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Determination of the Concentration of Tm^{3+} and Ho^{3+} Ions in the Glass and Crystalline Phases in Oxyfluoride Glass Ceramics by Absorption Spectra Analysis

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Abstract

Optical glass ceramics based on oxyfluoride glasses activated by rare earth ions have attractive properties for development of lasers and near-infrared amplifiers, since they combine properties of fluoride crystals with low phonon frequencies and chemical and mechanical properties of oxide matrices. Spectroscopic properties of activator ions in crystalline and glass phases of glass-ceramics can differ significantly. Thus, it is possible to determine impurity ions' distribution between these phases by means of absorption or luminescence spectra analysis. The main goal of this work was to develop a method for determining the concentration of Tm^{3+} and Ho^{3+} ions in the crystalline, PbF_2 and glassy phases of glass ceramics after secondary thermal treatment of thulium-doped and thulium-holmium co-doped oxyfluoride glasses. Spectroscopic characteristics of oxyfluoride glasses activated by Tm^{3+} ions and co-activated by Tm^{3+} and Ho^{3+} ions, as well as glass ceramics obtained from the original glasses as a result of secondary heat treatment were studied. It was established by X-ray phase analysis method that under certain heat treatment conditions crystalline β - PbF_2 phase is formed in those glasses. Absorption and luminescence spectra of Tm^{3+} and Ho^{3+} impurity ions in the original glass and in β - PbF_2 crystals were compared with their ones in glass ceramics. A method for determining the concentration of ions in the crystalline and glass phases of glass ceramics was proposed on the basis of this comparison. Dependence of Tm^{3+} and Ho^{3+} ions distribution between the glass and crystalline phases on different regime of glasses' secondary heat treatment was studied.

Keywords: oxyfluoride glass ceramics, ions of Tm^{3+} and Ho^{3+} , absorption and luminescence spectra

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Определение концентрации ионов Tm^{3+} и Ho^{3+} в стеклянной и кристаллической фазах в оксифторидной стеклокерамике в результате анализа спектров поглощения

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Оптическая стеклокерамика на основе оксифторидных стёкол, активированная ионами редкоземельных элементов, обладает привлекательными свойствами для разработки лазеров и усилителей в ближней инфракрасной области спектра, так как сочетает в себе свойства фторидных кристаллов с низкими частотами фононов и химические и механические свойства оксидных матриц. В стеклокерамических материалах спектроскопические свойства ионов-активаторов в кристаллической и стеклянной фазах могут иметь существенные различия. В этом случае спектральные методы исследования позволяют установить в какой степени примесные ионы распределяются между этими фазами. Целью данной работы являлась разработка спектрального метода определения концентрации ионов тулия и гольмия в кристаллической, PbF_2 , и стеклянной фазах стеклокерамик, полученных при вторичной тепловой обработке оксифторидных стёкол, активированных ионами Tm^{3+} и соактивированных ионами Tm^{3+} и Ho^{3+} . В работе изучались спектроскопические характеристики оксифторидных стёкол, активированных ионами Tm^{3+} и соактивированных ионами Tm^{3+} и Ho^{3+} , а также стеклокерамик, полученных из исходных стёкол в результате вторичной термообработки. Методами рентгенофазового анализа установлено, что при определённых условиях термообработки в них образуется кристаллическая фаза $\beta-PbF_2$. Проведено сравнение спектров поглощения и люминесценции примесных ионов Tm^{3+} и Ho^{3+} в исходном стекле, в кристаллах $\beta-PbF_2$ с их спектрами в стеклокерамике, и на основе этого предложен метод определения концентрации ионов в кристаллической и стеклянной фазах. Изучена зависимость распределения ионов Tm^{3+} и Ho^{3+} между стеклянной и кристаллической фазами в зависимости от режима вторичной термообработки стёкол.

Ключевые слова: оксифторидная стеклокерамика, ионы Tm^{3+} и Ho^{3+} , спектры поглощения и люминесценции

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Introduction

Transparent glass ceramics doped with ions of rare earth elements combine the mechanical and optical properties of a glass matrix and the spectroscopic characteristics of rare earth elements ions in a crystalline environment. In glass ceramics, rare earth ions are partially incorporated into the glass and into the crystalline phases, which makes it possible, to some extent, to "design" the spectroscopic properties of glass-ceramic materials. Oxyfluoride glass ceramics are attractive due to the low phonon frequencies of fluorides (CaF₂, SrF₂, PbF₂, etc.), which leads to a decrease in the probability of nonradiative decay of rare earth ions due to electron-phonon interactions. This is important for the development of lasers and amplifiers in the long-wavelength region of the spectrum [1–3].

A large number of works are devoted to the preparation of such materials and the study of their properties, for example, [4–10], where the creation of glass ceramics with Tm³⁺:PbF₂ [5–7], Er³⁺:PbF₂ [8], Nd³⁺:(CdF₂+PbF₂+YF₃) [9], Tm³⁺:(CdF₂+PbF₂+YF₃) [4], or glass ceramics co-activated by several types of rare earth ions, for example, PbF₂, with Yb³⁺, Eu³⁺ and Tm³⁺, Ho³⁺ or Er³⁺ ions [10] is reported. The temperature conditions for the formation of the crystalline phase were established based on the results of studying phase transitions using differential scanning calorimetry (DSC). Secondary heat treatment of the glasses, which resulted in the formation of a crystalline phase, was carried out at a temperature close to the glass transition temperature.

