



A study on microstructure and luminescent properties of oxyfluoride silicate glass-ceramics with (Ho³⁺, Yb³⁺):NaYF₄ crystallites

G. Dominiak-Dzik*, R. Lisiecki, W. Ryba-Romanowski, L. Krajczyk

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okólna 2, 50-950 Wrocław, Poland

ARTICLE INFO

Article history:

Received 1 July 2011

Received in revised form 7 September 2011

Accepted 8 September 2011

Available online 16 September 2011

Keywords:

Glass-ceramics

NaYF₄ nanocrystals

(Ho³⁺/Yb³⁺) luminescence

Excited-state dynamics

ABSTRACT

Glass-ceramics containing NaYF₄ nanocrystals were prepared by heat-treatment from oxyfluoride silicate-based glass doped with Ho³⁺ and Yb³⁺ ions. The formation of crystalline fluoride phase was confirmed by X-ray diffraction and transmission electron microscopy. Absorption and emission spectra revealed that a fraction of Ho³⁺ and Yb³⁺ ions is incorporated into the NaYF₄ ordered lattice influencing spectroscopic features of glass-ceramics in comparison with those of precursor glass. Green up-conversion emission (545 nm) originating in the ⁵S₂ level in glass-ceramics and up-converted red emission (650 nm) originating in the ⁵F₅ level in *as-melted* glass were observed under optical pumping into Yb³⁺ absorption band and analyzed. Although both emissions in both materials are achieved by two-photon excitations, the relation between green and red emission intensity in glass-ceramics and glass implies that processes relevant to up-conversion phenomena are different. Based on a careful analysis of relaxation dynamics of Ho³⁺ and Yb³⁺ excited states, the mechanisms involved in conversion of the infrared radiation into the visible emission in these materials are proposed and discussed.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Oxyfluoride glass-ceramics systems doped with rare earth ions have been researched widely in the last decade since they possess not only higher chemical and mechanical stability than fluoride glasses but also lower phonon energy than oxide ones. It has been reported in numerous papers that nano-sized crystalline phase like PbF₂, Pb_{1-x}Cd_xF₂, MeF₂ (Me = alkaline earth cations), LaF₃ or NaYF₄ can be created in glasses by controlled thermal treatment without loss of transparency. An interest in luminescent properties of trivalent holmium ion is related to laser emission achieved in the ⁵I₇ → ⁵I₈ transition around 2.2 μm (eye-safe spectral region) and to the visible emission achieved in up-converted processes. Since a direct excitation of Ho³⁺ with diode lasers is inefficient, Ho³⁺ ion is usually sensitized with Yb³⁺ that shows a very strong and broad absorption band at around 1.0 μm, easy available for commercial laser diodes. Energy exchange from Yb³⁺ to Ho³⁺ allows to pump holmium luminescent states for the infrared and visible emissions. Numerous published paper were devoted to luminescence properties of Ho³⁺ and (Ho³⁺, Yb³⁺) in various multicomponent glasses [1–4] and glass-ceramics containing LaF₃, PbF₂ or Pb_{1-x}Cd_xF₂ crystal phase [5–7]. However, to the best of our knowledge, optical studies of Ho³⁺ sensitized with Yb³⁺ in glass-ceramics systems with

the nanocrystalline phase of NaYF₄ have not been reported. The NaYF₄ has been recognized as very efficient up-conversion matrix [8] especially for Er³⁺ or Tm³⁺ with Yb³⁺ as a codopant [9,10]. These reported results were motivation to investigate spectroscopic features of silicate glass-ceramics with (Ho³⁺, Yb³⁺):NaYF₄ crystallites.

In this paper, we report the morphology of silica-based glass-ceramics with NaYF₄ nanocrystals, single- and double-doped with Ho³⁺ and Yb³⁺, and emission properties of Ho³⁺–Yb³⁺ co-doped glass and glass-ceramics materials under optical pumping into Ho³⁺ or Yb³⁺ absorption bands. Particular attention has been directed to relaxation dynamics of holmium and ytterbium excited states in order to explain mechanisms responsible for up-converted green emission originating in the ⁵S₂ level in the glass-ceramics and red emission from the ⁵F₅ state in glass.

2. Experimental

The mixture of high purity (4N, Sigma–Aldrich) reagents were melted to obtain the glass samples with the batch composition in mol%: 40SiO₂–25Al₂O₃–18Na₂CO₃–7NaF–(10–x–y)YF₃–xHoF₃–yYbF₃ (x=0, 0.5 and y=0, 1, 4). The anhydrous Na₂CO₃, NaF, YF₃ and LnF₃ (Ln=Ho, Yb) were used. Owing to a fluorine loss that may occur in the preparation procedure, a 10 mol% excess of YF₃ was used. The 20 g of starting reagents, thoroughly mixed and put in a covered corundum crucible in dry box, were introduced into a resistance furnace at 1450 °C and melted for one hour and fifteen minutes in normal atmosphere. The glassy liquid was poured into copper plate. To obtain glass-ceramics samples, the precursor (*as-melted*) glass ingots were cut into pieces and heat-treated at temperature ranging from 610 °C to 640 °C and time ranging from 2 to 4 h to find optimal crystallization conditions.

* Corresponding author. Tel.: +48 713954173; fax: +48 71 344 10 29.

E-mail address: G.Dominiak-Dzik@int.pan.wroc.pl (G. Dominiak-Dzik).

