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# Saturation effects in the upconversion efficiency of Er-doped fluorozirconate glasses

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## Abstract

A series of transparent erbium-doped fluorozirconate glasses has been investigated using differential scanning calorimetry, optical absorption, and upconverted fluorescence spectroscopy. The upconverted fluorescence intensity versus excitation power dependence shows that the ratio of the two-photon upconverted emission in the near infrared at 980 nm to the three-photon upconverted emissions in the visible at 530, 550, and 660 nm decreases with increasing excitation power. The integrated upconverted fluorescence intensity to excitation power ratio shows 'saturation' with increasing excitation power, while the point of saturation shifts to lower excitation power with increasing erbium concentration. The experimental lifetime of the upconverted fluorescence decreases with increasing erbium concentration.

## 1. Introduction

Low-phonon energy glasses are desirable hosts for rare-earth (RE) ions such as Er<sup>3+</sup> because they enable emission from RE energy levels that would be quenched in high-phonon energy glasses [1]. Upconversion occurs when the active RE ion is optically excited to emit visible light by the sequential absorption of two low-energy infrared photons. Of particular importance to the upconversion efficiency is the intermediate level lifetime of the RE ion, which depends on the phonon frequency of the host material and the concentration of the active RE ions. Such emissions are not only of interest for upconversion lasers but also for photovoltaic applications. Mono-gap solar cells like commercial silicon solar cells are unable to use the whole solar spectrum. In particular, photons with energy lower than the bandgap energy cannot be absorbed.

Er<sup>3+</sup>-doped materials, which convert two or more sub-bandgap photons into photons with an energy higher than the bandgap energy, are thus of great interest. Trupke *et al* [2] estimated that the efficiency of bifacial solar cells could be vastly improved by such an upconverting back layer. Several corresponding experiments where the external quantum efficiency (EQE) was measured for monochromatic excitation of Er<sup>3+</sup> around 1540 nm have been performed previously [3–5].

Fluorozirconate (FZ) glasses are characterized by low-phonon energies [6], a critical parameter leading to reduced non-radiative losses and increased upconversion efficiencies. In our previous work [7] we investigated the EQE of a relatively simple setup consisting of an Er<sup>3+</sup>-doped FZ upconversion glass on the top of a monocrystalline silicon solar cell. The results showed that a relatively moderate Er<sup>3+</sup> concentration of 9.1 mol% leads to an EQE of almost 1.6%. As stated above, the RE concentration has a significant influence on the upconversion efficiency. In this paper, an in depth study

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**Table 1.** Nominal composition (in mol%) and glass transition temperature (in °C) of the Er<sup>3+</sup>-doped FZ glasses.

No.	ZrF <sub>4</sub>	BaF <sub>2</sub>	NaF	LaF <sub>3</sub>	AlF <sub>3</sub>	InF <sub>3</sub>	ErF <sub>3</sub>	T <sub>g</sub>
1	51	20	20	3.5	3	0.5	2	268
2	48	20	20	3.5	3	0.5	5	275
3	48.2	18.2	18.2	3.2	2.7	0.5	9.1	290
4	46.1	17.4	17.4	3	2.6	0.4	13	290

of the influence of the Er<sup>3+</sup> concentration on the upconversion efficiency of FZ glasses is conducted.

## 2. Experiment

The Er<sup>3+</sup>-doped FZ glasses investigated are based on the well-known ZBLAN composition [8]. The nominal compositions of the glasses are summarized in table 1. For the 2 and 5 mol% doped samples, the ErF<sub>3</sub>-doping was done at the expense of ZrF<sub>4</sub> while for 9.1 and 13 mol% doping, the addition of ErF<sub>3</sub> is compensated by reducing the other components proportionally. The constituent chemicals were weighed in a platinum crucible in an inert atmosphere of nitrogen and melted at 750 °C for 1 h. The melt was poured into a brass mould that was at a temperature of 200 °C, i.e. below the glass transition temperature of approximately 260 °C for an FZ-based glass [8], before being slowly cooled to room temperature. The visible appearance of the glass is clear but it has a pink tinge due to the erbium starting material. The samples were cut into 7 mm × 7 mm plates and polished simultaneously by an identical process to a thickness of 2 mm and a surface roughness of about 3 μm.

