mainly as result of nonradiative processes from 3F_3 and 3F_2 levels. The third step of non-resonant Yb -Tm energy transfer results in population of 1G_4 level but quite high energetic disproportion exceeding 1500 cm^{-1} occurs. Consequently, we observe low efficiency of the 1G_4 up-converted luminescence as compared to the 3H_4 emission. These phenomena may be schematically described as follows:

The lower part of Fig. 6 displays the dependences of integrated up-converted emissions on excitation power at 975 nm. According to the determined slopes, two photon excitation process is needed to activate 3H_4 emission whereas the 1G_4 excited state is populated as result of tree photon excitation.

Comparison of these up-converted emissions reveals that for the glass-ceramic sample intensity of $^1G_4 \rightarrow ^3H_6$ and $^3H_4 \rightarrow ^3H_6$ luminescence increases respectively 12-fold and 9-fold in relation to adequate spectra measured for the as-melted glass. It may be seen that the thermal treatment results in substantial changes of these spectra i.e. the spectral shape of the up-converted emission spectra measured for our both samples is clearly different. Accordingly, the NIR emission band recorded for the glass-ceramic is characterized by two maxima at 793 nm and 801 nm while the blue emission band comprises prominent maximum at 476 nm and two weaker components at 472 nm and 486 nm. In glass-ceramic sample numerous optically active ions reside into the ordered $NaYF_4$ objects for which quantum efficiency of thulium excited states (3H_4 and 3F_4) responsible for promotion of up-converted luminescence is quite high.

Consequently, we observe substantial increase of anti-Stokes emission intensity in the heat-treated sample.

Figure 7 presents the up-converted luminescence spectra in the wavelength range of 650–850 nm for 1%Tm³⁺,3%Yb³⁺ co-doped oxyfluoride glass ceramic measured under excitation at 975 nm for various temperatures from 295 K up to 725 K. It may be discerned that at T=295 K the highest intensity is related to ³H₄ → ³H₆ Tm³⁺ emission at 795 nm while the thulium luminescence related to ³F_{3,2} → ³H₆ (695 nm) and ¹G₄ → ³H₆ (475 nm) transitions is considerably weaker. In relation to that at room temperature, the NIR Tm³⁺ transitions covers 90 % up-converted luminescence whereas red and blue thulium transitions are related to 4% and 6%, respectively. Actually, the peak position of the aforementioned emission bands is unchanged when the temperature increases, but the impact of higher temperature on their intensity is relevant. The NIR ³H₄ → ³H₆ up-converted emission intensity at 795 nm is gradually lowered with temperature increasing and at T=725 K this decrease is close to 50 %. The drop of emission effectiveness at higher temperatures takes place for ¹G₄ → ³H₆ transition as well. This effect is less spectacular comparing to NIR up-converted emission at 795 nm and 23% intensity reduction is observed at T=725 K. Contrary, the red ³F_{3,2} → ³H₆ emission intensity gradually increases with temperature elevating and we observe fairly two – fold intensity enhancement at highest temperature. It is result of the phenomena that is related to thermally coupled ³F_{3,2} and ³H₄ levels. The energy difference between these excited states is below 2000 cm⁻¹ and at higher temperatures ³F_{3,2} levels can be efficiently populated. In respect to that the special attention should be paid to the transitions from thermally coupled ³H₄ and ³F_{3,2} thulium excited levels. Fluorescence intensity ratio (FIR) between ³F_{3,2}–³H₆ and ³H₄–³H₆ emission lines can be applied as a temperature dependent parameter. The Boltzmann distribution governs the population of these excited states. It is known that the luminescence intensities are proportional

to the population of involved energy levels and FIR of two thermally coupled levels can be defined by following equation [22]:

$$FIR = \frac{I_{3F3,2}}{I_{3H4}} = B \exp\left(-\frac{\Delta E}{kT}\right) \quad (4)$$

where B is temperature independent constant, ΔE is the energy gap between the two thermally coupled levels and k is the Boltzmann constant. Figure 8 displays a transient of FIR (695/795) as a function of temperature for 1%Tm, 3% Yb co-doped glass – ceramic sample. The spectral limits of the integrated emission are 740–886 nm and 648–740 nm for 3H_4 – 3H_6 and $^3F_{3,2}$ – 3H_6 transitions, respectively. It can be seen that the acquired experimental data are reasonably fitted by the exponential Boltzmann equation and ΔE was found to be 1567 cm^{-1} .