The X-ray powder diffraction spectra were recorded with X'Pert PRO X-ray diffractometer (Cu, $K\alpha_1$ radiation: 1.54060 Å), in the range of $2\theta = 5\text{--}80^\circ$. Morphological studies encompassing transmission electron microscopy (TEM), and selected area electron diffraction (SAED) measurements were performed using a Philips Transmission Electron Microscope CM-20 Super Twin with 0.24 nm resolution at 200 kV. Absorption spectra were recorded using a Varian 5 UV–vis–NIR spectrophotometer. Low-resolution emission spectra were performed by microspectrometer Ocean Optics Model USB 200. Upconversion spectra were excited by an Apollo Instruments diode laser emitting continuous wave (cw) radiation at 980 nm with a maximum power up to 3 W. Resulting luminescence was dispersed by an Optron DongWoo DM711 monochromator with 750-mm focal length and detected by a Hamamatsu R-955 photomultiplier in UV–vis and by PbS detector in NIR spectral range. Luminescence decay curves were recorded upon a pulsed excitation delivered by a Continuum Surelite optical parametric oscillator (OPO) pumped with the third harmonic of Nd:YAG laser. The decays were measured with Hamamatsu R-955 photomultiplier or a cooled InSb Janson J10D detector (depending on the spectral range) connected to a Tektronix Model TDS 3052 digital oscilloscope. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Morphological characteristics

Fig. 1 presents the X-ray diffractograms of samples single-doped with Ho^{3+} (0.5% of HoF_3) and Yb^{3+} (1% of YbF_3), and double-doped with Ho^{3+} and Yb^{3+} (0.5% HoF_3 –4% YbF_3) that were heat-treated at temperatures from 610 to 630 °C. Sharp and intensive diffraction peaks are observed in the spectra of heat-treated glasses co-doped with Ho^{3+} and Yb^{3+} and single doped with Yb^{3+} ions whereas, the Ho^{3+} -doped glass not so easy undergoes structural modifications in the same thermal and temporal conditions regardless of holmium concentration (data not presented here). It seems that a tendency to crystallization may be controlled by ionic radii of lanthanide impurities. Ions from the beginning (Nd^{3+} , Pr^{3+}) and the end (Yb^{3+}) of lanthanide series were found as nucleating agents that promote evidently the crystallization of NaYF_4 phase in the systems [11,12]. The crystalline phase formed in the glass-ceramics has been

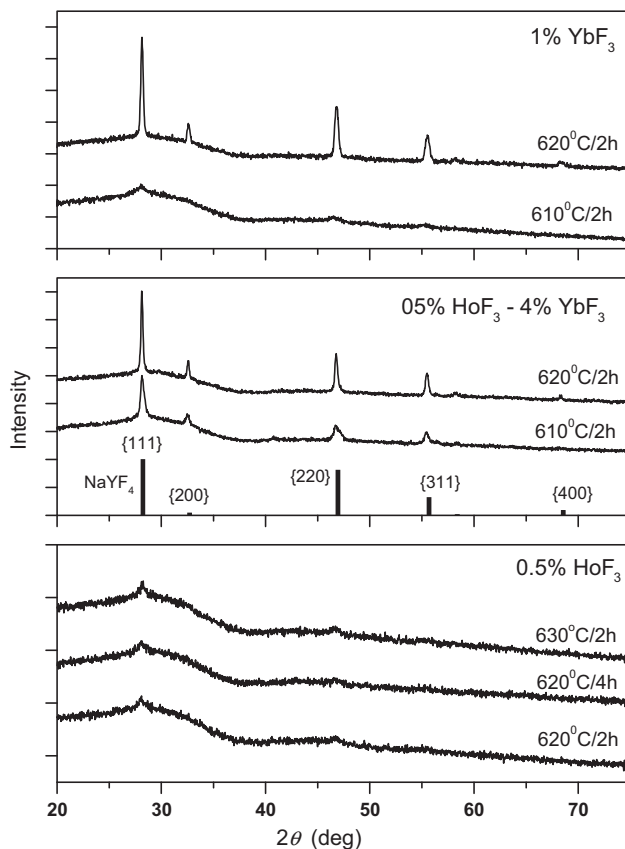


Fig. 1. X-ray diffraction patterns recorded for samples thermal treated at different temperatures. The cubic NaYF_4 pattern with 2θ and $\{hkl\}$ values are presented for the comparison.