The presence of a crystalline phase in glass ceramics can be determined by various methods. For

example, using X-ray phase analysis [4–10], electron transmission microscopy [4, 6, 9], Raman spectra [5, 8], absorption and luminescence spectra [5, 7, 10, 11]. It was shown in [11] that, under certain conditions, secondary heat treatment of oxyfluoride glasses with Tm₂O₃ leads to the appearance of a β-PbF₂ crystalline phase with thulium ions in them. The presence of a crystalline phase was manifested in a characteristic change in the shape of the spectral line of the thulium ions in the absorption spectrum in the region of 1700 nm.

The purpose of this work was to develop a spectral method for determining the concentration of thulium and holmium ions in the crystalline, β-PbF₂, and glass phases of glass ceramics obtained by secondary heat treatment of oxyfluoride glasses activated with Tm³⁺ ions and co-activated with Tm³⁺ and Ho³⁺ ions.

Objects and research methods

The synthesis of initial glasses of the composition SiO₂-GeO₂-PbO-PbF₂-CdF₂ with a variable content of Tm₂O₃ (glass series A) and with a variable content of Tm₂O₃ and Ho₂O₃ (glass series B) was carried out in an electric furnace at 950±50 °C at a maximum temperature for 30 min until the glass melt is clarified. The glasses were annealed at a temperature of 300 °C. The synthesized glasses are of good optical quality, homogeneous, and their amorphous nature is confirmed by X-ray diffraction. The concentration of thulium and holmium ions in each sample was determined based on the experimentally determined density using the Archimedes method and the molar content of thulium and holmium ions in the original glass (Table 1).

Table 1

Density of glasses, molar content of Tm₂O₃ and Ho₂O₃, concentration of thulium and holmium ions in the original glasses (series A and B)

	A1	A2	A3	A4	B1	B2	B3	B4
ρ, g/cm ³	5.93	6.08	6.04	6.13	5.97	5.87	6.06	6.08
Tm ₂ O ₃ , mol %	0.10	0.50	1.00	2.00	-	1.64	1.63	1.62
N _{Tm} , 10 ²⁰ cm ⁻³	0.64	3.24	6.32	12.4	-	7.19	7.3	7.33
Ho ₂ O ₃ , mol %	-	-	-	-	1.26	0.17	0.84	1.24
N _{Ho} , 10 ²⁰ cm ⁻³	-	-	-	-	5.55	2.72	3.64	5.37

To obtain glass ceramics, the glasses were subjected to secondary heat treatment. Heat treatment regimes are designated as follows: if, for example, the glass was heated at a temperature of $T1$ °C for $t1$ hours, then it was heated at a temperature $T2$ °C for $t2$ h, then this regime is designated as follows: $T1^{\circ}\text{C}/t1\text{h}+T2^{\circ}\text{C}/t2\text{h}$. The nature of the forming crystalline phase was determined from diffraction patterns obtained by X-ray diffraction on a *Bruker D8 Advance X-ray diffractometer*. Absorption spectra were recorded on a *Cary 5000 spectrophotometer (Varian (AgilentTech))* at room temperature. Stationary luminescence spectra were recorded using a laboratory setup based on an *MDR 23 monochromator (LOMO)*, a lock-in amplifier *SR830 (Stanford Research Systems)*, and a *PbS photodetector* with a preamplifier. Luminescence was excited by laser diode radiation, 800 nm, ≤ 1 W, focused on the edge of the wedge-shaped side of the samples to avoid reabsorption of luminescence, leading to distortion of the spectral line shape. The luminescence spectra were corrected for the spectral sensitivity of the recording system. The correction technique is described in [12].

A diagram of low-lying energy levels of thulium and holmium ions indicating absorption, luminescence transitions and the main channels of excitation energy transfer is presented in Figure 1.

Absorption and luminescence spectra of oxyfluoride glasses and lead fluoride crystals activated with thulium ions and co-activated with thulium and holmium ions

The absorption spectra of the original glass samples (series A) are presented in Figure 2. The

