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## Optical modulation of anti-stokes photoluminescence of the $Y_2O_2S:Er$

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The luminescence and excitation spectra of visible photoluminescence of  $Y_2O_2S:Er$  ceramics (1 at.%) at different optical pumping have been studied. It is shown that the anti-Stokes luminescence of single crystals doped with erbium has a high intensity when pumping the metastable state  $^4I_{13/2}$  of impurities. The resonant wavelengths of IR-photons for two-photon excitation of the visible glow  $Y_2O_2S:Er$  are determined. A method of photooptical modulation of anti-Stokes luminescence has been developed, which makes it possible to determine the nature of the corresponding electronic transitions inside the excited glow centers.

**Keywords:** Luminescence, excitation, photooptical modulation.

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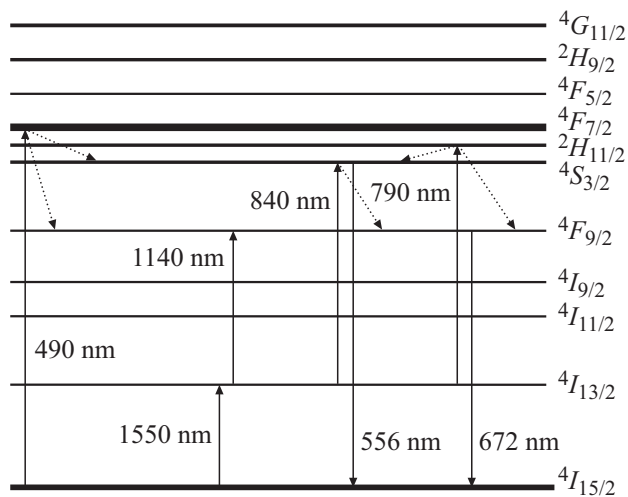
### 1. Introduction

Compounds doped with rare earth ions (REIs) have found wide application as luminophores, fiber lasers and amplifiers, optical memory devices, and three-dimensional displays. REIs such as  $Er^{3+}$ ,  $Tm^{3+}$ ,  $Ho^{3+}$ , and  $Yb^{3+}$  provide good anti-Stokes luminescence in transparent matrices for infrared (IR) light visualization. Increasing the efficiency of this type of luminescence requires reducing non-radiative recombination and using crystalline compounds with low phonon energy, REIs with long lifetimes of metastable excited states and the absorption cross section of these excited states in the IR-spectral region [1]. In this case, the probability of luminescence in the visible region from high lying states should be large. There are two mechanisms of excitation of anti-Stokes luminescence of REI excited states: due to optical absorption of the second IR-photon and due to non-radiative energy transfer from another excited rare-earth ion (for example,  $Yb^{3+}$ ) [2]. In the second case, the distance between two excited ions must be less than 2 nm, which requires a high REI concentration in the crystal and high IR-excitation intensities. For anti-Stokes luminescence at low IR-excitation intensities and low impurity concentrations, the first mechanism is predominant, but it requires resonant coincidence of the energies of the first and second phonons with the energy distances between the REI electron levels.

Yttrium oxosulfide  $Y_2O_2S:Er$  is interesting as an object of research not only because of the low phonon energy, but also because of high isomorphic capacity with respect to REI, optical transparency in a wide spectral range 0.12–10  $\mu m$ . This material can easily be obtained as a powder compound or pressed ceramic. For visualization of IR-radiation, the ease of introducing significant (up to  $10^{22} cm^{-3}$ ) concentrations of active ions into the crystal composition, high thermal conductivity, good transparency

and resistance of the material to external influences are very important [3,4]. In this case, IR-radiation can be modulated both in time and in space. One beam of light can modulate the optical properties of the medium (absorption, reflection, luminescence and refraction) for another infrared or visible light. The first beam of light changes the population of the metastable lower excited states of REIs [5], „creating“ impurity centers with new absorption for the second beam on the same REIs. Such photo-optical modulation is more efficient than modulation by an electric or magnetic field and can be used in various optical information processing devices. Therefore, the study of the mechanisms of absorption by excited centers and anti-Stokes photoluminescence is an urgent problem that requires more detailed study. Having many energy levels for  $Er^{3+}$  ions, it is logical to assume that the summation of the energies of IR-photons can be even more efficient for two photons of different energies, each of which is in resonance with its own electron transition up (Fig. 1). By selecting the resonant wavelengths of these two photons, one can obtain a sharp increase in the intensity of anti-Stokes luminescence compared to excitation by IR-photons with the same wavelength, which is usually used in experiments. Two-beam excitation of the medium will enable to use it to visualize IR-images and create a real three-dimensional image when scanning the intersection point of laser beams in space.

