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BLUE AND GREEN UPCONVERSION IN Er^{3+}-DOPED FLUOROINDATE GLASSES

R.Reiche*, L.A.O.Nunes, C.C.Carvalho, Y.Messaddeq and M.A.Aegerter
Instituto de Física e Química de São Carlos,
Universidade de São Paulo,
13560-970 São Carlos (SP), Brasil.

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The upconversion properties of Er^{3+} in fluoroindate bulk glasses (composition: $40InF_3$-$20ZnF_2$-$16BaF_2$-$(20-x)SrF_2$-$2GaF_3$-$2NaF$-$xErF_3$ with x=1,2,3 and 4 mole %) are investigated, following $^4F_{9/2}$ excitation with a red krypton laser. A strong green and a weaker blue luminescence is observed at room temperature corresponding to emissions from the thermally coupled $^4S_{3/2}$ and $^2H_{11/2}$ bands and the $^2H_{9/2}$ level respectively. Resonant energy transfer processes involving two excited erbium ions and a two-step absorption process are proposed to explain the upconversion phenomena. The emission intensities depend on the excitation power as P_{exc}^n with $1.5 \leq n \leq 1.7$ for the green and $1.6 \leq n \leq 1.9$ for the blue emission. The decay times and the relative intensities of the luminescences are also studied as a function of Er^{3+} concentration.

1. Introduction

Rare Earth doped Heavy-metal Fluoride glasses have a great potencial use in the laser and optical-fiber communications industries. The spectroscopic and fluorescent properties of fluoro zirconate glasses doped with erbium have been first reported by Reisfeld et al[1] and Shinn et al[2] and were found in good agreement with theoretical calculations upconversion due to the incorporation of rare-earth ions such as Er^{3+}, Ho^{3+}, Tm^{3+}, Pr^{3+} and Nd^{3+} into suitable glass hosts has been widely reported[3-12]. This phenomenon provides the possibi-lity of producing potentially attractive short-wavelength sources which can be pumped by near infrared light such as upconversion lasers and infrared light detectors.

In order to design a glass material with high upconversion efficiency the first step is the selection of a glass matrix with low non-radiative losses due to multiphonon relaxation. Oxide glasses as fluorescent hosts are not preferred because of their high phonon energy of more than 1000 cm^{-1} [4]. Reports on fluoride glasses[4,5] showed that the maximum phonon energy of these materials is lower than most oxide glasses[16,17]. They are therefore more favourable for upconversion processes than silica glasses[3,8,9] allowing the observation of a far greater upconversion efficiency via energy transfer. After choosing a glass host, the concentration of rare-earth ions required for optimum upconversion efficiency must be determined.

In this paper, we report on upconversion fluorescence of Er^{3+} in a new fluoride glass family of composition $40InF_3$-$20ZnF_2$-$16BaF_2$-$(20-x)SrF_2$-$2GaF_3$-$2NaF$-$xErF_3$, called hereafter IZBSGaNEr pumped by a red krypton laser at 647 nm. Samples with x=1,2,3 and 4 mole % of Er^{3+} are considered. The decay times and the relative intensities of the luminescences are also reported.

2. Experimental

Starting materials for the sample preparation were In_2O_3 and Ga_2O_3 from Preussag, Er_2O_3 from Fluka, SrF_2 and BaF_2 from B.D.H., and NaF from Aldrich. The oxides were fluorinated at 400°C in a platinum crucible with NH_4F,HF. The mixture of the desired composition (table 1) was then heated to T≈700°C for melting and 800°C for fining in a dry box under argon atmosphere. After the fining process, the melt was poured into a preheated brass mould (T≈290°C). The glasses had a mass density of about 5 g/cm^3. The average size of the glass samples having been under investigation was 5x9x14 mm^3 after mechanical polishing.

* Present address: Dresden University of Technology, Germany.