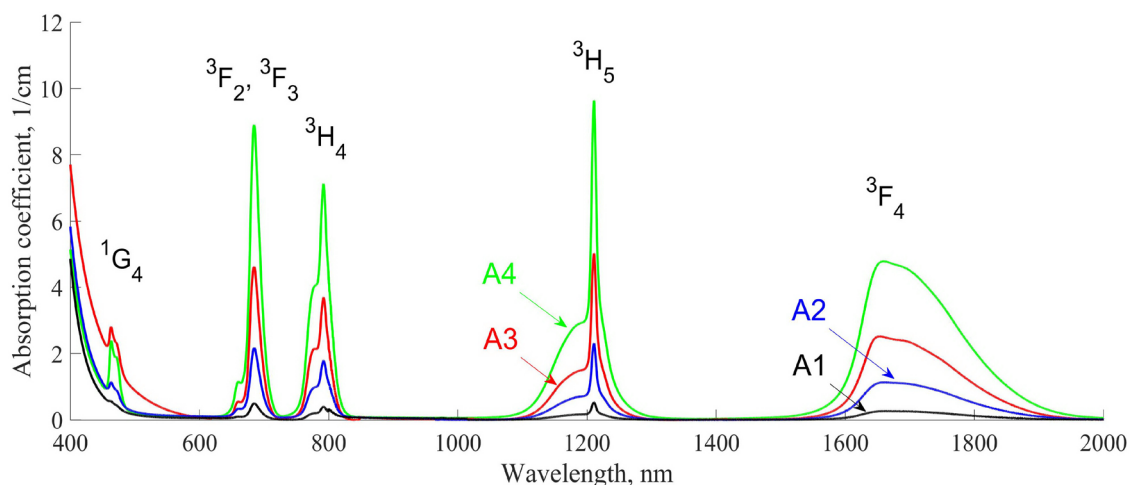


Figure 2 – Absorption spectra of the original oxyfluoride glasses of series A

assignment of spectral lines was made based on work [13].

The absorption spectra of series B glasses with thulium and holmium ions are shown in Figure 3. The assignment of spectral lines was made based on work [14]. The absorption spectra presented in Figures 1 and 2 are characterized by a typical set of spectral lines that correspond to transitions from the states of thulium ions, $^3\text{H}_6$, and holmium ions, $^5\text{I}_8$, with the lowest energy values to states with higher energy values indicated in the figures. The literature reports the results of a study of the spectroscopic characteristics of lead fluoride crystals with thulium and holmium ions: $\text{Tm}^{3+}:\text{PbF}_2$ [15, 16] and $\text{Ho}^{3+}:\text{PbF}_2$ [17–19].

Figure 4 shows the spectra of the absorption cross sections of these crystals in comparison with the spectra of the cross sections of the glasses under study at the transitions $^3\text{H}_6 \rightarrow ^3\text{F}_4$, (Tm^{3+}) and $^5\text{I}_8 \rightarrow ^5\text{I}_7$ (Ho^{3+}).

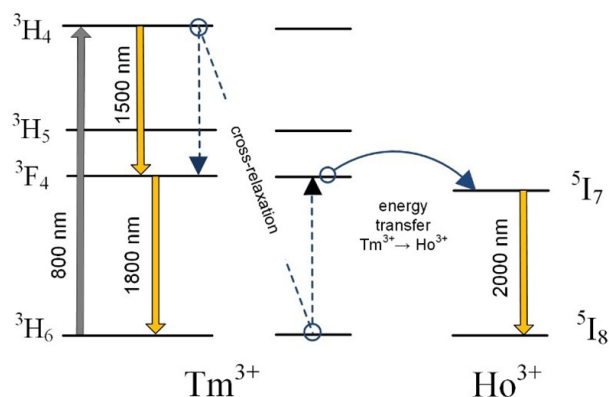


Figure 1 – Diagram of the lower energy levels of thulium and holmium ions

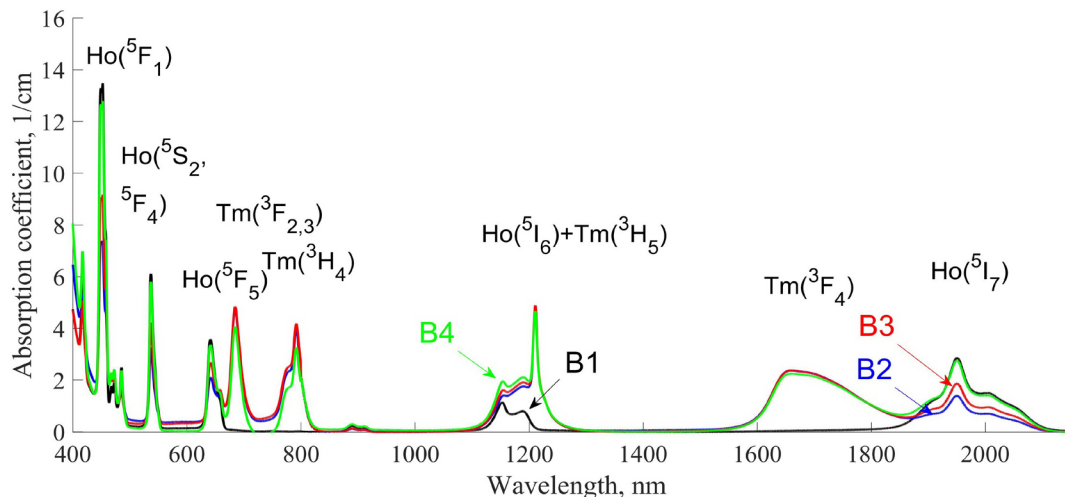


Figure 3 – Absorption spectra of the original oxyfluoride glasses of series B with thulium and holmium

