Upconversion emission obtained in Yb^{3+}-Er^{3+} doped fluoroindate glasses using silica microspheres as focusing lens

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Abstract: An intensity enhancement of the green upconversion emission from a codoped Er^{3+} -Yb^{3+} fluoroindate glass has been obtained by coating the glass surface with silica microspheres (3.8 μm diameter). The microspheres focus an incoming beam (λ ≈950 nm) on the surface of the fluoroindate glass. The green emission (λ ≈545 nm) of the Er^{3+} ions located in the microsphere focus was measured with a microscope in reflection mode, being the peak intensity 4.5 times the emission of the bare substrate. The transversal FWHM of the upconversion spot was experimentally determined by deconvolution with the experimental Point Spread Function of the system, obtaining a value of 309 nm. This value is in good agreement with Finite-Difference Time-Domain simulations taking into account the magnification of the image due to the microsphere.

OCIS codes: (110.0180) Microscopy; (160.2540) Fluorescent and luminescent materials; (350.3950) Micro-optics.

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1. Introduction

In the recent years a wide range of applications have been developed based in the research in dielectric microcavities such as microspheres and microcylinders. Among their known characteristics these systems exhibit high Q factors with narrow resonances [1] making them useful in several kinds of sensing applications [2,3] and microlasers [4].

Furthermore, under certain conditions, they can produce a narrow beam with a waist under the Abbe diffraction limit called photonic nanojet [5]. Experimental measurements of the 3-D intensity profile of a nanojet have been performed by P. Ferrand et al [6]. Their measurements reveal that a 3 μm diameter sphere under plane wave illumination at 520 nm can give rise to a focal spot with Full With at Half Maximum (FWHM) of 270 nm in good agreement with the Finite-Difference Time-Domain (FDTD) simulations.

The application of Photonic nanojets in a variety of fields as biomedicine, imaging, photonics and material science has been studied recently. In the work of Ref [7] several microspheres, arranged linearly as a chain, periodically focus the light, giving place to photonic nanojet induced modes that could be a tool to reach ultra precise laser surgery. Array structures are reported in Ref [8], where triangles and rings of 5, 6 and 7 nodes formed by dye coated microspheres emit in the far field in a similar way as fluorescence molecules. These structures have been called photonic molecules and can be used to manipulate photons in micrometric scale. In reference [9] Wang et al. have enhanced the resolution of a microscope under white light illumination up to 50 nm by locating a microsphere on the surface of a sample. This significant improvement in resolution opens the door to the imaging of virus, DNA and molecules.

On the other hand several studies have been focused on the enhancement of single molecule fluorescence in the vicinity of metal nanoparticles [10,11] and dielectric microspheres [12–14] with applications in biophotonics. Dielectric microspheres have been preferred because although metalic nanostructures are capable of generating strong electromagnetic fields in their vicinity, giving rise to a higher excitation of molecules, they also produce losses due to the quenching of the fluorescence emission.

In Ref [14] Gérard et al. obtained a tiny spot with subwavelength dimensions in both axial and transversal directions by illuminating a 2 μm dielectric microsphere with a tightly focused gaussian beam. Due to the interaction of the microsphere tiny spot and a single fluorescent molecule, they have obtained an enhancement of the fluorescence up to a factor of 2.2, being a key factor the axial confinement of the focal spot that cannot be obtained under plane wave illumination.

Non-linear processes have been studied in Ref [12] where silica microspheres were added to a rhodamine B dye solution. The authors observed a two-photon fluorescent enhancement

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of 30% in presence of microspheres when the sample was illuminated with a focused laser pulse. It has to be noticed that the results correspond to the emission averaged over a large area of the sample, and so the results of the enhancement of a single sphere were not reported.

