New invisible effective IR-phosphor in the basis of the ytterbium orthophosphate

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Recently one of the actual problems is the creation the invisible IR phosphors having at excitation by laser radiation of a range 0.94-0.98 microns the raised efficiency Stokses IR-luminescences in the field of 1.5-1.6 microns and minimal visible antiStokses luminescence. In process before the researches carried out by us the phosphor YbPO4: Er, having the enough intensive visible antiStokses and Stokses IR-luminescence in the field of 1.5-1.6 microns at excitation by laser radiation of a range 0.90-0.98mcm was developed. It was necessary to solve some problems for the creation on its basis the new invisible IR-phosphor, namely:

- to reduce the population of the top excited levels $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to which is connected the occurrence of the radiating visible antiStokses strips in the field of 520-680 nm (the transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$);
- to increase population of the bottom excited level $^4I_{13/2}$ from which occurs Stokses IR-luminescence in the field of 1.5-1.6 microns.

The specified problems may be decided successfully under next condition:

- the increases of the speed of the process unradiating relaxations of a state $^4I_{11/2}$ to become possible the increase of population of the bottom excited level $^4I_{13/2}$ and easing of the processes of the summation electronic excitations which are the reason of the visible antiStokses luminescence;
- the increases of the speed of the process unradiating relaxations of a states $^4S_{3/2}$ and $^4F_{9/2}$ as a result of the traditional donor-acceptors unradiating energy transfers which promotes the decreases of the visible antiStokses luminescence.

Coactivating YbPO4:Er by REE ions which are capable to isoenergetical and resonant absorbing transitions, in relation to considered transitions $^4S_{3/2}\rightarrow{}^4F_{9/2}$, $^4F_{9/2}\rightarrow{}^4I_{9/2}$ and $^4I_{11/2}\rightarrow{}^4I_{13/2}$ of Er^{3+} may be one of the ways for increase of the speed of the processes nonradiating relaxations of the excited levels $^4S_{3/2}$, $^4F_{9/2}$ and $^4I_{11/2}$ of Er^{3+}. For practical realization of this idea it is necessary to find a RE ion having such properties. The analysis of known data in the literature has allowed to establish, that among RE the ions, capable to make essential impact on the speed of processes unradiating relaxations of levels $^4S_{3/2}$, $^4F_{9/2}$ and $^4I_{11/2}$ the exclusive place occupies ion Ce^{3+}. Thanks to affinity of the power differences of pairs levels $^4S_{3/2}$ - $^4F_{9/2}$, $^4F_{9/2}$ - $^4I_{9/2}$, $^4I_{11/2}$ - $^4I_{13/2}$ ion Er^{3+} and $^2F_{5/2}$ - $^2F_{7/2}$ ion Ce^{3+} the following interionic unradiating cross-country-relaksatsionnye processes is possible:

$$^4S_{3/2}(Er^{3+}),\ ^2F_{5/2}(Ce^{3+}) \rightarrow {}^4F_{9/2}(Er^{3+}),\ ^2F_{7/2}(Ce^{3+})$$
$$^4F_{9/2}(Er^{3+}),\ ^2F_{5/2}(Ce^{3+}) \rightarrow {}^4I_{9/2}(Er^{3+}),\ ^2F_{7/2}(Ce^{3+})$$
$$^4I_{11/2}(Er^{3+}),\ ^2F_{5/2}(Ce^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}),\ ^2F_{7/2}(Ce^{3+}).$$

It should result for the account of increase of the speed unradiating relaxations of the conditions $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$ in intensity increase Stokses Ik-luminescences in area 1,5 -1,6 mcm and to easing of the visible antiStokses luminescences.

Considering, that a power difference of levels $^4S_{3/2}$ - $^4F_{9/2}$, $^4F_{9/2}$ - $^4I_{9/2}$, $^4I_{11/2}$ - $^4I_{13/2}$ ion Er^{3+} more than a power difference of the levels $^2F_{5/2}$ - $^2F_{7/2}$ ion Ce^{3+}, above-stated cross-country-relaksatsionnye processes should proceed with the phonon's generation of the phosphor's lattices.

