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Absolute thermal lens method to determine fluorescence quantum efficiency and concentration quenching of solids

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An absolute thermal lens method to determine fluorescence quantum efficiency and concentration quenching of solids is described in this work. The quantum efficiency of low silica calcium aluminate glasses doped with different concentrations of neodymium dioxide and melted under vacuum conditions to remove water has been measured by using mode-mismatched thermal lens spectrometry. It has been shown that the thermal lens signal amplitude is linearly dependent on neodymium concentrations up to 4.0 wt %, changing significantly from 4.5 to 5.0 wt %, indicating that there was quenching of the fluorescence only above 4.0 wt % neodymium dioxide. The quantitative treatment for the thermal lens effect provided the absolute value of the sample's fluorescence quantum efficiency. The technique is simple to perform and can be applied for a wide range of fluorescent materials. [S0163-1829(98)00714-0]

I. INTRODUCTION

Fluorescence quantum efficiency (ϕ) is one of the most important optical properties of fluorescent materials. The determination of its absolute value, especially for solid samples, has been shown to be difficult. Controversial results in the literature are due to the limitations of the employed experimental methods.$^{1-7}$ First, pure optical measurements such as the integrating sphere method, demand calibration of the detector. The fluorescent light is polychromatic, therefore introducing inaccuracy in the results. The use of fluorescence lifetime is also inadequate, especially for multilevel energy systems, because it depends on both the value of the nonradiative lifetime and the fluorescence decay. These do not obey a single exponential shape. The introduction of photothermal techniques to measure the quantum efficiency in the last decade has brought new perspectives to obtaining more accurate values for this parameter. These methods are based on the determination of the nonradiative quantum efficiency, and are therefore complementary to the purely optical procedures.^{1,2,4,5} A good review on the subject can be found in Ref. 1, which also presents the use of noncontact quadrature photopyroelectric spectroscopy to measure quantum efficiency of Ti:sapphire laser crystals.

In 1978, Brannon and Magde^{8} introduced the thermal lens spectrometry (TLS) to measure fluorescence quantum efficiency. Since then, the technique has been used to determine this parameter in fluorescent solutions^{9} and fluorescent polymers.^{10} In those experiments, single beam or mode-matched configuration have been used, and the data were analyzed through the parabolic model. However, it has been shown that this model is not realistic, since it cannot predict the rings observed in the far field during the experiments. Furthermore, the use of mode-mismatched experimental configuration has increased the sensitivity of the technique.

TLS is a noncontacting technique and can be performed in a low-frequency range (time resolved measurements) and in the steady-state mode. In these procedures, the ratio of the absorbed energy that is converted into heat and into fluorescence can be determined. This technique has received special attention in the last few years, particularly its dual-beam mode-mismatched configuration, which has been shown to be very sensitive and therefore appropriate for measurements in highly transparent materials. In this arrangement, the sample is positioned at the waist of the excitation beam, where the power density is maximum, and at the confocal position of the probe beam. By using this arrangement optical absorption coefficient as low as 10^{-7} cm^{-1} can be measured. The thermal lens effect is created when the excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the optical path length s and producing a lenslike optical element at the sample. The propagation of the probe beam through the TL will result in either a spreading or a focusing of the beam center, depending on the temperature coefficient of the thermal expansion and electronic polarizability of the sample.^{11} The theoretical model for thermal lens in the mode-mismatched configuration was developed by taking into account the absorbed energy that is converted into heat. This model considers both the aberrant nature of the thermal lens and the whole change in the optical path length induced by the laser beam. It provides a simple analytical expression to interpret the experimental results. This model has been applied successfully to measure quantitatively the thermo-optical parameters of transparent materials.^{11,12}

Rare-earth doped glasses are interesting for many optical

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applications, including active medium for glass lasers. The fluorescence quantum efficiency of these glasses decreases with the increase in the doping concentration. The fall in its value is highly dependent on the glass composition and structure. For silicate glasses the reduction in the radiative quantum efficiency becomes significant over 2% of Nd_2O_3, while in phosphate glasses with Nd_2O_3 concentration up to 6% the decrease in ϕ is very small.[13] Usually the quenching can be observed by monitoring the fluorescence lifetime (τ) of the sample. A decrease in τ value would indicate interaction between metal-metal and multiphonon relaxation processes, inducing a reduction in the fluorescence intensity. However, for quantitative measurements this is a limited procedure, since, as mentioned before, the fluorescence decay usually does not obey a single exponential shape.

