Journal of Alloys and Compounds 576 (2013) 363–368

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

# Study of the focusing effect of silica microspheres on the upconversion of $Er^{3+}$–$Yb^{3+}$ codoped glass ceramics

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ARTICLE INFO

*Article history:*
Received 22 February 2013
Received in revised form 8 May 2013
Accepted 31 May 2013
Available online 10 June 2013

*Keywords:*
Optical properties
Optical spectroscopy
Luminescence
Rare Earth alloys and compounds
Optical material

ABSTRACT

The upconversion emission properties of $Er^{3+}$–$Yb^{3+}$ codoped glass and glass ceramic samples with different Si/Al ratios and thermal treatments were analyzed by covering their surfaces with silica microspheres (3.8 μm diameter). A 950 nm laser beam is focused by the microspheres producing a set of photonic nanojets near the surface of the samples. After the upconversion processes of the $Er^{3+}$ ions located in each microsphere focus area, these ions emit light in the green and red regions. The red emission from each sample was measured, yielding an upconversion intensity in the focal areas three times higher than the emission from the bare substrate. To estimate the real size of the red emission area under a single microsphere, a deconvolution of the measured focal spots with the Point Spread Function of the experimental setup was performed, resulting in a Full Width at Half Maximum of 330 nm. The results obtained by Finite-Difference Time-Domain simulations are in good agreement with the experimental values.


## 1. Introduction

The employment of nanoscale materials as sensors seems advantageous since they confer local resolution while avoiding the spread of damaging perturbations in those systems in which they are used. These materials are of special interest in the field of biology, where they can be used simultaneously as nanothermometers and to produce a localized thermal treatment in a biological sample [1]. Research on new label probes [2] is also interesting in other fields, like microscopy. Efficient emitters are a key to achieving these goals, with non-toxicity being an additional requirement for biological applications. This explains the current trend of conducting research on obtaining sufficiently high optical intensities in nanoemitters [3,4]. However, this requirement on emitter efficiency when the sources have a reduced size is not a trivial issue [5], despite the emergence of low signal detectors that simplify the measurements of emissions from discretely incorporated nanoparticles.

Upconversion processes (UC) among Rare Earth (RE) ions are characterized by the sequential absorption of two or more photons that lead to the emission of light at wavelengths below the excitation wavelength. Upconversion emitters are starting to be considered as advantageous probes for fluorescence microscopy imaging because their luminescence is stable over time, their variety covers a wide spectral range and they can be synthesized as nanoparticles [6]. In an effort to improve the efficiency of the RE upconversion luminescence, different strategies are used, such as the design of the glass compositions, the combinations of different RE ions and the variation of doping concentrations, as well as the application of thermal treatments. With regard to this last approach, it was discovered that in many glass samples nanocrystals may appear after the thermal treatment, allowing the RE to be incorporated into these nanocrystals, thus improving their luminescence. Materials that combine a glass amorphous matrix with immersed nanocrystallites are known as glass ceramics. In general, the upconversion efficiency is higher with optimized glass ceramics as compared to the precursor glass since the distances between the RE ions in the crystallites of the former are shortened, favoring energy transfer among the ions. Additionally the crystalline phase in which the RE emitters are immersed results in decreased optical losses due to the reduction of the higher energy phonons [7,8].

Microspheres have been used to produce focal regions, known as photonic nanojets [9,10], whose sizes are below the micrometric scale. Previous research [11–14] has demonstrated experimentally and with simulations the use of microspheres in order to increase the signal intensity obtained in different experiments. In Ref. [11],

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http://dx.doi.org/10.1016/j.jallcom.2013.05.222

the authors reported a confirmation of the photonic jet in the microwave scale, observing the backscattering enhancement that occurred when metallic particles where introduced in the focus area. This backscattered emission was also analyzed in Refs. [12,13] but using dielectric microspheres illuminated in the optical range. In Ref. [12] a measurable enhancement of the backscattered light in the visible range was obtained when a gold nanoparticle was placed inside the photonic nanojet region produced by a dielectric microsphere with a 4.4 μm diameter. The authors concluded that this property could be advantageous for the visible detection of metallic nanoparticles even with diameters below 50 nm. In the work in Ref. [13], Hill et al. reported the backward emission from the fluorescence of a dye droplet excited with one, two or three photons. Moreover, Lecler et al. [14] measured a 30% increase in the fluorescence of a rhodamine B solution doped with microspheres. However, to our knowledge the use of nanojets produced by transparent microspheres in order to excite optical active materials, under upconversion processes with different numbers of excitation photons, has not been analyzed in the literature.

The aim of this work is to magnify the signal sent out by a small UC emitter by means of silica microspheres. These microspheres act as lenses focusing the excitation on the emitter and also collecting its luminescence towards the detector. $Er^{3+}$–$Yb^{3+}$ ions were included as codoping ions in the composition of glass and glass ceramic samples of a biologically compatible matrix, and their red upconversion emission was studied. This matrix corresponds to an oxyfluoride glass in which $CaF_2$ nanocrystals are formed under different thermal treatments. In these samples an efficient energy conversion of the 950 nm excitation wavelength occurs by the action of the $Er^{3+}$–$Yb^{3+}$ ions, resulting in an intense 650 nm emission.