Optical thermometer may be quantitatively characterized with absolute and relative thermal sensitivity. First of them reveals the absolute FIR change with temperature variation and is expressed as:

$$S_A = \frac{dFIR}{dT} = FIR \frac{\Delta E}{kT^2} \quad (5)$$

To reliably compare the thermometers quality, relative sensitivity is usually used because this parameter determines normalized change of FIR with temperature variation and is defined as [23]:

$$S_R = \frac{1}{FIR} \frac{dFIR}{dT} \cdot 100\% = \frac{\Delta E}{kT^2} \cdot 100\% \quad (6)$$

It was documented by Wei Xu et. al that sensitivity value of $2829.5/T^2$ for Tm^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramic is much higher than other RE ions fluorescence based sensors [20]. Moreover, the absolute sensitivities of Tm^{3+}/Yb^{3+} co-doped $LiNbO_3$ polycrystals was estimated to be $2129.23/T^2$ [24]. For our glass-ceramic this value $1567/T^2$ is significantly lower. Accordingly, in our optical system much lower energy separation between involved levels of thulium occurs and the thermalizing rate from the 3H_4 to the $^3F_{2,3}$ states is less effectively reduced at lower temperatures. It is worth to noticing that in the glass-ceramic sample some optically active ions are entered into fluoride nanoparticles with lower phonon energy environment. In consequence, up-converted luminescence originating in Tm^{3+}/Yb^{3+} co - doped oxyfluoride glass ceramic are expected to be ineffectively thermally quenched.

The lower part of Fig. 8 presents the relative sensitivities of the glass-ceramic sample as a function of temperature from 295 K up to 725 K. It can be perceived that the sensitivity increases up to 445 K and next gradually decreases at higher temperatures. It means that our Tm^{3+}/Yb^{3+} co-doped glass – ceramic is most suitable for the optical sensor within quite wide temperature range. We estimate maximal relative sensitivity to $0.35 \%K^{-1}$ at $T=445K$. For the comparison substantially lower $S_R=0.12 \%K^{-1}$ was found for $SiO_2-PbF_2-Tm_2O_3-Yb_2O_3$ oxyfluoride glass ceramic [20] and higher value of $S_R=1.84 \%K^{-1}$ at $T=435 K$ [19] was estimated for $0.1\%Tm^{3+}, 1\%Yb^{3+}$ co-doped glass-ceramic considering $^1G_4-^3H_6/^3F_{3,2}-^3H_6$ transitions.

Relaxation of excited states

Experimental lifetimes of luminescent levels were determined from luminescence decay curves measured under direct excitation of excited states in question with pulses delivered by OPO. Results of this examination for the as melted glass and for the glass-ceramic sample are collected in Table 1. It stems from this study that thermal treatment results in an effective

increase of the 1G_4 and 3H_4 experimental lifetimes. Accordingly, for the as melted glass 98 μs 3H_4 lifetime elevates to be 247 μs in glass-ceramic while 46 μs 1G_4 lifetime estimated for the as melted glass rises to value of 90 μs for the glass-ceramic sample. This effect is less pronounced in the case of Yb^{3+} excited state and solely 20 % increase of $^2F_{5/2}$ excited state lifetime is observed in the glass-ceramic. Furthermore, effect of heat-treatment on the first thulium excited state 3F_4 lifetime appears to be negligible. It is related to the fact that the 3F_4 level decays mainly radiatively in both as-melted and glass - ceramic samples and quite large energy gap between this excited state and 3H_6 ground state exceeds 5800 cm^{-1} . On the other hand, it can be assumed that more efficient multiphonon relaxation occurs in depopulation of 1G_4 and 3H_4 excited states. Consequently, influence of thermal treatment on lifetimes of these levels is more effective. The highest phonon energy corresponding to the Si–O vibrations in silicate hosts is equals to 1100 cm^{-1} [25] but considerably lower phonon mode 418 cm^{-1} was found in $NaYF_4$ [26]. In fact, glass-ceramic sample contains numerous ordered fluoride nanoparticles and consequently ion-lattice coupling is expected to be lower. As a result of that we observe longer experimental lifetimes of higher-lying thulium excited states in the glass-ceramic sample. Figure 9 compares the semi-log plots of luminescence decay curves for the 1G_4 and 3H_4 levels of thulium measured with the as-melted and glass-ceramics samples. It can be seen that for the as-melted glass strongly nonexponential decay curves were recorded. It means that optically active ions reside into numerous different local positions and various relaxation rates may be considered. In the case of sample containing crystalline precipitates, reduction of intrinsic relaxation rate occurs and consequently nearly single exponential and longer decays are observed.