It is desirable, therefore, to have a quantitative and accurate method to determine concentration quenching of doped samples without using lifetime measurements.

The effects induced by the introduction of large amounts of rare earth on both the glass structure and the fluorescence quantum efficiency have not yet been investigated in low silica calcium aluminate glasses. These glasses are transparent in the infrared spectral range up to 6 μm, for samples melted under vacuum conditions. Low silica calcium aluminate glasses are interesting because they can be obtained without using the traditional network former.[14–16] Their excellent qualities, good chemical durability and high transformation temperatures, allow their use in hostile environments,[14] such as the cavity of solid-state lasers. The addition of rare-earth oxides to these glasses demands the determination of their quantum efficiency (ϕ) for the different doping concentration.

The addition of a rare earth increases the thermal lens effect. The absorbed incident light is converted into heat and fluorescence, and the ratio between the two depends on the temperature induced optical path length change (ds/dT) in the sample. The theoretical treatment for the mode-mismatched TL effect has been used quantitatively to determine ds/dT of silicate glasses by using an analytical expression for the thermal lens signal which permits evaluation of the fraction of energy that is converted into heat.[11] The advantage of this method compared with lifetime measurements is that the absorbed energy that is converted into heat is taken into account quantitatively. Furthermore, the method is very sensitive and simple to perform.

The aim of this work is to present the mode-mismatched TL as a quantitative method to determine absolute fluorescence quantum efficiency and the concentration quenching of solids. The experiments have been performed in low silica calcium aluminate glasses prepared with different concentrations of neodymium dioxide. For comparison, the quantum efficiency values were also obtained through the Judd-Ofelt model.

II. EXPERIMENTAL

The glasses were prepared by melting low silica calcium aluminate glasses doped with different concentrations of neodymium dioxide in graphite crucibles. The sample compositions were 41.5 wt % Al_2O_3-X, 47.4 wt % CaO, 7 wt % SiO_2, 4.1 wt % MgO, where $X = 0.5$, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 wt % of Nd_2O_3. The mixture was melted under vacuum conditions at 1500 °C. After two hours of melting the heater was switched off and the crucible moved to a cooled chamber close to room temperature. The samples obtained were cut and polished, resulting in disks of approximately 1 cm in diameter and 3 mm in thickness. They were analyzed using both x-ray diffraction and optical microscopy in order to investigate their homogeneity. All of them presented good optical quality with a low level of scattering and no evidence of devitrification. The doping concentration for all samples was verified by measuring the optical absorption coefficient in the peak of the absorption band at 590 nm.

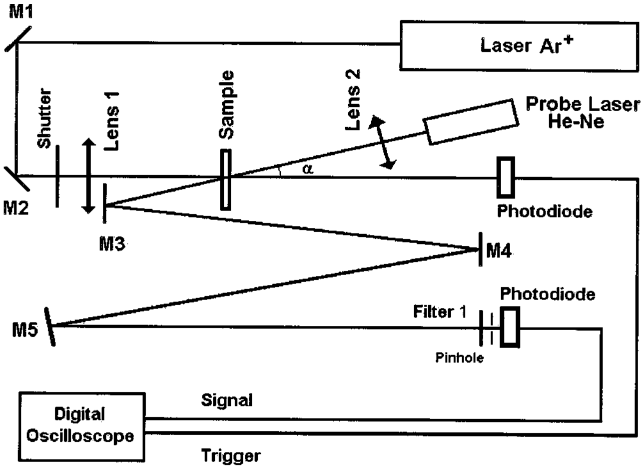

FIG. 1. Mode-mismatched thermal lens experimental setup.