Table 1. Composition of the glasses

Batch	Composition (mole %)						
	InF_3	ZnF_2	BaF_2	SrF_2	GaF_3	NaF	ErF_3
1	40	20	16	19	2	2	1
2	40	20	16	18	2	2	2
3	40	20	16	17	2	2	3
4	40	20	16	16	2	2	4

Absorption spectra were obtained with a CARY 17 spectrophotometer (spectral bandwidth 0.1 nm). Upconversion lumines-cence was excited by a krypton laser (647.1 nm) and analysed by a SPEX 1403 double monochromator equipped with a RGA 31034 photomultiplier connected to a PAR-128A lock-in amplifier. Conventional fluorescences were excited by a XBA-450 W OSRAM xenon arc lamp coupled to a 25 cm ORIEL monochromator and with a krypton laser (330.0 nm). The emission was analysed by a 50 cm Jarrell-Ash monochromator. The signal was detected by an IFW 130 photomultiplier and processed with a PAR-124A lock-in amplifier. Fluorescent decay times were measured by time resolution spectros-copy. The pulse light used was a third harmonic of a Quanta Ray Nd: YAG laser; the typical characteristics of this laser are 5 kW peak power, pulse duration of 5 ns and repetition rate of 10 Hz. The complete rejection of the laser radiation was done by employing colour filters.

3.Upconversion

Threefold upconversion to the $^4S_{3/2}$ level of Er^{3+} incorporated in several fluoride glass fibers using a absorption (ESA)[14], this energy transfer process may also populate the ^4G_J manifold. Two excited erbium ions, one in the $^4F_{9/2}$ and the other one in the $^4I_{9/2}$ state, are necessary for promoting one ion to the $^2K_{15/2}$ state. After this or the ESA process, the excited erbium ion decays into the $^2H_{9/2}$ blue upconversion level resulting in emission of 407 nm photons while relaxing into the $^4I_{15/2}$ ground state.

The processes that lead to the green upconversion are ESA and PET as well (fig.1c). As described above the metastable $^4I_{9/2}$ and $^4I_{11/2}$ levels can be populated by a red photon. However, non-radiative decay also occurs from the excited $^4F_{9/2}$ state to the $^4I_{13/2}$ level. This state can be further excited by the pump wavelength to the $^4F_{5/2}$ state. The energy transfer process mentioned above involves either two ions being excited to the metastable $^4I_{11/2}$ level or individual ions in both the $^4I_{9/2}$ and $^4I_{11/2}$ states. Two neighbouring ions interact with each other in such a way that through energy transfer the acceptor is promoted to the $^4F_{7/2}$ or to the $^4F_{3/2}$ level respectively, while the donor ion returns to the ground state. For this process to be effective, the excited ions must be sufficiently close to one another. Therefore the

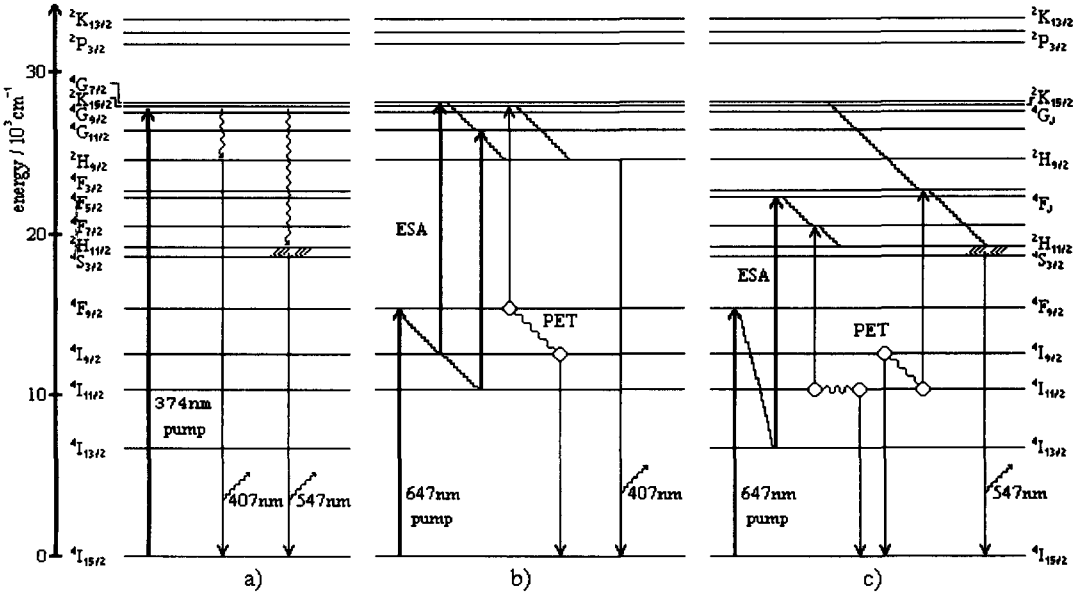

Fig.1. a) Energy levels of Er^{3+}, absorption and luminescence transitions.
b) Blue (407 nm) upconversion process.
c) Green (547 nm) upconversion process.

