Time-resolved Z-scan and thermal lens measurements in Er^{+3} and Nd^{+3} doped fluoroindate glasses

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Abstract

In rare earth ion doped solids, a resonant non-linear refractive index, n_2, appears when the laser pumps one of the ion excited states and the refractive index change is proportional to the excited state population. In these solids there are usually thermal and non-thermal lensing effects, where the non-thermal one is due to the polarizability difference, $\Delta\alpha$, between excited and ground states of the ions. We have used the time resolved Z-scan and a mode-mismatched thermal lens technique with an Ar^+ ion laser in Er^{+3} ($20ZnF_2$–$20SrF_2$–$2NaF$–$16BaF_2$–$6GaF_3$–$(36-x)InF_3$–$xErF_3$, with $x = 1, 2, 3$ and 4 mol%) and Nd^{+3} ($20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–$2NaF$–$(40-x)InF_3$–$xNdF_3$, with $x = 0.1, 0.25, 0.5$–1 mol%) doped fluoroindate glasses. In both samples we found that the non-linear refraction is due to the thermal effect, while the non-thermal effect is negligible. This result indicates that in fluoride glasses $\Delta\alpha$ is very small (less than 10^{-26} cm^3). We also measured the imaginary part of the non-linear refractive index (n_2'') due to absorption saturation.

1. Introduction

Non-linear properties of optical materials are very important in laser active media because standing waves in laser cavities produce light-induced gratings that cause effects such as hole-burning, self-focusing, temporal and spatial self-phase modulation, etc. Thermal effects, like the thermal variation of the refractive index, thermal expansion and thermally-induced stress are considered in solid-state laser design [1]. Several kinds of non-linear experiments, such as interferometric measurements, laser induced gratings, transverse self-phase modulation [2], bi-stability, four and two wave mixing [3], and Z-Scan [4], have been made particularly in Cr^{+3} [2–4] and rare earth [5–7] doped solids (glasses and crystals). In these materials, the non-linear effect originates from dopant ion excited state population, which has a complex susceptibility different from that of ground state, so the medium susceptibility changes proportionally to the excited state population pumped by the laser. This effect is known as Population Lens (PL) effect [8]. Usually, part of the decay from the excited state is non-radiative with the emission of phonons. Consequently, as the laser heats the sample, a refractive index change occurs because of the temperature coefficient of refractive index (dn/dT), the so-called thermal lens (TL) [9,10,12].

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The propagation of a TEM_{00} mode with a radial Gaussian distribution of energy, either the excitation laser beam itself or a probe beam, is affected by the refractive index profile (PL and/or TL). This effect results in beam spreading, with a reduction in its on-axis intensity, or beam focusing with an increase in on-axis intensity. By measuring the beam on-axis intensity in the far field, the non-linear and/or thermo–optical properties of the sample can be obtained. This is the fundamental idea used in both Z-scan [11] and thermal lens [10] techniques which are sensitive but experimentally simple. The determination of the signal response time by time-resolved methods permits the distinction between PL and TL. In most of the works related to Cr^{+3} [2–4], Nd^{+3} [5,6] and Er^{+3} [7] doped solids, the TL effect was found to be negligible in comparison with PL. However, using a time resolved photothermal deflection spectroscopy method on Nd^{+3}-doped ED-2 silicate glass, a ratio of 0.6 for the PL and TL was observed [6].

In the present work, time resolved Z-scan and mode mismatched thermal lens [10,12] measurements were performed in Er^{+3} ($20ZnF_2$–$20SrF_2$–$2NaF$–$16BaF_2$–$6GaF_3$–$(36-x)InF_3$–$xErF_3$, with $x = 1$, 2, 3 and 4 mol%) and Nd^{+3} ($20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–$2NaF$–$(40-x)InF_3$–$xNdF_3$, with $x = 0.1$, 0.25, 0.5–1 mol%) doped fluoroindate glasses. We used an Ar^+ laser, in resonance with the ions absorption lines, in order to pump the excited state population. In both materials, PL effect was found negligible in comparison with TL and they behave like saturable absorbers.