Among fluorescence materials the choice of glasses doped with Rare Earths (RE) seems to be advantageous since they are efficient emitters that present well known upconversion processes. In upconversion processes two or more photons are sequentially absorbed leading to the emission in a shorter wavelength. From these processes emissions in the infrared, visible and UV can be obtained. The upconversion intensity depends on the n-th power of the excitation intensity, where n is the number of photons involved. In this work a glass doped with Er^{3+} and Yb^{3+} has been covered with silica microspheres with the aim of producing an enhancement of the upconversion intensity in the focal region of each microsphere. The microsphere focus the incident beam in a small region of the sample, producing a gain in the excitation per unit area in the focal region. Furthermore, due to the upconversion process, the sample emits with the nth power of the excitation intensity, optimizing the emission compared, as an example, with fluorophores whose emission has a linear dependence with the excitation intensity. Moreover at low powers fluorophores can suffer from the photobleaching that destroys their fluorescence after some characteristic time. On the contrary glasses doped with RE ions show a luminescence stable in time.

2. Experimental description

The sample was obtained from a precursor Er-Yb codoped glass based on a fluoroindate matrix with the following composition in mol %: $37InF_3$, $20ZnF_2$, $20SrF_2$, $20BaF_2$, $0.75YbF_3$ and $2.25ErF_3$ (see Ref [15] for details). The microspheres (Cospheric Santa Barbara) were diluted in a conical tube and sonicated for 10 minutes to avoid clustering. A drop of the solution was taken with a micropipette and deposited on the sample. Finally, the sample surface was imaged by a microscope to ensure that microspheres were not stacked. A collimated 950 nm beam from a laser diode (L3-MSF03 JDS Uniphase) in continuous mode is collected by a microscope objective (Olympus Plan, NA = 0.9) giving rise to a converging beam which illuminates the sample. In order to calibrate the laser power a thermopile power sensor (Gentec UP19K-15S-H5-DO) was located on the sample's position, setting the laser power to a value of 2 mW. Each microsphere focuses the incident beam in a narrow region of the glass, exciting the Er^{3+}-Yb^{3+} ions, resulting in emissions centered at 545 nm and 660 nm due to upconversion processes. The light emitted by the sample re-enters the microscope objective and is focused by a lens in a CCD camera (ATK-16HR). Suitable filters (shortPass 600 nm FES0600 Thorlabs and shortPass 800 nm NT64-325 Edmundoptics) have been located before the CCD to select the green upconversion emission. The experimental set-up is shown in detail in Fig. 1. The PSF of the system has been measured using as point sources Tm^{3+}-Yb^{3+} doped SrF_2 nanoparticles with sizes below 8 nm diluted in distilled water. The procedure employed to avoid the formation of aggregates in the preparation of this sample is similar to the one described in the protocol of Ref [16]. Under excitation at 950 nm in the same experimental setup it is possible to detect upconversion emission from the individual nanoparticles at 480 nm. Fitting the measured emission spot to a gaussian distribution, a value of 350 nm for the transversal FWHM of the system PSF has been obtained.

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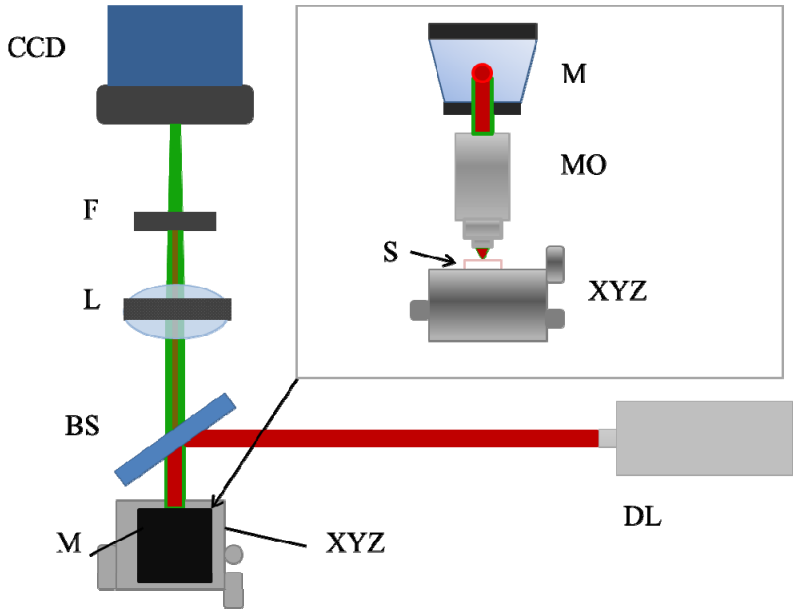

