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LUMINESCENCE OF OXYFLUORIDE GLASSES CONTAINING Yb^{3+}–RE^{3+} IONS

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The optical absorption and up-conversion luminescence of oxyfluoride glasses in the system SiO_2–PbO–PbF_2–CdF_2 coactivated by Yb^{3+}–RE^{3+} ions (where RE = Er, Tm, Ho, Dy, Pr, or Tb) are investigated. Excitation with a laser diode in the IR range (960 nm) gives intense green, blue, and red luminescence. The color characteristics of the up-conversion luminescence in the CIE 1931 system are determined. The efficiency of energy transfer from the Yb^{3+} to the RE^{3+} ions is found to be 70% for RE = Er, Tm, and Ho. The efficiency of cooperative energy transfer reaches 10% for glass with Yb–Tb ions.

***Key words*:** oxyfluoride glasses, ions of rare-earth elements, absorption, luminescence, up-conversion.

Up-conversion is a process in which the absorption of two or more photons results in the emission of one photon with a shorter wavelength than that of the exciting light [1]. Specifically, up-conversion materials make it possible to convert IR radiation into visible light of different colors and are used in luminophores, solar cells, temperature sensors, and luminescent marks. The phenomenon of up-conversion luminescence is associated with a transition of active ions to high-lying excited states. Trivalent ions of rare-earth elements RE^{3+} possessing a developed energy-level structure are attractive for creating up-conversion materials based on them.

An ion pair Yb^{3+}–RE^{3+} is often used to improve the luminescence properties of such materials [2, 3]. Ytterbium ions Yb^{3+} afford high absorption efficiency for the IR-exciting light (for example, from InGaAs of laser diodes emitting at the wavelength about 960 nm), since they are characterized by a wide and intense absorption band associated with the transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$. But, the ions $RE^{3+} = Er^{3+}$, Tm^{3+}, Ho^{3+} and others are 'responsible' for the intense emission in the visible range of the spectrum, whose color depends on the type and concentration of the activators. The transfer of electronic excitation energy from Yb^{3+} to RE^{3+} ions occurs by an energy transfer mechanism.

It is known that the efficiency of up-conversion processes is higher in fluoride than oxide materials. This is because fluoride matrices possess lower phonon (lattice vibrations) energies, of the order of about 400 – 500 cm^{-1} versus about 1000 cm^{-1} for oxide matrices; correspondingly, they are characterized by a lower probability of nonradiative relaxation. At the same time the low thermal and mechanical properties (low thermal conductivity, large CLTE, low hardness) limit the applicability of purely fluoride materials, many of which are hygroscopic or possess low chemical stability in air. But oxide matrices usually do not have these drawbacks.

A compromise solution of the problem is to use oxyfluoride materials, specifically, oxyfluoride glasses and transparent glass ceramics (sitals) [4, 5], which combine the advantages of fluoride and oxide matrices. Oxyfluoride materials possess low lattice vibration energies and, correspondingly, intense luminescence, as well as high strength and comparatively high thermal conductivity; in addition, they are chemically stable. Oxyfluoride glasses (for example, the classical two-component lead-containing glass $50SiO_2 – 50PbF_2$ [4]) possess lower synthesis temperature about 900°C. An important problem is optimization of the glass composition which imparts on the one hand good spectral-luminescence properties and on the other hand, stability of the glassy state upon the introduction of fluorides and oxides of different rare-earth elements with molar content of several percent.

This article presents the results of a comparative investigation of the optical absorption and up-conversion luminescence of oxyfluoride glasses coactivated by Yb^{3+}–RE^{3+} ions.

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TABLE 1. Energy Transfer Efficiency η_{ET} ($Yb^{3+} \rightarrow RE^{3+}$) and Color Characteristics of Glass Luminescence in the System *Commission Internationale de l'Éclairage* (CIE 1931)

Active ions	η_{ET}, %	$(x; y)$	λ_d, nm	p_e	Luminescence color
Yb–Er	84	(0.283; 0.713)	547	0.99	Green
Yb–Tm	73	(0.166; 0.140)	473	0.75	Blue
Yb–Ho	72	(0.308; 0.676)	551	0.99	Green
Yb–Dy	2	(0.370; 0.473	–	–	Yellow-green
Yb–Pr	6	(0.469; 0.347)	–	–	Rose-tinted
Yb–Tb	10	(0.311; 0.640)	549	0.84	Green
Yb–Eu	12	(0.636; 0.363)	613	0.98	Red

Notations: $(x; y)$ — color coordinates; λ_d — dominant wavelength; p_e — color purity.