2. Theory

When a rare earth (RE) doped solid is pumped, in resonance with a RE absorption line, both thermal and non-linear effects are proportional to the ion excited state population, N_{ex}. Using rate equations, the normalized excited state population, $n_{ex} = N_{ex}/N_0$ (where N_0 is the total ion concentration), is given by [2]

$$n_{ex} = (1 - e^{-t/\tau})\frac{I/I_s}{1 + I/I_s}, \tag{1a}$$

where

$$\tau^{-1} = \tau_0^{-1}(1 + I/I_s) \tag{1b}$$

and $t = 0$ is the time of the chopper opening, I is the laser intensity, and τ_0 is the excited state lifetime. The saturation intensity is given by $I_s = h\nu/\sigma\tau_0$, where $h\nu$ is the pump photon energy and σ isthe absorption cross-section.

In our theoretical model we assume that the laser beam has a gaussian TEM_{00} intensity profile that at focus position is given by

$$I(r) = I_0 \exp\left(-\frac{2r^2}{\pi w_0^2}\right), \tag{2}$$

where w_0 is the beam radius (where the intensity is I_0/e^2), $I_0 = 2P/\pi w_0^2$ is the peak (on-axis) intensity and P the laser power. The real part of the refractive index can be written as $n'(t) = n'_0 + \Delta n'(t)$, where $\Delta n'$ is the real part of the laser induced refractive index variation due to PL and/or TL. In the far field, the intensity dependence of the sample transmittance through an aperture is proportional to the laser induced phase shift. We should point out that the PL refractive index profile is given only by the $n_{ex}(r)$ profile (determinated by Eqs. (1a) and (2)), while the TL profile also depends on radial heat diffusion.

We first consider the PL effect, where the laser induced refractive index profile is given by [2]

$$\Delta n_p(r, t) = n_{ex}(r, t)\, n_2 I_s, \tag{3a}$$

with the complex non-linear refractive index with $n_2 = n'_2 - in''_2$:

$$n'_2 = (2\pi/n_0) f_L^2 N_0 \Delta\alpha/I_s, \tag{3b}$$

$$n''_2 = -c\Delta\sigma/2\omega I_s, \tag{3c}$$

where $f_L = (n'_0 + 2)^2/3$ is the Lorenz local field correction factor. Eqs. (3a), (3b) and (3c) shows that n'_2 is proportional to the polarizability difference, $\Delta\alpha$, between excited and ground states and n''_2 is proportional to the absorption cross-section difference, $\Delta\sigma$, between excited and ground states. The PL phase shift expressed in terms of the on-axis ($r = 0$) index change at focus: $\Delta\phi_p(t) = (2\pi/\lambda)\Delta n_p(0, t) L_{eff}$, where $L_{eff} = (1 - e^{-AL})/A$ and A is the linear absorption coefficient. From Eqs.

(3a), (3b) and (3c), $\Delta\phi_p(t)$ is proportional to the on-axis excited state population, $n_{ex}(0, t)$, and $\Delta\alpha$ as follows:

$$\Delta\phi_p(t) = \frac{(f_L 2\pi)^2 N_0 n_{ex}(0, t)\Delta\alpha L_{eff}}{n_0'\lambda}. \quad (4)$$

The thermal lens (TL) effect is caused by deposition of heat, via a non-radiative decay process, after laser energy has been absorbed by the sample. In this situation, a refractive index change, Δn_{th}, is established because of the temperature coefficient of refractive index (dn/dT). The TL phase shift is given by [10]

$$\Delta\phi_{th} \approx \frac{PAL}{K\lambda}\varphi\frac{ds}{dT}, \quad (5)$$

where P is the laser power, A the absorption coefficient, K the thermal conductivity and φ the fraction of absorbed energy converted into heat per photon. The optical path change with temperature is given by $ds/dT = (n-1)(1+\nu)\gamma + dn/dT$, where ν is the Poisson's ratio and γ the linear temperature coefficient of thermal expansion [10].

Effects of excited state absorption can be considered similarly to the derivation of Eqs. (3a), (3b) and (3c). In this case A must be replaced by A_s:

$$A_s = N_0(\sigma_1 + n_{ex}\Delta\sigma), \quad (6)$$

where the first term, $N_0\sigma_1$, is just the ground state absorption, A and the second term is due to the excited state absorption, which is related to n_2'' given by Eq. (3c).