Fig. 1. Top view of the experimental setup. DL. Diode Laser, M. Mirror, XYZ. Three axis translation stage, BS. Beamsplitter, L. Lens, F. Filter and CCD. CCD detector. In the inset shows the front view of the ensemble designated by the arrow. S. sample and MO. Microscope objective.

3. Results and discussion

An image of an arrangement of five microspheres above the flat surface of an Er^{3+}-Yb^{3+} codoped fluoroindate glass is shown in Fig. 2(a) and a 3-D representation of the intensity distribution of the green emission in Fig. 2(b). It can be observed that an intensity enhancement due to the upconversion emission has been obtained compared to the emission of the bare substrate. The intensity gain, defined as the ratio of the maximum intensity and the mean value of the emission from the substrate, was calculated obtaining a value of 4.5.

The microspheres focus the incoming beam affecting the emission from the substrate in the area covered by each microsphere. On the one hand, the black region of the image in Fig. 2(a) is related to the fact that the microsphere concentrates the incoming light in a small region surrounding the contact point with the glass. Consequently there is a reduction of the excitation and the emission near the microspheres borders (as can be seen in Fig. 2(b)). This shadowing behaves as a mask effect to the luminescence of the substrate. On the other hand, in the contact point of the silica microspheres, the emission coming from the ions in the glass is enhanced due to the focusing of the incident excitation light.

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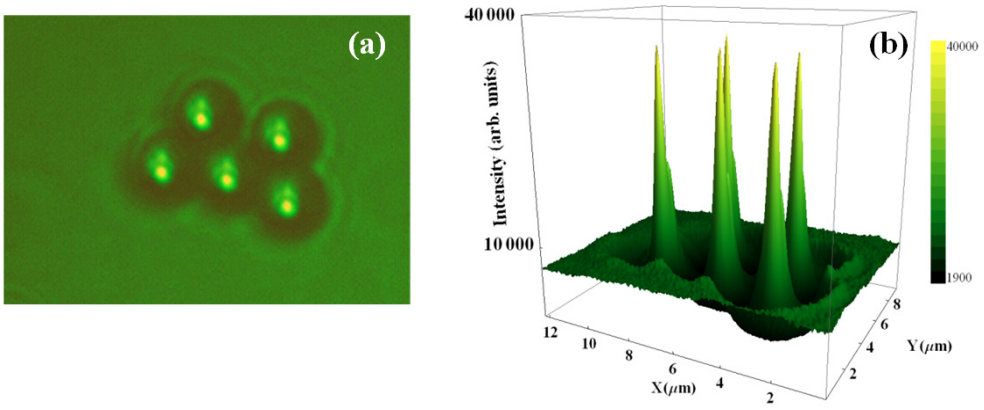

Fig. 2. (a) Left: Green upconversion emission of five microspheres located above an Er^{3+}-Yb^{3+} codoped fluoroindate glass. (b) Right: 3D graph of the spatial intensity distribution of the green upconversion intensity corresponding to the left image.

In order to know the characteristic of this emission, the emission spectrum of a bulk fluoroindate glass codoped with Er^{3+}-Yb^{3+} has been measured under excitation at 950 nm as it is shown in Fig. 3. The spectrum has been obtained selecting a region without microspheres. The main emission bands due to Er^{3+} electronic transitions are centered in the green at 545 nm ($^4S_{3/2}$ ($^2H_{11/2}$)→ $^4I_{15/2}$) and in the red at 660 nm ($^4F_{9/2}$ → $^4I_{15/2}$). These emissions are supported by the Excited State Absorption (ESA) of the Er^{3+} ion and/or the Energy Transfer (ET) processes from the $^2F_{5/2}$ level of the Yb^{3+} ion, resonant with the $^4I_{11/2}$ level of Er^{3+} ion as it is shown in the diagram of the inset of Fig. 3. By choosing a proper filter the 545 nm green emission has been selected.

