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Structure and Anti-Stokes Luminescence of Yb-containing Glass Co-doped with Eu, Ho and Er

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The aim of our work was synthesis of transparent silicious media high-doped with Yb–Er, Yb–Ho and Yb–Eu and determination of the media structure and spectral-luminescent properties in the anti-Stokes region at excitation through the Yb^{3+} ions.

Keywords: Anti-stokes luminescence, Up-conversion, Yb-containing silicious glass, Er^{3+}, Eu^{3+} and Ho^{3+} ions.

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1. INTRODUCTION

The Er–Yb-containing glasses are extensively used as active media of laser operating at $\lambda \approx 1.55$ µm [1]. In additional, similar media may be used for visualization of IR-radiation which is absorbed by Yb^{3+} ions as well as for obtaining of laser effect in their anti-Stokes luminescence band. The glassy matrixes which provide formation of complex Er–Yb centers and characterized by an absence in them of oscillators with high vibration frequencies are promising for solving of the problems indicated above. It is known that the Yb-containing phosphors co-activated with certain rare-earth ions are widely used for visualization of infrared radiation absorbed by the Yb^{3+} ions [2]. A high transparent media co-activated by these ions, in principle, may be used as active elements of up-conversion lasers. The present work problems are the following: preparation of silicious glassy media co-doped with ytterbium, erbium, europium, holmium and investigation of their structural and spectral-luminescent properties.

2. MATERIALS AND EXPERIMENTAL

The scheme of synthesis of the Yb-containing material is given in Fig. 1. The basic source materials were tetraethylorthosilicate $Si(OC_2H_5)_4$ and salts of ytterbium, erbium, europium, holmium and buffer element. The synthesis method includes tetraethylorthosilicate hydrolysis in water solution of hydrochloric acid to obtain a sol, preparation of the colloid by adding aerosil into the sol, the neutralization of the sol-colloid system up to pH ≈ 3.0, liquid slip casting, gel-formation, drying and heat treatment to obtaining of monolithic xerogels, impregnation of the xerogels by a water-alcohol solution of the rare-earth co-dopes salts, subsequent drying, vitrification in air and inertial cooling.

The structural investigation of synthesized samples was carried out by an X-ray diffraction (D8 Advance) and scanning electron microscope (LEO-1420REM). These samples absorption and luminescence spectra were investigated with use of a spectrophotometer (Cary 500) and a spectrofluorimeter (SDL-2), respectively. The luminescence decay kinetics were explored oscillographicly at excitation by a monopulse laser radiation with λ = 266, 380 and 970 nm and $\Delta t \approx 10$ ns.

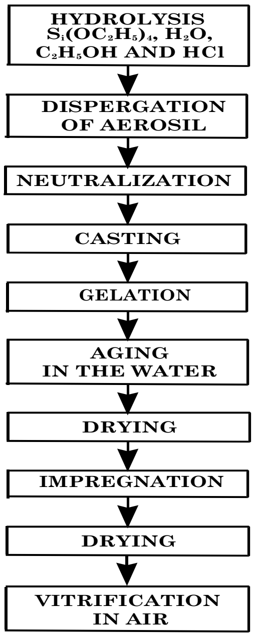

Fig. 1 – The scheme of synthesis of Yb-containing silicious glassy media.

3. RESULTS AND DISCUSSION

All synthesized samples were characterized by a high transparence (track of a He-Ne laser ray was absent) and with total concentration of the rare-earth oxides up to 15 mass %. A containing of OH^--groups in them was about 0.2 mass %. The phase and microscopical analyses showed an absence of obvious features of any crystalline particles. This fact permitted us to conclude that the media inhomogeneous are lesser than some nm.

The anti-Stokes luminescence spectra of all samples in visible region obtained at excitation by radiation of a semiconductor CW laser (λ = 970 nm) with a power density about 6 kW/cm² are displayed in Fig. 2. It is seen that the spectra of Yb- (Fig. 2*a*) and Yb–Eu-

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containing samples (Fig 2*b*) are characterized by intense bands caused by cooperative $2(^2F_{5/2} \rightarrow {}^2F_{7/2})$ transitions of Yb^{3+} pairs ($\lambda \approx$ 500 nm) and $^5D_0 \rightarrow {}^7F_2$, $^7F_1$ ones of Eu^{3+} ions ($\lambda \approx$ 613 and 585 nm, respectively). Besides of, the luminescence spectrum of Yb–Eu-containing sample reveals presence of the low intense $^5D_1 \rightarrow {}^7F_0$ ($\lambda \approx$ 536 nm) and $^5D_2 \rightarrow {}^7F_0$ ($\lambda \approx$ 460 nm) bands. This later presence testifies to realization of successive sensitization of Eu^{3+} luminescence by the paired and isolated Yb^{3+} ions. The same name spectrum of Yb–Er-containing sample is characterized by disappearance of the cooperative luminescence band and appearance of three relatively intense anti-Stokes luminescence bands $^2H_{11/2} \rightarrow {}^4I_{15/2}$ ($\lambda \approx$ 522 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ ($\lambda \approx$ 547 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ ($\lambda \approx$ 660 nm) caused by Er^{3+} ions (see Fig. 2*c*). A disappearance of the Yb^{3+} pairs cooperative luminescence and the relatively high intense of anti-Stokes luminescence from the $^2H_{11/2}$ level which is located on ~800 cm^{-1} [3] above the $^4S_{3/2}$ one in the Yb–Er-containing media is a worth argument in a favour of formation of nanocrystalline $(Yb_{1-x}Er_x)_2O_3$ particles. Here it should be noted that the main feature of Yb–Er-containing glassy media at the monopulse excitation is a dramatic dependence of relative intensity of Er^{3+} anti-Stokes luminescence bands on the Yb^{3+} excitation power (Fig. 2c, cf. curves *1* and *2*). This fact we explain mainly by essential distinction of filling speeds of the corresponding luminescent levels. The spectrum of Yb–Ho-containing sample (Fig. 2*d*, curve *1*) is close to spectrum in Fig. 2*a*. However, the difference spectrum of Yb–Ho- and Yb-containing samples (Fig. 2*d* curve *2*) reveals a weak band at $\lambda \approx$ 480 nm caused by the $^5F_3 \rightarrow {}^5I_8$ transition of Ho^{3+} ions. It has been established that a weak up-conversion luminescence of the Yb–Ho-containing sample is caused mainly by the back excitations transfer according to the $Ho^{3+}(^5F_4 \rightarrow {}^5I_6)$–$Yb^{3+}(^2F_{7/2} \rightarrow {}^2F_{5/2})$ scheme.