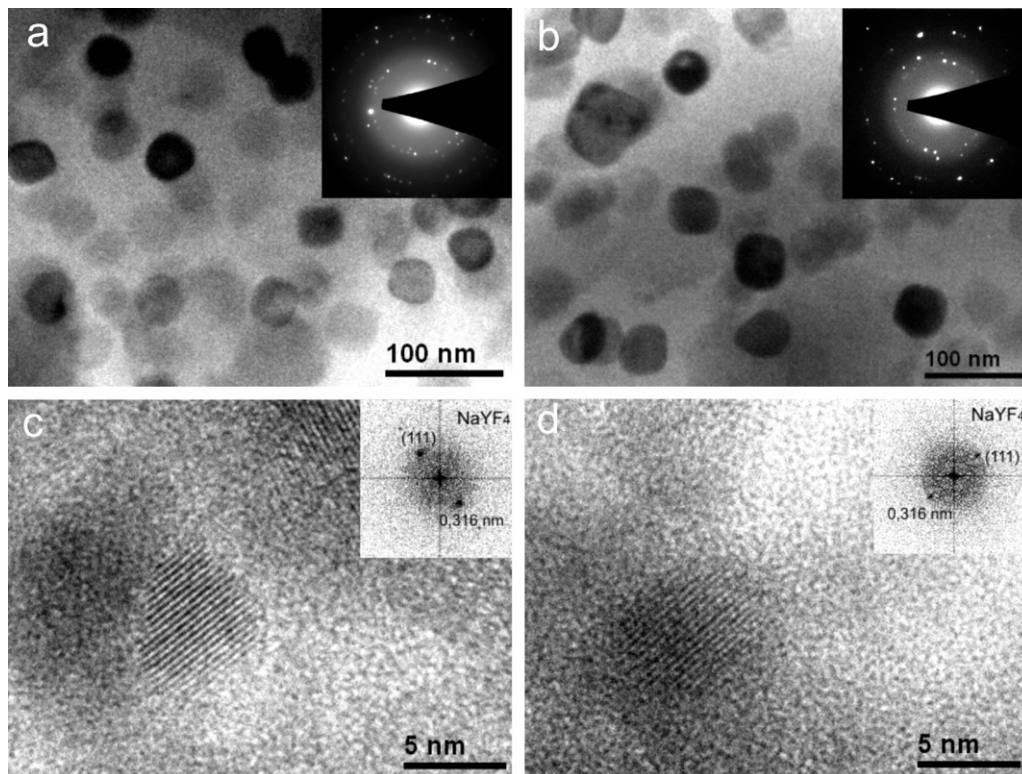


Fig. 2. TEM micrographs with corresponding SAED (insets) of glass-ceramics created at 620 °C and containing 1% of YbF_3 (a) and 0.5% of HoF_3 –4% of YbF_3 (b). The HRTEM images with corresponding fast Fourier transforms (FFT – insets) of the samples with 1% YbF_3 (c) and 0.5% HoF_3 (d) heat-treated at 610 °C and 620 °C, respectively.

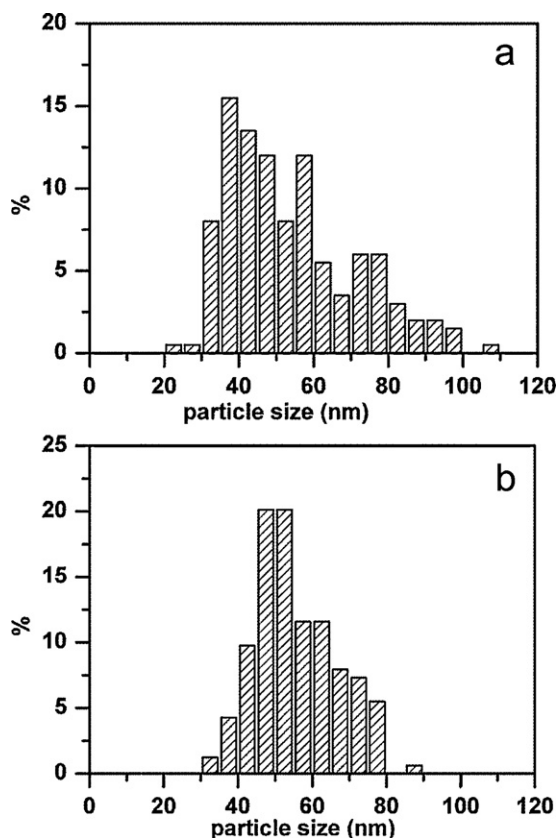


Fig. 3. Histograms of spherical particle size obtained from TEM images for glass-ceramics created at 620 °C and containing 1% of YbF₃ (a), and 0.5% of HoF₃-4% of YbF₃ (b).

identified as a α -NaYF₄ belonging to fluorite structure (space group Fm-3m, $Z=4$) with unit cell parameter of $a=5.470 \text{ \AA}$ [13], in which Y³⁺ and Na⁺ ions are randomly distributed in the cationic sublattice. The X-ray diffractograms of *as-melted* glasses confirmed their amorphous state.

To obtain more detailed insight into morphology of systems heat-treated in similar thermal and temporal conditions and into size variations of formed crystalline particles, the transmission electron microscopy techniques were used. Results are presented in Fig. 2. TEM micrographs of the glass-ceramics samples with 1%YbF₃ and 0.5%HoF₃-4%YbF₃ created at 620 °C are presented in panels (a) and (b). The images portray the spherical in shape and nearly monodisperse particles embedded into amorphous phase. The selected area electron diffraction pattern (SAED) of a single particle confirmed crystalline nature of species. Panels (c) and (d) present high-resolution images and fast Fourier transforms (FFT) obtained for samples single doped with 1% of YbF₃ and 0.5% of HoF₃ and heat-treated at 610 and 620 °C, respectively. In these samples much smaller number of crystalline species was observed in amorphous matrix. It can be seen that single particles exhibit crystalline nature with the calculated d -spacing value of $d_{(111)}=3.16 \text{ \AA}$, typical of the cubic NaYF₄ [13]. Histograms, derived from TEM micrographs on the basis of size measurements of 250–300 particles for each sample, are presented in Fig. 3. The average particle size in both samples was found to be around 50 nm.