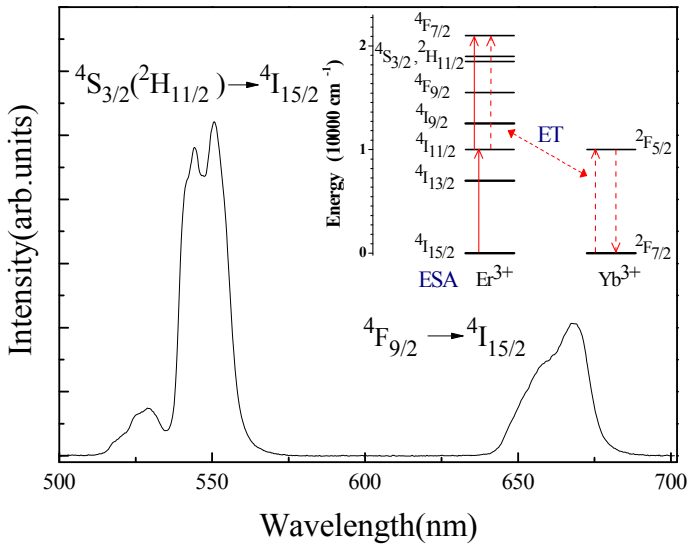

Fig. 3. Upconversion emission spectrum of a Er^{3+}-Yb^{3+} codoped fluoroindate glass sample under excitation at 950 nm. Inset: Diagram energy levels of Er^{3+} and Yb^{3+} ions detailing ESA and ET upconversion process.

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As a previous step to the measurements it has been checked if the presence of the silica microspheres has affected the dynamics of the upconverted green emission. Following this purpose the pump power dependence of the upconverted green band has been measured inside and outside a microsphere (directly from the sample surface). The measurements were performed by taking images at different pumping powers. The current of the laser diode was changed to modulate the pumping intensity which was again calibrated using the thermopile meter to ensure a proper sampling. In Fig. 4 the results obtained for the intensity of the emission band centered at 545 nm Er^{3+} are shown in a double-log scale. It can be seen that the intensities collected inside the microsphere (squares) are higher than the values obtained from the surface emission (circles). A mean increment about a factor 4.5 has been obtained. As it is known the upconversion emission intensity I_{UP} will be proportional to the nth power of the IR excitation intensity I_{IR}, i.e. $I_{UP} \propto I_{IR}^{n}$, where n is the number of IR photons absorbed per visible photon emitted. In a double log scale the dependence of the intensity upconversion with the power pump appears linear. The slopes of the two data sets obtained by linear fitting are 1.71 and 1.61 for the data collected inside and outside of the microsphere respectively. Both slopes approximate to the theoretical value 2. In Ref [15], similar slopes have been obtained in upconversion processes in fluoroindate glasses doped only with Er^{3+} ions. In this reference, ESA and ET are the proposed mechanisms to produce green emission in bulk samples. As was explained in Ref [17] the nth power dependence of the intensity in the upconversion processes usually decreases when the upconversion rate is efficient. Moreover, the laser beam profile does not affect the intensity dependence of Fig. 4 for ET or ESA mechanism (see Ref [17] for details). This allows to conclude that in both cases the emission is due to a two-photon upconversion mechanism. This result demonstrates that the microsphere does not change the dynamics of the green emission in the glass, being the only difference a higher IR excitation.

