Temperature dependence of thermo-optical properties of fluoride glasses determined by thermal lens spectrometry

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In this work we report on the use of the thermal lens spectrometry to determine the absolute values of thermal diffusivity, thermal conductivity, and temperature coefficient of optical path-length change of several fluoride glasses. The results showed that flouride glasses doped with minor quantities of Ga, In, and Zn exhibit thermal conductivities and thermal diffusivities roughly 20% larger than that of fluorozirconate (ZBLAN) glasses, whereas their temperature coefficients for the optical path-length change was found to be 50% smaller. This suggests that these fluoride glasses may be considered as promising candidates for high power laser applications. We have also demonstrated how this technique can be used for the complete thermo-optical properties characterization as a function of temperature. [S0163-1829(99)01342-9]

INTRODUCTION

Fluoride glasses have been a subject of increasing interest mainly due to their high transparency at long wavelength, up to 10 μm.[1,2] When doped with rare-earth ions these glasses present very low nonradiative decay rates as compared to the oxide glasses. These two features are essentially due to their low-field strength and weak chemical bonds.[1] However, this also implies in poor physical and chemical properties, namely high expansion coefficients, low values of both thermal conductivity (K) and thermal diffusivity (D) and high-temperature coefficient of the optical path-length change (ds/dT).[3–6] These thermo-optical properties are among the most important characteristics determining the figures of merit of optical glasses. They essentially determine the glass servicing conditions such as thermal shock and thermal stress resistance,[5] thermal lens effect, and so on. The thermal diffusivity measures essentially the thermalization time of a given material and it is known to be strongly dependent upon the compositional and microstructural variables as well as processing conditions,[7–10] while ds/dT describes the thermally induced distortion of a laser beam after its passing through the sample.[7] Furthermore, it is also important to know the thermal properties in a wide temperature range, up to the glass transition temperature (T_g), since they affect the fiber pulling, glass formation and devitrification processes.[11]

The thermal lens (TL) technique has proved to be a valuable method to study the thermo-optical properties of transparent materials.[9,10,12–16] It allows the determination of thermal diffusivity and thermal conductivity,[9,10,15] the temperature coefficient of optical path length,[9,13] optical absorption coefficient,[16] and fluorescence quantum efficiency.[12,13] Since this is a remote technique the measurement on a sample inside a furnace presents no extra difficulty, allowing therefore the measurements to be performed as a function of the temperature.

In the thermal lens effect, the propagation of a TEM_{00} Gaussian laser beam (either the excitation laser beam itself or a probe beam) is affected by the refractive index profile, or more generally, by a profile of the optical path length s. This results in beam spreading (when $ds/dT<0$) with a reduction in its on-axis intensity, or beam focusing (when $ds/dT>0$) with an increase in on-axis intensity.

There are several experimental configurations for the thermal lens spectrometry. The two-beam mode-mismatched experimental arrangement has shown to be the most sensitive one.[17] The theoretical model for the thermal lens effect in this configuration has been developed and an analytical expressions to treat the thermal lens effect quantitatively was obtained.[9,18,19] By measuring the beam on-axis intensity in the far field and using this theoretical model the thermo-optical properties of the sample can be obtained.

Considering the importance in determining the thermo-optical properties of fluoride glasses and the difficulties in measuring these properties using conventional calorimetry, a simple and accurate method to determine the temperature dependence of these properties is of utmost importance. In this work the two-beam mode-mismatched TL technique is used to determine the absolute value of thermal diffusivity, thermal conductivity, and the temperature coefficient of the optical path-length change of several fluoride glasses. For the ZBLAN glass doped with 0.2% mol CoF_2 we have measured the temperature behavior of the thermal diffusivity and ds/dT from 25 °C up to 315 °C. This range of temperature includes the temperature transformation of the glass (T_g), which is around 298 °C.