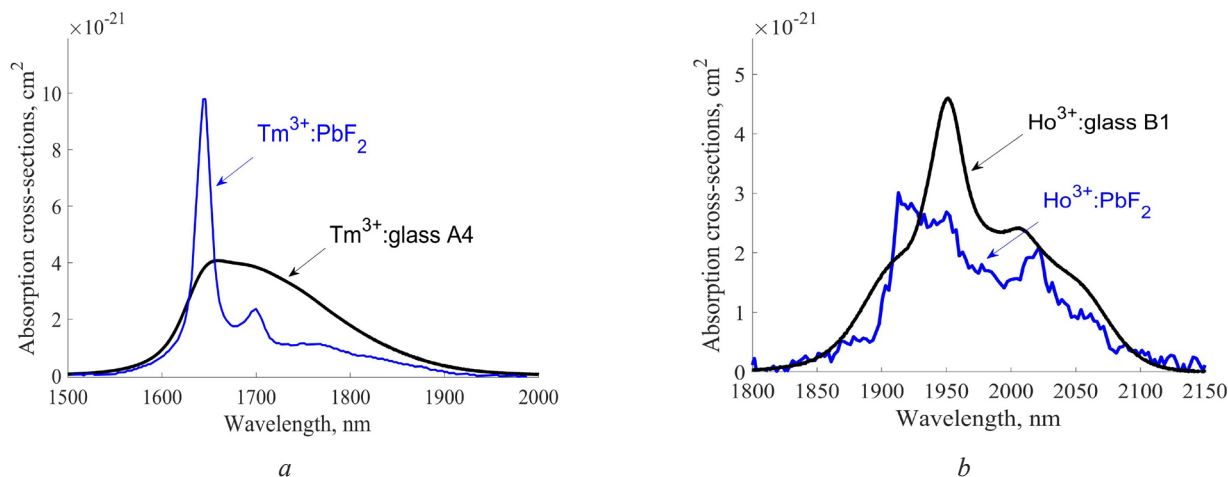


Figure 4 – Spectra of absorption cross sections of crystals $\text{Tm}^{3+}:\text{PbF}_2$ [15] (a), $\text{Ho}^{3+}:\text{PbF}_2$ [17] (b) and spectra of absorption cross sections of thulium (a) and holmium (b) ions in glasses of series A and B

As can be seen from the presented data, the spectra of the absorption cross sections of thulium and holmium ions in a lead fluoride crystal and in glasses are significantly different qualitatively from each other.

The luminescence spectra of thulium and holmium ions in the PbF_2 crystal, calculated on the basis of the data presented in [15, 19], and in glasses, recorded by us, on the transitions ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ (Tm^{3+}), and ${}^5\text{I}_7 \rightarrow {}^5\text{I}_8$ (Ho^{3+}), on the contrary, do not have significant qualitative differences (Figure 5). The luminescence spectra of thulium ions in glasses excited to the ${}^3\text{H}_4$ level show two lines: in the region of 1500 nm and 1800 nm (Figure 5a), corresponding to the transitions ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$, respectively. The intensity of the first line decreases relative to the intensity of the second with an increase in the concentration of thulium ions, due to an increase in the probability of non-radiative transfer of excitation energy from

the ${}^3\text{H}_4$ level to the ${}^3\text{F}_4$ level according to the cross-relaxation mechanism: ${}^3\text{H}_4 + {}^3\text{H}_6 \rightarrow {}^3\text{F}_4 + {}^3\text{F}_4$ [20] (Figure 1). In the luminescence spectra of glasses co-activated with thulium and holmium ions (Figure 5b), two lines are distinguished: the first, in the region of 1800 nm, corresponds to the transition ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ (Tm^{3+}), the second, in the region of 2000 nm, refers to the transition ${}^5\text{I}_7 \rightarrow {}^5\text{I}_8$ (Ho^{3+}). As the concentration of holmium ions increases, the intensity of the second line increases relative to the first, which is due to an increase in the probability of nonradiative transfer of excitation energy according to the following scheme: ${}^3\text{F}_4(\text{Tm}^{3+}) \rightarrow {}^5\text{I}_7(\text{Ho}^{3+})$ [14] (Figure 1). The results obtained show that the lines in the absorption spectra of thulium and holmium ions, corresponding to transitions between lower levels, are convenient for analyzing what fraction of thulium and holmium ions enters the crystalline phase and what remains in the glass phase in glass ceramics based on oxyfluoride glasses.