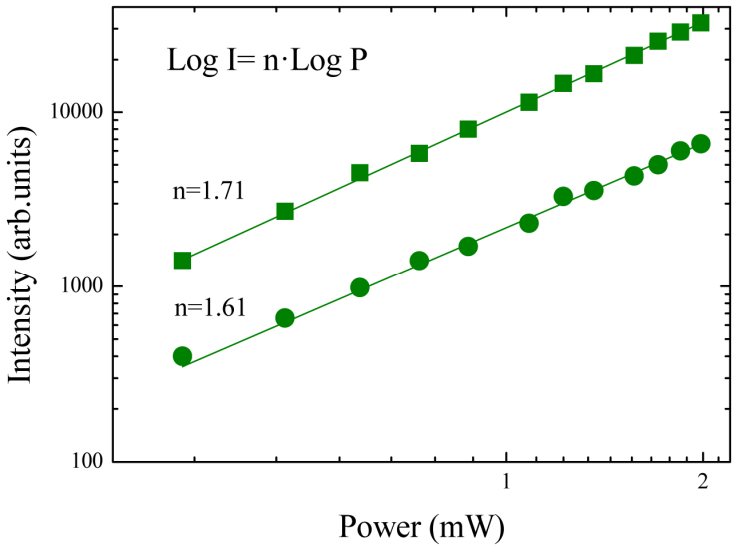

Fig. 4. Emission intensity as a function of the incident pump power for the 545 nm band collected from the glass flat sample (circles) and through the sphere (squares).

The mean value of the FWHM of the intensity peaks shown in Fig. 2 has been estimated by fitting the data to Gaussian profiles (see Fig. 5 for a representative peak), obtaining a value of 609 nm. The FWHM of the focal spot produced by the sphere is enlarged by both the PSF of the system and the fact that the light emitted by the sample goes through the microsphere in its way to the CCD camera.

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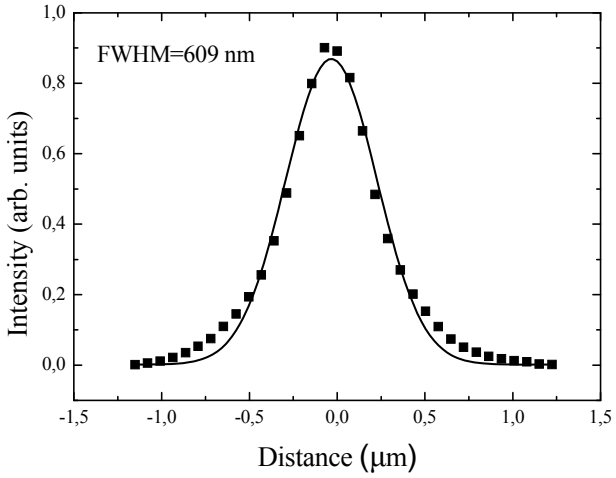

Fig. 5. Intensity profile (dots) in a line that cross the center of a microsphere and Gaussian fitting (continuous line).

The FWHM of the focal spot has been calculated by FDTD simulations, similar to the reported in Refs [6,18,19], obtaining a value of 453 nm. The intensity distribution at the microsphere output is shown in Fig. 6(a) and the transversal distribution at best focus in Fig. 6(b). The two photons upconversion is proportional to the square of the excitation power, reducing the FWHM in a factor of √2, resulting in a FWHM of 320 nm. The microsphere magnification has been measured by covering a diffraction grating (1200 lines/mm) with the microspheres under study and observing the grating lines though the sphere. The value of the experimental magnification is about 1.5. Taking into account this magnification and the properties of the deconvolution of Gaussian functions [6], the experimental FWHM is related to the FWHM of the PSF and the upconversion spot by the expression [6]:

$$W_{EXP}{}^2 = (W_{UPC} \cdot \beta)^2 + W_{PSF}{}^2 \quad (1)$$

where W_{EXP}, W_{UPC} and W_{PSF} represent the FWHM of the experimental measurement, the upconversion spot and the experimental PSF respectively and β is the microsphere magnification. Applying Eq. (1) a value of 332 nm has been obtained for the FWHM of the upconversion spot. It has to be noticed that the PSF has been measured at 480 nm instead of the emission wavelength 545 nm. Due to this wavelength difference the real PSF is around 10% wider than the PSF here considered. This change in the PSF has been estimated from the theoretical formula (see Ref [16]). Taking this into account in Eq. (1) the FWHM of the upconversion spot has a corrected value of 309 nm, in good agreement with the theoretical simulation (320 nm).