3.2. Optical investigation

Fig. 4 compares absorption spectra related to the $^2F_{7/2}$ - $^2F_{5/2}$ transition of Yb³⁺ ions in *as-melted* and heat-treated glass containing 0.5% of HoF₃ and 4% of YbF₃. These spectra deserve some

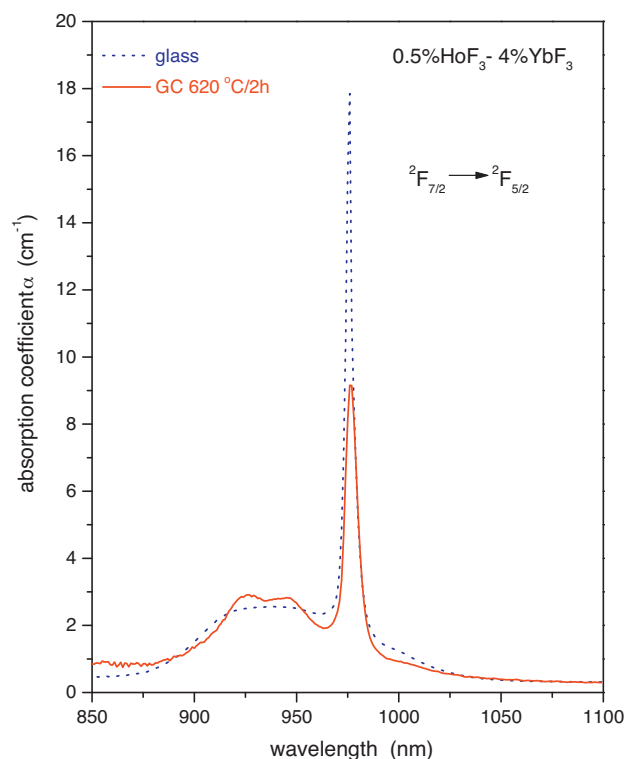


Fig. 4. Absorption spectra of Yb³⁺ ion in glass containing 0.5% of HoF₃ and 4% of YbF₃ and glass-ceramics created at 620 °C.

attention since they show peculiarities of the band that is used for optical pumping with InGaAs laser diode. It can be seen that the thermal treatment brings about significant changes of the spectra. In particular, a broad and smooth part of the spectrum in the region between 915 nm and 960 nm becomes more narrow and assumes a form of a double band after heat-treatment. The most spectacular change consists however in the decrease of the intensity (roughly by a factor of two) at band maximum around 976 nm. The explanation of the effect of thermal treatment is not straightforward. When considering peculiarities of the $^2F_{7/2}$ - $^2F_{5/2}$ band of Yb³⁺ ions one should remember that in virtually all hosts the transition in question is vibronic in character. As a general rule, the absorption band of Yb³⁺ ions contains a relatively narrow line appearing on the long-wavelength part of the spectrum related to transition from the lowest crystal-field component of the ground state to the lowest crystal-field component of the excited state (0-0 line), and a much broader part consisting of overlapping electronic transitions and phonon sidebands. The shape of the latter part depends on the degree of structural disorder on the one hand, and on the importance of the electron-phonon coupling on another. The supposition that a fraction of ytterbium ions is incorporated into the ordered structure of NaYF₄ crystalline phase that appears as a consequence of the heat-treatment can account for observed change in absorption spectrum. The decrease of intensity of the no-phonon 0-0 line accompany with the increase of the band width as a consequence of the heat-treatment stem from the fact that ytterbium ions in fluoride and oxygen surrounding contribute to absorption spectrum.

Fig. 5 compares emission spectra related to the 5I_7 - 5I_8 transition of Ho³⁺ ions in *as-melted* glass samples and thermally treated samples both co-doped with ytterbium and holmium. The spectra were excited into Yb³⁺ absorption band by an InGaAs diode laser emitting radiation at 980 nm. The influence of heat-treatment on emission band shapes is rather weak because the overlap of great number of inhomogeneously broadened lines related to transitions between

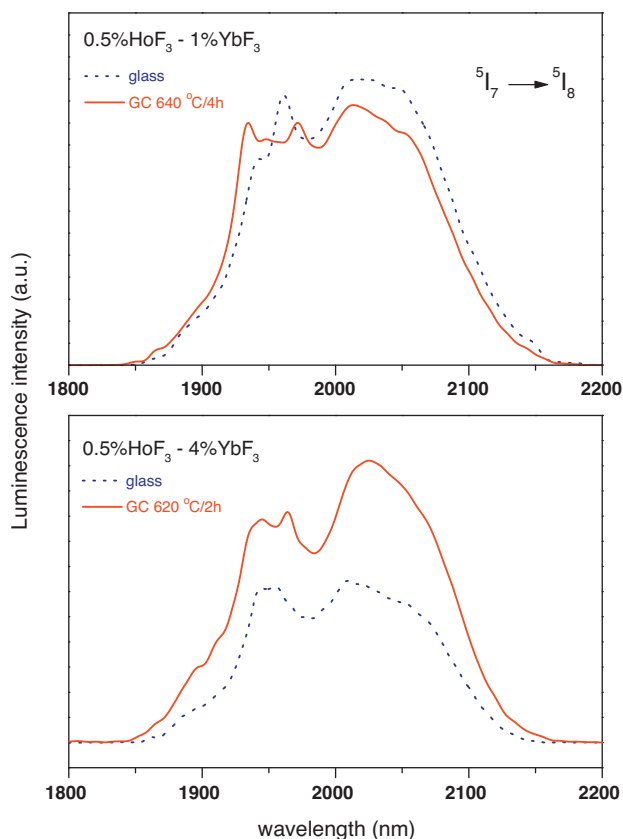


Fig. 5. Room temperature emission spectra corresponding to the 5I_7 – 5I_8 transition of Ho^{3+} in glass and glass-ceramics.

crystal-field levels of the ground and excited states combined with the electron–phonon broadening prevents the appearance of a fine structure. It has been observed during this experiment that strong visible emission emerges from pumped region of the samples. Rather curiously; *as-melted* samples showed red emission whereas glass-ceramics emitted green light.