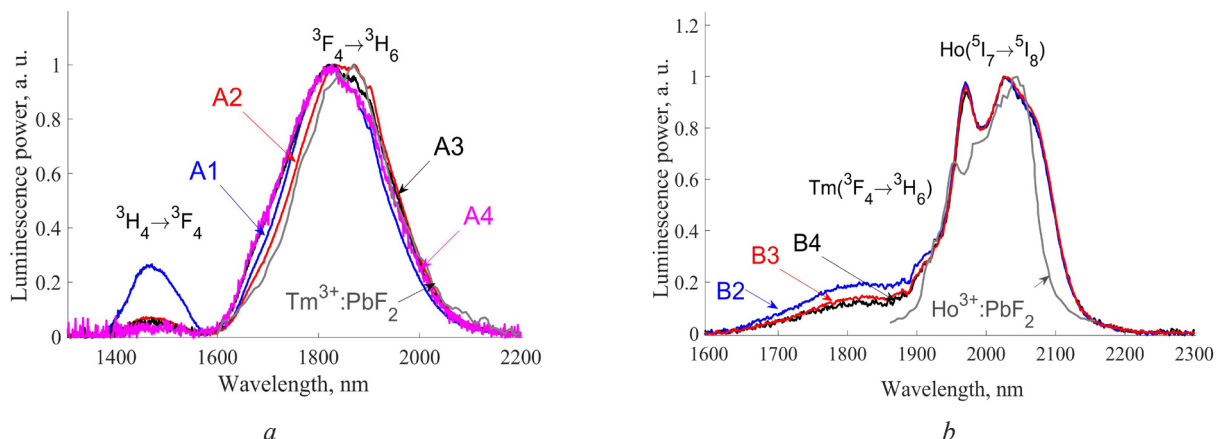


Figure 5 – Luminescence spectra of Tm^{3+} and Ho^{3+} in glasses of series A (a) and B (b) and in PbF_2 crystals [15, 19]

Changes in the absorption spectra of thulium ions during secondary heat treatment of oxyfluoride glasses

At the first stage, changes in diffraction patterns and absorption spectra of glass samples with thulium ions (series A glass) were analyzed during the formation of a crystalline phase in them. For this purpose, the glasses were subjected to a secondary heat treatment at a temperature close to the glass transition temperature, $T_g = 384.5\text{ }^\circ\text{C}$, which was determined from the DSC curves (Figure 6). When the heat treatment of the initial glasses is $350\text{ }^\circ\text{C}/2\text{ h}$, the X-ray diffraction patterns are diffuse and do not show signs of the formation of a crystalline phase.

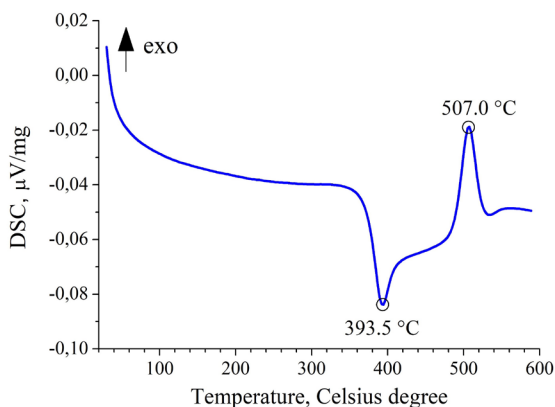


Figure 6 – Differential scanning calorimetry curve of series A glass

There are also no qualitative changes observed in the absorption spectra. When the secondary heat treatment temperature increases to $400\text{ }^\circ\text{C}$, changes which are typical for glass-ceramic materials were revealed in the diffraction pattern of glass A4 with the formation of a crystalline phase of lead fluo-

ride $\beta\text{-PbF}_2$ with space symmetry group $Fm\bar{3}m$ (Figure 7). The position of the peaks is slightly shifted relative to the reflections of a nominally pure "bulk" PbF_2 crystal, which is due, in our opinion, to the inclusion of Tm^{3+} ions into the PbF_2 crystals with partial replacement of Pb^{2+} ions [10].

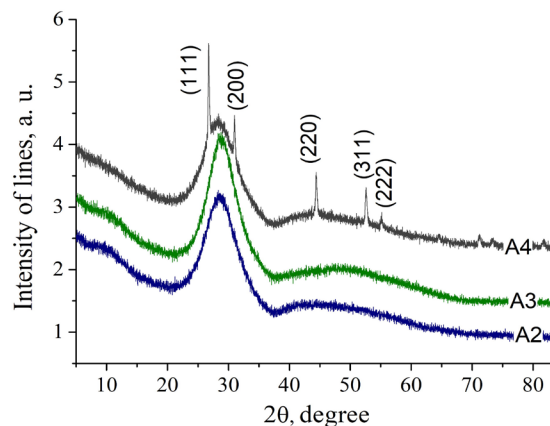


Figure 7 – Diffraction patterns of heat-treated glasses of series A at $350\text{ }^\circ\text{C}/2\text{h} + 400\text{ }^\circ\text{C}/3\text{h}$

The absorption spectra of glass samples A4 and A3 after secondary heat treatment, $350\text{ }^\circ\text{C}/2\text{h} + 400\text{ }^\circ\text{C}/3\text{h}$, are presented in Figure 8. As can be seen, here only the spectrum of sample A4 reveals characteristic signs of the entry of thulium ions into the PbF_2 crystalline phase.

With an increase in the time of secondary heat treatment at a temperature of $400\text{ }^\circ\text{C}$, the formation of a crystalline phase also occurs in sample A3. Thus, Figure 9 shows the absorption spectra of samples A4 and A3 after they were heated at a temperature of $400\text{ }^\circ\text{C}$ for 9 h, where characteristic signs of the entry of thulium ions into the PbF_2 crystalline phase are clearly visible.