The idea of this work is to control the color characteristics of the luminescence of such glass by introducing different impurity ions RE^{3+} into the same glass matrix.

The initial glass was synthesized in the system SiO_2–PbO–PbF_2–CdF_2 by means of the conventional glass technology. The following chemical reagents were used as the raw materials: amorphous silicon dioxide, lead oxide, lead fluoride, and cadmium fluoride. The glass matrix was activated by the oxides of rare-earth elements: Er_2O_3, Tm_2O_3, Ho_2O_3, Dy_2O_3, PR_2O_3, Tb_2O_3, or Eu_2O_3 (0.5 mol.%) and ytterbium fluoride (1 mol.% YbF_3). The results of the investigations of the glasses coactivated by the oxides Eu_2O_3 and YbF_3 are described in detail in [6].

The components of the batch were carefully mixed and placed in 25 ml corundum crucibles. The glass was synthesized in 0.5 h in air at temperature 900 ± 50°C in an electric furnace. The ready glass melt was extracted onto a smooth metal surface, after which the glass was subjected to annealing at temperature about 300°C in an electric muffle furnace and allowed to cool freely to room temperature. The obtained glasses had a pinkish (RE = Er, Eu), greenish (Pr), or yellowish (RE = Tm, Ho, Dy, Tb) hue with no indications of opalescence.

A Varian Cary 5000 spectrophotometer was used to measure the absorption spectra of the experimental glasses. The glasses containing only Yb^{3+} ions were studied first. The absorption spectrum of the glass doped with 1 mol.% YbF_3 is shown in Fig. 1. The wide band from 900 to 1050 nm is associated with the transition $^2F_{7/2} \rightarrow {}^2F_{5/2}$. Maximum absorption is observed at the wavelength 976 nm ($\alpha = 2.8\ cm^{-1}$) and the intense plateau in the region 920 – 970 nm furnishes the absorption coefficient about 0.8 cm^{-1}. Doping the glass

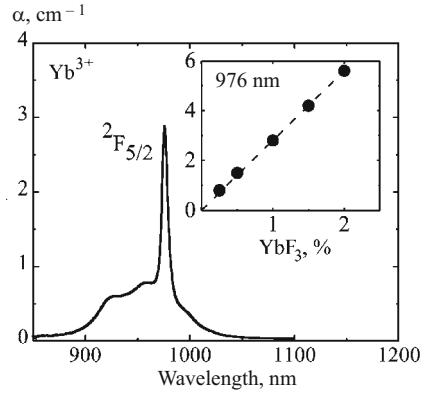

Fig. 1. Absorption spectrum of oxyfluoride glass doped with 1 mol.% YbF_3; inset: absorption coefficient α_{abs} at the wavelength 976 nm versus the YbF_3 molar content.

with YbF_3 in different concentrations (0.25 – 2 mol.%) preserves the linear dependence of the absorption coefficient α on the ytterbium fluoride concentration, i.e. Beer's law holds (see inset in Fig. 1). The glass possesses high transmission in the visible range of the spectrum; the UV-absorption edge corresponds to radiation with wavelength about 340 nm.

The absorption spectra of the synthesized oxyfluoride glasses with RE^{3+} ions are displayed in Fig. 2, where the absorption bands are interpreted with an indication of the ionic excited states into which the transitions occur. The ground states for the RE^{3+} ions are: $^4I_{15/2}$ (for RE = Er), $^3H_6$ (Tm), $^5I_8$ (Ho), $^6H_{15/2}$ (Dy), $^3H_4$(Pr), and $^7F_6$ (Tb). The high transmission of the glasses makes it possible to resolve the absorption bands in the short-wavelength region of the spectrum that correspond to transitions into excited states participating in up-conversion processes.

Up-conversion luminescence (UCL) in oxyfluoride glasses with the ions Yb^{3+}–RE^{3+} was excited by radiation from an InGaAs-laser diode at the wavelength about 960 nm; an MDR-23 monochromator, synchronous amplifier, and Hamamatsu C5460-01 sensitive photodetector were used to measure the spectra. The UCL spectra and their interpretation are shown in Fig. 3. The color coordinates of the luminescence of the glasses in the *Commission Internationale de l'écalirage* system (CIE 1931) as well as the dominant wavelength λ_d in the spectrum and the color purity p_e were determined on the basis of the spectrum.

