Temperature dependence of thermo-optical properties of optical glasses determined by Thermal Lens Spectrometry

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In this work we report on the use of thermal lens spectrometry to determine the temperature dependence of the thermo-optical properties, namely, thermal conductivity, thermal diffusivity, temperature coefficient of optical path length change and fluorescence quantum efficiency of ZBLAN and Nd\textsubscript{2}O\textsubscript{3}-doped low silica calcium aluminosilicate glasses. The results indicates that this technique can be used for the complete characterization of the thermo-optical properties of optical glasses as a function of temperature.

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Thermo-optical properties are among the most important characteristics determining the figures of merit of optical materials. They essentially determine the servicing conditions such as, thermal shock and thermal stress resistance, thermal lens effect, and so on[1]. The thermal diffusivity (D) measures essentially the thermalization time of a given material and it is known to be strongly dependent upon the sample composition. The temperature coefficient of the optical path length change (\(ds/dT\)) describes the thermally induced distortion of a laser beam after its passing through the sample, while fluorescence quantum efficiency (\(\phi\)) is one of the most important optical properties of fluorescent materials, specially in the case of ions-doped glasses used as a laser hosts. Furthermore, it is also important to know these thermo-optical properties in a wide temperature range, since they affect the material processing conditions and also its response in the working temperature range.

The Thermal Lens (TL) technique has proved to be a valuable method to study the thermo-optical properties of transparent materials [2-12]. It allows the determination of thermal diffusivity and thermal conductivity, the temperature coefficient of optical path length, optical absorption coefficient and fluorescence quantum efficiency. Since this is a remote technique measurement of samples inside a furnace present no extra difficulty, allowing therefore the experiments to be performed as a function of the temperature.

In this work we describe the results of our research regarding the application of the two beam mode mismatched TL technique to determine the temperature dependence of the thermo-optical properties of optical glasses. For the fluoride (ZBLAN) glasses the experiments were performed in the temperature range where the phase transition occurs. For Nd\textsubscript{2}O\textsubscript{3}-doped low silica calcium aluminosilicate glasses (LSCAS) the fluorescence quantum efficiency was determined in the temperature range from 22 °C up to 200 °C.

**Experimental**

In the two beam arrangement the TL effect is created when an excitation laser beam passes through the sample and the absorbed energy is converted into heat, changing the refractive index of the sample and therefore producing a lens-like optical element within the sample. The propagation of the probe beam laser through the TL results in either a defocusing (\(ds/dT < 0\)) or a focusing (\(ds/dT > 0\)) of the beam center. The theoretical treatment of the TL effect considers the aberration of the thermal lens as an optical path length change to the probe laser beam, which can be express as an additional phase shift on the probe beam wave front after its passing through the sample. The analytical expression for absolute determination of the thermo-optical properties of the sample is given by [2-12]:

\[
I(t) = I(0) \left(1 - \frac{\theta}{2} \tan^{-1} \frac{2n:\nu}{(l + 2n^2 + t^2)k_{\lambda_0} / (2) + 1 + 2n + t^2} \right)^2
\]

Where

\[
\theta = - \frac{P_e A_n}{K_{\lambda_n}} \left( \frac{ds}{dT} \right)_p
\]
\[
V = \frac{Z_t}{Z_c}
\]
\[
m = \left( \frac{\alpha_p}{\alpha_0} \right)^2
\]

In eq. (1) \(I(t)\) is the temporal dependence of the probe laser beam at the detector, \(I(0)\) is the initial value of \(I(t)\), \(\theta\) is the thermally induced phase shift of the probe beam after its passing through the sample, \(\alpha_0\) and \(\alpha_p\) are the probe beam and excitation beam spot sizes at the sample, respectively, \(P_e\) is the excitation beam power, \(A_n\) is the optical absorption coefficient of the sample at the excitation beam wavelength, \(Z_c\) is the confocal distance of the probe beam, \(Z_t\) is the distance from the probe beam waist to the sample, \(k_0\) is the sample thickness, \(K\) is the thermal conductivity, \(\lambda_p\) is the probe beam wavelength, \(t_e\) is the characteristic thermal lens time constant, and \((ds/dT)_p\) is the temperature coefficient of the optical path length change at the probe beam wavelength.

The TLS experiments have been performed with the mode mismatched configuration. The set up is shown in fig. 1. In the time resolved measurements, \(\theta\) and \(t_e\) are
straightforwardly obtained from the fitting of the experimentally observed profile of the developing thermal lens to Eq. (1). Therefore, it can be observed that by having the experimental value of \( \theta \), the thermal conductivity and optical absorption coefficient determined from complementary techniques, the absolute value of the parameter \( ds/dT \) of the sample can be determined.

