Journal of Luminescence 130 (2010) 2491–2494

Contents lists available at ScienceDirect

Journal of Luminescence

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

Concentration dependent fluorescence quantum efficiency of neodymium doped phosphate glass matrix

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ARTICLE INFO

Article history:
Received 9 April 2010
Received in revised form
16 August 2010
Accepted 18 August 2010
Available online 24 August 2010

Keywords:
Fluorescence quantum emission
Rare-earth ions
Laser materials
Thermal lensing
Phosphate glasses

ABSTRACT

In this work, we have studied the optical and thermal properties of Nd-doped phosphate glass matrix. The studied samples have concentration ranging from 0.5 to 5 wt% of Nd_2O_3. Here we report the measurements of fluorescence quantum efficiency, η, obtained through the thermal lens technique using a reference sample. Also, the refractive index, n, specific heat, c_p, mass density, and the thermal diffusivity and conductivity measurements were performed. The knowledge of these characteristics as a function of neodymium concentration is very important to design optical devices, especially high power solid state lasers.

1. Introduction

The glass science is always pursuing materials with large applicability ranging, for example, from detection of ionizing radiation to telecommunication devices. In particular, the search of glassy materials used in optical devices still has attracted attention of the involved community. Good thermal characteristics as high thermal diffusivity and good mechanical performance are desired to improve the performance of lasers in the high pump powers domain. In these systems the control of heat generation is a very important issue. In order to improve such control in the laser design, glass matrices with precisely known photothermal properties should be used. Indeed, it is well known that depolarization losses, beam distortion, thermal lensing, and even fracture in high power laser systems can be assigned to the heating of the active medium [1].

In this work, a new phosphate glass matrix is proposed and for the first time its optical and photothermal properties were studied. It is well known that the neodymium ion (Nd^{3+}) is one of the most studied rare earths, both in crystal and glass, since it presents as a four level system [2]. The samples were doped with increase in concentration of Nd_2O_3. Several optical and photothermal properties were obtained. Also, using the thermal lens (TL) technique, we have investigated the fluorescence quantum efficiency, and observed it decreasing with increase in dopant concentration.

2. Experimental

Samples were synthesized in glass matrix PAN with nominal compositions $40P_2O_5 \cdot 20\ Al_2O_3 \cdot 40Na_2CO_3$ (mol%) adding xNd_2O_3 (wt%), with $x=0.5$, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The preparation process consisted of melting the powder mixtures in an alumina crucible at 1250 °C for 60 min, in air atmosphere. In the sequence, the crucible containing the melted mixture underwent quick cooling to room temperature. In a second step, thermal annealing of this melted and cooled glass matrix was carried out at 350 °C for 24 h to reduce, partially, the internal stresses. In third step, the samples were polished for the optical and photothermal measurements.

Optical absorption spectra were obtained using a HR4000 Ocean Optics spectrophotometer operating between 350 and 1000 nm. Photoluminescence (PL) measurements were recorded using a SPEX-750M monochromator equipped with a Joban-Yvon CCD 2000 800-3. For these spectra, and for the subsequent experiments, the samples were optically excited by the 514.5 nm line of an Argon-ion laser. In addition, mass density measurements were carried out using the picnometer method [3]. In this case a 10 ml picnometer, a 4 digit precision scale, and a reference sample (acetone, $\rho=0.79$ g/cm^3), were used. In order to obtain the refractive index a Michelson–Morley interferometer was used, at 632 nm, with an accuracy of ± 0.01, following the method described in Ref. [4]. Moreover, we have performed specific heat measurements, c_p, using a thermal relaxation method with a laser beam as the heat source. In this method the temperature variation at the sample is monitored as a function of the time the sample is exposed to a pump laser, as described in Ref. [5].

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0022-2313/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.08.018

Finally, to find the thermo-optical parameters the photothermal analysis is carried out in this work, which is based on the thermal lens technique [6]. Here, the energy absorbed, provided by an excitation laser, is converted into light (fluorescence) and/or heat. The induced heating follows the incident beam profile and changes the sample refractive index. Hence for Gaussian beams the index profile has a lens-like shape that changes the incident wavefront, making it focalize or defocalize, depending on the thermal properties of the sample. A second beam, with a higher spot size at the sample, to improve the sensibility, is then used to prove the induced thermal lens. This configuration is known as the time-resolved mode mismatched one, and is described in more detail elsewhere [6]. The TL spectrometry has been shown to be a useful method to measure thermo-optical properties of materials with a wide range of optical absorption coefficients. The theoretical modeling for the thermal lens effect in this configuration has been developed and an analytical expression to treat the thermal lens quantitatively has been derived [7]. Here, the propagation of the probe beam through the TL results in a variation of its on-axis intensity, which is monitored in the far-field [7]. In this technique the transient probe signal amplitude is proportional to the phase variation, θ, given by

$$\theta = -P_{abs} C \varphi \tag{1}$$

here $P_{abs}=P_e A_e L_{eff}$, where P_e is the power of the excitation input beam, A_e the absorption coefficient of the sample at the excitation wavelength, $L_{eff}=(1-e^{-A_e L})/A_e$ the effective length of the sample, with L being the sample thickness; $C=(K\lambda_p)^{-1} ds/dT$ with λ_p the probe beam wavelength, K the thermal conductivity, and ds/dT the temperature coefficient of the optical path length, and finally φ the fraction of absorbed energy converted into heat (also known as thermal loading). The term ds/dT describes the thermally induced distortion of a laser beam during its passage through the sample. In solids, it has contributions due to the refractive index temperature coefficient, dn/dT, the expansion of the sample and the photo-elastic effect [6]. For luminescent samples, when there is only one emitting level, the thermal loading can be described as

$$\phi = 1-\eta \frac{\lambda_e}{\langle \lambda_{em} \rangle} \tag{2}$$

where η is the fluorescence quantum efficiency, λ_e the excitation/pump wavelength, and $\langle \lambda_{em} \rangle$ the average emission wavelength. For non-luminescent samples $\varphi=1$.