Intense bands in the green region of the spectrum (522 and 542 nm), associated with transitions from the excited states $^2H_{11/2}$ and $^4S_{3/2}$ into the ground state $^4I_{15/2}$, which determine the color of the green luminescence, with high color purity ($p_e = 0.99$) are observed for glass with Yb–Er ions. The weaker band in the red region (transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (652 nm)) lies at the boundary of the color correspondence functions for the eye and for this reason does not make a significant contribution to the change in the color of the UCL. At the same time, for glass ceramic with high Er concentration [7] this band dominates in the spectrum, which deter-

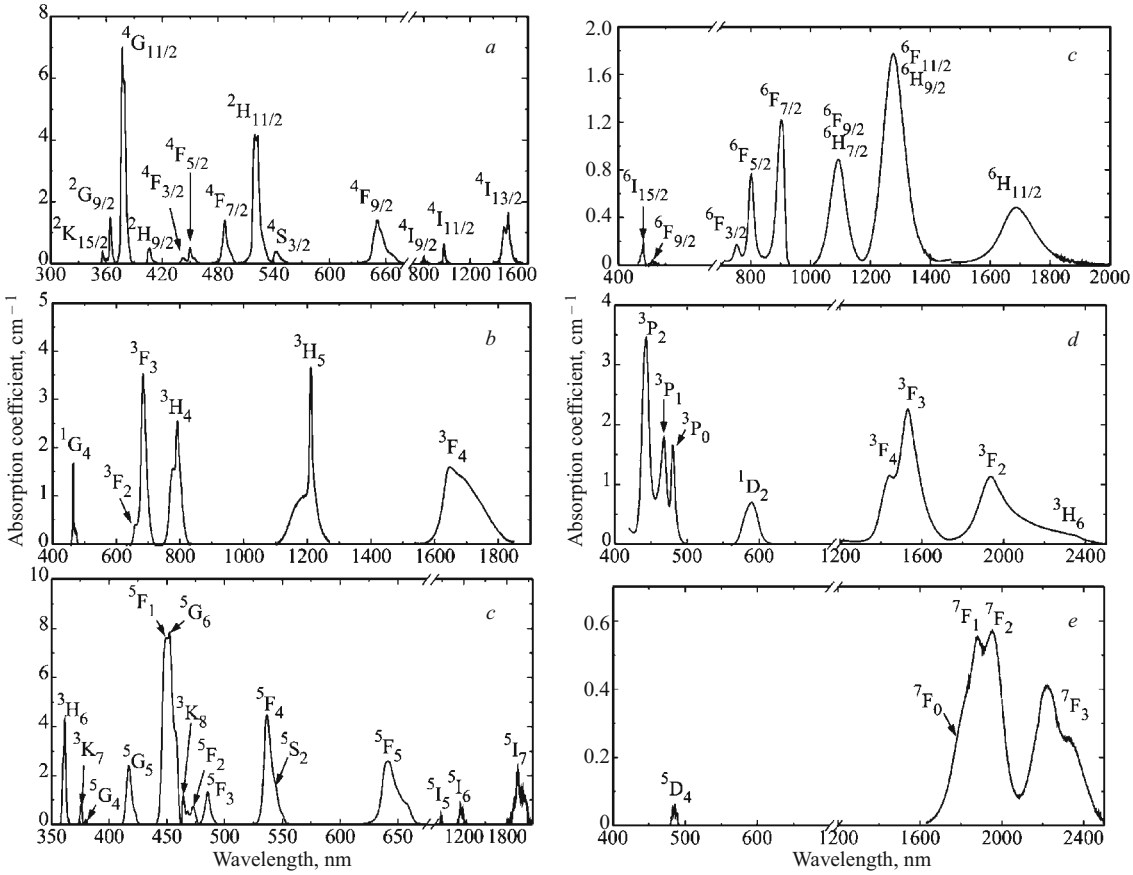

Fig. 2. Absorption spectra of oxyfluoride glasses doped with (0.5 mol.%) Er_2O_3 (*a*), Tm_2O_3 (*b*), Ho_2O_3 (*c*), Dy_2O_3 (*d*), Pr_2O_3 (*e*), and Tb_2O_3 (*f*) with interpretation of the absorption bands.

mines the yellow color of the luminescence. The excitation of Er^{3+} occurs by a direct transfer of energy from the Yb^{3+} ions to the Er^{3+} ions, whose excited states are in energy resonance: $^2F_{5/2}(Yb) \rightarrow {}^4I_{11/2}(Er)$.