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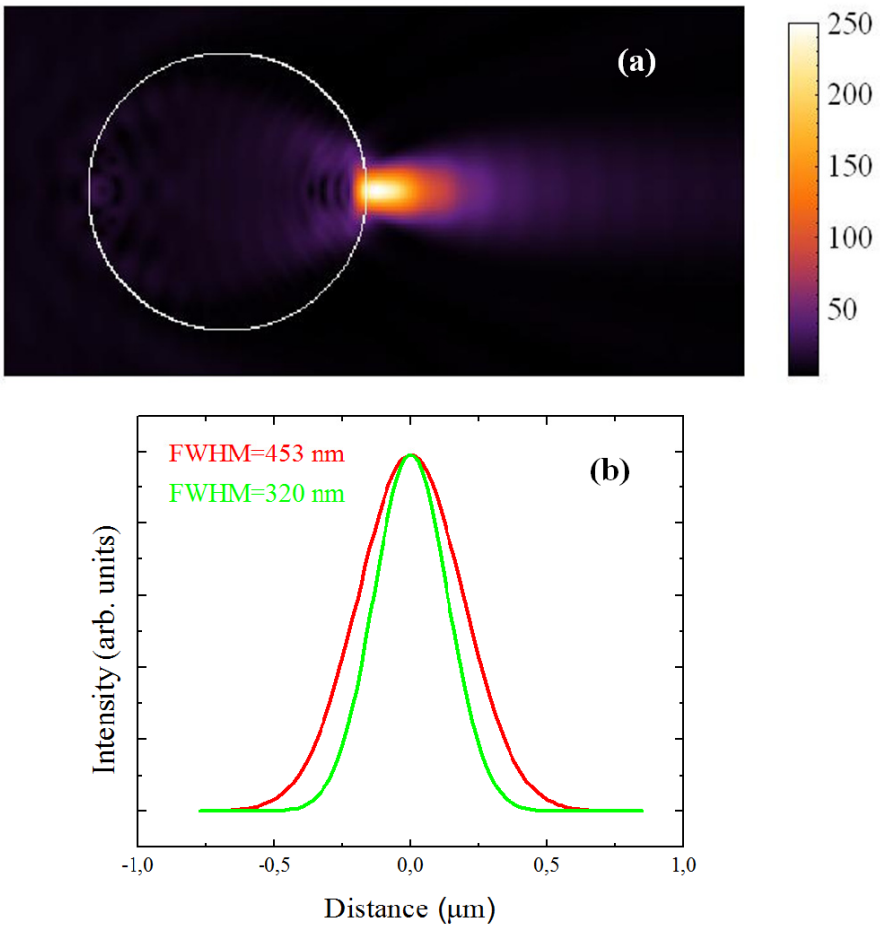

Fig. 6. (a) Intensity distribution computed by FDTD under plane wave illumination (950 nm). (b) Transversal intensity profile at best focus (red line) and upconversion intensity (green line).

4. Conclusions

In a simple optical setup and with an easy sample preparation an intensity enhancement of 4.5 for the green upconversion emission of an Er^{3+}-Yb^{3+} codoped fluoroindate glass has been obtained by focusing the incoming beam with a 3.8 μm silica microsphere. This value could be improved by properly choosing the size and refractive index of the microspheres. Measurements of the variation of the intensity emitted by the sample in the microsphere focus area and outside of the microsphere with the pump power allow to conclude that the microspheres do not affect the ESA and ET upconversion mechanisms. The size of the emitting area has been experimentally determined obtaining a FWHM of 309 nm in good agreement with the Finite-Difference Time-Domain simulations (320 nm). This size could be reduced by using upconversion processes requiring more participating photons (three or four) at shorter wavelengths. These results open a new method to improve the upconversion emission intensity in biological samples with rare earth doped nanoparticles that can be used as nano-sensors. Furthermore, in this kind of applications, it could be interesting to use optical trapping in order to shift the microspheres over the sample.

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