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Up-conversion and IR Luminescence of Ytterbium–Erbium Oxyfluoride Silicate Glassceramics

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The paper studied the luminescent properties of lead fluoride silicate nanostructured glassceramics doped with ytterbium and erbium ions. We have measured luminescence spectra of glassceramics in the visible and near-IR ranges at temperatures of 300 and 77 K and under their pumping at a wavelength of 975 nm. We have examined changes in the luminescence spectra of glassceramics depending on the time of their secondary thermal treatment, concentration of dopant ions, specimen temperature, and power of excitation radiation.

Keywords: Up-conversion Luminescence, Ytterbium–Erbium Glassceramic, IR Luminescence, Low Temperature Luminescence, Solar Cell.

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1. INTRODUCTION

In recent years, optical materials doped with rare-earth ions have been of increased interest for investigations, since they are becoming more and more widely used in various fields of science and technology, for example, as phosphors for solar cells, white light-emitting diodes and sensors, active media for fiber lasers and optical amplifiers, and mini- and micro-chips lasers. Of trivalent rare-earth ions, erbium attracts the greatest attention because of its upconversion characteristics. However, the low absorption cross section of erbium at a wavelength of 980 nm restricts its commercial applicability. Ytterbium ions have strong and broad absorption bands, which coincide with the radiation range of InGaAs-based laser diodes; also, they are efficient sensitizers for erbium. It is well known that oxygen-free glass matrices, e.g., the fluoride matrix, are more favorable than are oxygen-containing matrices. This is related to a decrease in the probability of nonradiative energy transfer from the rare-earth ion to surrounding matrix ions. However, synthesis of fluoride materials is complicated and laborious. Special precautions are required to prevent contact of the material to be synthesized with the atmosphere. In addition, the chemical and thermal stability of these materials and their mechanical strength are low compared to oxide glasses. It should also be noted that optical fiber drawing based on oxygen-free fluoride glasses presents a significant problem. At present, a simpler and less expensive way for obtaining materials with a low-phonon spectrum is synthesis of oxide–fluoride glassceramics doped with rare-earth ions (such as, e.g., erbium, ytterbium, etc.) that are incorporated in nanocrystalline phase. Glassceramics combines the best properties of glasses and crystals and has wide range of advantages. If rare-earth ions enter into the crystal phase, the spectral–luminescent properties of such glassceramics are close to the properties of corresponding single-crystal analogs. As drawbacks of these materials, one can note the complexity of the technology of their production, as well as light scattering at boundaries between glassy and crystalline phases. In order to reduce the light-scattering effect and obtain required properties of glassceramics, it is necessary to optimize the main parameters of the crystalline phase, such as the size and volume fraction. In turn, these parameters depend on the temperature and duration of the secondary thermal treatment (i.e., thermal treatment under which a spontaneous growth of the crystalline phase in the glass matrix is observed). Decreasing the size of the crystalline phase to 10–50 nm makes it possible to considerably reduce the light scattering in glassceramics and classify the heterophase structure as an optical material or, if this medium is doped with rare-earth ions, as a laser material.

In [1], the possibility of creation of a new laser material – nanostructured lead fluoride silicate glassceramics doped with rare-earth ions and that contains nanocrystals of lead lanthanide oxyfluorides with a size of 10–40 nm has been shown. In [2, 3], the spectral–luminescent properties of new lead fluoride silicate nano-glassceramics have been investigated. Based on X-ray diffractometry and optical spectroscopy, the authors of [1–3] experimentally showed that rare-earth ions enter into the nanosized crystalline phase. The objective of this work was to study effects of thermal treatment time, the power of excitation radiation, and the concentration of erbium ions on the luminescence spectra of nanostructured lead fluoride glassceramics at temperatures of 300 and 77 K.

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2. TECHNOLOGY AND EXPERIMENTS

In the work, we investigated samples of the following composition: $30SiO_2$–$18PbF_2$–$15AlO_{3/2}$–$5ZnF_2$–$29CdF_2$–$3YbF_3$–$xErF_3$ (x = 0.05–0.5). The concentration of ytterbium fluoride was constant, being 3 mol %, the concentration of ErF3 was varied from 0.05 to 0.5 mol %.

Based on the obtained DSC data, the thermal treatment was performed at a temperature of 515°C, i.e., at the beginning of the peak of the volume crystallization. The time of secondary thermal treatment was varied between 30 and 600 min. The choice of thermal-treatment temperature is determined by the possibility of controlling the rate growth of nanocrystals and their size (not greater than 60 nm in diameter) in order to reduce losses for scattering.

The luminescence spectra were measured in the wavelength ranges 350–700 nm and 1400–1650 nm with a step of 0.1 nm at temperatures of 300 and 77 K. Luminescence was excited with diode laser (975 nm). The luminescence spectra in the visible range were normalized to unity based on the peak in the red spectral range (~650–670 nm).