For glass with Yb–Tm ions the most intense UCL band lies in the region 477 nm (transition $^1G_4 \rightarrow {}^3H_6$), determining the blue color of the luminescence. At the same time the bands in the red region of the spectrum with a maximum at 650 nm ($^1G_4 \rightarrow {}^3F_4$) and 698 nm ($^3G_4 \rightarrow {}^3H_6$) lead to a reduction of the color purity to $p_e = 0.75$ and a violet hue of the luminescence. Similarly, for glass with Yb–Ho ions the strongest UCL band lying at 542 nm, associated with a transition from the excited states $^5S_2 + {}^5F_4$ into the ground state $^5I_8$, determines the green color of the luminescence. The much weaker bands in the red region of the spectrum with maxima at 655 nm ($^3F_5 \rightarrow {}^5I_8$) and 750 nm ($^5S_2 + {}^5F_4 \rightarrow {}^5I_7$) does not have a large effect on the color purity ($p_e = 0.99$). Just as for the system Yb–Er, in the systems Yb–Tm and Yb–Ho the transfer of energy is due to the close values of the energies of the excited states $^5H_5$(Tm), $^2F_{5/2}$(Yb) and $^5I_6$(Ho), $^2F_{5/2}$(Yb), respectively.

For glasses with Dy, Pr, and Tb ions the mechanism of UCL is associated with a structural feature of the energy levels, specifically, the presence of a long-lived (metastable) excited state — $^4F_{9/2}$(Dy), $^3P_0$(Pr), and $^5D_4$(Tb). The quite large energy gap between the metastable and low-lying excited levels gives rise to the long lifetime of the ions. This is especially sharply manifested for the ions Tb^{3+}, for which the metastable level $^5D_4$ lies about 15,000 cm^{-1} above $^7F_0$, as one can see from the absorption spectrum (see Fig. 2). As a result of the relaxation in the system of excited states a large part of the ions 'accumulates' in a metastable state and UCL is observed precisely from this state.

Indeed, UCL for glass with the ions Yb–Tb is associated with the transitions $^5D_4 \rightarrow {}^7F_J$, where $J = 6$ (the band peaking at 482 nm), 5 (537 nm, the most intense band, determining the green color of the luminescence), 4 (579 nm), and 3 (615 nm). Since Tb^{3+} does not possess a state which is in energy resonance with the excited state $^2F_{5/2}$(Yb), energy transfer in the system Yb–Tb is cooperative [6, 8]. In other words it occurs from the excited pair Yb^{3+}–Yb^{3+} to a close lying ion Tb^{3+}. This mechanism has been described in detail for oxyfluoride glass with the ions Yb–Eu [9].

Finally, for glasses with the ions Yb–Dy and Yb–Pr a series of bands is present in the UCL spectrum. This gives rise to 'mixing' of the UCL color, which in accordance with the CIE 1931 system is yellow-green and rose, respectively.