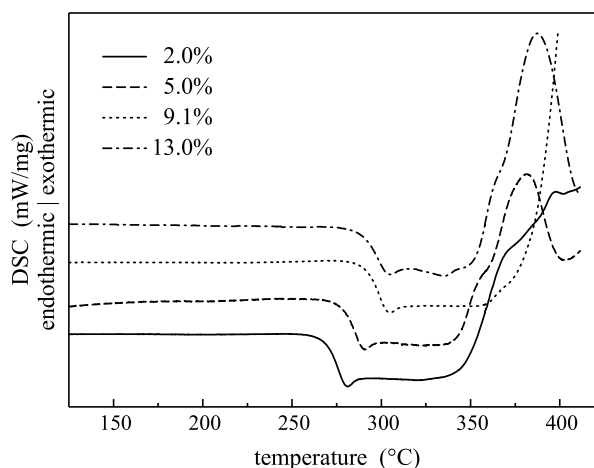
Differential scanning calorimetry (DSC) measurements were performed with a DSC 204 F1 Phoenix instrument (Netzsch).

The transmission spectra were recorded with a commercial UV–VIS–NIR absorption spectrometer.

For fluorescence measurements a monochromator with 0.32 m focal length (Horiba Jobin Yvon iHR320) was used. The excitation for upconverted fluorescence was carried out with a continuous wave (cw) infrared laser diode operating at 1540 nm (Anritsu GB5A016); the laser beam was focused with a lens down to several tens of micrometres. The upconverted fluorescence was detected in the visible and the near infrared range with a high-speed silicon detector (Thorlabs DET36A) in reflection mode using a lock-in technique with a modulation frequency of <10 Hz. The spectra have been corrected for the sensitivity of the detector, but not for the transfer function of the monochromator.

For the power dependence measurements of the upconverted fluorescence intensities a power meter (Thorlabs PM300E) with an InGaAs sensor (Thorlabs S144A) was used to measure the excitation power.

For the time-resolved fluorescence measurements the infrared laser diode was switched on and off with a square wave signal from a generator (Rhode & Schwarz AFS); the repetition frequency was set at 5 Hz. The upconversion signal was detected with a photomultiplier (Hamamatsu R2658P) and recorded with a digital oscilloscope (Tektronix TDS 2022B).



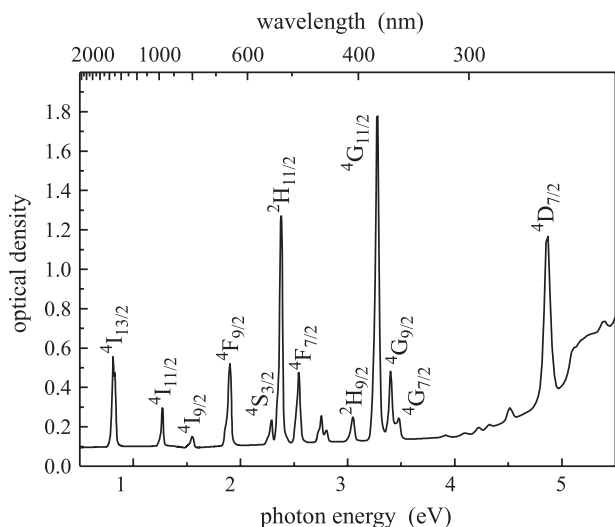
**Figure 1.** DSC data for 2, 5, 9.1, and 13 mol% Er-doped FZ glasses. The curves are vertically displaced for clarity.