Fig. 6 shows survey emission spectra in the visible region for *as-melted* glass and glass-ceramics containing 0.5% of HoF_3 and 4% of YbF_3 excited at 980 nm (upper) and at 476 nm (lower) for the reference. Presented spectra are instrumentally broadened owing to the instrumental resolution. Nevertheless, the relation of their intensities is clearly seen. Spectra excited into Ho^{3+} absorption band) are related to the ${}^5S_2 \rightarrow {}^5I_8$ transition at 545 nm (green emission) and ${}^5F_5 \rightarrow {}^5I_8$ one at 650 nm (red emission). A weak band at around 750 nm corresponds to ${}^5S_2 \rightarrow {}^5I_7$ emission. In these spectra the ratio of integrated intensities of red to green emission (I_{650}/I_{545}) is roughly 1:4 for both glass and glass-ceramics. Spectra excited by a radiation at 980 nm emitted by a laser diode are different. For *as-melted* sample the ratio of red to green emission I_{650}/I_{545} is 1:0.03. After heat-treatment process a green emission dominates and the I_{650}/I_{545} amounts to 1:1.5. Qualitatively similar results have been obtained with glass and glass-ceramics containing 0.5% of HoF_3 and 1% of YbF_3 . To get a more close insight into phenomena of up-conversion, the high-resolution emission spectra of studied glassy and glass-ceramics samples were recorded and dependence of up-converted emission intensity on excitation power was measured. Results are shown in Fig. 7. One can see that spectra recorded with heat-treated samples display fine structure; maxima of band components are clearly seen at 536, 541, 545 and 549 nm.

The dependencies of integrated intensities of up-converted emissions on the excitation power at 980 nm are presented in the

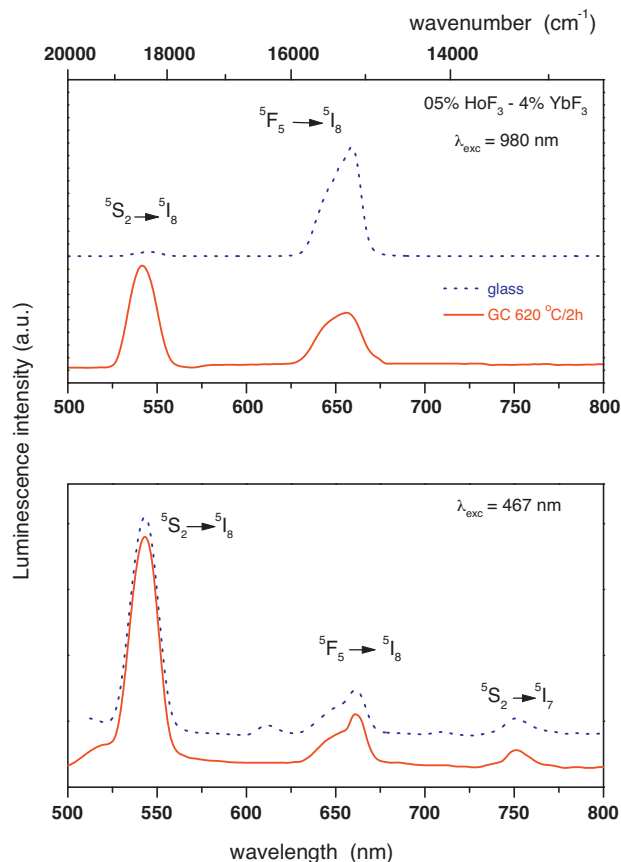


Fig. 6. Survey emission spectra recorded in the visible for glass and glass-ceramics with 0.5% of HoF_3 and 4% of YbF_3 upon excitation at 980 and 467 nm.

insets of Fig. 7. The plots can be well approximated by straight lines. The slopes of lines of about 2 suggest that up-converted emission originating from both 5S_2 and 5F_5 levels is excited by a sequential absorption of two photons. Although the slopes of fitted lines for green and red emissions are almost the same, the relation between intensities of up-converted light obtained for glassy and glass-ceramics samples implies that processes relevant to up-conversion phenomena are different. It is well known that no level of Ho^{3+} ion is in energetic resonance with the ${}^2F_{5/2}$ state of Yb^{3+} ion. It means that to conserve energy, phonon-assisted processes must be involved in the excitation of holmium states in $\text{Yb} \rightarrow \text{Ho}$ energy transfer and up-conversion processes. A mean energy of the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} in studied materials is higher by about 1600 cm^{-1} than that of the ${}^5I_8 \rightarrow {}^5I_6$ transition of Ho^{3+} and the $\text{Yb}({}^2F_{5/2}) \rightarrow \text{Ho}({}^5I_6)$ energy transfer will occur with a simultaneous emission of several phonons. The up-conversion excitation pathways for $\text{Ho}^{3+}/\text{Yb}^{3+}$ ion couples in these materials are shown in Fig. 8. The two-step mechanism of excitation of red emission is represented by the case (b). In the first step, the excitation of the ${}^2F_{5/2}$ level of Yb^{3+} is transferred non-radiatively to the 5I_6 level of Ho^{3+} . Next, the 5I_7 level is fed by multiphonon relaxation from the 5I_6 state. In the second step, the 5F_5 level is populated by excited state absorption (ESA) from the 5I_7 level and/or by second energy transfer process (ETU) in which ytterbium ions undergo the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and coupled holmium ions make the ${}^5I_7 \rightarrow {}^5F_5$ transition. For the efficiency of this process the 5I_7 level should be long-lived and the 5I_6 level should relax rapidly by multiphonon relaxation. The mechanism mentioned above has been considered to explain occurrence of red up-converted emission in several matrices co-doped with ytterbium and holmium [2,7]. The mechanism involved in the excitation of up-converted green emission is