The mode-mismatched thermal lens experimental setup is shown in Fig. 1. The excitation laser used was an argon ion laser (Coherent Innova 90 Plus) at 514.5 nm and a He-Ne laser as the probe beam at 632.8 nm. The sample was placed at the waist of the excitation beam and at the confocal position of the probe beam. The probe beam and excitation beam spot sizes at the sample were 236 μm and 64.7 μm, respectively. The experiments were performed by using both time resolved and steady-state methods. In the time resolved procedure the exposure of the sample to the excitation beam was controlled by a shutter. The signal was recorded for about 30 ms during the buildup of the thermal lens. For the steady-state method the thermal lens signal was recorded after 2 s of illumination. For each sample, the signal was obtained as a function of the excitation laser beam power.

The optical absorption coefficients were determined using the same experimental configuration applied for the TL measurements. The transmitted light of the argon laser at 514.5 nm was recorded for different incident power. The reflections at the two sample surfaces were taken into account.

The fluorescence quantum efficiency value was also obtained by using the Judd-Ofelt model by following the same procedure described in Refs. 17 and 18.

III. THEORY

In the aberrant theoretical model for the mode-mismatched TL configuration, the thermal lens effect is treated as an optical path length change to the probe laser beam, which can be expressed as an additional phase shift on the probe beam wave front after its passing through the sample. The variation of the intensity in the center of the probe beam at the detector caused by the thermal lens can be expressed as[11,12]

$$I(t)=I(0)\left[1-\frac{\theta}{2}\times\tan^{-1}\left(\frac{2mv}{[(1+2m)^2+v^2]\,\frac{t_c}{2t}+1+2m+v^2}\right)\right]^2, \tag{1}$$

where

$$m=\left(\frac{\omega_{1p}}{\omega_e}\right)^2;\quad v=\frac{Z_1}{Z_c}\ \text{when}\ Z_c\gg Z_2;\quad t_c=\frac{\omega_e^2}{4D};$$

$$\theta=-\frac{P_eA_el_0}{K\lambda_p}\frac{ds}{dT}. \tag{2}$$

Here, t_c is the characteristic thermal lens time constant, ω_e is the excitation laser beam radius at the sample, D is the sample thermal diffusivity (cm^2/s), K is thermal conductivity ($J\ \mathrm{s}^{-1}\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$), P_e is excitation laser beam power (mW), A_e is the optical absorption coefficient at the excitation beam wavelength (cm^{-1}), l_0 is the sample thickness (cm), Z_c is the confocal distance of the probe beam, Z_1 is the distance between the probe beam waist and the sample, Z_2 is the distance between the sample and the detector, ω_{1p} is the probe beam radius at the sample, θ is approximately the phase difference of the probe beam at $r=0$ and $r=2^{1/2}\ \omega_e$ induced by the thermal lens, λ_p is the probe beam wavelength and $I(0)$ is the value of $I(t)$ when the transient time t or θ is zero.

The above expressions are valid when all the absorbed energy is converted into heat. For fluorescent samples a factor must be introduced in order to take into account the energy emitted. This can be accomplished rewriting the equation for θ as

$$\theta=-\frac{P_el_0}{K\lambda_p}\frac{ds}{dT}\left[A_0+(A_D-A_0)\left(1-\phi\frac{\lambda_e}{\langle\lambda_{em}\rangle}\right)\right], \tag{3}$$

where ϕ is the sample radiative quantum efficiency, λ_e is the excitation beam wavelength and $\langle\lambda_{em}\rangle$ is the average wavelength of the fluorescence.