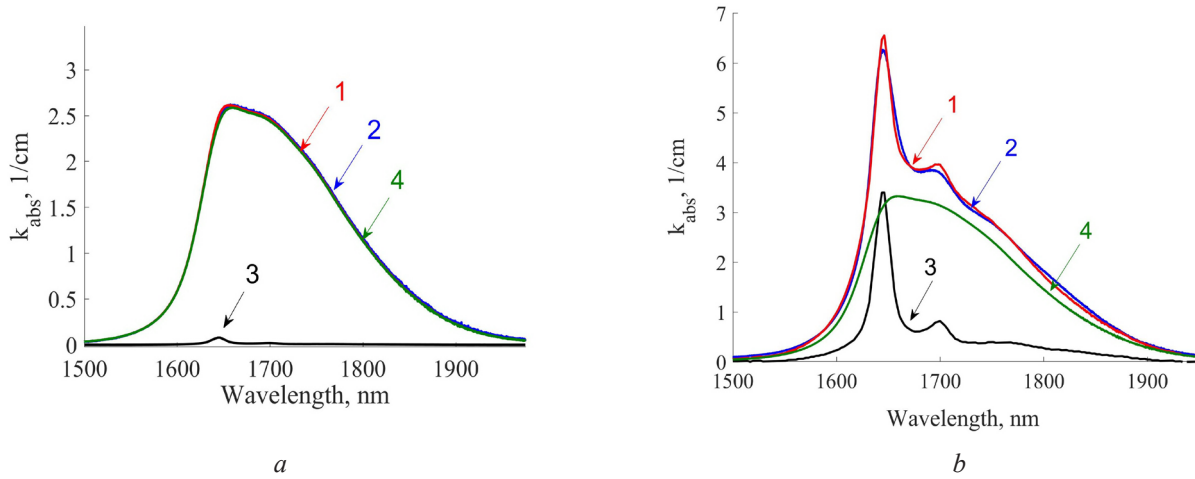


Figure 8 – Absorption spectra of glass ceramic samples obtained from glasses A3 (a) and A4 (b). Secondary heat treatment: 350 °C/2h + 400 °C/3h. 1 – calculation; 2 – experiment; 3 – $Tm^{3+}:PbF_2$; 4 – Tm^{3+} : glass

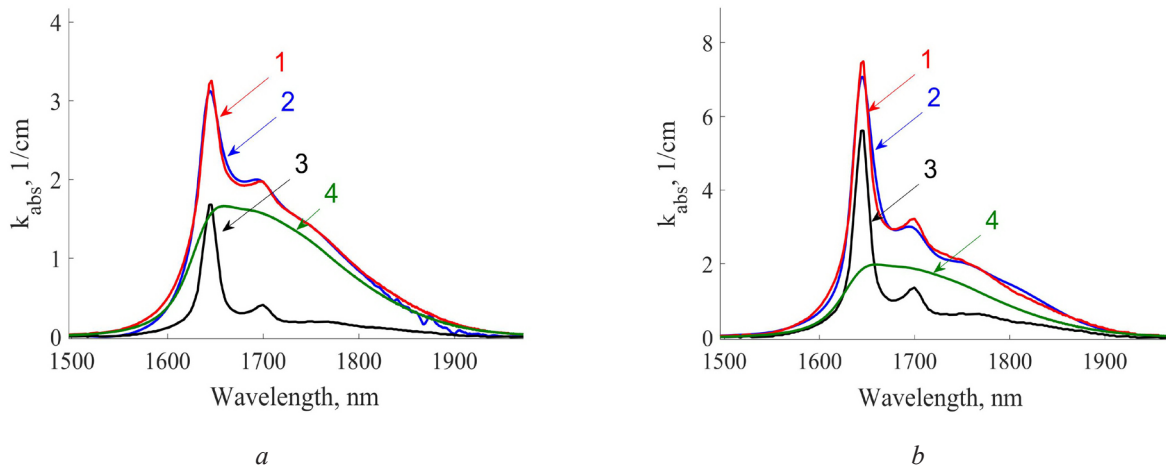


Figure 9 – Absorption spectra of glass ceramic samples obtained from glasses A3 (a) and A4 (b). Secondary heat treatment: 350 °C/2h+400 °C/9h. 1 – calculation; 2 – experiment; 3 – $Tm^{3+}:PbF_2$; 4 – Tm^{3+} : glass

Note that during heat treatment, opaque areas or "clouding" appeared in some glass ceramic samples, which is apparently due to the nonuniform distribution of the crystalline phase in the volume of the sample.

To analyze changes in the absorption spectra during the formation of glass ceramics from initial glasses during secondary heat treatment, we use the approach proposed in [11], where the spectrum of the glass ceramic absorption coefficient $k_{abs}(\lambda)$ is presented in the form:

$$k_{abs}(\lambda) = \sigma_{abs}^{gl}(\lambda) N_{Tm}^{gl} + \sigma_{abs}^{cr}(\lambda) N_{Tm}^{cr} = \sigma_{abs}^{gl}(\lambda) N_{Tm} X_1 + \sigma_{abs}^{cr}(\lambda) N_{Tm} X_2, \quad (1)$$

where $\sigma_{abs}^{gl}(\lambda)$, $\sigma_{abs}^{cr}(\lambda)$ are the absorption cross sections of thulium ions in the glass and crystalline phases, respectively; N_{Tm} , $N_{Tm}^{gl} = N_{Tm} X_1$, $N_{Tm}^{cr} = N_{Tm} X_2$ are the concentrations of thulium ions in the original

glass sample, in the glass and crystalline phases of the transparent part of the glass ceramics, respectively; X_1 and X_2 are parameters that characterize the relative content of thulium ions in the glass and crystalline phases, respectively. Then, the part of thulium ions, X_0 , which is located in the opaque part of the sample can be defined as $X_0 = 1 - X_1 - X_2$.