Table 1Decay time constants for Ho³⁺ and Yb³⁺ emissions in glasses and glass-ceramics. All values are in μ s and relate to room temperature measurements.

Sample		Ho ³⁺				Yb ³⁺
		⁵ S ₂	⁵ F ₅	⁵ I ₇	⁵ I ₆	² F _{5/2}
0.5% HoF ₃ –1% YbF ₃	Glass	1.0	0.8	2770	12	480
	Glass-ceramics	1.4	1.2	2440	1106	640*
0.5% HoF ₃ –4% YbF ₃	Glass	0.9	0.8	2497	30	176*
	Glass-ceramics	0.9	1.1	2487	303	320

Symbol * denotes mean time calculated according to the formula [14]: $\tau_{\text{mean}} = (\int_{t=0}^{\infty} tI(t) dt / \int_{t=0}^{\infty} I(t) dt)$ where $I(t)$ is the intensity of luminescence at the time t .

represented by a case (a). In the first step, Ho³⁺ ions are excited to the ⁵I₆ state by a non-radiative energy transfer from the ²F_{5/2} level of Yb³⁺. In the second step, the ⁵S₂ level is populated by excited state absorption (ESA) from the ⁵I₆ level and/or by second energy transfer process (ETU) in which ytterbium ions undergo the ²F_{5/2} → ²F_{7/2} transition and coupled holmium ions make the ⁵I₆ → ⁵S₂ transition. For this process to be efficient the ⁵I₆ level should be long-lived. This mechanism has been supposed to be responsible for green up-converted emission in fluoroindate and fluoroalate germanate glasses [1,4], SiO₂–LaF₃ [5], and glass-ceramics containing Pb_xCd_{1-x}F₂ [6]. It follows from the above consideration that the ⁵I₆ lifetime can be considered as a controlling factor that

determines the colour of the up-converted emission in hosts doped with holmium and ytterbium. Accordingly, the change of red emission to green emission in our samples as a consequence of heat-treatment must be due to lengthening of the ⁵I₆ lifetime. To verify this supposition, lifetimes of excited levels involved in up-conversion processes were determined from luminescence decay curves recorded upon direct excitation of levels in question with pulses delivered by OPO. Results of this measurement for two samples with different ytterbium concentrations are gathered in Table 1. A reliability of lifetime data in Table 1 deserves some comments. The uncertainty of the ⁵S₂ and ⁵F₅ lifetime values is believed to be within 10%. That for the ⁵I₆, ⁵I₇ and ²F_{5/2} levels is considerably higher, in the range of 30%, because the phenomenon of self-absorption tends to lengthen their luminescence decays. It can be seen that thermal treatment brings about a significant increase of the ⁵S₂ and ⁵F₅ levels except for the ⁵S₂ lifetime for the sample containing 4% of YbF₃, likely because the high concentration of ytterbium tends to accelerate a back energy transfer from holmium to ytterbium. Effect of heat-treatment on the ⁵I₇ lifetime appears to be negligible but the lengthening of the ⁵I₆ lifetime is important thus corroborating the supposition mentioned above. It may be interesting to notice that the thermal treatment influences the lifetimes of the ⁵S₂, ⁵F₅ and ⁵I₆ levels while leaving the ⁵I₇ lifetime practically unchanged. This stems from the fact that owing to large energy gap between the ⁵I₇ and ⁵I₈ states ($\Delta E \sim 5100 \text{ cm}^{-1}$),