## 3. Results and discussion

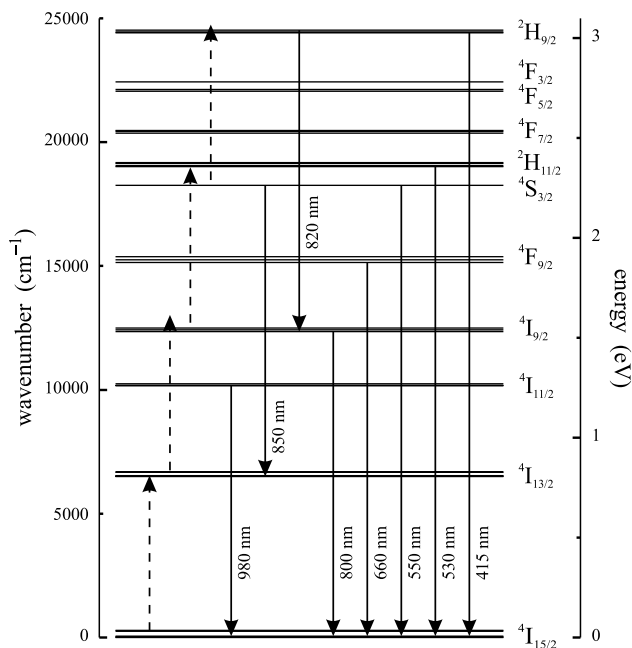
Figure 1 shows the DSC data for the Er-doped FZ glasses. For the 2 mol% Er-doped sample the glass transition temperature is at 268 °C, in good agreement with that observed in a pure FZ glass [8]. Increasing the Er<sup>3+</sup> concentration from 5 to 9.1 mol% and then to 13 mol% leads to a significant shift in the glass transition temperature from 275 °C for 5 mol% to 290 °C for both the 9.1 and 13 mol% samples. For all DSC measurements the experimental uncertainty is ±1 °C. Looking closely at table 1, the most significant change in composition going from 2 to 13 mol% is in the amount of ErF<sub>3</sub>. Although there is an overall drop in the level of ZrF<sub>4</sub>, this is insignificant between the 5 mol% and the 9.1 mol% sample, as it is for all other chemicals besides ErF<sub>3</sub>, yet there is still a significant change in T<sub>g</sub> between these two samples. In synthesizing the samples, it becomes increasingly difficult to incorporate higher levels of ErF<sub>3</sub>, which is obvious from the appearance of the glass. At higher levels of Er-doping, the glass becomes milky, indicating partial crystallization. It is likely that somewhere in the region between 9.1 and 13 mol% ErF<sub>3</sub> incorporation the glass becomes saturated with Er so that T<sub>g</sub> does not change further. To test this hypothesis, sample synthesis is planned to attempt an even higher incorporation of ErF<sub>3</sub>, nominally 20 mol% along with chemical analysis (such as inductively coupled plasma mass spectroscopy) of the sample for both anion and cation concentrations. It is known from ion chromatography that a significant amount of fluorine and chlorine is lost but the loss of cations has not yet been measured.

Figure 2 shows the optical density of the 5 mol% Er<sup>3+</sup>-doped FZ sample. As already described in [9, 10] the material has strong Er<sup>3+</sup> absorption at 254, 377, and 520 nm and very weak absorption at 229, 274, and 800 nm. At other wavelengths the absorption strengths are intermediate. In addition to the observed Er<sup>3+</sup> absorption bands, the material shows some background absorption below 300 nm.

The upconversion experiments were carried out with an excitation wavelength of 1540 nm in resonance with the



**Figure 2.** Optical density of the 5 mol% Er<sup>3+</sup>-doped FZ glass sample. The sample thickness was 2.2 mm. The labelled transitions start from the <sup>4</sup>I<sub>15/2</sub> ground state level and end on the levels indicated.