The investigation of the samples luminescence decay kinetics showed that the average decay duration of the states $^2F_{5/2}$ (Yb^{3+}), $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ (Er^{3+}) consists of about 450, 80, 90 and 12 ms, respectively. A comparison of the values with the corresponding radiative lifetime testifies to sufficiently high quantum yield of the luminescence. In particular, for the Yb-containing sample it is close to 70%.

4. CONCLUSION

It is shown that the Yb–Ln-containing (Ln = Eu, Ho, Er) silicious glassy media are characterized by a high transparence and, with the exception of Ln = Ho, sufficiently effective anti-Stokes luminescence at excitation in the Yb^{3+} absorption band. These properties permit us to propose the materials as promising active media for visualization of the IR radiation and, perhaps, obtaining of laser effect at up-conversion pumping.

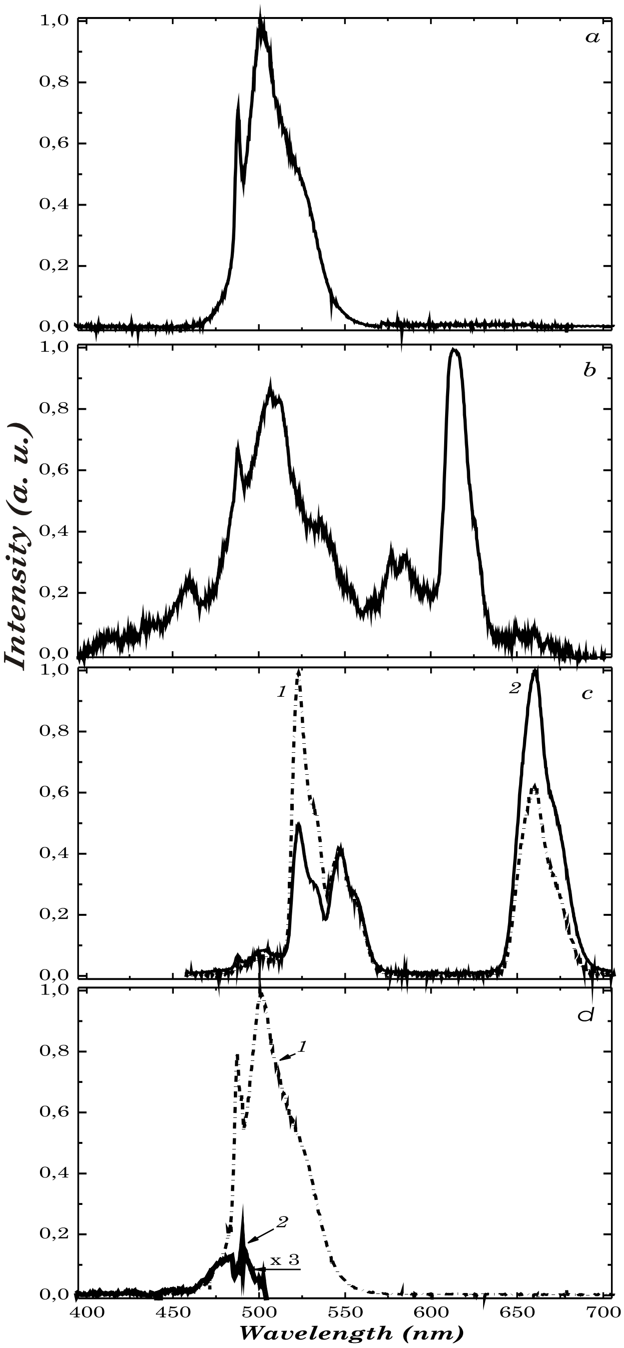

Fig. 2 – Up-conversion luminescence spectra of Yb- (*a*), Yb–Eu- (b), Yb–Er- with specific power 3.5×10^5 (*c*, curve *1*) and 7×10^5 (*c*, curve *2*) W/cm^2, Yb–Ho-containing (*d*, curve *1*) samples, *d,* curve *2* is difference spectrum of Yb–Ho- and Yb-containing samples.

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