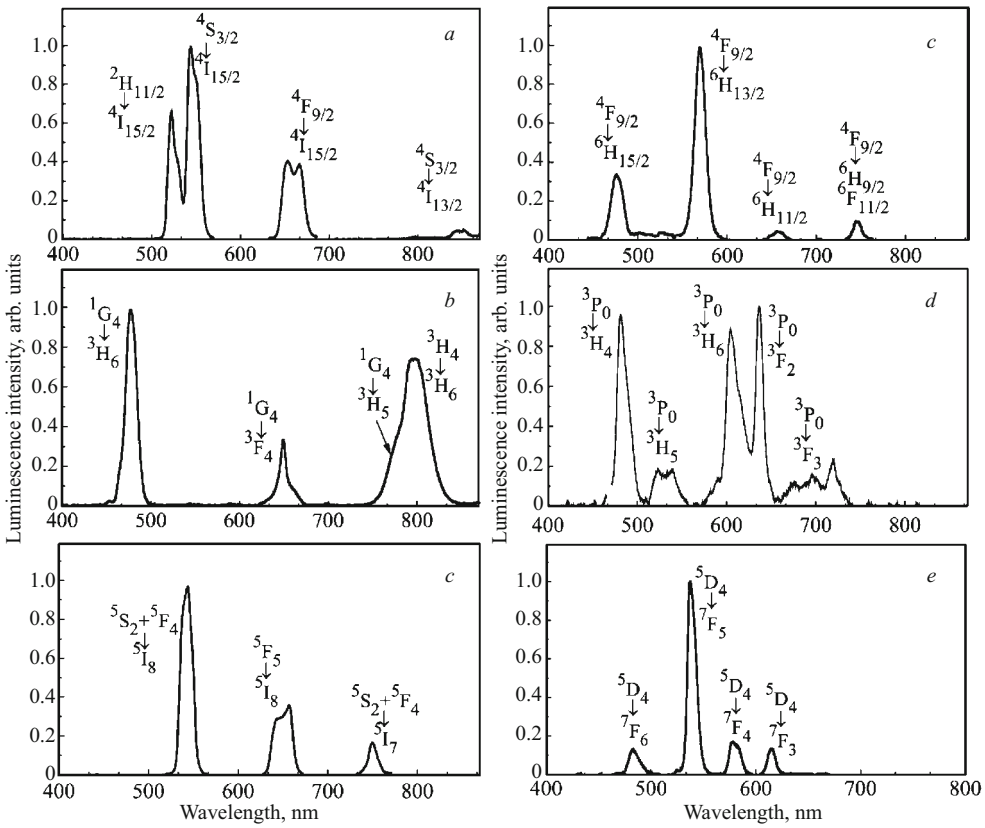

Fig. 3. Up-conversion luminescence spectra (UCL) of oxyfluoride glasses doped with 1 mol.% YbF_3 and 0.5 mol.% Er_2O_3 (*a*), Tm_2O_3 (*b*), Ho_2O_3 (*c*), Dy_2O_3 (*d*), Pr_2O_3 (*e*), and Tb_2O_3 (*f*) with interpretation of the UCL bands.

It should be noted that 'cooperative' luminescence [10] of Yb^{3+}-ion pairs, which is observed near 500 nm, is absent in the UCL spectra; this indicates absence of clusterization of ions in the experimental glasses and, therefore, high glass quality.

An important parameter determining the prospects for up-conversion luminescing materials based on the ion pair Yb^3–RE^{3+} is the efficiency η_{ET} of energy transfer between them. In the present work η_{ET} was determined according to the lifetime reduction for the Yb^{3+} ions in the state $^2F_{5/2}$; the lifetime τ_{Yb} itself was determined from the decay kinetics of the luminescence of the Yb^{3+} ions at the wavelength 1030 nm. For glass containing only the ions Yb^{3+} the lifetime τ_{Yb} equals 1.02 msec, which corresponds to the values for commercial laser ytterbium glasses (0.7 – 2 msec, the most typical value about 1 msec).

A considerable lifetime τ_{Yb} reduction to 152, 266, and 280 msec is observed for glasses coactivated by Yb ions and Er, Tm, and Ho ions. This indicates high energy transfer efficiency in these glasses. The energy transfer efficiency η_{ET} ($Yb^{3+} \rightarrow RE^{3+}$) and the color characteristics of the luminescence of the glasses (*x*, *y* — color coordinates, λ_d — dominant wavelength, p_e — color purity) are presented in Table 1. The efficiency η_{ET} equals 84% for glass with the ions Yb–Er, 73% for Yb–Tm, and 72% for Yb–Ho.

For glasses with the ions Dy, Pr, Er, and Tb the highest efficiency is observed in glass with the ions Yb–Tb (10%) and Yb–Eu (12%) [9]. The lowest values are associated with a lower probability of 'cooperative' energy transfer, which determines the mechanism of UCL for these ions.

In summary, the use of the proposed glass as a matrix for activation by rare-earth ions makes it possible to obtain 'multicolor' UCL — green (Er, Ho, Tb, Dy), blue (Tm), or red (Eu, Pr). The glasses developed hold promise as a base for obtaining luminophores converting IR radiation of semiconductor laser diodes into visible light with high efficiency. These glasses can also be used as a base for synthesis of transparent glass ceramic with nanocrystals of lead fluoride RE^{3+} : PbF_2 with improved spectral-luminescence properties.

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