The aim of this article is to study a new photooptical effect in the study of photoluminescence (PL) spectra and excitation of visible fluorescence of the  $Y_2O_2S:Er$  compound for determination of all possible resonant frequencies of two sequentially absorbed IR-photons. Achieving this result required the use of an original technique for excitation of anti-Stokes luminescence by a frequency-tunable infrared radiation source simultaneously with pumping the crystal by radiation from a high-power laser LED with a wavelength of



**Figure 1.** Scheme of the energy levels of the erbium ion  $\text{Er}^{3+}$  and the corresponding electronic transitions during their two-photon excitation and radiation of ceramics  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$ .

1.55  $\mu\text{m}$ . As a result, the presence of a significant intensity of anti-Stokes luminescence of erbium ions in the regime of two-photon resonant excitation of ceramics modulated at the frequency of the pump LED was found. A method for optical modulation of anti-Stokes photoluminescence is proposed for determining the maxima of excited-state absorption (ESA) of erbium.

## 2. Experiment

In this article, luminophores with composition  $\text{Y}_{1.99}\text{Er}_{0.01}\text{O}_2\text{S}$  obtained by solid-phase synthesis by reacting yttrium oxide, erbium oxide, and sulfur are studied [6]. The concentrations of rare earth elements were determined based on the composition of the initial mixture. Taking into account the extreme sensitivity of anti-Stokes luminophores to microimpurities, especially pure oxides with a substance content of 99.995–99.999 at.% were used for the synthesis of samples. The crystal lattice parameters and the content of various phases (oxosulfide and various oxides) in the final compound were controlled by X-ray diffraction methods. According to X-ray diffractometry data, we immediately note the presence of only the yttrium oxosulfide phase in the obtained  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$  luminophores. For the convenience of measurements, the powdered material was pressed into pellets 20 mm in diameter by cold pressing followed by annealing in inert (argon) atmosphere at 1100°C for 1 h.

Diffuse reflectance spectra of luminophores were recorded in the visible and infrared regions of the spectrum with MDR-12 monochromator and FEU-106 and FEU-62 photodetectors. In this case, radiation from „Narva-100“ incandescent lamp with a continuous spectrum, which passed through a mechanical obturator, was used. The signal was recorded at modulation frequency of 30 Hz, and the spectral resolution in all measurements was

0.1 nm or better. The diffuse reflectance spectra of a strongly scattering material actually record its optical transmission spectra, since most of the scattered light has passed through this material.

The photoluminescence (PL) spectra were recorded upon excitation by the light of a „Narva-100“ incandescent lamp passed through an MDR-12 monochromator and a mechanical obturator. Luminescence of the sample entered an optical waveguide located at an angle of 45° to its surface at a distance of 10 mm from it, and was analyzed using an MDR-6 spectrometer and „Unipan-237“ AC signal amplifier paired with the computer. When recording the luminescence excitation spectra, the wavelength on the MDR-6 spectrometer was recorded at the corresponding PL band, and the excitation wavelength on the MDR-12 monochromator varied in the range of visible or infrared wavelengths. Sometimes, to populate the upper energy levels  $4I_{13/2}$  of erbium with electrons, simultaneously with the radiation of an incandescent lamp passed through MDR-12 monochromator, the luminophore was also irradiated by an ML9XX10 infrared semiconductor laser diode with a length waves 1550 nm and power 200 mW, to which an alternating voltage was applied. In this case, the measurements were carried out at the modulation frequency of the LED. All studies were carried out at room temperature of the samples of 300 K.