3. Experimental

The erbium doped fluoride glasses were prepared with batch compositions $20ZnF_2$–$20SrF_2$–$2NaF$–$16BaF_2$–$6GaF_3$–$(36-x)InF_3$–$xErF_3$, with $x = 1$, 2, 3 and 4 mol%. The concentration range (1–4%) corresponds to 2.0–8.0×10^{20} Er^{+3} ions/cm^3. The InSbZnGdN glasses were prepared with batch compositions $20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–$2NaF$–$(40-x)InF_3$–$xNdF_3$. The $x = 1$ mol% Nd doped glass correspond to a concentration 2.3×10^{20} Nd^{+3} ions/cm^3. The mixture was melted in a platinum crucible at 800°C for 1 h then held at 850°C for 1 h for fining, both treatments were performed in a dry box under argon atmosphere. The melt was cast into a preheated mold at 260°C and cooled to room temperature.

When the non-linear refractive index change is slow, due to a long-lived excited state, transient response measurements can be used in order to eliminate parasitic linear effect. Immediately after the chopper opening ($t = 0$) there is no non-linear phaseshift, so the signal can be normalized by taking $I(t)/I(t=0)$ via a data-acquisition system. The microcomputer also allows the average of several points, collected at each position as a way to improve signal-to-noise ratio. This time-resolved method is used in both Z-Scan [4] and mode-mismatched thermal lens [10] measurements performed in this work.

4. Results

In the case of the Nd^{+3} ion, when a green (0.514 μm) photon is absorbed, phonons are emitted as the system rapidly decays to the $^4F_{3/2}$ metastable state, which then decays radiatively to the $^4I_{9/2}$, emitting an infrared 1.06 μm photon [5,6]. As a first approximation, we supposed that for every 0.514 μm absorbed photon, part of its energy is reemitted as a 1.06 μm photon and the other part converted in heat [5]. We can estimate that $\varphi \sim 1 - 0.514/1.06 \sim 0.5$. Fig. 1 show Z-scan measurements in InSBZnGdN (1% Nd) glass, excited with an Ar^+ laser at 0.514 μm. Fig. 1a shows the measurement with a closed aperture (aperture factor $S = 0.5$ as defined in Ref. [11]) with $\Delta T_{p-v} = 4\%$. This curve indicates a negative laser induced refractive index variation, Δn, because the peak appears between the focal point and the lens. In order to investigate the origin of non-linearity, we did transient measurements and observed a response time of ~ 1 ms, which is much longer than the $^4F_{3/2}$ decay time of 470 μs. This lifetime value was measured by fitting infrared luminescence decay curves obtained with chopped Ar^+ laser excitation and a photodiode. This difference indicates that the PL effect is not responsible for the real part of the non-linear refraction and the longer response time is due to TL effects. The imaginary part of the non-linear refractive index (n_2'') can be obtained by performing the Z-scan measurement with

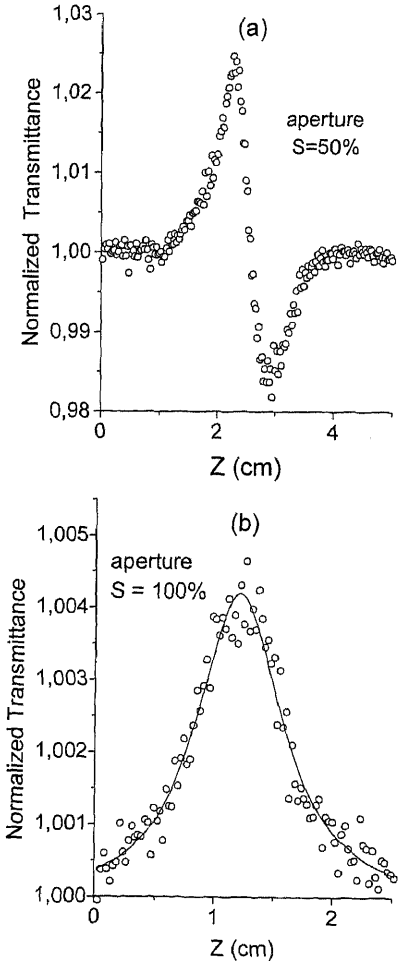

Fig. 1. Z-scan of a InSbZnGdN (1% Nd) 1.7 mm thick sample at $\lambda = 514$ nm, with $P = 1.5$ W, $w_0 = 27$ μm. (a) non-linear refraction measurement done with aperture $S = 0.5$. (b) non-linear absorption measurement done no aperture ($S = 1.0$). The solid line represents the best theoretical fit.