THEORY

In the mode mismatched thermal lens measurement, the sample is illuminated by a TEM_{00} Gaussian laser beam. As a result of the optical energy absorption, a local temperature rise is produced within the sample due to the nonradiative decay processes. The change of the refractive index with the

TABLE I. Comparisons of the fluoride glasses studied in this work (mol %).

Acronym	ZrF_4	YF_3	LaF_2	AlF_3	GaF_2	InF_3	CaF_2	SrF_2	BaF_2	ZnF_2	PbF_2	NaF
ZBLAN	53		4.5	3.5					29			10
YABC		20		40			20		20			
PGIZCa					20	15	20			15	30	
ISZn					6	34		20	16	20		4
InSBZnGdN					$2GdF_3$	40		20	16	20		2

temperature produces a lenslike element within the heated region. A weak probe beam propagating through this heated region will experience an optical path-length change, resulting in a variation of its intensity at the beam center in the far field. The resulting change of the center probe beam intensity due to the thermal lens can be expressed as[9,18,19]

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

where

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

Here, t_c is the characteristic thermal lens time constant, ω_e is the excitation laser beam radius at the sample, $D=K/\rho C\,(\mathrm{cm^2\,s^{-1}})$ is the thermal diffusivity, $\rho\ (\mathrm{g\,cm^{-3}})$ is the density, $C\ (Jg^{-1}\,\mathrm{K^{-1}})$ is the specific heat, 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, and $I(0)$ is the value of $I(t)$ when the transient time t or θ is zero. The TL transient signal amplitude is proportional to its phase shift θ, given by[9]

$$\theta=-\frac{PA_eL}{K\lambda_p}\frac{ds}{dT}, \quad (3)$$

where 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, $P(W)$ is the excitation laser power, $A_e(\mathrm{cm^{-1}})$ is the absorption coefficient at the excitation beam wavelength, $K(\mathrm{W\,K^{-1}\,cm^{-1}})$ is the thermal conductivity, $\lambda_p\,(\mathrm{cm})$ is the probe beam wavelength, L (cm) is the sample thickness and $ds/dT\,(\mathrm{K^{-1}})$ is the optical path-length change with temperature, which is given by[9,20]

$$\frac{ds}{dT}=\frac{(n-1)}{L}\left(\frac{dL}{dT}\right)_{T_o}+\left(\frac{dn}{dT}\right)_{T_o}, \quad (4)$$

where n and L are the sample's refractive index and length, respectively, at the initial temperature T_o. We note that the above expression for ds/dT is a normalized quantity taking into account both thermal expansion and refractive index changes. According to Refs. 9 and 20 ds/dT can be expressed as

$$\frac{ds}{dT}=(n-1)(1+\nu)\gamma+\frac{dn}{dT}, \quad (5)$$

where $\gamma\ (\mathrm{K^{-1}})$ is the linear thermal expansion coefficient, n is the refractive index, and ν is Poisson's ratio. Since the first term in Eq. (4) is always positive, glasses with negative dn/dT are required to minimize ds/dT. So far all glasses with ds/dT are fluoride glasses or glasses containing fluorine. In order to analyze the magnitude of ds/dT it is convenient to express it as proportional to $[\phi-\eta\beta]$,[9] 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. It can be seen that the values of ϕ and β determine the absolute value of ds/dT.

We have performed time-resolved TL experiments in several fluoride glasses, using the two-beam mode-mismatched TL configuration. From the transient TL signal data fitting the parameters θ and t_c are obtained from which the values of D, K, and ds/dT are deduced.

EXPERIMENT

The fluoride glasses are very transparent, presenting a very low absorption coefficient ($A\sim10^{-3}$–$10^{-4}\,\mathrm{cm^{-1}}$) 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 them with low concentrations of Cobalt fluoride, CoF_2, in order to improve the signal-to-noise ratio.