In order to validate and evaluate the sensitivity of the proposed method we have also carried out complementary measurements of the samples specific heat, using the transient heat method [13] and differential thermal analyser (DTA) for the evaluation of the glass transition temperature.

The fluoride glasses are very transparent, presenting a very low absorption coefficient (\( A \sim 10^{-3} - 10^{-4} \text{cm}^{-1} \)) in the visible and an even lower coefficient in the mid infrared. Since the TL signal is proportional to \( A \), the signal of undoped matrixes is very low. We have accordingly increased the absorption of these glasses by doping the sample with 0.2 mol% CoF\(_2\), in order to improve the signal to noise ratio. The basic sample composition was ZrF\(_4\) (53 mol%), LaF\(_3\) (4.5 mol%), AlF\(_3\) (3.5 mol%), BaF\(_2\) (29 mol%), NaF (10 mol%).

The LSCA glasses were prepared by melting the samples with different concentrations of neodymium dioxide in graphite crucible and under vacuum conditions [4,7,8]. The compositions of the samples were 27.7 mol% Al\(_2\)O\(_3\)-X; 57.5 mol% CaO, 7.9 mol% SiO\(_2\), and 6.9 MgO [4,7,8]. Where X is Nd\(_2\)O\(_3\) concentration.

Results and Discussion

In Fig. 2 we show a typical transient thermal lens signal for the ZBLAN glass at room temperature.

The solid line corresponds to the data fitting of Eq. (1) to the TL experimental data leaving \( \theta \) and \( t_c \) as adjustable parameters. The values we obtained were \( \theta=(0.3010 \pm 0.0005) \) and \( t_c=(0.55 \pm 0.01) \text{ ms} \). Using for \( t_c=(\omega_e^2/4D) \) we obtained \( D=(2.52 \pm 0.1) \times 10^{-3} \text{ cm}^2/\text{s} \), for the thermal diffusivity.

The same procedure was carried out for measurements as a function of temperature in the range of 25 °C up to 320 °C. This upper limit for the temperature excursion was essentially dictated by the glass transition temperature, \( T_g \), of this material. The glass transition temperature was independently measured using a Differential Thermal Analyzer (DTA), and the value found for \( T_g \) was 298 °C. The results of our DTA measurements for the ZBLAN doped with 0.2% CoF\(_2\) are shown in Fig.3.

In Fig. 4 we show the resulting temperature dependence of the thermal lens signal (\( \theta \)) and the thermal diffusivity (D) of the ZBLAN sample as obtained from the TL measurements. As before, the values of these parameters were obtained from the transient TL signal data fitting to Eq. (1).

In Fig. 3 we show the Differential Thermal Analyzer (DTA) curve of the 0.2 % mol of CoF\(_2\) doped ZBLAN glass.

We note from Fig. 4 that both parameters exhibit a marked change around \( T_g \). The thermal diffusivity, after remaining practically constant up to 280 °C, passes through a sharp minimum at \( T_g \). The overall decrease of the D values in the temperature range close to \( T_g \) is of a factor of 12. The values of \( \theta \) show a sharp jump around \( T_g \). The solid line was obtained by using a gaussian fitting in the (\( \theta/PA \)) data. The arrow indicates the inflection point of this curve. To further explore the \( T_g \)
identification using the $\theta$ data we have taken the temperature derivative of the $\theta$ fitted curve shown in fig. 4. The result is shown in fig. 5 in which we note the close resemblance between $d\theta/dT$ and DTA at the glass transition.

![Figure 5](image_url)

**Figure 5.** Temperature dependence of the $(1/PeA_0)(d\theta/dT)$.

Considering that $K=\rho CD$, Eq.(2) can be rewritten as [9]:

$$\theta = \left( \frac{P_A A_0}{D \lambda_p} \right) \left( -\frac{1}{\rho C} \left( \frac{ds}{dT} \right)_p \right)$$  \hspace{1cm} (4)

The first term on the right-hand side is essentially the energy deposited by the pumping beam within a probe beam characteristic volume consisting of a cylinder of unit area and length equal to the probe beam wavelength, $\lambda_p$. The second term, namely, $-(\rho C)^{-1} ds/dT$, henceforth denoted by $-ds/dQ$, is a sample's characteristic response function telling us how the optical path changes with the heat deposited per unit volume. That is, it is a measure of the thermal lens distortion induced within a given material by a pumping beam. From the point of view of glass laser design, it may appear that this quantity is indeed the one we should be looking at when investigating the laser beam profiles and distortions within the active medium under high power operation conditions. Using our data for the 0.2% CoF$_2$ doped ZBLAN glass we have plotted in Fig. 6 $-ds/dQ$ as a function of temperature. It follows from Fig. 6 that up to 250°C, $-ds/dQ$ remained roughly constant. Between 250 and 280°C it increased with increasing temperature. As the temperature crosses the glass transition temperature, between 280 and 300°C, $-ds/dQ$ passes through a minimum to finally exhibit a sharp jump above 300°C.