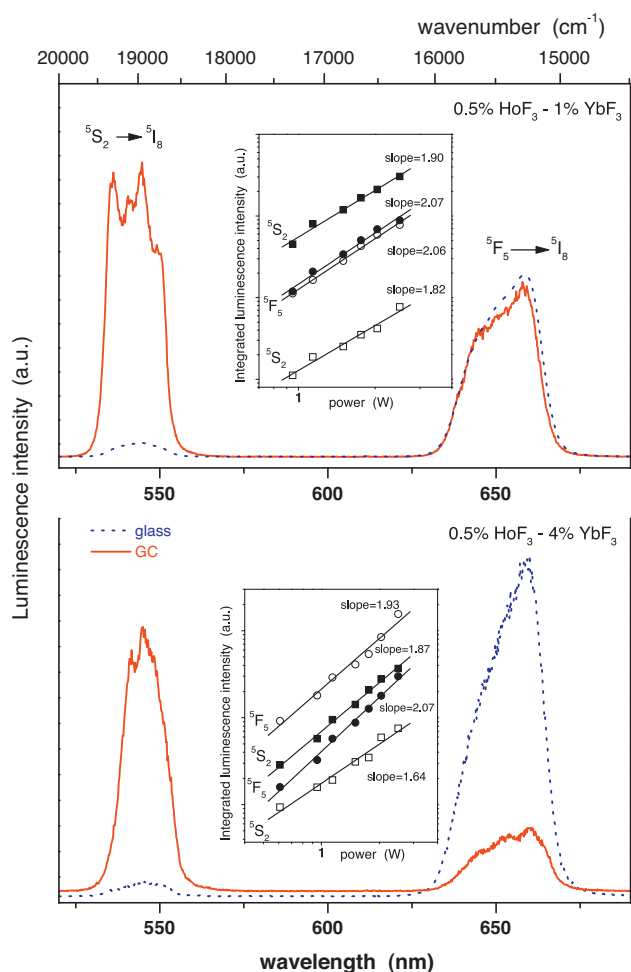


Fig. 7. Up-conversion luminescence spectra of Ho³⁺ ion in glass (dotted line) and glass-ceramics (solid line) registered under the 980 nm excitation. The insets present integrated emission intensities of the ⁵S₂–⁵I₈ and ⁵F₅–⁵I₈ transitions vs excitation power measured both for glass (open symbols) and glass-ceramics (solid symbols). Samples denoted as 0.5%HoF₃–1%YbF₃ and 0.5%HoF₃–4%YbF₃ were heat-treated at 640 °C and 620 °C, respectively.

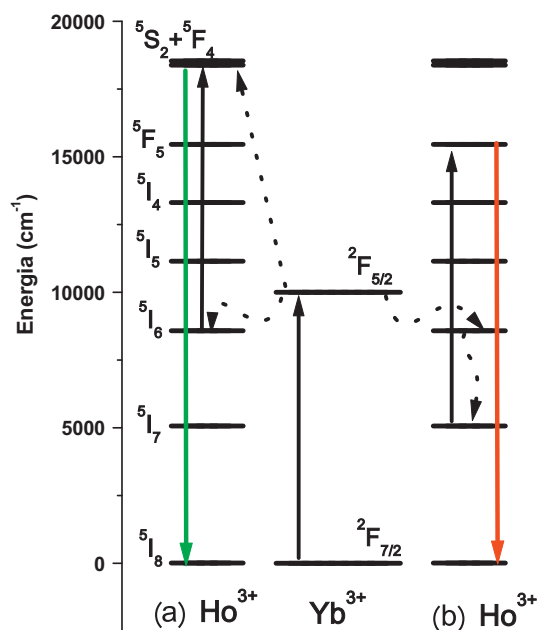


Fig. 8. Energy diagram and up-conversion mechanisms considered for Ho³⁺–Yb³⁺ doped oxyfluoride silicate systems under study. Solid arrows indicate transitions with absorption or emission of photons. Dotted arrows depict non-radiative transitions.

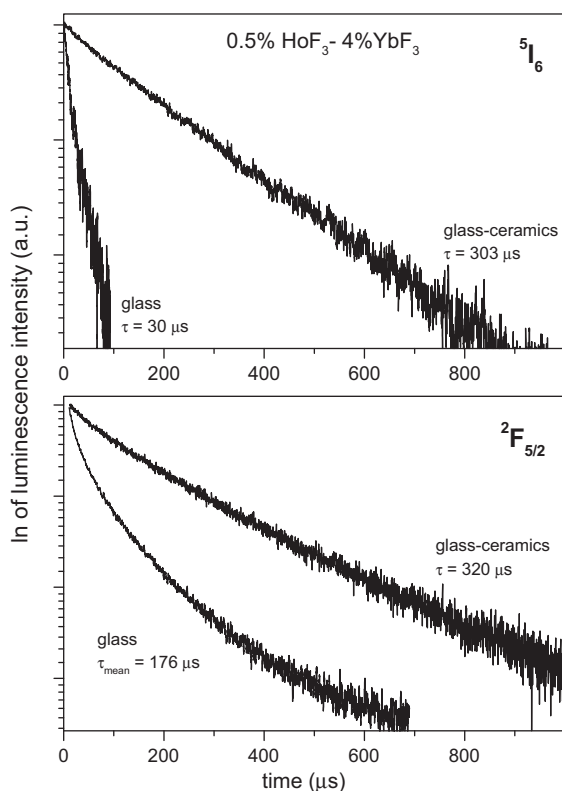


Fig. 9. Semi-logarithmic decay profiles of the 5I_6 (Ho^{3+}) and $^2F_{5/2}$ (Yb^{3+}) luminescence acquired at 300 K from glass (0.5% HoF_3 -4% YbF_3) and glass-ceramic created at 620 °C.

the 5I_7 level decays mainly radiatively in both *as-melted* and glass-ceramics samples. Decays of remaining levels mentioned above, in *as-melted* samples are governed mainly by multiphonon relaxation as a consequence of smaller energy gaps ($\Delta E = 2000\text{--}3000\text{ cm}^{-1}$) to lower-lying states. The gaps may be easily covered by not more than three highest energy phonons corresponding to the Si–O vibrations ($\hbar\omega_{\text{max}} = 1000\text{--}1100\text{ cm}^{-1}$) of silicate host. Thus, the 5S_2 and 5F_5 states with the energy gap of 3060 cm^{-1} are strongly bridged by three host phonons through multiphonon relaxation. As a result, the 5F_5 state is populated giving the luminescence observed at around 660 nm under the 467 excitation (Fig. 6). Significantly lower phonon modes of 298, 370 and 418 cm^{-1} in NaYF_4 [10] lead to much weaker the ion-lattice coupling because the number of the highest phonon modes needed to cover the energy gap of $2000\text{--}3000\text{ cm}^{-1}$ is larger and amounts from 5 to 7, respectively.