In our setup a 950 nm laser beam impinges first onto a set of 3.8 μm diameter silica microspheres located above the sample, producing a set of focal regions inside the sample matrix in which these ions are embedded. Because of the increase in the excitation per unit area in these focal regions, the upconverted emission, also coming from this area, attains a higher intensity value with respect to the bare substrate. Moreover, the microspheres can collect a certain solid angle of the total emission and redirect it in the backward direction resulting in an enhanced number of counts recorded by a properly positioned detector. From the detected image, the Full Width at Half Maximum (FWHM) of the emission in the focal area was obtained by deconvolution with the Point Spread Function (PSF) of the experimental system and compared with the theoretical value obtained with Finite-Differences Time-Domain (FDTD) simulations.

## 2. Experimental description

### 2.1. Preparation of the glass and glass ceramic samples

The samples were prepared using reagent-grade chemicals: (opti pure) $SiO_2$ (Alfa-aesar89709), $Al_2O_3$ (Alfa-aesar42571), $CaF_2$ (MERCK 102840 precipitated pure) $ErF_3$ (Alfa-aesar 13653) and $YbF_3$ (Across 31616) as raw materials. The batch compositions were mixed in agitate mortar for 10 min in a glove box with a humidity of less than 10%. The glass samples were prepared by melting the mixtures of the aforementioned materials in covered platinum crucibles at 1450 °C in an electric kiln for 90 min. The glasses were then annealed at 480 °C (close to the glass transition temperatures) for 3 h. The resulting samples were cut and polished to form 30 mm × 30 mm × 2 mm rectangular slices. The glass crystallization temperatures were determined by differential thermal analysis (DTA; Polymer Laboratories 1640, Amherst, MA). The ratio of $SiO_2$ to $Al_2O_3$ was chosen as 1.8 and 2.18 to fabricate two precursor glasses, fixing in both the dopant contents to 0.5 mol% of $ErF_3$ and 2 mol% of $YbF_3$ and the $CaF_2$ to 35 mol%. In what follows these glasses are referred to as SA1.8EY and SA2.18EY, respectively. In order to name the glass ceramic samples obtained from these precursor glasses, the thermal treatment temperature applied in each case was added to these names.

The glasses were heat treated in an electric kiln at three different temperatures (630, 675, and 690 °C) for 48 h, as per the DTA results, at a heating rate of 10 K/min. The crystalline phases, precipitated during the heat treatment, were identified with a Philips X'Pert Pro diffractometer equipped with a primary monochromator, Cu Kα radiation, and an X'Celerator detector. The presence of $CaF_2$ nanocrystals was confirmed with XRD patterns collected with a step of 0.016° in the $2\theta$ angular range from 10° to 90° and an acquisition time of 2 h. The Debye–Scherrer formula yielded an average size of 25 nm for these nanocrystals.

### 2.2. Optical measurements with microspheres

The surface of each polished sample was covered with drops of a distilled water and silica microsphere solution (3.8 μm CoSpheric, Santa Barbara) and dried at room temperature so as to randomly spread the microspheres on the glass surface. The experimental setup in which the samples were imaged is shown in Fig. 1. The excitation beam from a 950 nm diode laser (L3-MSF03 JDS Uniphase) is directed by a beamsplitter to a microscope objective (Olympus Plan, 80x, NA = 0.9) used to produce a converging beam to illuminate the sample. After that, each microsphere focuses the 950 nm illumination near the surface of the sample, producing upconversion processes in the focal region. The excited $Er^{3+}$–$Yb^{3+}$ ions emit at wavelengths centered on 545 nm and 650 nm, which can be easily detected. The emitted light goes through the microsphere and re-enters the microscope objective, being focused by a lens in a CCD camera (ATK-16HR). In order to select the red emission a proper combination of filters is placed before the CCD detector. The imaging system is characterized by its PSF with a value for the FWHM of 369 nm, which was obtained by the theoretical formula in Ref. [15] for this experimental setup.

## 3. Results and discussion

The emission spectra of the $Er^{3+}$–$Yb^{3+}$ codoped SA1.8EY and SA2.18EY glasses and glass ceramics treated at 675 °C obtained under excitation at 950 nm are shown in Fig. 2a. The spectra were obtained from the bulk samples before covering them with microspheres. The main emission bands are in the green (at

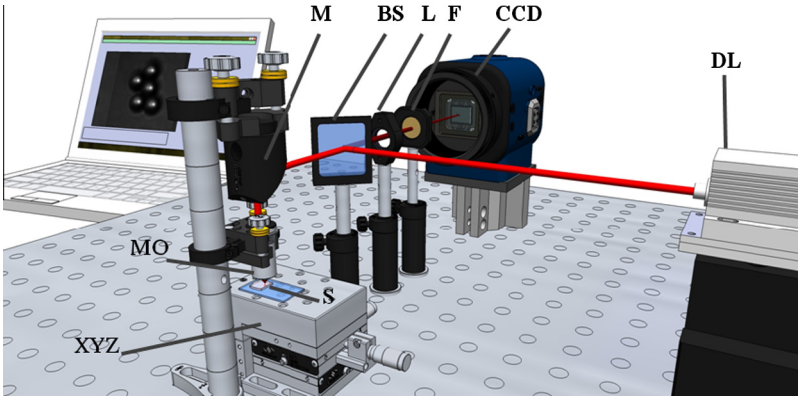


**Fig. 1.** Experimental setup. S. sample, XYZ. Three axis translation stage, M. Mirror, MO. Microscope objective, BS. Beamsplitter, L. Lens , F. Filter and DL. Diode Laser.