From these data the quantum efficiency can be calculated by taking the ratio of Eq. (3) for the doped and undoped samples as follows:

$$\frac{\theta_D}{\theta_0}=\frac{A_0+(A_D-A_0)\left(1-\phi\frac{\lambda_e}{\langle\lambda_{em}\rangle}\right)}{A_0}. \tag{4}$$

Here, θ_0 and θ_D are the probe beam phase shift for the undoped and doped samples, respectively (normalized to the excitation beam power and sample thickness) and A_0 and A_D their optical absorption coefficients. The doped sample absorption coefficient is considered to be comprised of two contributions coming from the doping and the sample itself, such as

$$A_D=A_0+A_{\mathrm{Nd}},$$

where A_{Nd} is associated to the neodymium optical absorption coefficient.

Therefore, by measuring the sample optical absorption coefficient and taking the average wavelength of the fluorescence $\langle\lambda_{em}\rangle$ for neodymium as approximately 1.054 μm, the values of the quantum efficiency ϕ can be obtained.

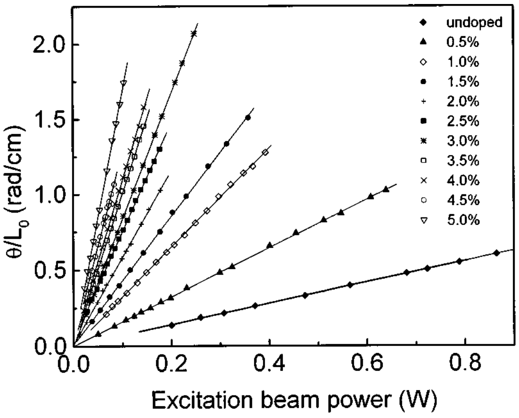

FIG. 2. Normalized thermal lens signal for different excitation laser beam power at 514.5 nm. The probe beam wavelength is 632.8 nm.

IV. RESULTS AND DISCUSSION

In Fig. 2 the steady-state thermal lens results are shown for different excitation beam power for the samples doped with Nd_2O_3. From the linear curve fitting, the values of θ (normalized to the sample thickness and excitation beam power) were determined for each sample and represented in Fig. 3. The time resolved measurements provided similar results for the θ values, as expected. It can be seen that the thermal lens signal increased linearly with neodymium concentration up to 4% wt Nd_2O_3. Above 4% wt Nd_2O_3, the

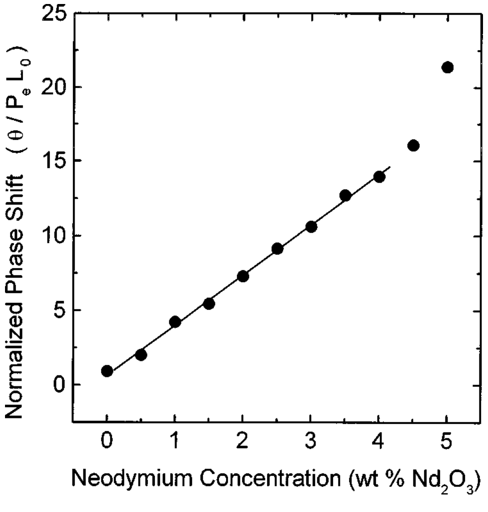

FIG. 3. Normalized thermal lens signal vs different Nd_2O_3 concentration in low silica calcium aluminate glasses.

thermal lens signal increased faster than observed for low doping concentration. This result suggests that the fluorescence rate is constant up to 4% wt Nd_2O_3 and that there was quenching of the fluorescence only for the samples with 4.5% wt and 5.0% wt of Nd_2O_3.