Parameters X_1 and X_2 were determined in the process of fitting the calculated spectrum (1) to the experimentally determined one of the absorption coefficient of series A glass material in the region of 1700 nm, ${}^3H_6 \rightarrow {}^3F_4$, after secondary heat treatment. Fitting was carried out using the direct search method [21]. Note that the parameters X_1 and X_2 varied independently of each other. The spread of their values for different initial fitting conditions did not exceed 5%. The calculation results are presented in Figures 8 and 9.

Figure 10 shows the dependences of the obtained parameters X_1 and X_2 on the time of secondary heat treatment of glass at 400 °C.

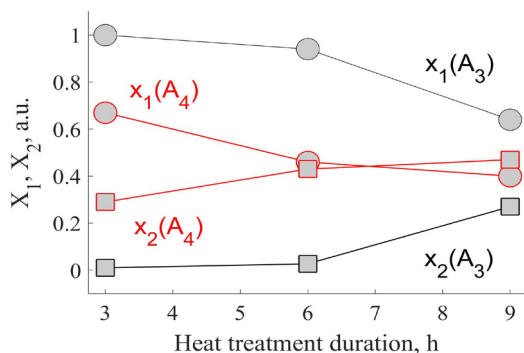


Figure 10 – Dependences of parameters X_1 and X_2 on the duration of secondary heat treatment of glasses A3 and A4 at 400 °C

As can be seen from the presented results, with increasing time of thermal treatment of glass, the proportion of thulium ions in the crystalline phase increases. It should also be noted that in this case, the portion of thulium ions, which is concentrated in the scattering (opaque) regions of the glass material, also increases. Thus, about 10 % of thulium ions are contained in the opaque regions of glass ceramics obtained from glasses A3 and A4 with a secondary annealing duration of 9 h.

Changes in the absorption spectra of thulium and holmium ions during secondary heat treatment of oxyfluoride glasses

Secondary heat treatment regimes for series B glasses were also selected based on DSC curves (Figure 11). Glass transition temperature is 386 °C. At a heat treatment temperature of 350 °C with a duration of 25 h, all obtained X-ray diffraction patterns have a diffuse shape characteristic of amorphous materials. The absorption spectra of all series B glasses also do not change during this secondary heat treatment, both for the bands related to thulium and holmium ions. However, when the temperature increases to 360 °C, the diffraction patterns corresponding to samples B3 and B4 with a secondary heat treatment time of more than 30 h show the appearance of several peaks indicating the formation of a crystalline phase, see Figure 12. Positions of the observed diffraction peaks, as in the case of series A, correspond

to a crystal structure with space group symmetry $Fm\bar{3}m$ and indicate the cubic phase of $\beta\text{-PbF}_2$. The unit cell parameter of this phase increases slightly with increasing holmium oxide concentration [22].

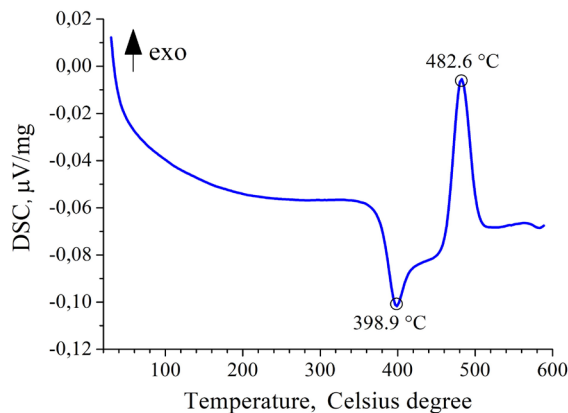


Figure 11 – Differential scanning calorimetry curve of glass series B

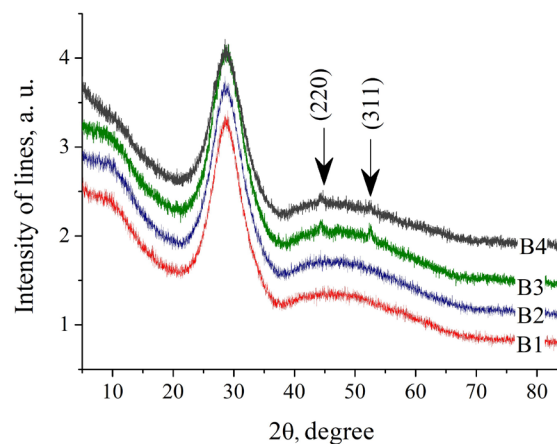


Figure 12 – Diffraction patterns of heat-treated glasses of series B at 350 °C/30h + 360 °C/50h

Analysis of the absorption spectra of samples B3 and B4 during the formation of a crystalline phase in them shows that the band in the region of 1700 nm, which corresponds to the ${}^3\text{H}_6 \rightarrow {}^3\text{F}_4$ transition of Tm^{3+} ions, undergoes a change. In the spectral region of 2000 nm, corresponding to the ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ transition, no significant changes are observed. To quantitatively analyze changes in the absorption spectra of series B glasses, a formula similar to formula (1) was used:

$$k_{abs}(\lambda) = \sigma_{Tm}^{gl}(\lambda) N_{Tm} X_1 + \sigma_{Tm}^{cr}(\lambda) N_{Tm} X_2 + \sigma_{Ho}^{gl}(\lambda) N_{Ho} X_3 + \sigma_{Ho}^{cr}(\lambda) N_{Ho} X_4. \quad (2)$$

By varying the parameters $X_{i,i} = 1, 2, 3$ and 4, the calculated absorption spectrum was fitted to the experimentally obtained one. Figure 13 shows examples of such fitting.