The starting materials used for the preparation of our glasses were fluorides (BDH and Strem products) and oxides as In_2O_3, ZnO, and Ga_2O_3 (MetalEurop). The ammonium bifluoride was used to transform oxides into fluorides. The mixtures were heated in a platinum crucible for melting and refining. Finally, the melt was poured into a brass mold preheated few degrees below T_g temperature to prepare samples 4-mm thick. All these operations were carried out in a glove box with controlled inert atmosphere whose relative moisture was kept below 10 ppm. Table I summarizes the glass compositions used in this work. They are fluoroindates (PGIZCa, ISZn, InSBZnGdN), fluoroaluminate (YABC), and fluorozirconates (ZBLAN). The Co^{2+} doped glasses presented a wide ($\sim$ 130 nm) absorption band, centered at 550 nm with significant absorbance at 514.5 nm. The density of the samples were measured using the buoyancy method with CCl_4 as the

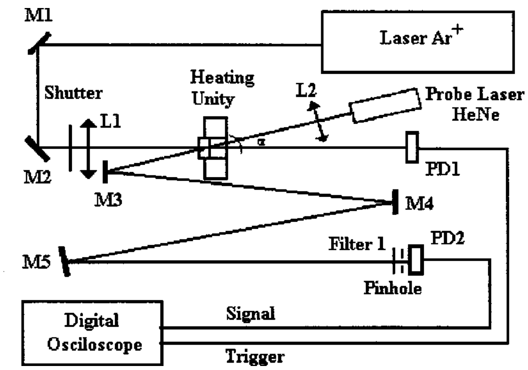

FIG. 1. A schematic diagram of the mode-mismatched thermal lens experimental apparatus, where M_1, M_2, M_3, M_4, and M_5 are mirrors, PD_1 and PD_2 are detectors, and L_1 and L_2 are lenses. Sample is placed inside the heating unity.

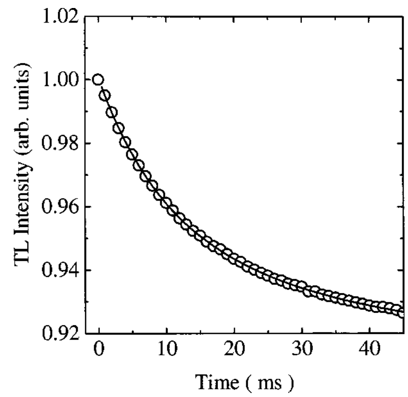

FIG. 2. Transient TL signal at room temperature for the 0.2% CoF_2 ZBLAN sample. The line indicates the curve fitting using Eq. (1) of the text.

immersion liquid. The samples' specific heat were measured by using the thermal relaxation method.

The mode-mismatched thermal lens experimental setup is shown in Fig. 1. We have used an Ar^+ laser as an excitation beam and a HeNe laser as the probe beam. The sample was positioned at the waist of the excitation laser beam, where the power density is maximum. The excitation beam was focused with a $f_1=15$-cm lens (L_1), and the sample was positioned at its focal plane. The exposure of the sample to the excitation beam was controlled by means of a shutter. The probe laser beam was focused using a converging lens (L_2) with focal length $f_2=25$ cm at an angle $\alpha<1.5°$ with respect to the excitation beam and centered to pass through the thermal lens to maximize the TL signal. The excitation beam was incident on a detector (PD_1) and used as a trigger. The adjustable mirrors M_3, M_4, and M_5 were used to get a long optical length (~2 m) from the sample to an iris mounted before the detector (PD_2). For the measurements at different temperatures, the sample was placed in an oven. The experiments were carried out in the temperature range between 25 °C up to ~350 °C. Using the same TL experimental configuration we have also measured the optical absorption coefficients of our samples, by measuring the transmitted Ar^+ laser light as a function of the incident power.