an open aperture ($S = 1$), as shown in Fig. 1b. The transmittance increase at the focus indicates that the absorption decreases when the excited state is populated ($\Delta\sigma < 0$), the material behaves like a saturable absorber. The normalized transmittance variation, $\Delta T(z)$, is used to calculate n_2'' using the following expression (valid for small ΔT):

$$\Delta T(z) = \frac{2}{\lambda} L_{\text{eff}} n_2'' \frac{e^{-\alpha L} P}{w_0^2\left(1 + z^2/z_0^2\right)}, \qquad (7)$$

where $Z_0 = \pi w_0^2/\lambda$ is the diffraction length of the beam. In Fig. 1b we present the experimental data for $S = 1$ with least square fit using Eq. (7). The fit gives $z_0 = (0.44 \pm 0.022)$ cm and $\Delta T(z = 0) = (4.35 \pm 0.2) \times 10^{-3}$, we calculated $n_2'' = (1.9 \pm 0.1)10^{-12}$ cm^2/W.

For the Er^{+3} doped fluoroindate glasses, we used the 0.488 μm Ar^+ laser line in resonance with the $^4F_{7/2}$, which then decays to several metastable levels [13]: $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$. Consequently, as opposed to Nd^{+3}, several excited states have significant population and contribute to the PL effect. Besides the spontaneous emission decay, excited state absorption and cooperative effects also appear, consequently, the population dynamics are complicated. However, the main peak in the emission spectrum is at 0.555 μm so, as a first approximation, we can estimate that $\varphi \sim 1 - 488/555 = 0.12$. The Z-scan results obtained with closed aperture ($S = 0.5$) were similar to those obtained in Nd^{+3} doped samples, with a negative $\Delta n'$ and a response time of 1.1 ms. We believe that for Er^{+3} doped fluoroindate glasses, TL is also the dominant effect of the laser induced refraction. For a 2.1 mm thick 1% Er^{+3}-doped sample, at 488 nm, with $S = 0.5$ and $I_0 = 6.6 \times 10^4$ W/cm^2, we obtained $\Delta T_{p-v} = 9.4\%$. The non-linear absorption measurement gave $n_2'' = (1.6 \pm 0.1) \times 10^{-11}$ cm^2/W.

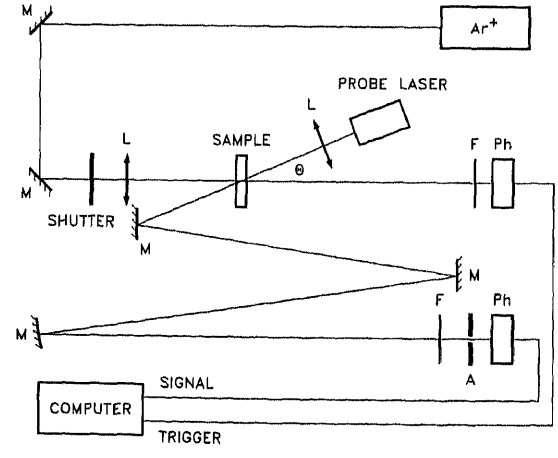

Fig. 2. Schematic diagram of the time-resolved thermal lens apparatus with an Ar^+ ion laser ($\lambda = 515$ or 488 nm) as excitation beam and a HeNe ($\lambda = 633$ nm) laser as probe beam. M are mirrors, L lens, F neutral density filters and Ph photodiodes detectors.

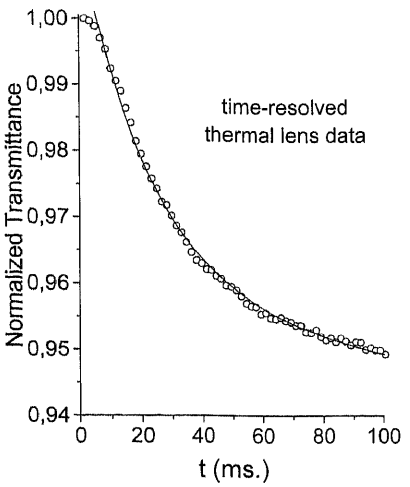

Fig. 3. Time-resolved mode-mismatch TL experimental data of 2% doped Er^{+3} sample and their best fit curve in solid line. Sample length $L = 3$ mm, excitation power $P_e = 0.3$ W (at 488 nm where $A_e = 0.6$ cm^{-1}). The solid line represents the least square theoretical fit which gives $t_c = 3.73$ ms and $\Delta\phi_{th} = 0.0495$.