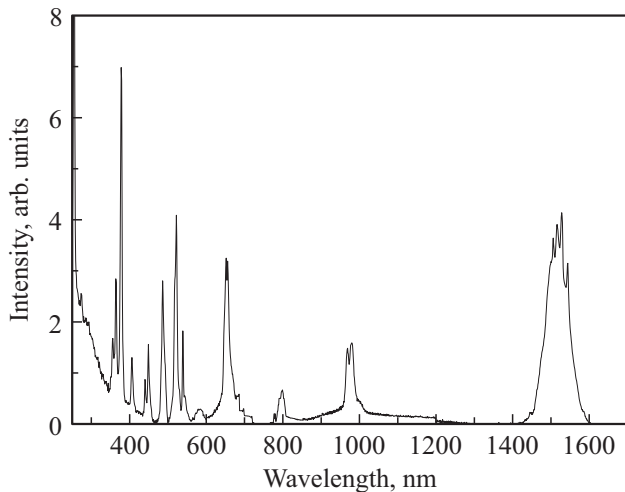
## 3. Results and discussion

The optical properties of a material are determined by its electronic system, which can be influenced by electric, magnetic, acoustic, or thermal external fields. But the influence of resonant light fields, which lead to a change in the wave functions of electrons or a change in the population of energy levels, is much stronger. In this case, the optical properties for the second light beam change drastically even for low pump and signal beam intensities (photooptical effect). We used resonant pumping of the level  $4I_{13/2}$  of erbium ions by a laser with a wavelength of 1550 nm, creating population of these long-lived (10 ms) metastable states and reducing the number of electrons in the main  $4I_{15/2}$  state (Fig. 1) [7].

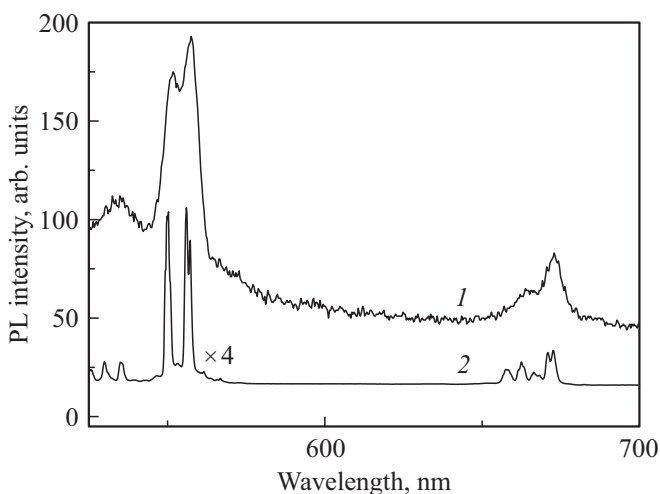
Figure 2 shows the absorption spectra of monochromatic light transmitted through  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$  ceramics with REI concentration of 1 at.%. The presence of many absorption peaks is characteristic of erbium ions. The position of the absorption maxima for erbium-doped yttrium oxosulfide and the corresponding excited levels of the  $\text{Er}^{3+}$  ion, upon transitions to which from the ground state  $4I_{15/2}$  light absorption occurs, are shown below: 410 nm —  $2H_{9/2}$ , 450 nm —  $4F_{5/2}$ , 490 nm —  $4F_{7/2}$ , 525 nm —  $2H_{11/2}$ , 550 nm —  $4S_{3/2}$  and 660 nm —  $4F_{9/2}$  (Fig. 2). The central position of several narrow lines is indicated, which are due to the splitting of the excited states by the crystal field of the compound. In the absorption spectra of the luminophore  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$ , measured in the infrared region (Fig. 2), at least

three maxima with wavelengths of 790, 980 and 1540 nm are clearly distinguishable for the maximum concentration. In this case, the maximum 790 nm can be associated with the  $^4I_{15/2} - ^4I_{9/2}$  transitions, while the maxima 980 and 1540 nm — with  $^4I_{15/2} - ^4I_{11/2}$  and  $^4I_{15/2} - ^4I_{13/2}$  electron transitions inside erbium ions.

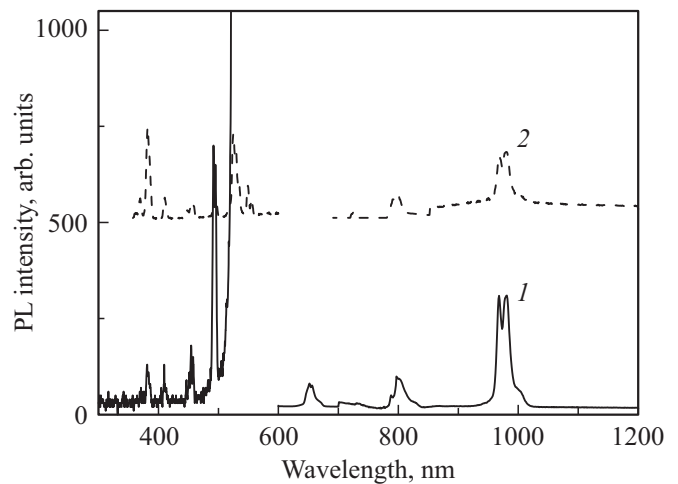
To record the visible emission bands of the luminophore  $Y_2O_3S:Er$ , we used the excitation of one of the previously detected absorption bands by blue light passed through a monochromator with a wavelength 490 nm (Stokes luminescence) and IR-excitation 970 nm (anti-Stokes luminescence) (Fig. 3). We note the presence luminophore in the PL spectra, in addition to the characteristic erbium lines in the red region with wavelengths of 672 and 663 nm, three rather narrow luminescence bands in the green (with maxima 556, 550, and 530 nm) spectral region (curve 1). Features of the red fluorescence can be associated with radiative transitions