RESULTS AND DISCUSSION

Figure 2 shows a typical TL signal for the ZBLAN with 0.2% mol of CoF_2. The experimental data fitting to Eq. (1) yielded $\theta=0.3010\pm0.0005$ and $t_c=0.55\pm0.01$ ms. Using Eq. (2) for t_c we obtained $D=(2.5\pm0.1)\times10^{-3}$ cm^2/s, for the thermal diffusivity. The same procedure was carried out with all the other fluoride samples, and the resulting values for thermal diffusivity are summarized in Table II. In particular, for the case of the ZBLAN glasses, we have performed the measurements with four samples with different concentrations of CoF_2, namely, 0.1, 0.2, 0.3, and 0.38 mol %. The results obtained for their thermal diffusivities in this concentration range is practically constant and equal to $D=(2.6\pm0.1)\times10^{-3}$ cm^2/s, as shown in Table II. From this value of D, and the measured values of ρ and C also shown in Table II, the thermal conductivity for these samples was calculated as $K=(7.6\pm0.1)\times10^{-3}$ W/cm K. For the other fluoride samples the thermal conductivity values are summarized in Table II.

In this way, we could perform a complete thermal properties characterization of the fluoride glass samples using the thermal lens technique. In particular, we note from Table II that the introduction of Ga, In, and Zn fluorides in the base composition of the fluoride glasses results in an improvement of the thermal properties of these glasses, without affecting the good optical properties of these materials. The thermal diffusivity and thermal conductivity of the first three glasses in Table II are roughly between 25 and 35% higher than those of ZBLAN. For laser applications, this represents a considerable gain in terms of heat dissipation, especially for the case of high power applications.

We have next used the above values of the thermal conductivity of these samples, together with the corresponding measured values for their optical-absorption coefficients and θ, to calculate ds/dT. The results are summarized in Table II. All fluoride glasses studied presented positive θ, which [cf Eq. (1)] indicates negative ds/dT values. The reason for this is that fluoride glasses are known to present very large thermal expansion coefficient β, which combined with the small values of ϕ for the fluoride ions, results in negative dn/dT and ds/dT.[21–23] It can be seen from Table II that for the first three samples, containing the Ga, In, and Zn fluorides, ds/dT is roughly 50% smaller as compared to the ZBLAN sample values. That is, the addition of these fluorides to the base composition not only improves their thermal properties but also makes the optical path within these materials less susceptible to temperature changes. Considering that ds/dT is proportional to $[\phi-\eta\beta]$, the observed decrease in the value of ds/dT for the samples 1, 2, and 3 can be associated with a better combination of the two parameters ϕ and β minimizing the values of ds/dT for these samples as compared to the ZBLAN glasses. The observed decrease of ds/dT for these samples is quite interesting. It indicates that these glasses should exhibit lower thermal distortions, at the same time that it suggests that further modification in the samples composition may lead to an improvement in lowering the ds/dT values for these samples.

Finally, to further demonstrate the usefulness of the TL technique for the complete thermo-optical characterization of glass samples, we have performed some measurements of the thermal properties as a function of temperature. These mea-

TABLE II. Optical absorption coefficient Θ/P, thermal diffusivity, thermal conductivity, and ds/dT of the fluoride glasses determined at room temperature.