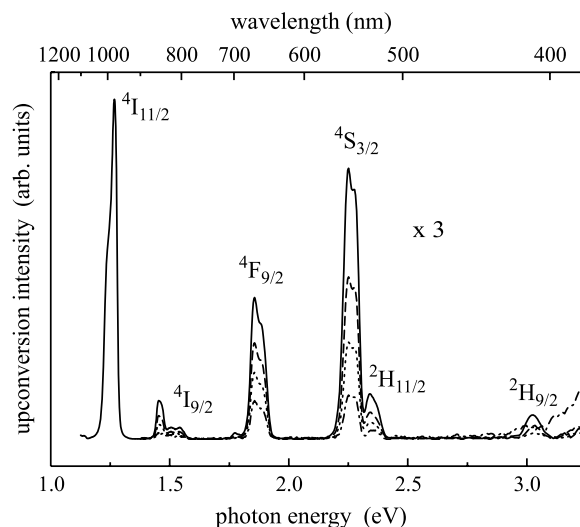


**Figure 3.** Energy level diagram of Er<sup>3+</sup> in FZ glasses. Possible upconversion routes (dashed arrows) and assignments of the main upconverted emissions (solid arrows) are indicated [11, 12].

transition from the <sup>4</sup>I<sub>15/2</sub> ground state to the <sup>4</sup>I<sub>13/2</sub> excited state. Note, that the high Er<sup>3+</sup> concentration and the sample thickness of 2 mm are responsible for the relatively high optical density. Self-absorption of the emitted light by Er<sup>3+</sup> will probably affect the shape of the upconverted fluorescence spectrum.

Figure 3 shows the energy level diagram of Er<sup>3+</sup> in FZ glasses [11, 12]. Possible upconversion routes and assignments of the main upconverted emission bands are also shown.

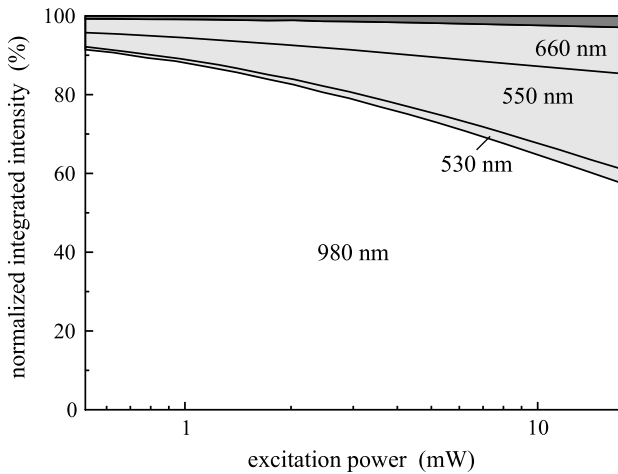
Upon excitation with the light of a cw laser diode operating at 1540 nm the Er<sup>3+</sup>-doped FZ glasses show intense



**Figure 4.** Upconverted fluorescence spectra of the 9.1 mol% Er<sup>3+</sup>-doped FZ glass sample. Excitation is carried out with a cw laser diode operating at 1540 nm with 17.2 (solid curve), 7.8 (dashed), 3.55 (dotted), and 1.15 mW (dash-dotted). The range from 900 down to 400 nm was blown up by a factor of 3. The labelled transitions start from the levels indicated and end on the <sup>4</sup>I<sub>15/2</sub> ground state level. The NIR emission at 850 nm is caused by a transition from the <sup>4</sup>S<sub>3/2</sub> to the <sup>4</sup>I<sub>13/2</sub> state. All spectra have been normalized to the two-photon NIR emission at 980 nm. The intensity increase below 400 nm is caused by the detector correction for the case of low signal-to-noise ratios.