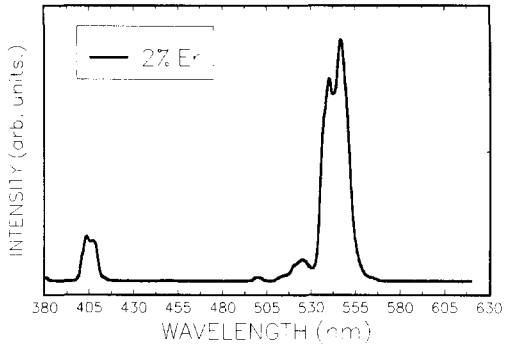

Fig.2. Typical green and blue fluorescences of IZBSGaN doped with 2 mole% Er measured at 300 K.

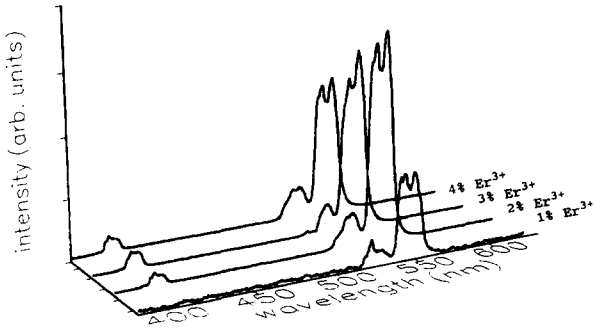

Fig.3. Upconversion spectra of IZBSGaNEr glasses measured at 300 K. Excitation: krypton laser, 647.1 nm, 500 mW.

process rate and fluorescent decay times will depend on the doping concentration[13]. From the ^4F_J manifold the ions may branch into the thermally coupled bands $^2H_{11/2}$ and $^4S_{3/2}$. In addition to this, non-radiative decays from the ^4G_J manifold will also populate the green emission levels. Finally, the erbium ions having been excited this way emit green light at about 547 nm and 526 nm.

The blue upconversion emission is weaker than the green one. As the PET process is of second order, the blue emission profits mainly from the two-step absorption process. Yet the upper blue level converts only part of the energy provided by ESA into a blue emission, and the main part is fed to the green upconversion bands. As the Er^{3+} concentration rises, the PET process contributes even more strongly to the population of the emission levels.

4.Dependence on Er^{3+} concentration

Four samples with 1,2,3 and 4 mole % Er^{3+} concentration have been considered (table 1). Figure 3 shows the upconversion spectra. Green emission is observed for each sample. A summary of the results of the relative intensities of the green and the blue luminescence and of various fluorescent decay time measurements is listed in table 2.

The fluorescence measurement for which an example is shown in figure 2 confirm the assignment of the green upconversion to the transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ as the shape and the wavelength location are identical. For confirmation of the suggested blue upconversion $^2H_{9/2}\rightarrow{}^4I_{15/2}$ transition we used a krypton laser at 330.0 nm. The samples provided a blue response identical to that of the blue upconversion luminescence (fig.2).

The dependence of the fluorescent lifetimes on Er^{3+} concentration of the red and green luminescence is similar. They all decrease as the Er^{3+} concentration increases, indicating Er-Er cooperative effects. The decay time of the blue emission was found practically independent of it. It is worthwhile to note the very short lifetime

Table 2.
(1) Relative intensity of upconversion's most intensive line at 550 nm, $I_x/I_{2\%}$ (2% = 1.0); excitation: red krypton laser, 647.1 nm, 500 mW.
(2) Relative intensity of fluorescence at emission peak (550 nm), $I_x/I_{2\%}$ (2% = 1.0); excitation: xenon arc lamp, 374 nm.
(3) Upconversion intensity ratio of the blue to the green emission, I_{blue}/I_{green}; excitation: red krypton laser, 647.1 nm, 500 mW.
(4) Fluorescent decay times τ in μs; excitation: 5ns-pulsed Nd laser, 355 nm.

Type of measurement	Er^{3+} concentration x (mole %) 1	2	3	4
(1) $I_x/I_{2\%}$ upconversion	0.45	1.00	0.94	0.74
(2) $I_x/I_{2\%}$ fluorescence	0.72	1.00	0.69	0.66
(3) I_{blue}/I_{green}	-	0.06	0.09	0.11
(4) τ_{blue} (μs) [$^2H_{9/2}$]	19	15	20	16
τ_{green}(μs) [$^4S_{3/2}$]	573	185	86	84
τ_{red} (μs) [$^4F_{9/2}$]	645	407	302	349
τ_{IR} (μs) [$^4I_{11/2}$]	-	10634	9839	9412

of the blue emission and the increase of the lifetime in the order of blue, green and red. Except for the green $^4S_{3/2}$ emission, all the decay times observed at 300 K for 2% Er doping are longer than those reported in references 1 and 2. A study of their temperature variation is presently underway and will be reported elsewhere.