**Figure 2.** Absorption spectra of the compound  $Y_2O_3S:Er$  ( $T = 300$  K).



**Figure 3.** PL spectra in the visible region of the spectrum of the  $Y_2O_3S:Er$  compound upon excitation by radiation: 1 — 490 nm and 2 — 970 nm ( $T = 300$  K).

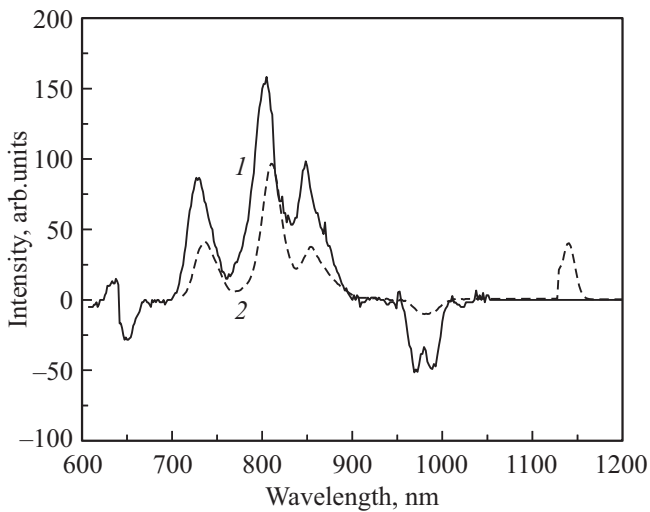


**Figure 4.** Excitation spectra of  $Y_2O_3S:Er$  ceramics in the visible (Stokes) and IR (anti-Stokes) regions of the spectrum: 1 — for 556 nm FL line and 2 — for 672 nm FL line at  $T = 300$  K.

of electrons from the excited level  $^4F_{9/2}$  to the lower ground level  $^4I_{15/2}$  of erbium ions split by the crystal field (Fig. 1). Intense peaks of green fluorescence with maxima 556 and 550 nm correspond to electron transitions from the excited level  $^4S_{3/2}$  to the ground level  $^4I_{15/2}$ . While the 530 nm band is determined by the erbium ion transitions from the  $^2H_{11/2}$  level to the lower  $^4I_{15/2}$  level. Above we are talking about Stokes photoluminescence since the energy of excitation photons was higher than the energy of registered photons of the visible spectrum. For anti-Stokes PL (curve 2), the luminescence intensity was an order of magnitude smaller, and the width of the luminescence lines is less.

It is interesting to study the excitation spectra of Stokes and anti-Stokes visible luminescence, respectively, in the short and long wavelength regions of the spectrum (Fig. 4). Figure 4 shows the excitation spectra of the 556 and 672 nm luminescence lines of the  $Y_2O_3S:Er$  ceramics in the photon energy region outside the luminescence bands. It can be seen that the Stokes PL excitation spectrum of  $Er^{3+}$  ions mainly consists of several series of narrow bands centered at wavelengths of 380, 410, 450, 490, and 525 nm, respectively. These excitation bands arise when the incident radiation of an incandescent lamp is absorbed by erbium ions and lead to electron transitions from the ground  $^4I_{15/2}$  state to excited energy levels split by the crystal field. According to the literature data, these excitation bands appear at wavelengths and at transitions similar to those indicated above in the description of the absorption spectra (Fig. 2).