upconverted fluorescence. The corresponding spectra for the 9.1 mol% Er-doped sample in the 400–1100 nm spectral range can be seen in figure 4. Besides the 980 nm emission in the near infrared (NIR) spectral range, the most intense bands in the visible are located in the green (530 and 550 nm) and red spectral range (660 nm). The NIR emission at 980 nm can be attributed to a transition from the <sup>4</sup>I<sub>11/2</sub> excited state to the <sup>4</sup>I<sub>15/2</sub> ground state. The weak 800 nm band arises from the <sup>4</sup>I<sub>9/2</sub> state. The <sup>4</sup>I<sub>9/2</sub> and <sup>4</sup>I<sub>11/2</sub> levels are accessible with two 1540 nm photons; the <sup>4</sup>I<sub>11/2</sub> level via a subsequent non-radiative relaxation from the <sup>4</sup>I<sub>9/2</sub> level. The NIR emissions at 850 nm and 820 nm are caused by a transition from the <sup>4</sup>S<sub>3/2</sub> to the <sup>4</sup>I<sub>13/2</sub> state and a transition from the <sup>2</sup>H<sub>9/2</sub> to the <sup>4</sup>I<sub>9/2</sub> state, respectively [12, 13]. The visible emissions can be attributed to transitions from the <sup>2</sup>H<sub>11/2</sub> (530 nm), <sup>4</sup>S<sub>3/2</sub> (550 nm), and <sup>4</sup>F<sub>9/2</sub> (660 nm) excited states to the <sup>4</sup>I<sub>15/2</sub> ground state. These levels are energetically accessible with three 1540 nm photons. Four-photon upconverted fluorescence can be observed at 415 nm, which arises from a transition from the <sup>2</sup>H<sub>9/2</sub> state to the ground state. All transitions to the <sup>4</sup>I<sub>15/2</sub> ground state are split by about 0.03 eV which is caused by the crystal field splitting of the ground state.

In addition, figure 4 shows that the relative intensity of the upconverted fluorescence bands depends significantly on the excitation power. Upon increasing the excitation power from 1.15 mW (dash-dotted curve) to 17.2 mW (solid) the relative intensity ratio between the two-photon upconverted emission at 530, 550, and 660 nm changes in favour of the three-photon

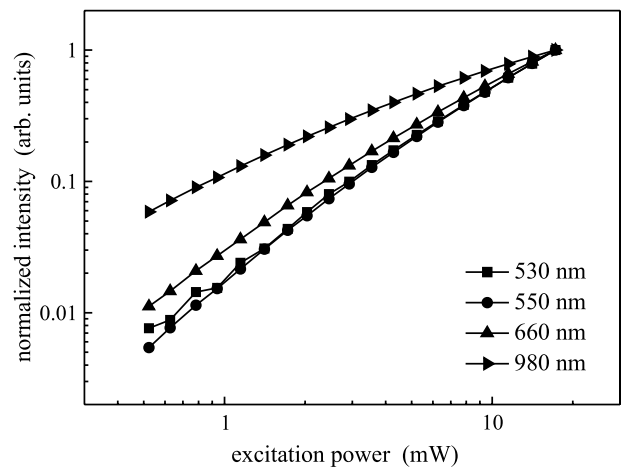


**Figure 5.** Relative contribution of the two-photon upconverted emission at 980 nm (white) and the three-photon upconverted emissions at 530, 550, and 660 nm (light grey) in the 9.1 mol% sample; all other upconverted emissions play only a minor role for the overall upconversion efficiency and are summarized as ‘others’ (dark grey).

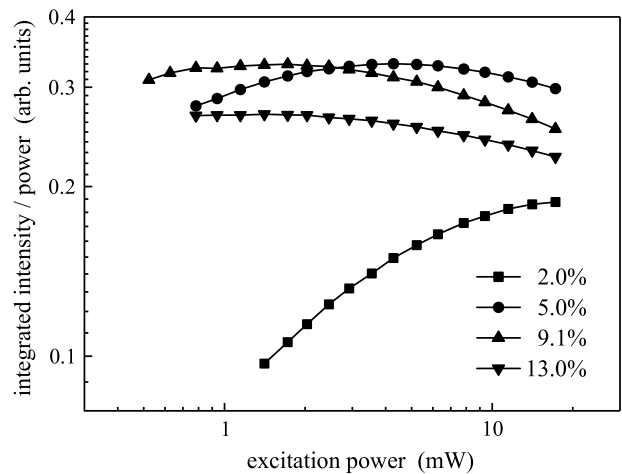
upconversion. Note, that all spectra in figure 4 are normalized to the NIR emission at 980 nm for better comparison.