Thus, the cited data specify in basic possibility of reception new "invisible" IR-phosphor on a basis the yttrium oxisulfide with the raised intensity of the IR-luminescence in the field of 1,5 -1,6 micron by Ce^{3+} coactivation of $YbPO_4$: Er.

The purpose of the present work - research of possibility of practical realisation of the given idea and creation the new IR-phosphor.

As objects of research a concentration series of samples $Yb_{1-x-y}Ce_xEr_yPO_4$ (0 x 0.25, 0 y 0.5) served. Samples have been received by heat treatment of the mix Yb_2O_3, Er_2O_3, CeO_2, $(NH_4)HPO_4$ and mineralizer at temperature 1200 C within one hour. Considering extreme sensitivity of the antiStokses phosphors to microimpurity РЗЭ [3], for synthesis of samples used especially pure yttrium and erbium oxides with the maintenance of substance of 99.999 %.
According to the results received by us the basic strips of radiation of ion Er^{3+} in $YbPO_4$: Er in a range 0,5-1,6 microns can be interpreted as follows: the strip in the field of 0,520 - 0,535 microns is result of optical transition $^2H_{11/2}\rightarrow{}^4I_{15/2}$; a strip 0,540 - 0,560 microns - transition $^4S_{3/2}\rightarrow{}^4I_{15/2}$, a strip 0,660 -0,680 microns - transition $^4F_{9/2}\rightarrow{}^4I_{15/2}$, a strip 0,80 -0,83 microns - transition $^4I_{9/2}\rightarrow{}^4I_{15/2}$, a strip 0,97 -1,03 microns - transition $^4I_{11/2}\rightarrow{}^4I_{15/2}$ and a strip 1,5 -1,6 microns - transition $^4I_{13/2}\rightarrow{}^4I_{15/2}$ (drawing). antiStokses and Stokses strips of ion Er^{3+} in $YbPO_4$: Er have difficult structure which is caused by transitions between shtarkses components of the raised levels $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and the basic condition $^4I_{15/2}$.

