Journal of Luminescence 180 (2016) 8–13

Contents lists available at ScienceDirect

Journal of Luminescence

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

Full Length Article

Glass heating through submicron spots produced with silica microspheres

L. Labrador-Páez [a,*], C. Pérez-Rodríguez [a,b], S. Ríos [a], I.R. Martín [a,b]

[a] Departamento de Física, Universidad de La Laguna, San Cristóbal de La Laguna, Santa Cruz de Tenerife 38206, Spain
[b] MALTA Consolider Team and Instituto de Materiales y Nanotecnología (IMN), Universidad de La Laguna, San Cristóbal de La Laguna, Santa Cruz de Tenerife 38200, Spain

ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form
2 August 2016
Accepted 4 August 2016
Available online 9 August 2016

Keywords:
Microsphere
Heating
Photonic nanojet
Lanthanide

ABSTRACT

The emission spectra of phosphate glasses doped with different concentrations of Nd^{3+} ions have been measured and the dependence of the emission intensity on the concentration of doping ions has been explained using energy transfer models. Thus, the optimum concentration in order to obtain the maximum heating of the glass has been theoretically estimated. The glass sample doped with a Nd^{3+} concentration closest to the optimum was covered with silica transparent microspheres with different diameters (2, 7, and 25 μm). The incident laser light at 532 nm was focused through the microspheres producing submicron spots (known as photonic nanojets) that excite the doping ions in the glass and heat the matrix due to non-radiative processes. From this, the heating as a function of the microsphere diameter has been analysed.

1. Introduction

Microspheres are spherical transparent dielectric cavities with diameters in the micrometre range, usually made of silica compounds. They must have higher refractive index than their enclosing medium in order to generate total internal reflection and, consequently, morphology-dependent resonances. Due to minimal reflection losses and very low material absorption, these resonators can reach exceptionally high quality factors, which lead to very high energy density [1]. Their spherical symmetry enables their use as resonant cavities, what produces the effect known as whispering gallery modes (WGMs).

Under certain conditions, microspheres can also produce the non-resonant phenomenon named photonic nanojet by tightly focusing an incident beam. It is a non-evanescent beam that propagates keeping a subwavelength transverse width through a distance as long as $\sim 2\lambda$. It has a high energy concentration, respect to the incident beam, and transversal size under the diffraction limit (as small as $\sim\lambda/3$). This occurs for a wide range of microsphere diameters (from 2λ up to 40λ) and for certain conditions in the refractive index contrast to the surrounding medium [2–4]. On the other hand, by introducing a nanoparticle within the nanojet, the far-field backscattered power could be considerably modified [2]. The characteristics of the photonic nanojets make them interesting for applications in sensing; sizing and manipulating nanoscale objects; subdiffraction-resolution surface nanopatterning and nanolithography [5,6]; more precise ophthalmic laser surgery [7,8]; dry cleaning of surfaces [9]; low-loss optical waveguiding; ultrahigh-density optical storage; enhancement of the optical excitation and harvesting of luminescence [3,4,10] among others [2,11].

The aim of the first part of this study is to optimise the Nd^{3+} concentration in the doped phosphate glass in order to obtain the maximum heating capability. This type of glasses are of great interest due to their frequent use in the fields of optical transmission, detection, sensing, and laser technologies [12]. Phosphate glasses show unique characteristics such as a great solubility of lanthanide trivalent ions, high transparency, low linear and nonlinear refractive indexes, low melting point, good thermal stability, low dispersion, and high gain density [13]. In order to analyse the emission of Nd^{3+} ions, the energy transfer processes which take place among these ions in the studied bulks were reviewed. When the concentration of ions grows, the mean distance between them decreases. As a consequence, the interaction between them increases. Therefore, non-radiative energy transfer processes between doping ions are more likely to happen. When the migration processes between donor ions are important, the model proposed by Parent can be used to describe the temporal variation of the emission intensity [14]. This model includes the Inokuti-Hirayama model as a particular case [15], in which the

Abbreviations: WGM, whispering gallery mode; FIR, fluorescence intensity ratio

* Corresponding author. Present address: Fluorescence Imaging Group, Departamento de Física de Materiales, Universidad Autónoma de Madrid, Madrid, 28049, Spain.
E-mail address: lucia.labrador@uam.es (L. Labrador-Páez).

http://dx.doi.org/10.1016/j.jlumin.2016.08.013
0022-2313/

migration between donor ions is not considered. The dependence of the emission intensity with the doping ion concentration can be calculated from the fit of the experimental data to the theoretically estimated emission intensity. From this, the optimal concentration of doping ions can be obtained.

The second part of this work consists in locating transparent silica microspheres over the surface of a phosphate glass doped with Nd^{3+} ions with the aim of producing high energy density submicron spots (photonic nanojets) that excite the Nd^{3+} ions of the bulk in the small area where the photonic nanojet spreads. These ions absorb a part of the energy of the photonic nanojet and thus a heating process of the glass matrix is produced due to the non-radiative relaxations of the excited ions. Among the available glass samples, the one with the concentration of Nd^{3+} ions closest to the optimum (with the highest probability of non-radiative relaxation) was chosen.