![Figure 6](image_url)

**Figure 6.** Characteristic optical path changes with deposited heat ($-ds/dQ$) as a function of temperature.

This behavior of $-ds/dQ$ is closely related to that of the DTA measurements as follows. Between 200 and 280°C, the DTA measurements tell us that the sample tends to lose heat so that $-ds/dQ$ should increase with increasing temperature. In the temperature range between 280 and 300°C, the DTA data tell us that the sample tends to retain heat so that one expects $-ds/dQ$ to decrease with increasing temperature. Finally, the sudden rise above $T_g$ is basically attributed to the larger increase in the thermal expansion coefficient, and consequently of the optical path, which is observed in a glass transition.

The same procedure used for the ZBLAN glass was adopted in the study of LSCAS doped with Nd$_2$O$_3$. In Fig. 7 the normalized temperature dependence of $\theta/P_A$ is shown.

It can be observed that the parameter $\theta$ is almost constant in this temperature range. Since this doped glass is fluorescent, in order to determine the temperature dependence of the sample fluorescence quantum efficiency, $\phi$, eq. (2) must be modified, as follows[8]:

$$\theta = \frac{P_A A_0}{K \lambda_p} \left( \frac{dS}{dT} \right)_p A_D \left( 1 - \frac{\lambda_e}{\lambda_{em}} \right)$$  \hspace{1cm} (5)

Where $\phi$ is the sample radiative quantum efficiency, $\lambda_e$ is the excitation beam wavelength and $\langle \lambda_{em} \rangle$ is the average wavelength of the fluorescence, and $A_D$ is the doped sample optical absorption coefficient.

![Figure 7](image_url)

**Figure 7.** Temperature dependence of the normalized TL signal for Nd$_2$O$_3$-doped LSCA.

![Figure 8](image_url)

**Figure 8.** Temperature dependence of the thermal conductivity.
From eq. (5) we observe that to obtain the \( \phi \) value the parameters \( \lambda_{em} \), AD, ds/dT and K need to be known. In order to obtain the thermal conductivity, K, we have performed independent measurements of the specific heat and the mass density as a function of the temperature. With these data the temperature dependence of the K values was obtained, as shown in Fig. 8.

The parameter AD was obtained by measuring the optical transmittance of the sample in 514.5 nm in the same temperature range where the TL experiments have been performed. The value of \( \lambda_{em} \) determined from the luminescence spectra was 1.054 nm, while ds/dT was considered constant in this temperature range and equal to 6.0.10^{-6} K^{-1}.

Figure 9 shows the fluorescence quantum efficiency results for different concentration of Nd\(_2\)O\(_3\)-doped low silica calcium aluminosilicate glasses. There was a decrease of about 30% in their values for the sample doped with 2 wt% of Nd\(_2\)O\(_3\) and around 40% for the one doped with 4.5 wt% of Nd\(_2\)O\(_3\) when the temperature was increased from 22 °C up to 200 °C.

This is the first time that TL spectrometry is applied to determine the absolute value of fluorescence quantum efficiency as a function of the temperature.

In conclusion, in this work we have shown the results of our recent work using thermal lens spectrometry to perform a complete evaluation of the thermo-optical properties of optical glasses as a function of the temperature. For fluoride glasses, two interesting aspects emerged from these measurements. First, it was shown that the thermal diffusivity exhibits a sharp minimum at 298 °C which coincides with the T\(_g\) value measured by DTA. Secondly, using the data for the thermal diffusivity and the probe beam phase shift, we calculated the rate of change of the optical path with respect to the heat absorbed. It was shown that this parameter is closely related to the behavior of the DTA measurements. For low silica calcium aluminosilicate glasses doped with Nd\(_2\)O\(_3\), we have determined the temperature dependence of the fluorescence quantum efficiency in the range from 25 °C up to 200 °C.

We believe that the sensitiveness together with its simplicity and its remote character may render this technique as a valuable tool for the complete characterization of the thermo-optical properties of transparent materials as a function of the temperature.

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References