The intensity of the green emission is strongest in sample doped with 2 mole % Er^{3+}; above this value it seems to saturate and/or decay. The saturation effect for samples with higher Er^{3+} concentration is also apparent from the results of the lifetime measurements. On the other hand, the intensity of the blue fluorescence was found practically constant in samples with 2%, 3% and 4% Er^{3+}, but no signal was observed with 1% Er^{3+} doping. Similar results have been observed by Reisfeld and Eckstein[19] in Er^{3+} doped tellurite glasses. Therefore the blue upconversion process depends strongly on Er^{3+} concentration below ≈1.5 mole % Er^{3+}, and from two per cent on, the fluorescence signal is saturated.

The dependence of upconversion on the incident pump power was studied using a krypton laser emitting 647.1 nm. We measured the upconversion at 408 nm and 544 nm under a pump power range of 100 to 1000 mW (fig.4). As expected from the proposed nature of the upconversion process, the dependence of the output intensity as a function of the input power varies as P_{exc}^n with $1.5 \leq n \leq 1.9$ depending on the Er^{3+} concentration. Strictly speaking, the output intensity of the green upconversion emission changed with increasing Er^{3+} concen-tration from $P_{exc}^{1.7}$ to $P_{exc}^{1.5}$, whereas the output intensity of the blue emission changes from $P_{exc}^{1.9}$ to $P_{exc}^{1.6}$. This result underlines the rising contribution of the PET process to the blue and green upconversion fluorescence as the Er^{3+} concentration increases, with a stronger influence of energy transfer processes on the green emission. Reasons for the deviation from a quadratic dependence, as it would be expected for a two-photon process[15], are the sharp focus of the pump beam on the sample and the excitation of several long-lived intermediate levels such as the $^4I_{11/2}$[6]. Measurements of upconversion at 407 nm and 550 nm in the same pump power range showed the same dependence.

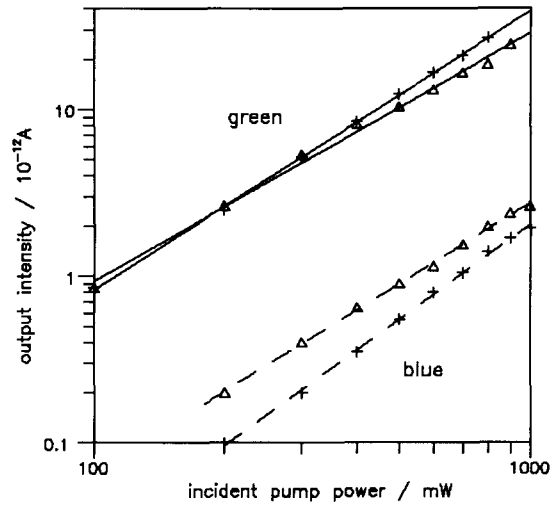

Fig.4. Output intensity as a function of pump power for IZBSGaNEr glasses measured at 300 K. Excitation: krypton laser, 647.1 nm.

5.Conclusion

The absorption, luminescence and fluorescent decay times of Er^{3+} in a new fluoroindate glass family (IZBSGaN) have been reported. Excitation by photons provided by a red krypton laser resulted in broad upconversion emissions around 407 nm and 547 nm at room temperature. Models involving sequential doubly resonant photon absorption (ESA) and cross-relaxation processes (PET) are suggested to explain the upconversion processes. Glass doped with 2% Er^{3+} showed the most efficient upconversion for green emission. The blue upconversion fluorescence was found practically independent on Er^{3+} concentration. The dependence of the green upconversion emission intensity on the pump intensity varies as P_{exc}^n with $1.5 \leq n \leq 1.7$, but its relative intensity decreases with in-creasing Er^{3+} concentration. The blue upconversion intensity changes its dependence on the excitation power from $P_{exc}^{1.9}$ to $P_{exc}^{1.6}$ with increasing Er^{3+} concentration. These behaviours are qualitatively discussed in terms of ESA and PET processes. This new material appears very promising for developing optical devices, such as a green upcon-version laser.

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