Figure 4 also shows the excitation spectra of the anti-Stokes luminescence of  $Y_2O_3S:Er$  ceramics in the region of photon energy lower than the luminescence photon energy. We can clearly distinguish a broad excitation peak with a maximum of 970 nm, which is due to two successive processes of absorption of infrared photons with transitions  $^4I_{15/2} - ^4I_{11/2}$  and then  $^4I_{11/2} - ^4F_{7/2}$  inside erbium ions



**Figure 5.** Excitation spectrum of  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$  ceramics modulated by 1550 nm radiation in the visible and IR-spectral regions for the anti-Stokes FL line: 1 — 556 nm and 2 — 672 nm at  $T = 300$  K.

(Fig. 1). As a result, the population of metastable energy levels  $^4I_{11/2}$  of erbium ions increases, creating conditions for electron transitions to higher energy levels upon absorption of the second IR-photon [8]. This photon has the same energy as the first one in the case of using one source of IR-spectrum to excite anti-Stokes luminescence. Excitation peaks with wavelengths of 800 and 650 nm also arise when two identical photons are absorbed by neighboring erbium ions, followed by non-radiative recombination of the electron energy to the metastable  $^4I_{11/2}$  level. Then there is a non-radiative energy transfer from one erbium ion to another and the electron is ejected to a high energy level  $^4F_{7/2}$ . If two different IR-sources of excitation are used for anti-Stokes luminescence, then sequentially absorbed photons can have different energies.

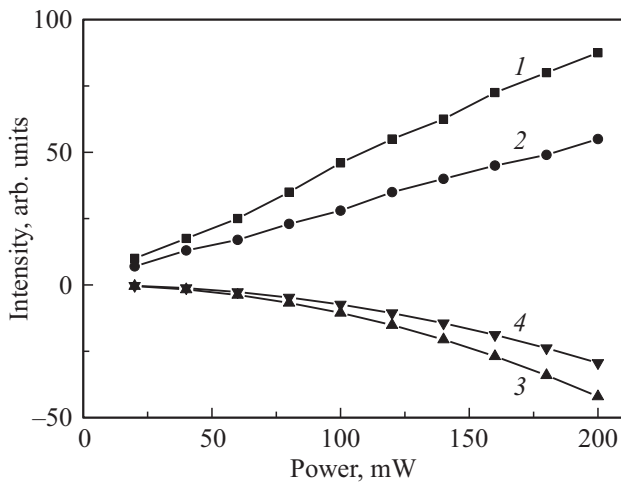
We use radiation from a 1550 nm laser with variable frequency as pump light, which enables to populate the metastable lower excited level  $^4I_{13/2}$  of erbium ions with electrons (Fig. 5). In this case, the population of the ground level will decrease at the moment of laser irradiation. Recording of excitation spectra of visible luminescence by the second IR-beam at the modulation frequency gives positive or negative peaks during phase detection, depending on whether the excitation occurs from the  $^4I_{13/2}$  level (positive peaks) or from  $^4I_{15/2}$  level (negative peaks).

It can be seen that this modulated spectrum is more diverse than without laser illumination, and several new narrow positive excitation peaks with wavelengths of 645, 710, 790, and 840 nm are clearly visible. It is logical to assume that these peaks are related to electron transitions from the  $^4I_{13/2}$  level pre-populated by laser pumping to higher energy levels of erbium ions [9]. To understand what level the electron will go to as a result of successive absorption of two IR-photons, it is necessary to sum the energy of the LED pump photon  $E_0 = 0.80$  eV, and the

energy of each of the photons in the IR excitation peaks (Fig. 5, curve 2)  $E_1 = 1.92$  eV,  $E_2 = 1.75$  eV,  $E_3 = 1.57$  eV and  $E_4 = 1.48$  eV. As a result, we obtain the energy distance of the erbium ion excited levels from the ground lower level: 2.72 eV —  $^4F_{5/2}$ , 2.55 eV —  $^4F_{7/2}$ , 2.37 eV —  $^2H_{11/2}$  and 2.28 eV —  $^4S_{3/2}$  (here the designations of electronic terms corresponding to these levels are also indicated) [10]. Further, from these high levels of erbium ions, electrons radiatively or non-radiatively recombine to the  $^4S_{3/2}$  level, the transition from which to the ground  $^4I_{15/2}$  level gives anti-Stokes green or red luminescence, which is recorded in the IR-excitation spectra (Fig. 5). In this case, the intensity of anti-Stokes luminescence is much higher when the erbium ion successively absorbs two IR-photons not with the same energy of 1.28 eV (970 nm), but with different energies. Therefore, the intensity of the excitation peaks at 790 and 840 nm is higher than that of the 970 nm peak (Fig. 5, curve 1). The main difference of the excitation spectra of the 672 nm anti-Stokes red PL with laser illumination is the appearance of an additional peak at 1140 nm. The maximum with a wavelength of 1140 nm (Fig. 5, curve 2) is typical only for red anti-Stokes PL, since the energy of two photons is only enough to eject an electron to the  $^4F_{9/2}$  level. On the other hand, at the second photon wavelength of 840 nm, mainly green anti-Stokes PL is excited, since there is a resonant ejection of electrons to the  $^4S_{3/2}$  level (Fig. 1). The negative peaks at 650 and 970 nm (Fig. 5) correspond to two-photon excitation from the ground level of erbium with the participation of photons of the same indicated wavelength [11,12].