Samples	L (cm)	A_e (cm^{-1})	Θ/P (W^{-1})	D (10^{-3} cm^2/s)	ρ (g cm^{-3})	C J/g K	K (10^{-3} W/K cm)	ds/dT (10^{-6} K^{-1})
PGIZCa 0.2 CoF_2	0.366 ± 0.001	0.90 ± 0.04	1.200 ± 0.002	2.9 ± 0.1	5.359 ± 0.004	0.67 ± 0.03	10.4 ± 0.9	-2.4 ± 0.3
IsZn 0.2 CoF_2	0.324 ± 0.001	1.0 ± 0.1	0.700 ± 0.001	3.1 ± 0.1	4.761 ± 0.004	0.67 ± 0.03	9.9 ± 0.8	-1.3 ± 0.2
InSBZnGdN 0.3 CoF_2	0.272 ± 0.001	0.80 ± 0.02	0.700 ± 0.001	3.2 ± 0.1	4.753 ± 0.004	0.67 ± 0.03	10.2 ± 0.8	-2.1 ± 0.2
YABC 0.38 CoF_2	0.212 ± 0.001	1.80 ± 0.03	1.500 ± 0.002	3.3 ± 0.1	3.704 ± 0.004	0.67 ± 0.03	8.2 ± 0.7	-2.0 ± 0.2
ZBLAN 0.1 CoF_2	0.31 ± 0.001	0.40 ± 0.05	1.500 ± 0.003	2.6 ± 0.1	4.445 ± 0.004	0.67 ± 0.03	7.7 ± 0.7	-5.9 ± 1.3
ZBLAN 0.2 CoF_2	0.349 ± 0.001	0.70 ± 0.01	3.100 ± 0.004	2.5 ± 0.1	4.445 ± 0.004	0.67 ± 0.03	7.4 ± 0.7	-6.0 ± 0.6
ZBLAN 0.3 CoF_2	0.322 ± 0.001	1.50 ± 0.02	6.000 ± 0.001	2.5 ± 0.1	4.445 ± 0.004	0.67 ± 0.03	7.4 ± 0.7	-5.8 ± 0.6
ZBLAN 0.38 CoF_2	0.268 ± 0.001	2.20 ± 0.10	7.400 ± 0.001	2.7 ± 0.1	4.445 ± 0.004	0.67 ± 0.03	8.0 ± 0.7	-6.4 ± 0.9

surements were carried out with the ZBLAN sample with 0.2% CoF_2. The sample was positioned inside an oven and the temperature was varied from 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 Figs. 4 and 5 we show the resulting temperature dependence of the thermal lens signal parameter θ and thermal diffusivity of the ZBLAN sample as obtained from the TL measurements, respectively. As before, the values of these parameters were obtained from the transient TL signal data fitting to Eq. (1). We note from Figs. 4 and 5 that both parameters exhibit a marked change around T_g. The parameter θ exhibits a sharp jump around T_g, whereas the thermal diffusivity, after remaining practically constant up to 280 °C, it passes through a sharp minimum at T_g. The overall decrease of the thermal diffusivity in the temperature range close to T_g is of a factor of 12. On the other hand, from differential scanning calorimetry measurements on ZBLAN glasses,[11] it has been shown that the specific heat of these glasses exhibits a sharp increase of about 1.6 close to T_g. Assuming that this is actually the case, and noting that the thermal conductivity is related to D and C by $K=\rho CD$, we conclude that at the glass transition temperature the thermal conductivity should decrease by a factor of 8.

To get further insight into the observed temperature dependence of θ we address ourselves to its definition. As given by Eq. (3), θ is essentially a measure of the probe beam phase shift between $r=0$ and $r=\sqrt{2}\omega_e$ induced by the thermal lens. Writing the thermal conductivity K in terms of the thermal diffusivity, namely, $K=\rho CD$, Eq. (3) can be rewritten as

$$\theta=\left(\frac{PA_eL}{D\lambda_p}\right)\left(-\frac{1}{\rho C}\frac{ds}{dT}\right). \tag{6}$$

The first term on the right-hand side of Eq. (6) is essentially the energy deposited by the pumping beam within a probe beam characteristic volume consisting of a cylinder of unit

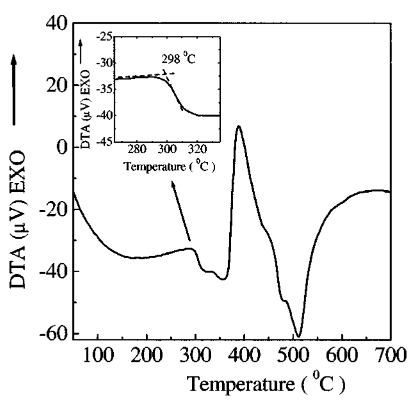

FIG. 3. Differential thermal analyzer (DTA) curve of the 0.2% mol of CoF_2 doped ZBLAN glass.