Figure 5 shows the relative contribution of the different upconverted emissions for the 9.1 mol% Er-doped FZ glass. The main contribution to the overall upconverted fluorescence intensity comes from the two-photon (980 nm) and from the visible three-photon upconverted emissions (530, 550 and 660 nm). All the other emissions play only a minor role; their contribution is summarized as ‘others’. It can be seen that the contribution from the two-photon upconversion decreases significantly upon increasing the excitation power while the contribution of the three-photon upconverted emissions, in particular of the 550 nm band increases: for an excitation power of approximately 0.5 mW, the contribution of the main emissions to the total intensity is 0.7% (530 nm), 3.5% (550 nm), 3.5% (660 nm), and 91.4% (980 nm) while it is 3.6% (530 nm), 24.2% (550 nm), 11.8% (660 nm), and 57.6% (980 nm) for an excitation power of 17 mW. A similar behaviour can be observed for the 2, 5, and 13 mol% ErF<sub>3</sub>-doped glass samples (not shown).

Figure 6 shows the dependence of the normalized emission intensities on the 1540 nm excitation power for the NIR two-photon upconverted fluorescence band at 980 nm and the visible three-photon upconverted fluorescence bands at 530, 550, 660 nm. Fluorescence spectra were recorded over two orders of magnitude of excitation power, e.g. from approx. 17 mW (maximal LD output power) down to a few tenths of a mW. The intensity of upconverted fluorescence that is excited by the sequential absorption of  $n$  photons has a dependence on absorbed excitation power  $P_{exc.}$ , which may range from  $P_{exc.}^n$  in the limit of infinitely small upconversion rates down to  $P_{exc.}^1$  for the upper state and less than  $P_{exc.}^1$  for the intermediate states in the limit of infinitely large upconversion rates [14]. For the two-photon upconverted emission at 980 nm, the average slope is  $n = 0.81 \pm 0.02$  with a decreased slope for higher excitation powers, i.e. the emission intensity is already



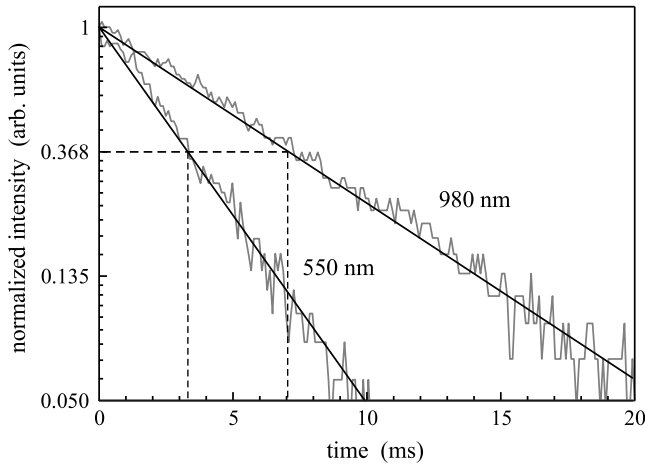
**Figure 6.** Normalized power dependence (in double-logarithmic scale) of the upconverted fluorescence intensities in the 9.1 mol% Er-doped FZ glass sample, recorded at the wavelengths indicated under cw laser diode excitation at 1540 nm. The lines are a guide to the eye.



**Figure 7.** Power dependence of the integrated upconverted fluorescence intensity divided by the excitation power of Er-doped FZ glasses. Excitation is carried out with a cw laser diode operating at 1540 nm.

affected by saturation effects. For the bands at 530, 550, and 660 nm, the average slope is significantly larger, namely  $n = 1.43 \pm 0.02$ ,  $1.49 \pm 0.02$ , and  $1.29 \pm 0.02$ , respectively, but still significantly smaller than ‘3’ as expected for infinitely small upconversion rates. Saturation effects are also clearly noticeable.