From these data the quantum efficiency was calculated by performing the linear curve fitting shown in Fig. 3 for the θ values of the undoped and doped samples with neodymium concentrations up to 4%. Taking the linear angular coefficient, the optical absorption coefficient of the sample and by using Eq. (3), the fluorescence quantum efficiency was determined to be 0.92 ± 0.05. For the samples with 4.5% wt and 5.0% wt of Nd_2O_3, the values of ϕ were 0.86 ± 0.04 and 0.67 ± 0.04, respectively. The standard deviation of the results was observed to be controlled by the measurements of the optical absorption coefficient, which was about 3% for all measured samples. The results shown in Figs. 2 and 3 were repeated 5 times and the deviations found for each measurement sequence were always below 1.5%. The standard deviation of ϕ values provided by thermal lens in this work are smaller than those accepted in the literature for the Judd-Ofelt model, which are higher than 10%.[19]

Uhlmann *et al.*,[20] analyzing four different compositions of calcium aluminate glasses doped with 0.5% wt of Nd_2O_3, have found that the value of the quantum efficiency was around 0.83, higher than those of silicates, attributing this difference to the lower phonon energy of aluminates. Our results of 0.92 are even higher than those of the authors, and may be associated to the fact that our samples are melted under vacuum conditions, removing the water, and therefore reducing the contribution of the OH to fluorescence quenching.

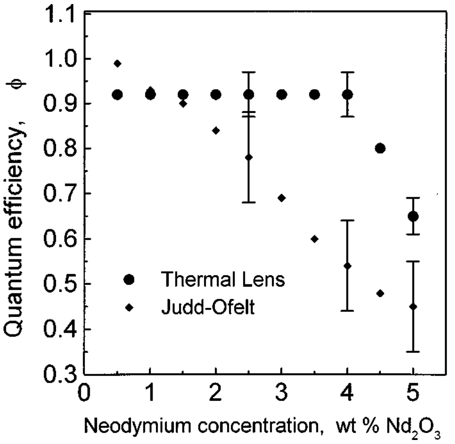

FIG. 4. Fluorescence quantum efficiency vs different Nd_2O_3 concentration determined by thermal lens and Judd-Ofelt methods.

In Fig. 4 the values of the quantum efficiency obtained by TL are compared with those determined through the Judd-Ofelt model in the same samples. If we consider 10% as the standard deviation of the data obtained through the Judd-Ofelt model, the results provided by the two methods are in good agreement for doping concentrations up to 2.0% wt of Nd_2O_3. In contrast, for higher doping concentrations, the Judd-Ofelt model, which considers the experimental radiative lifetime, showed quenching of the fluorescence at lower concentrations than those from TL results. It is well known that the increase in ion concentration induces interactions between the pairs of ions, depopulating the ${}^4F_{3/2}$ level. The lifetime of this level thus is reduced with a consequent decrease in its emission. The depopulation of the ${}^4F_{3/2}$ level has been attributed to the following cross relaxation process: $({}^4F_{3/2}, {}^4I_{9/2}) \rightarrow ({}^5I_{15/2}, {}^4I_{15/2})$, followed by a nonradiative decay to ground state, generating heating.[21] Our results indicate that an additional process, not taken into account by the Judd-Ofelt theory, might be involved. A fraction of those photons would populate higher energy levels, with consequent emission in the visible or UV, with no generation of heat or TL signal. The latter mechanism may explain the difference observed between the two methods. The TL method provides therefore the total fluorescence, while the Judd-Ofelt model determines the emission from the ${}^4F_{3/2}$.

In conclusion, our results provided quantitative information about the thermal lens effect in low silica calcium aluminate glasses doped with neodymium. Fluorescence rates appear to be constant for the investigated samples with concentrations up to 4.0 wt % of Nd_2O_3. Quenching of the fluorescence was significant only for the samples doped with 4.5% wt and 5% wt of Nd_2O_3. The experimental configuration used is very sensitive and we have presented a new method to determine the sample quantum efficiency and, therefore, to evaluate the fraction of the radiative and nonradiative processes in these glasses. The method has been shown to be useful to investigate concentration effects on neodymium fluorescence. The technique is simple to perform, is noncontacting and its high sensitivity indicates that it can be applied for a wide range of fluorescent materials. Furthermore, our results have shown that by melting the glasses under vacuum conditions the fluorescence quantum efficiency of the doping is increased, indicating that calcium aluminate glasses are strong candidates to be used as an active medium for solid-state lasers.

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