The impact of temperature on relaxation dynamic of some thulium luminescent levels has been examined. Figure 10 presents experimental lifetimes of the 3F_4 first thulium excited state, the 3H_4 level, and additionally, the 1G_4 level of Tm^{3+} in the glass ceramic sample measured as a function of temperature in the 295–675 K region. It can be seen that 3F_4 experimental

lifetime gradually decreases with temperature increasing. Among processes responsible for relaxation of excited states, multiphonon relaxation and nonradiative energy transfer between neighbouring lanthanide ions are temperature dependent. Taking into account that it is first thulium excited state and that energy difference between this level and 3H_6 ground state is quite large, contribution of nonradiative cross-relaxation and multiphonon relaxation appears to be insignificant. On the other hand this temperature quenching may be result of a migration-accelerated energy transfer to unintentional defects acting as energy traps. Effect of multiphonon relaxation and cross-relaxation processes on experimental lifetimes of higher-lying 3H_4 level should be more efficient. Relaxation of 1G_4 excited state is mainly governed by the cross-relaxation process due to a large energy gap between this level and the next lower energy level of thulium. Actually, in contrast to Tm^{3+} first excited state, as it is presented on Fig. 10 experimental lifetimes of these Tm^{3+} higher energy levels are unchangeable up to $T=675$ K.

4. Conclusions

The oxyfluoride glass and glass-ceramic samples co-doped with thulium and ytterbium were manufactured. The precipitation of the fluoride crystalline phase was initiated during heat-treatment of the as-melted glass. Study on structural, morphological and spectroscopic properties of the glass-ceramic imply that Tm^{3+} and Yb^{3+} ions can reside advantageously into $NaYF_4$ fluoride nanocomponents. The significantly different spectroscopic features were found for the glass and glass-ceramic samples considering VUV-VIS-NIR range. The visible emission may be excited effectively in the VUV–UV region, particularly in the spectral range of the intense $4f^n-4f^{n-1}5d$ transitions of thulium. The visible thulium luminescence was observed as well when exciting in NIR region into Yb^{3+} absorption band at 975 nm. Consequently, the

substantial enhancement of up-converted luminescence was found for glass – ceramic sample. Optical spectra and luminescence decay curves were measured as a function of temperature in the 295 K–725 K region. It was observed that 3F_4 - 3H_6 Tm^{3+} and $^2F_{5/2}$ - $^2F_{7/2}$ Yb^{3+} emissions are weakly affected by temperature up to $T=500$ K. Furthermore, the potential application of material under study as luminescence temperature sensor was verified and maximal relative sensitivity of $0.35\ \%K^{-1}$ was estimated at $T=445$ K.

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Table 1. Measured lifetimes of luminescent levels of Tm and Yb in as-melted glasses and glass-ceramic system.

Glass / <i>Glass-Ceramic</i>	$^2F_{5/2}$ [μs] (Yb)	3F_4 [μs] (Tm)	3H_4 [μs] (Tm)	1G_4 [μs] (Tm)
1 % Tm, 3 % Yb	257	1197	98	46
<i>1 % Tm, 3 % Yb (640°C 2h)</i>	330	1175	247	90

Figures

Fig. 1 Structure of the NaYF₄ forms and X-ray diffraction patterns of as-melted glass, glass-ceramic sample (GC) as well as the NaYF₄ - cubic reference pattern.

Fig. 2 Bright field TEM image of the glass-ceramic sample (A), high resolution TEM image showing nanocrystals embedded in the glassy host (B,C), the Fast Fourier Transform (FFT) of the image equivalent to the corresponding electron diffraction pattern, identified as the cubic NaYF_4 structure (D).

Fig. 3 Excitation spectra of $^1D_2 \rightarrow ^3F_4$ Tm³⁺ luminescence at 450 nm (upper) and emission spectra of thulium in glass and glass-ceramic samples excited at $\lambda = 183$ nm.

Fig. 4 Emission spectra related to the $^1G_4 \rightarrow ^3F_4, ^3H_5$ Tm^{3+} (upper) and $^2F_{5/2} \rightarrow ^2F_{7/2}$ Yb^{3+} (lower) transitions measured for 1%Tm, 3%Yb - doped glass and glass-ceramic (GC).

Fig. 5 NIR emission spectra of ytterbium $^2F_{5/2}-^2F_{7/2}$ Yb³⁺ (upper) and thulium $^3F_4-^3H_6$ Tm³⁺ (lower) measured as function of temperature for 1%Tm,3%Yb - doped glass ceramic.

Fig. 6 Up-converted emission of glass and glass ceramic excited at 975 nm (upper) and integrated luminescence intensity versus excitation power (lower).

Fig. 7 Up-converted emission of 1%Tm,3%Yb -doped glass ceramic measured as function of temperature in the range of 295 – 725 K.

Fig. 8 Fluorescence intensity ratios attributed to $^3F_3-^3H_6 / ^3H_4-^3H_6$ Tm^{3+} transitions as well as corresponding relative thermal sensitivity estimated for 1%Tm,3%Yb -doped glass ceramic.

Fig. 9 Decay curves of 1G_4 and 3H_4 luminescence measured for 1%Tm,3%Yb – doped glass and glass-ceramic.

Fig. 10 Plots of lifetime values versus temperature for luminescent levels of Tm^{3+} in 1%Tm,3%Yb – doped glass-ceramic sample.