The time resolved Z-scan method [4] we used is completely equivalent to the single beam TL technique. In order to investigate thermal origin of the $\Delta n'$, we performed measurements with the mode-mismatched dual-beam method, which is more sensitive than the mode-matched dual-beam or single-beam method [11]. In the experimental arrangement for mode mismatched TL (shown in Fig. 2), a continuous wave TEM_{00} Gaussian beam illuminates a sample, causing a thermal lens. A weak TEM_{00}, Gaussian probe beam, which is almost co-linear to the excitation beam, passes through the sample to probe the thermal lens. In the time resolved method, the time development of the probe beam signal is measured [10]. We used a 6 W Ar^+ as the excitation laser and a 4 mW HeNe as the probe laser. The beam radius at the sample position was $w_e = 101$ μm and $w_p = 430$ μm for the excitation and probe beams respectively. Fig. 3 shows a typical result for a 2% Er doped sample. The transient signal amplitude is proportional to the phase 2 shift, $\Delta\phi_{th}$ (given by Eq. (5)), and the thermal response time is given by $t_c = W_e^2/4D$, where w_e is the excitation beam radius at sample position and D the thermal diffusivity ($D = K/\rho c$, where c is the specific heat and ρ is the density). The least square fit of the experimental data of Fig. 3, with Eq. 10 of Baesso et al. [10], gives $t_c = 3.73$ ms and $\Delta\phi_{th} = 0.0495$. Using the t_c and w_e values, we calculated diffusivity $D = (2.0 \pm 0.1) \times 10^{-3}$ cm^2/s. Using $\Delta\phi_{th}$ obtained from the fit, and assuming a typical fluoride glass thermal conductivity [15] of 6 mW cm^{-1} · K^{-1} and $\varphi \sim 0.12$, we determined that $ds/dT = -3.9\ 10^{-6}$ K^{-1}. From a similar measurement for a InSBZnGdN (1% Nd) sample, using 515 nm excitation, we obtained $D = (4.5 \pm 0.1) \times 10^{-3}$ cm^2/s and $ds/dT = -6.7 \times 10^{-7}$ K^{-1}.

5. Discussion

We point out that $ds/dT \alpha [\phi - \eta\beta]$, where ϕ and β are the temperature coefficients of the electronic polarizability and volume expansion respectively, and η is a constant that depends on the glass refractive index and the Poisson ratio ν. Contrary to most oxide glasses, we obtained a negative value for ds/dT. This is an indication of a small ϕ factor for the glasses in this study. Our results on fluoroindate glasses are comparable with those obtained using interferometric techniques for fluorozirconate glasses [14], ds/dT varies in the range $(-2$ to $-6) \times 10^{-6}$ K^{-1}, dn/dT $(-8$ to $-5) \times 10^{-6}$ K^{-1} and expansion coefficient, γ, typically is 15×10^{-6} K^{-1}.

Another relevant fact is that no PL have been observed in the real part of the laser induced refractive index variation, Δn, so PL is responsible only for the non-linear absorption (n_2''). Consequently, supposing that $\Delta\phi_p$ is at least one order of magnitude smaller than $\Delta\phi_{th}$, by Eqs. (4) and (5), we estimate that in Nd^{+3}-doped InSBZnGdN $\Delta\alpha$ is smaller than 10^{-26} cm^3. Bubnov et al. [5] observed $\Delta\alpha \sim 10^{-25}$ in several Nd^{+3} doped glasses. An interesting systematic study was performed by Powell et al. [5] in order to investigate the dependence of $\Delta\alpha$ on the host media for Nd^{+3} materials (crystals and glasses were studied). It was observed that $\Delta\alpha$ can vary by up to one order of magnitude, in the range 10^{-26}–10^{-25} cm^3, depending on host media, the effect being larger for oxides than for fluorides.

6. Conclusion

With open aperture, our Z-scan measurements indicate that both kinds of glasses studied in this

work behave like saturable absorbers. The closed aperture Z-scan measurements indicates negative values of n_2, which are attributed to a thermal effect. Our thermal lens measurements indicates negative ds/dT, with magnitude similar to those previously obtained in fluorzirconate glasses.

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