3. RESULT AND DISCUSSION

In work [1], X-ray analysis showed that a new compound of lead lanthanide oxyfluorides ($PbLnF_3$) was precipitated in glass host as a nanosized crystal composition PbYb(1 – x)ErxOF3. The size of crystals was about 30–40 nm. With increasing concentration of Er^{3+} ions in ytterbium-erbium nanoglassceramics, the volume of the crystalline phase increases. Comparison the luminescence spectra of the glass and glassceramics at room temperature showed that six peaks are observed in the luminescence spectrum of the nanoglassceramics. However, in the spectrum of the glass, only five peaks in the visible range are observed and there is no band in the UV range. That is, after the thermal treatment, the probabilities of radiative transitions change. The intensity of the luminescence peak at 415 nm increases (the radiative probability increases), whereas the luminescence in the entire remaining spectral range 450–575 nm decreases with respect to the normalization peak (the radiative probability decreases). Let us compare the luminescence spectra obtained at different measurement temperatures (Fig. 1).

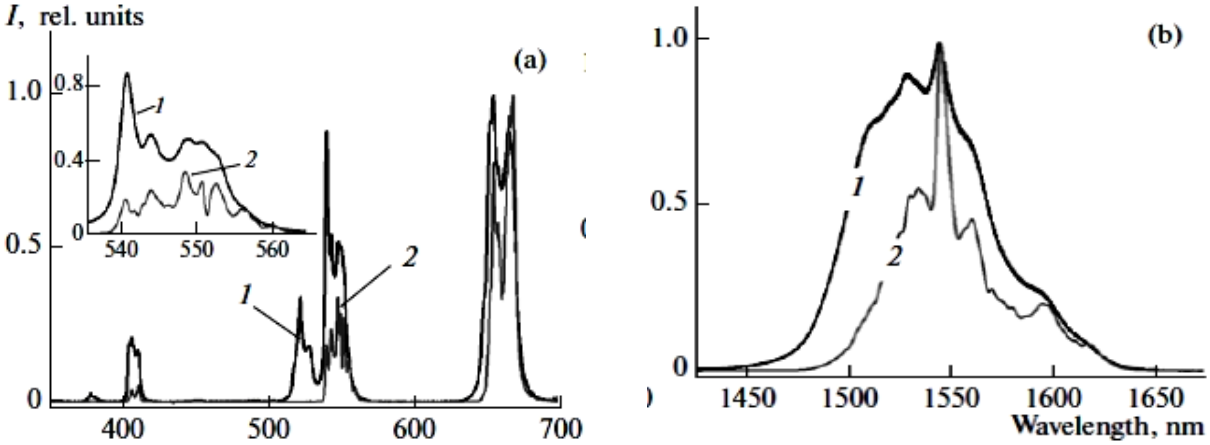

Fig. 1 – The effect of the temperature of the specimen on the luminescence spectra of nano_glass_ceramics: (*1*) 300 and (*2*) 77 K (the concentration of ErF_3 is 0.5 mol %). The inset shows the luminescence band 530–590 nm.

At room temperature, in the visible spectral range, one observes luminescence bands with maxima at 520 and 550 nm, which correspond to the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$, respectively (Fig. 1a); however, at 77 K, the peak with the maximum at 520 nm is not observed. This is related to the fact that the mechanism by which the level $^2H_{11/2}$ is populated occurs because of the excitation transfer from the lower-lying energy level $^4S_{3/2}$ at the expense of the thermal energy. At 77 K, the thermal energy (kT) is too low for the transition between the levels $^2H_{11/2}$ and $^4S_{3/2}$ to occur; i.e., temperature redistribution does not occur. The lowering of the temperature leads to a narrowing of the luminescence spectra in the IR range from 68 to 23 nm (Fig. 1b). Comparison of the shapes of the luminescence spectra for the initial glass and glassceramics shows that the spectrum of the glassceramics is more clearly structured and a greater number of Stark sublevels are observed. This proves that erbium ions enter the crystalline phase upon thermal treatment. Also, as the time of the thermal treatment increases, it is observed that the relative intensity of the luminescence bands 375–575 nm increases; i.e., the probabilities of radiative transitions from different levels depend on the crystal size. The luminescence intensity is significantly affected by a change in the concentration of dopant ions in the composition of the specimen. Upon an increase in the concentration of erbium, the luminescence relative intensity decreases in the entire investigated spectral range, namely, of the bands at 415, 475, and 550 nm. Also in order to gain a deeper insight into mechanisms of upconversion luminescence, we measured the dependence of luminescence intensity on pumping power. With an increase in the excitation power, the luminescence intensity in the blue range increases with respect to the intensity of the red band of the spectrum, while the intensity in the green range decreases.

4. CONCLUSIONS

In this work, we have examined the luminescent properties of nanostructured glassceramics doped with

ytterbium and erbium ions at room temperature (300 K) and temperature of liquid nitrogen (77 K).

Upon an increase in the time of the secondary thermal treatment, the ratio of peak intensities with respect to the normalization peak changes; namely, there is an increase in the intensity of peaks in the range of 415 and 520–550 nm. Also, we have observed intense upconversion luminescence in the blue (415 nm), green (475, 520, and 550 nm), and red (~ 670 nm) spectral ranges.

Obtained ytterbium-erbium nano-glassceramics can be used as material for solar cell.

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