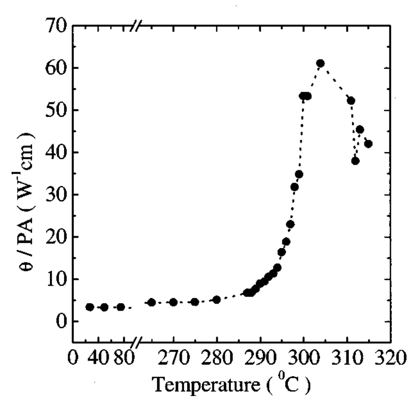

FIG. 4. Temperature dependence of the normalized thermal lens phase shift of the 0.2% mol of CoF_2 doped ZBLAN glass.

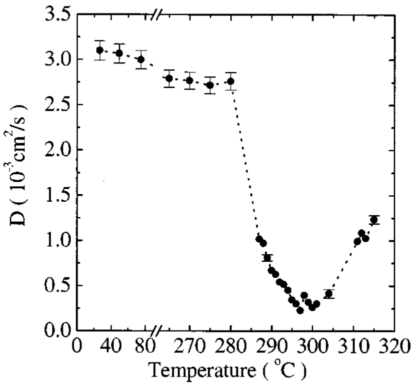

FIG. 5. Temperature dependence of the thermal diffusivity of the 0.2% mol of CoF_2 doped ZBLAN glass.

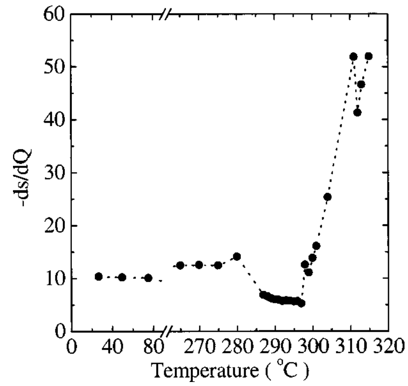

FIG. 6. Characteristic optical path changes with deposited heat ($-ds/dQ$) as a function of temperature for the 0.2% mol of CoF_2 doped ZBLAN glass.

area and length equal to the probe beam wavelength λ_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. 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.

CONCLUSION

In this paper we have demonstrated the usefulness of the thermal lens spectrometry to determine the thermal diffusivity, thermal conductivity, and the temperature coefficient of optical path-length change of fluoride glasses. The results showed that glasses containing Ga, In, and Zn exhibited improved thermo-optical properties as compared to the ZBLAN formulation. Especially in the case of high power laser applications, the thermal parameters play an essential role. For these applications one requires glasses with high thermal conductivity in order to effectively dissipate the heat generated within the laser action region, at the same time that a small temperature coefficient of optical path length is also desired for smaller thermally induced laser beam distortions.

It is well known that fluoride glasses do not have thermo-optical properties suitable for high power laser applications. Our results indicate that fluoroindate and fluoroaluminate glasses, which have very good optical properties, exhibit thermal conductivity and thermal diffusivity roughly 18 and 23%, respectively, greater than those of ZBLAN, while the temperature coefficient of optical path length was about 50% smaller. This better combination of the thermo-optical properties indicates that these glasses are promising candidates for laser applications. Finally, we have also demonstrated the ability of the thermal lens spectrometry to perform the thermo-optical characterization of glasses as a function of temperature. This was demonstrated for the case of the ZBLAN doped with 0.2% CoF_2. 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. Second, 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 not only reflects the characteristic dependence of the refractive index and thermal expansion coefficient with temperature, but is also closely related to the behavior of the DTA measurements.

This application of the thermal lens spectrometry completely evaluates the thermo-optical properties of fluoride glasses, including their temperature dependence. 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 a wide range of transparent materials, especially as a function of temperature.

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