In this connection, it is interesting to study the dependence of the anti-Stokes PL intensity in the visible region of  $\text{Y}_2\text{O}_2\text{S}:\text{Er}$  ceramics (1 at.%) at [two-photon excitation by a 1550 nm laser and 840 (1), 1140 (2), 970 (3) and 650 nm (4) irradiation by incandescent lamps on the power of the latter (Fig. 6). The point is that the anti-Stokes luminescence depends linearly on the power of the pump laser 1550 nm for all peaks in Fig. 5 when recording at the modulation frequency of this laser. But if in Fig. 6 for the second photon wavelengths of 840 nm (curve 1) and 1140 nm (curve 2) the dependence of the anti-Stokes luminescence intensity on the signal photon power is linear, for these photons with a wavelength of 970 nm (curve 3) and 650 nm (curve 4) it is quadratic. In general, all positive peaks of the modulated excitation (Fig. 5) have linear, and negative -quadratic dependence of the intensity on the power of the second IR-photon source (incandescent lamp).

To explain the obtained dependences of the anti-Stokes PL intensity, we consider two-photon successive absorption of photons 1550 nm (with intensity  $P_{12}$ ) and 840 nm (with intensity  $P_{23}$ ) in a three-level system  $^4I_{15/2}$  (level-1),  $^4I_{13/2}$  (level-2) and  $^4S_{3/2}$  (level-3) of the erbium ion (Fig. 1). In the simplest approximation, for low powers of IR-radiation, the electron population of the ground ( $N_1$ ) and two excited ( $N_2$  and  $N_3$ ) states are related to the pump



**Figure 6.** Dependence of the anti-Stokes PL intensity of  $Y_2O_3:Er$  ceramic at two-photon laser excitation 1550 nm and radiation: 1 — 840 nm; 2 — 1140 nm; 3 — 970 nm or 4 — 650 nm on the power of the latter.  $T = 300$  K.

intensities as follows

$$N_2/\tau_2 = \alpha^* N_1 P_{12} \quad \text{or} \quad N_2 = \alpha^* N_1 P_{12} \tau_2, \quad (1)$$

$$N_3/\tau_3 = \beta^* N_2 P_{23} \quad \text{or} \quad N_3 = \beta^* N_2 P_{23} \tau_3, \quad (2)$$

where:  $\alpha \propto 1/\tau_{21}^r$  and  $\beta \propto 1/\tau_{32}^r$  are proportionality coefficients equal to the probabilities of the corresponding optical radiative transitions of electrons, while  $\tau_2$  and  $\tau_3$  are the lifetime constants of excited levels, which depend on the lifetime of radiative and non-radiative transitions:  $1/\tau_2 = 1/\tau_{21}^r + 1/\tau_{21}^{nr}$  and  $1/\tau_3 = 1/\tau_{31}^r + 1/\tau_{31}^{nr} + 1/\tau_{32}^r + 1/\tau_{32}^{nr}$ . Consequently, the longer the lifetimes of the metastable states of 2 and 3 erbium ions, the higher the population of these energy levels under IR-pumping. Thus, the number of electrons ejected by the light from the lower level is equal to the number of recombining carriers, and the population of the uppermost level -3 depends on the power of the IR-sources as follows

$$N_3 \propto 1/\tau_{32}^r * 1/\tau_{21}^r * N_1^* P_{12}^* \tau_2^* P_{23}^* \tau_3. \quad (3)$$

But this is the dependence of the anti-Stokes PL intensity, which in our case is  $\propto N_3/\tau_{31}^r$ . To increase its intensity, it is necessary not only to increase the impurity concentration  $N_1$  and the intensity of IR-photons, but also to use metastable excited erbium levels with minimal non-radiative recombination or larger  $\tau_{21}^{nr}$ ,  $\tau_{31}^{nr}$  and  $\tau_{32}^{nr}$ . This is achievable in crystalline matrix materials with low energy of optical phonons responsible for non-radiative recombination of this type.