In this work the TL experiment was performed using an Ar^+ laser at 514 nm as the excitation beam and a He–Ne laser at 632.8 nm, of very low intensity, as the probe beam. A converging lens of focus $f=15.0$ cm was used to focus the excitation beam at the sample. A chopper controlled the exposure time of the sample to the excitation beam. The probe beam was focused by another lens ($f=25.0$ cm) arranged in such a way that the sample is positioned nearby its confocal position ($Z_1 \approx 1.73 Z_c$). An angle $< 1.5^\circ$ is used to deviate the probe beam to the TL detection plane positioned in the far-field. In this experiment, a computer controlled data acquisition system is used to record the TL signal buildup. Its temporal evolution depends on a characteristic formation time, t_c, which is related to the thermal diffusivity $D=w_e^2/4t_c$, where w_e is the excitation beam spot size at the sample. On the other hand, D is related to the thermal conductivity, K, through $K=\rho c_p D$, with ρ the matrix mass density, and c_p its specific heat.

3. Results and discussion

3.1. Optical properties

As mentioned before, the absorption spectra for all the samples were obtained at the visible and near IR regions. A typical spectrum, of the 5 wt% Nd_2O_3 doped sample, can be seen in Fig. 1. All the observed absorption bands can be related to the well known electronic transitions of Nd^{3+} ion [8–10]. Also, the absorption coefficient, at 514 nm, presented a linear behavior with increase in concentration, not shown. Inset in Fig. 1 shows a linear behavior of the absorbance integrated spectra as a function of increase in concentration, thus indicating the absence of Nd^{3+} ions clusters inside the glass matrix. This demonstrates the high solubility of Nd^{3+} ions inside the glass matrix.

Fig. 2 shows the PL spectrum of the 2 wt% Nd_2O_3 doped sample, at 300 K, excited with 514 nm Ar^+ laser line. The three emission peaks shown, centered at 881, 1061, and 1333 nm, can be ascribed to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ e $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. Therefore, all significant emissions arise from the $^4F_{3/2}$ level, which is a fundamental condition to use a thermal lens approach to achieve the luminescent quantum efficiency. An average emission wavelength, $\langle \lambda_{em} \rangle$ from this level can be derived from

$$\langle \lambda_{em} \rangle = \frac{\int \lambda I_{em}(\lambda) d\lambda}{\int I_{em}(\lambda) d\lambda} \tag{3}$$

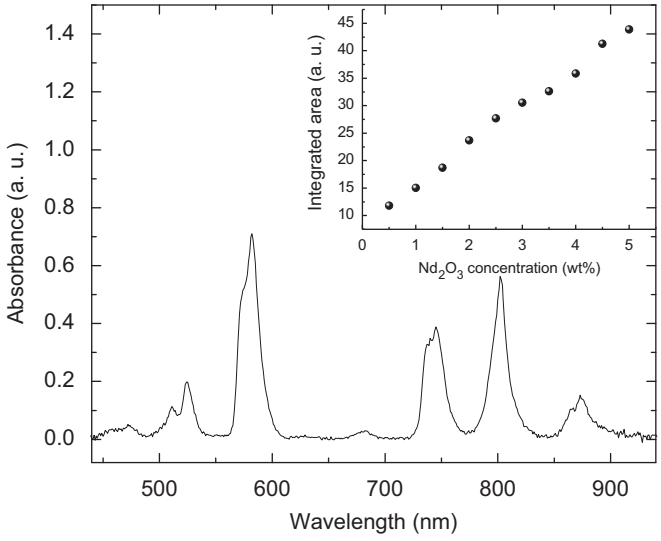

Fig. 1. Absorption spectrum of the 5 wt% Nd_2O_3 doped sample, excited at 514 nm. The inset shows the absorbance spectra integrated area versus the Nd_2O_3 content.

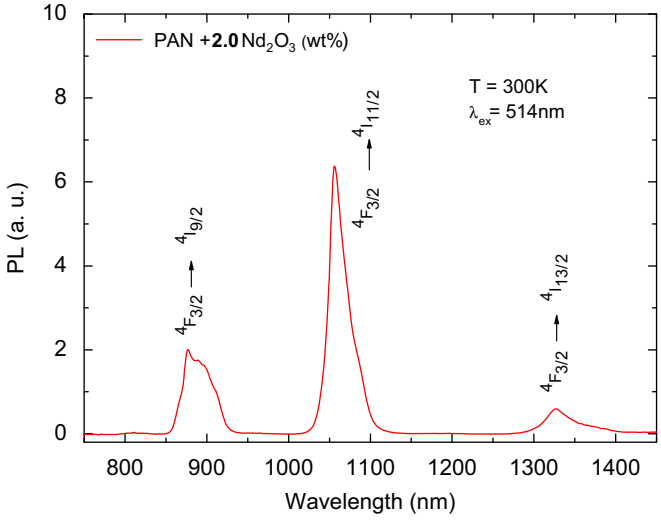

Fig. 2. Photoluminescence, PL, obtained from the 2 wt% Nd_2O_3 doped sample.