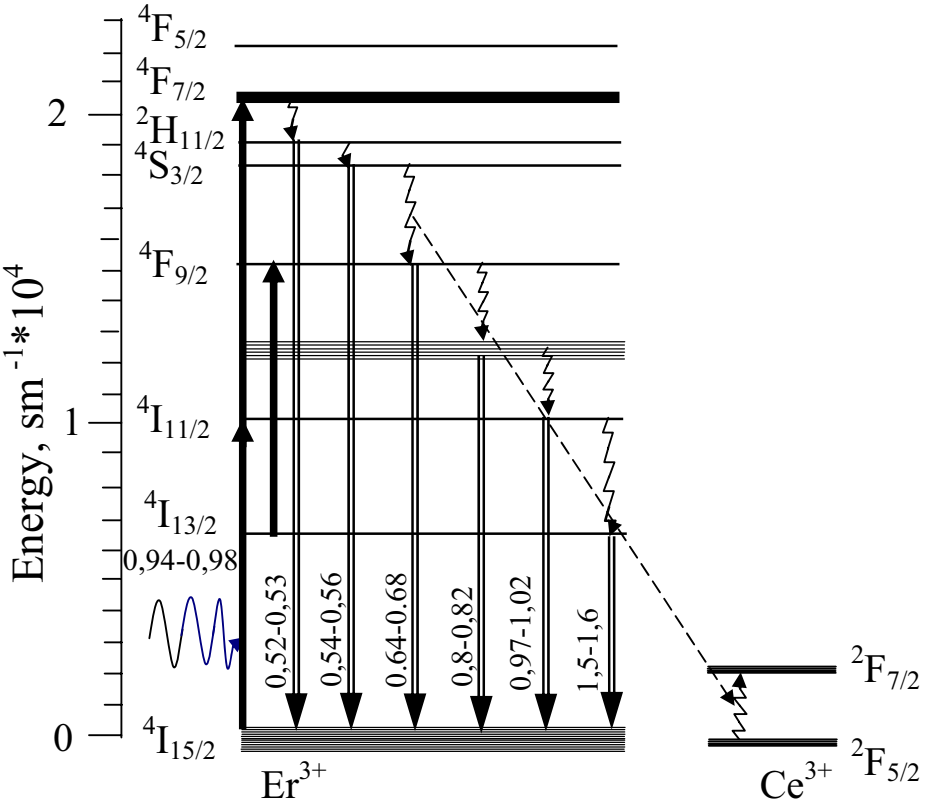

Fig. The diagram of the possible optical transitions between the ions Er^{3+} and Ce^{3+} at IR-excitation in the range 0.94-0.98 microns.

Comparison of the stationary luminescence spectra for samples $Yb_{0.99-x}Er_{0.01}Ce_xPO_4$ at lasers excitation of IR-radiation with maxima 0.965 and 0.975 microns has allowed to establish, that introduction the Ce^{3+} into $YbPO_4$:Er in all studied range of concentration does not lead to occurrence of the new radiation strips and does not change structure of the antiStokses and Stokses Er^{3+} radiation strips, and renders essential influences only on their intensity.

According to the data resulted in the table, the coactivation $YbPO_4$: Er by ions Ce^{3+} leads to occurrence of the predicted effect, namely to reduction of brightness of a visible antiStokses luminescence up to its full suppression at the raised Ce^{3+}concentration.

The table

The comparative luminescence characteristics of the samples $Yb_{1-x-y}Ce_xEr_yPO_4$ in visible and IR spectrum ranges at excitation by the IR-radiating laser with different wavelengths.

X	Relative brightness of a seen luminescence, %		IR-luminescence							
	Laser 965 nm	Laser 975nm	Range 0.97-1.02 mcm				Range 1.5-1.6 mcm			
			Laser 965 nm		Laser 975nm		Laser 965 nm		Laser 975nm	
			λ_{max}, nm	I, %	λ_{max}, nm	I, %	λ_{max}, nm	I, %	λ_{max}, nm	I, %
0	100	100	1002	100	1002	100	1506	100	1506	100
0.0001	99	98	1002	100	1002	100	1506	103	1506	102
0.001	95	91	1002	95	1002	96	1506	107	1506	105
0.005	33	27	1002	75	1002	78	1506	115	1506	110
0.010	21	16	1002	62	1002	65	1506	116	1506	118
0.025	10	9	1002	53	1002	57	1506	106	1506	107
0.05	4	3	1002	44	1002	48	1506	102	1506	103
0.075	2	0	1002	39	1002	41	1506	99	1506	99
0.10	0	0	1002	35	1002	37	1506	93	1506	91
0.25	0	0	1002	21	1002	25	1506	57	1506	65

Such character of the brightness visible antiStokses luminescences dependence at IR-excitation from the Ce^{3+} concentration, can be caused first of all reduction of the level $^4I_{11/2}$ population for the following reason. According to the known scheme [2] the population of the excited levels $^2H_{11/2}$ and $^4S_{3/2}$ in $YbPO_4$: Er at excitation by IR-radiation of a range 0,90 -0,98 microns directly depend on population of level $^4I_{11/2}$ which is initial at the second stage of process of the summation electronic exitations. The specified interrelation gives the basis to believe, that any change of the level's $^4I_{11/2}$ population should lead to practically similar changes of the levels $^2H_{11/2}$ and $^4S_{3/2}$ population, and as consequence, to the same changes the intensity of the visible strips of radiation in the field of 0,520 -0,535 microns (transition $^2H_{11/2}\rightarrow{}^4I_{15/2}$) and 0,545 -0,560 microns (transition $^4S_{3/2}\rightarrow{}^4I_{15/2}$) which, basically and define the brightness of a visible luminescence $Yb_{1-x-y}Ce_xEr_yPO_4$ at IR-excitation. The reduction of the level's $^4I_{11/2}$ population in $YbPO_4$:Er at the Ce^{3+} introduction it is possible to explain influence interionic non radiating cross – relaxating transition $^4I_{11/2}$ (Er^{3+}), $^2F_{5/2}$ (Ce^{3+}) → $^4I_{13/2}$ (Er^{3+}), $^2F_{7/2}$ (Ce^{3+}), providing at excitation by range radiation 0,90 -0,98 microns essential increase of the relaxation $^4I_{11/2}\rightarrow{}^4I_{13/2}$ process speed. As, the intercentre