It can be seen from the dependence of the anti-Stokes PL intensity (3) that when visualizing IR-light upon absorption of two identical photons of low power, we have a quadratic dependence on the intensity of the incident light and weak visible radiation. To increase the quantum yield of visible

luminescence, it is better to use two different IR-beams — powerful laser pumping 1550 nm (with intensity  $P_{12}$ ) and weak signal light 840 nm (with intensity  $P_{23}$ ). In this case, the visible fluorescence will be more intense and linearly depend on the power of the detected IR-light. Interestingly, for media with low non-radiative recombination  $\tau_2 = \tau_{21}^r$  (with low phonon energy or low temperature), the probability of anti-Stokes luminescence does not depend on the lifetime of the excited states (3) and the effect can be strong even for short-lived -2 energy levels, but all processes occur in a thinner surface layer. It can also be enhanced by pumping through more absorbing  $^4I_{11/2}$  level, followed by fast recombination to the  $^4I_{13/2}$  level.

## 4. Conclusion

Powdered luminophores with composition  $Y_{1.99}Er_{0.01}O_2S$  were obtained from oxides of rare-earth elements by solid-phase synthesis in a sulfur atmosphere. The absorption, excitation, and photoluminescence spectra of this compound were analyzed for the Stokes and anti-Stokes excitation mechanisms. It is shown that the anti-Stokes luminescence of yttrium oxosulfide doped with erbium has high intensity at different energies of infrared illumination photons and for high concentrations of REIs. The resonant wavelengths of IR-photons and the mechanisms of energy transitions inside erbium ions (Fig. 1) for two-photon excitation of the visible fluorescence of  $Y_{1.99}Er_{0.01}O_2S$  ceramics are determined by the method of optical luminescence modulation.

As regards the modulation of the optical properties of crystals, the use of a pump laser to populate metastable electronic levels significantly changes the electronic subsystem of impurity atoms. This change is much greater than when the electron wave functions are perturbed by a non-resonant electric, magnetic or acoustic field in electric, magnetic and acoustic modulation methods. Therefore, the technique of photooptical modulation of absorption, refraction, or luminescence of crystals is much more promising for the creation of solid-state IR-visors and switching devices of various types.

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## Conflict of interest

The author declares that he has no conflict of interest.

## References

- [1] R. Brede, E. Heumann, J. Koetke, T. Danger, G. Huber, B. Chai. *Appl. Phys. Lett.* **63**, 2030 (1993).
- [2] F. Auzel. *Chem. Rev.* **104**, 139 (2004).
- [3] L.A. Bausa, G. Lifante, E. Daran, P.L. Pernas. *Appl. Phys. Lett.* **68**, 3242 (1996).

- [4] P. Rogin, J. Hulliger. *J. Cryst. Growth* **172**, 200 (1997).
- [5] S.Kh. Batygov, L.A. Kulevsky, A.M. Prokhorov, A.D. Saveliev, V.V. Smirnov, V.V. Osiko. *Kvant. Elektronika*, **1**, 2633 (1974) (in Russian).
- [6] D.N. Karimov, O.N. Komarkova, N.I. Sorokin, V.A. Bezhanov, S.P. Chernov, P.A. Popov, B.P. Sobolev. *Kristallografiya* **55**, 556 (2010) (in Russian).
- [7] A.M. Prokhorov. *Spravochnik po lazeram. Sov. radio, M.* (1978). V. 2, 503 p. (in Russian).
- [8] P.L. Boulanger, J.L. Doualan, S. Girard, J. Margerie, R. Moncorge. *Phys. Rev. B* **60**, 11380 (1999).
- [9] R. Brede, E. Heumann, J. Koetke, T. Danger, G. Huber. *Appl. Phys. Lett.* **63**, 2030 (1993).
- [10] J. Koetke, G. Huber. *Appl. Phys. B* **61**, 151 (1995).
- [11] A.N. Gruzintsev. *Neorgan. materialy* **56**, 7, 801 (2020) (in Russian).
- [12] A.N. Gruzintsev, D.N. Karimov. *FTT* **59**, 1, 116 (2017) (in Russian).

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