The temperature achieved by this glass in the submicron spots zone must be estimated to achieve a controlled heating. The possibility of controlling the temperature reached by the heated material during the process opens many opportunities for the development of potential applications and improvement of the existent ones [3–10]. For this purpose, the changes in the emission spectra of the Nd^{3+} ions as a function of temperature have been analysed as proposed in [16,17], where this type of calibration has been performed in other matrix doped with Er^{3+} and Nd^{3+} ions. The spectra obtained for the radiation emitted by the heated sample were analysed by means of the Fluorescence Intensity Ratio technique (FIR), which compares the fluorescence intensities emitted from two adjacent thermalized energy levels, that is to say, levels which experiment a thermally induced population redistribution between them by means of non-radiative transitions [18]. The $^4F_{3/2}$ and $^4F_{5/2}$ levels of Nd^{3+} ions are adequate so as to apply the FIR technique [17].

2. Material and methods

The employed glasses are a set of Nd^{3+} doped materials with the following composition in mol%: 44 P_2O_5, 17 K_2O, 9 Al_2O_3, (30-x) CaF_2, and x Nd_2O_3, where x=0.1, 0.5, 1.0, and 2.0 mol%. These glasses were prepared by a standard melt quenching method. P_2O_5, K_2O, Al_2O_3, CaF_2, and Nd_2O_3 with 99.99% purity (Aldrich Chemical Co.) were used in the glass preparation as starting materials. Approximately 10 g of batch chemicals were thoroughly mixed and crushed. The mixture was melted in a platinum crucible inside an electric furnace at 1150 °C for one hour. After that, the melt was then poured onto a preheated brass plate and air quenched. Then, the glasses were annealed for twelve hours and cooled slowly to room temperature to remove the thermal stress caused during the quenching process. Finally, all the glasses were polished to optical quality prior to the optical measurements.

The intensity decay measurements were performed by exciting the diverse Nd^{3+} doped samples at 532 nm by means of a pulsed Nd: YAG laser (pulses of 5 ns with an energy of 1 mJ) and detecting with a TRIAX 180 monochromator and a photomultiplier tube.

The absorption spectrum of the 2 mol% of Nd^{3+} doped glass in the range from 750 to 950 nm was measured with the spectrophotometer Cary 5000 so as to obtain the value of the energy mismatch between the thermally coupled levels of neodymium.

The emission spectra of the 2 mol% of Nd^{3+} doped glass for diverse temperatures in the 300–520 K range were taken using an electric furnace and exciting the sample at 532 nm by means of a diode laser, similarly to the procedure in Refs. [16,19].

The microspheres employed as focusing lens are made of silica (Bangs Laboratories, Inc). Microspheres with 2, 7, and 25 μm of diameter were chosen in order to analyse their heating capability. For this purpose, the emission spectra of the 2 mol% of Nd^{3+} doped bulk glass with the microspheres acting as focusing lenses were obtained exciting at 532 nm with a commercial continuous wave diode pumped solid state laser and employing a home-made microscope similar to the experimental setup described by Pérez-Rodríguez et al. in [4].

3. Theory

3.1. Energy transfer processes

If the concentration of optically active ions in the sample is high enough, the mean distance between them decreases, which would cause that interaction processes such as energy transfer were appreciable.

Considering the existence of non-radiative energy transfer processes and multipolar interaction between optically active ions as the predominant interaction, the temporal evolution of the emission intensity after the excitation pulse, I(t), should obey the following models.

3.1.1. Inokuti-Hirayama model

When migration processes among donors are not considered, the temporal evolution of the emitted intensity, I(t), is proposed by Inokuti and Hirayama in [15] to be described as

$$\mathrm{I}(t) = \mathrm{I}(0)\exp\left[-\frac{t}{\tau} - Q\left(\frac{t}{\tau}\right)^{3/S}\right] \tag{1}$$

where $I(0)$ is the intensity in arbitrary units at time $t=0$; τ is the intrinsic lifetime of the engaged donor level; S is a dimensionless parameter that depends on the type of interaction between the ions (for dipole–dipole interaction, $S=6$); and, Q, the dimensionless energy transfer parameter, if there is only a type of acceptor ion, is given by

$$Q = \frac{4\pi}{3}\Gamma\left(1-\frac{3}{S}\right)A(\mathrm{C_{DA}}\tau)^{3/S} \tag{2}$$

where Γ is the well known gamma function [20], A is the concentration of doping ions, and C_{DA} is the donor–acceptor energy transfer parameter [15].

The dependence of the emitted intensity, I, on the concentration of doping ions, A, is given by

$$I \propto N^* = \frac{6\phi\mathbf{A}}{\frac{1}{\tau}+\mathrm{W_T}} \tag{3}$$

where N^* is the number of excited doping ions, ϕ is the flow of photons per cm^2, and W_T is the transfer probability, that can be calculated using

$$W_T = \frac{\eta_T}{\tau(1-\eta_T)} \tag{4}$$

where η_T is the transfer efficiency.

Inokuti-Hirayama model allows to obtain the transfer efficiency for dipole–dipole interaction from [15]

$$\eta_T = \sqrt{\pi}\, x \exp(x^2)\left[1-\mathrm{erf}(x)\right] \tag{5}$$

where erf(x) is the error function and x is given by

$$x = \frac{2\pi}{3}\sqrt{\pi}\, A\, {C_{\mathrm{DA}}}^{1/2}\tau^{1/2} \tag{6}$$

Finally, considering Eq. (2) for the case $S=6$, x can be expressed in terms of Q as

$$x = \frac{Q}{2} \tag{7}$$