multiphonon relaxation $^4I_{11/2} \rightarrow {}^4I_{13/2}$ is the basic mechanism of settling of level $^4I_{13/2}$ [3], the increase in speed of this process should be accompanied, besides suppression visible antiStokses luminescences, also reduction Stokses IR-luminescences in the field of 0.97-1.03 microns (transition $^4I_{11/2} \rightarrow {}^4I_{15/2}$) and intensity increase Stokses IR-luminescences in area 1.5-1.6 microns (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$). We will consider further as these assumptions will be co-ordinated with experimental data.

The introduction of Ce^{3+} ions into $YbPO_4$:Er leads to intensity reduction Stokses of the IR-luminescence in area 0.97-1.03 microns according to the results presented in the table. Hence this part of experimental results completely confirms the come out assumptions.

The analysis of the results of measurements presented in the table has allowed to establish, that Ce^{3+} ions depending on their quantitative maintenance in $YbPO_4$:Er can act in a sensitizer or quencher role Stokses IR-luminescences in area 1,5-1,6 microns.

At small concentration ($0 \le x \le 1*10^{-2}$) the increase in the maintenance of ions Ce^{3+}, in the specified limits is accompanied by intensity increase Stokses IR-luminescences in area 1,5-1,6 microns which reaches the maximum value at $x=1*10^{-2}$. Thus reduction of relative brightness visible antiStokses luminescences is simultaneously observed. The visible luminescence is insignificant for IR-phosphor with optimum structure $Yb_{0.98}Er_{0.01}Ce_{0.01}PO_4$, and with the maximum intensity IR-luminescences in area 1,5-1,6 microns. Thus, in the above-stated range of concentration the Ce^{3+} ions are carried out by two functions: a role of a selective sensitizer Stokses IR-luminescences in area 1,5-1,6 microns and a quencher visible luminescences. Hence, the received results allow to draw the conclusion important for practical purposes, that co activation $YbPO_4$: Er ions Ce^{3+} in certain concentration limits allows to solve successfully a problem of creation the new "invisible" IR-phosphor on a ytterbium orthophosphate basis with the raised intensity of the IR-luminescence in area 1,5-1,6 microns. From the received data also follows, that coactivation of the $YbPO_4$:Er by Ce^{3+} ions can be used in practice as a way of the directed and reproduced reception IR-phosphors with an adjustable parity of the intensity antiStokses and Stokses strips of the Er^{3+}.radiation.

At the maintenance of ions Ce^{3+} in firm solutions $Yb_{1-x-y}Ce_xEr_yPO_4$ above optimum ($x > 1*10^{-2}$) it is observed both reduction Stokses IR-luminescences in area 1,5-1,6 and the further intensites decrease all other strips radiations. Hence, at enough high concentration ions Ce^{3+} act already only in a role of an effective quencher for all strips of the ion's Er^{3+} luminescence.

The conclusion

For the first time it is established, that coactivation of the $YbPO_4$:Er by Ce^{3+} allows at excitation by laser radiation (0.90-0.98 microns) simultaneously to suppress visible antiStokses a luminescence and to raise Stokses the IR-luminescence in area 1,5-1,6 microns. The found out effect is used for creation new "invisible" IR-phosphor on a **ytterbium orthophosphate** basis, possessing the raised efficiency Stokses IR-luminescences at 1,5-1,6 microns.

The literature

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