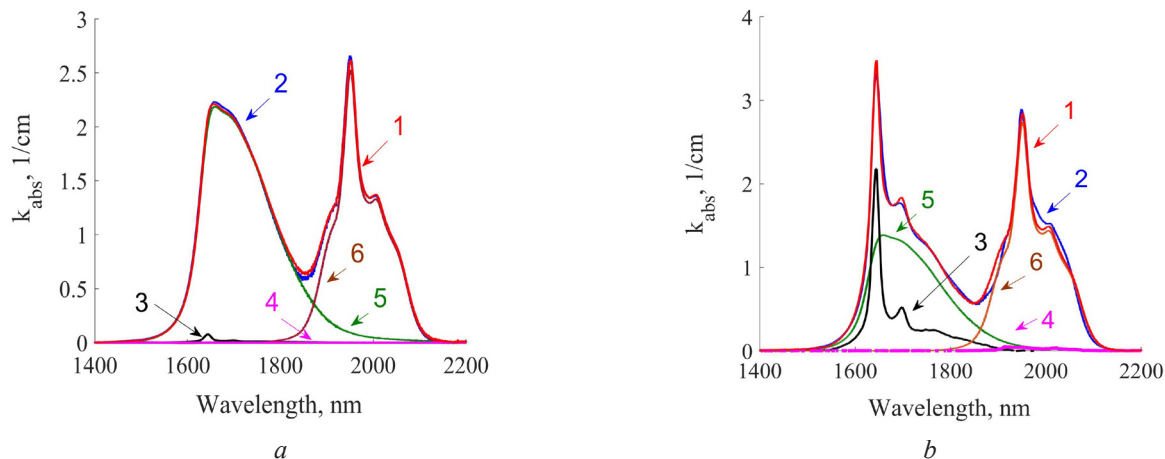


Figure 13 – Absorption spectrum of glass B4 with secondary heat treatment at 350 °C/25h (a) and glass B4 with secondary heat treatment at 350 °C/30h + 360 °C/50h (b). 1 – calculation; 2 – experiment; 3 – $\text{Tm}^{3+}:\text{PbF}_2$; 4 – $\text{Ho}^{3+}:\text{PbF}_2$; 5 – $\text{Tm}^{3+}:\text{glass}$; 6 – $\text{Ho}^{3+}:\text{glass}$

Calculations using formula (2) revealed that the value of coefficient X_3 is close to one, and coefficient X_4 is close to zero for both B3 and B4 glass samples. This indicates that holmium ions under such conditions of secondary heat treatment do not enter the crystalline phase of series B glasses. However, it follows that an increase in the content of holmium oxides, starting from 0.84 mol %, promotes the entry of thulium ions into the crystalline phase of the resulting glass ceramics, see Figure 14.

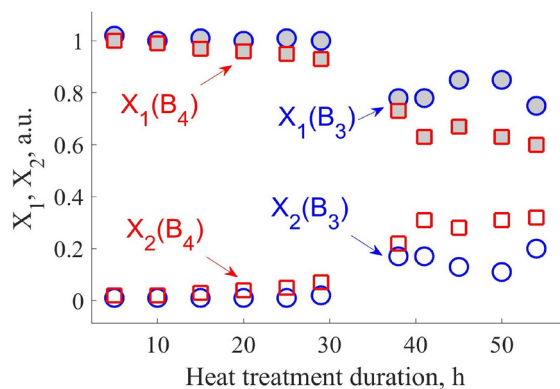


Figure 14 – Values of parameters X_1 and X_2 at different heat treatment times at 360 °C

An annealing duration of more than 40 h does not lead to a significant increase in the content of thulium ions in the crystalline phase. It should also be noted that glass ceramics of series B have better optical quality compared to glass ceramics of series A; the content of thulium ions in opaque areas with an annealing duration of 40 h or more is about 5 %.

Conclusion

It is shown that the analysis of lines in the absorption spectra corresponding to the transitions ${}^3\text{H}_6 \rightarrow {}^3\text{F}_4$, (Tm^{3+}) and ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ (Ho^{3+}), allows us to establish in what proportion thulium and holmium ions are distributed between the glass and crystalline, $\beta\text{-PbF}_2$, phases in the resulting glass ceramics and find the corresponding concentrations of impurity ions. It was established that an increase in the content of holmium oxide in the thulium and holmium co-doped original glass promotes the entry of thulium ions into the crystalline phase, while no spectroscopic manifestations of the entry of holmium ions themselves into the crystalline phase were detected. In general, such a spectroscopic method can be used to study glass ceramics with other ions of rare earth elements.

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