It can be seen in Table 1 that the $^2F_{5/2}$ lifetime is also affected by heat-treatment and becomes longer in glass-ceramic samples. The interpretation of this finding is not straightforward since the change in the $^2F_{5/2}$ relaxation is governed by a change of intrinsic decay rate induced by incorporation of a fraction of Yb^{3+} ions into an ordered lattice of the NaYF_4 crystalline precipitates combined with the change of ytterbium–holmium energy transfer rate. In Fig. 9 we compare semi-log plots of luminescence decay curves for the 5I_6 level of Ho^{3+} and $^2F_{5/2}$ level of Yb^{3+} recorded with *as-melted* and glass-ceramics samples containing 0.5% of HoF_3 and 4% of YbF_3 . Nearly single exponential time dependence of the 5I_6 state with the time constant of $303\text{ }\mu\text{s}$ in the glass-ceramics seems to indicate that

the luminescence originates mainly in ions in fluoride surrounding. Strongly nonexponential and relatively short decay ($176\text{ }\mu\text{s}$) of the $^2F_{5/2}$ level in *as-melted* sample points at an efficient energy transfer to Ho^{3+} ions in agreement with the static, Forster-like time dependence. The longer $^2F_{5/2}$ lifetime ($320\text{ }\mu\text{s}$) measured for sample containing crystalline precipitates points at the decrease of the rate of energy transfer and/or decrease of intrinsic relaxation rate. The latter reason seems to be much more relevant since rare earth ions that enter the cubic NaYF_4 host are expected to reside in sites with O_h symmetry [15] which forbids pure electric dipole transitions and solely vibronic and magnetic dipole transitions contribute to their decay.

4. Conclusions

Investigation performed revealed that heat-treatment of multicomponent oxyfluoride silicate-based glass brings about the precipitation of NaYF_4 nano-sized crystals thus forming a glass-ceramics. Results of spectroscopic measurements indicate that a fraction of Ho^{3+} and Yb^{3+} ions residing in amorphous glass enter the ordered lattice of NaYF_4 crystalline precipitates during thermal treatment process. Spectroscopic features of *as-melted* glass and glass-ceramics systems relevant to potential laser operation employing the $^5I_7 \rightarrow ^5I_8$ transition of Ho^{3+} with optical pumping into the Yb^{3+} absorption band were found to be similar. However, phenomena of conversion of the infrared radiation into the visible emission in these systems are different. Based on careful analysis of relaxation dynamics of excited levels involved in up-conversion processes, it has been concluded that the red up-converted emission in *as-melted* glass turns to green emission in glass-ceramics due to the decrease of multiphonon relaxation rates resulting from the incorporation of luminescent ions in the fluoride phase.

Acknowledgment

The work supported by Polish Ministry of Science and Information Society Technologies (project NN508400377).

References

- [1] I.R. Martin, V.D. Rodríguez, V. Lavín, U.R. Rodríguez-Mendoza, J. Alloys Compd. 275–277 (1998) 345–348.
- [2] Li Feng, Jing Wang, Qiang Tang, Lifang Liang, Hongbin Liang, Qiang Su, J. Lumin. 124 (2007) 187–194.
- [3] Wang Weizhong, Qu Wanchun, Yang Kuisheng, Li Yan, He Guanghai, J. Rare Earths 24 (2006) 187–190.
- [4] A.S. Gouveira-Neto, L.A. Bueno, R.F. do Nascimento, E.A. da Silva Jr., E.B. da Costa, V.B. do Nascimento, Appl. Phys. Lett. 91 (2007), 091114-1-091114-3.
- [5] J.J. Velázquez, A.C. Yanes, J. del Castillo, J. Méndez-Ramos, V.D. Rodríguez, Phys. Stat. Sol. (a) 204 (2007) 1762–1768.
- [6] Janbei Qiu, Akio Makishima, Sci. Technol. Adv. Mater. 5 (2004) 313–317.
- [7] Jiajia Pan, Rongrong Xu, Ying Tian, Kefeng Li, Lili Hu, Junjie Zhang, Opt. Mater. 32 (2010) 1451–1455.
- [8] N. Menyuk, K. Dwight, J.W. Pierce, Appl. Phys. Lett. 21 (1972) 159–161.
- [9] -J.Ch. Boyer, L.A. Cuccia, J.A. Capobianco, Nano Lett. 7 (2007) 847–852.
- [10] J.F. Suyver, J. Grimm, M.K. van Veen, D. Biner, K.W. Krämer, H.U. Güdel, J. Lumin. 117 (2006) 1–12.
- [11] Feng Liu, Yuansheng, Daqin Chen, Yunlong Yu, Mater. Sci. Eng. 136 (2007) 106–110.
- [12] G. Dominiak-Dzik, J. Nanosci. Nanotechnol. 9 (2009) 2525–2531.
- [13] D.M. Roy, R. Roy, J. Electrochem. Soc. 111 (1964) 421–429.
- [14] M. Inokuti, F. Hirayama, J. Chem. Phys. 43 (1965) 1978–1989.
- [15] K. Narasinha Reddy, M.A.H. Shareef, J. Mater. Sci. Lett. 2 (1983) 83–84.