Figure 7 shows the power dependence of the integrated upconverted fluorescence intensity normalized to the excitation power. On a double-logarithmic scale, for each of the four curves a ‘saturation’ of the upconversion intensity can be observed. The point of saturation depends critically on the ratio between excitation power, intermediate energy level lifetime, and the relative contribution of excited state absorption (ESA) and energy transfer upconversion (ETU) processes to the overall upconverted fluorescence. The maximal EQE is at more than 10 mW excitation power for the 2 mol% doped sample,



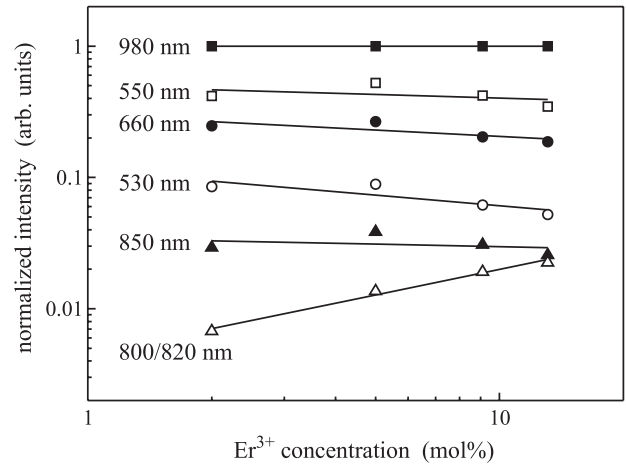
**Figure 8.** Normalized upconverted fluorescence decay in the 13 mol% Er-doped FZ glass sample. The fluorescence was detected at 550 and 980 nm. The excitation was carried out with a cw laser diode at 1540 nm.

**Table 2.** Lifetime of the NIR emission at 980 nm ( ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ ) and the visible emission at 550 nm ( ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ ).

Er <sup>3+</sup> concentration (mol%)	Lifetime (ms)	
	550 nm	980 nm
2	4.7 ± 0.3	8.5 ± 0.5
5	4.1 ± 0.3	8.7 ± 0.5
9.1	3.5 ± 0.3	8.1 ± 0.5
13	3.3 ± 0.3	7.1 ± 0.4

at 4–5 mW for a concentration of 5 mol%, approximately 1–2 mW for the 9.1 mol% sample, and about 0.8 mW (with a trend to even lower values) for the 13 mol% Er-doped glass.

Figure 8 shows the radiative decays of the  ${}^4S_{3/2}$  to  ${}^4I_{15/2}$  (550 nm) and the  ${}^4I_{11/2}$  to  ${}^4I_{15/2}$  (980 nm) transition, recorded for the 13 mol% sample upon optical excitation at 1540 nm. The lifetimes are  $(3.3 \pm 0.3)$  ms and  $(7.1 \pm 0.4)$  ms for the 550 and the 980 nm emission, respectively. The lifetimes depend slightly on the Er<sup>3+</sup> concentration; there is a trend to shorter lifetimes for higher Er<sup>3+</sup> concentration (see table 2). Previous experiments on 1 mol% ErF<sub>3</sub>-doped fluorozirconate and fluorochlorozirconate glasses [15] yielded a radiative lifetime of the  ${}^4S_{3/2}$  to  ${}^4I_{15/2}$  transition (550 nm) of  $(0.37 \pm 0.04)$  ms upon excitation at 380 nm. This value is approximately one order of magnitude smaller than the values observed for the 1540 nm excitation (see table 2). Rubin *et al* [16] attributed this lengthening to energy transfer processes, namely a  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  transition of erbium ion #1 combined with a  ${}^4I_{11/2} \rightarrow {}^4S_{3/2}$  transition of erbium ion #2, which occurs to populate the  ${}^4S_{3/2}$  level via an energy transfer upconversion (ETU) process between two erbium ions. However, a  ${}^4I_{11/2}$ ,  ${}^4I_{11/2} \rightarrow {}^4F_{7/2}$ ,  ${}^4I_{15/2}$  ETU process followed by a non-radiative decay to the  ${}^4S_{3/2}$  level would be a better match. Assuming energy transfer processes between pairs of excited ions it was stated that the depopulation of the  ${}^4S_{3/2}$  energy level is mainly determined by  $N(t) \approx \exp(-2t/\tau)$  (see equation (7) in [16]) with a decay time which is half the decay time of the  ${}^4I_{11/2}$  level. This is in good agreement with the observed lifetimes.



**Figure 9.** Upconverted fluorescence intensity ratio  $I/I_{980 \text{ nm}}$  versus Er<sup>3+</sup> concentration. The upconverted fluorescence was excited at 1540 nm.

The upconverted fluorescence intensity of the different emission bands versus the Er<sup>3+</sup> concentration is plotted in figure 9. For each concentration the intensity is normalized to the most intense emission, i.e. the  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  transition at 980 nm, which is due to a two-photon upconversion process. The slope of the curves gives information on the upconversion mechanisms.

In figure 9 it can be seen that the  $I/I_{980 \text{ nm}}$  ratio of the three-photon upconversion process enabling emissions at 530, 550, 660, and 850 nm does not show a strong dependence on the Er<sup>3+</sup> concentration. These emissions originate from the  ${}^2H_{11/2}$  (530 nm), the  ${}^4S_{3/2}$  (550 and 850 nm), or the  ${}^4F_{9/2}$  level (660 nm). Excited state absorption (ESA) and energy transfer upconversion (ETU) are the most efficient mechanisms to populate the  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$  energy levels. Compared to ESA processes, ETU processes are usually strongly dependent on the dopant concentration, since the interatomic distance determines the dipole–dipole interaction. Since all transitions are normalized to the  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  emission any ETU contributions to upconversion steps from the  ${}^4I_{9/2}$  energy level would result in a positive slope in figure 9 for the three-photon upconversion bands. Since the emissions from the  ${}^2H_{11/2}$  (530 nm), the  ${}^4S_{3/2}$  (550 and 850 nm), or the  ${}^4F_{9/2}$  level (660 nm) do not show a concentration dependence when normalized to the 980 nm emission, it can be assumed that ESA is the most important upconversion process for the  ${}^4I_{9/2}$  to  ${}^2H_{11/2}$  transition; a  $({}^4I_{13/2}; {}^4I_{9/2}) \rightarrow ({}^4I_{15/2}; {}^2H_{11/2})$  ETU process does not play a significant role in populating the  ${}^2H_{11/2}$  level.

The 820 nm band can be attributed to a  ${}^2H_{9/2} \rightarrow {}^4I_{9/2}$  transition, whose excitation requires four photons, i.e. three upconversion steps. However, the intensity of the  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$  emission at 800 nm was comparable to that of the  ${}^2H_{9/2} \rightarrow {}^4I_{9/2}$  transition. Since the two bands are spectrally very close together, they could not be resolved as two separate peaks and the intensity was determined by integrating over both bands. The increased  $I_{800/820 \text{ nm}}/I_{980 \text{ nm}}$  ratio for higher Er<sup>3+</sup> concentrations indicates that the 800/820 nm band has

significant ETU contributions. As the 800 nm band is populated by the same mechanism as the 980 nm band no concentration dependence would be expected for this band. This means that ETU is important for the population of the  $^2H_{9/2}$  level and thus for the four-photon upconversion process.

#### 4. Conclusion

Er-doped ZBLAN shows intense upconverted fluorescence upon excitation with a laser diode operating at 1540 nm. The different emissions can be attributed to different upconversion processes. The emission of the two-photon upconversion is at 980 nm, whereas the three-photon upconversion can be found in the visible spectral range. The ratio of these emissions depends significantly on the excitation power, i.e. the higher the excitation power the lower the contribution of the two-photon upconversion to the integrated intensity. This effect can be attributed to a saturation of the  $^4I_{9/2}$  energy level for high excitation power. This assumption is supported by the power dependence of the upconverted emissions. The slopes of all emissions are quite low, i.e. the NIR as well as the visible upconverted emissions are subject to saturation effects.

The integrated intensity normalized to the excitation power gives initial insight into the upconversion efficiencies of the different systems. For all  $Er^{3+}$  concentrations a maximum is found, which is shifted to lower excitation power for higher concentrations.

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