Thermal Diffusivity Measurements of Fluoride Glasses Using the Thermal Lens Method

S.M. Lima[1], T. Catunda[1], E. Hersoug[1], R. Lebullenger[1],
A.C. Hernandes[1], J.A. Sampaio[1], M.L. Baesso[2] and S. Gama[3]

[1]*Instituto de Física de São Carlos, USP*
C.P. 369, CEP 13560-970, São Carlos, SP
[2]*Departamento de Física, Universidade Estadual de Maringá, UEM*
Av. Colombo 5790, CEP 87020-900, Maringá, PR
[3]*Instituto de Física Gleb Wataghin, UNICAMP*
CEP 13083-970, Campinas, SP

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The time-resolved mode-mismatched thermal lens technique has been used to determine an absolute value for the optical path change with temperature (ds/dT), thermal diffusivity (D) and conductivity (K) in CoF_2 doped solids. We present for the first time thermal diffusivity and conductivity results for of fluoride glasses. The method is simple and can be applied for a wide range of fluorescent materials.

I. Introduction

The thermal lens (TL) technique [1] has proved to be a valuable to study transparent materials [2-7]. Since the first report of the TL effect the sensitivity of the technique has been improved by changing the experimental configuration. The two-beams mode-mismatched method is the most sensitive one.

The 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 transverse temperature gradient is established, owing to the temperature coefficient of refractive index (dn/dT), a refractive index gradient is produced, creating a lens-like optical element, the so-called TL. Like the probe laser beam passes through the sample, its propagation is affected resulting in a spreading or focusing of the beam center. By measuring its beam center intensity variation in the far field, the thermo- optical properties of the sample can be determined. The time-resolved method is used to study the temporal evolution of the TL effect allowing the determination of sample thermal diffusivity.

The thermal diffusivity of a materials is known to be dependent upon the effects of compositional and microstructural variables as well as processing conditions. In this work, apply the TL technique in several fluoride glasses determine an absolute value for the optical path change with temperature (ds/dT), thermal diffusivity (D) and conductivity (K).

The fluoride glasses are very transparent, presenting very low absorption coefficient ($\sim 10^{-3}$ - 10^{-4}cm^{-1}) in the visible and even lower in the mid infrared. Consequently the TL signal from undoped matrixes are very low. In order to improve the signal to noise ratio of our experiment, we doped the glasses with low concentrations of CoF_2.

II. Theory

The theoretical treatment of TL is done using Fresnel diffraction theory [8]. An analytical expression can be obtained for probe beam intensity $I(t)$ [3]:

$$I(t) = I(0)\left\{1 - \frac{\theta}{2} atan\left[\frac{2mV}{[(1+2m)^2+V^2]t_c/2t + 1 + 2m + V^2}\right]\right\}^2 \quad (1)$$

where

$$m = \left(\frac{\omega_{1p}}{\omega_{oe}}\right)^2; \qquad V = \frac{Z_1}{Z_c} \quad \text{when} \quad Z_c << Z_2 \ . \quad (2)$$

Here, Z_c is the confocal distance of the probe beam, Z_1 is the distance between probe beam waist and sample, Z_2 is the distance between the sample and the photodiode (2), ω_{1p} is probe beam radius at the sample, ω_{oe} excitation laser beam radius at the sample, t_c is the characteristic thermal lens time constant, θ is approximately the phase difference of the probe beam at $r = 0$ and $r = \sqrt{2}\,\omega_{oe}$ induced by the thermal lens, and $I(0)$ is the value of $I(t)$ when the transient time t, or θ is zero.

The TL effect can be treated through the calculation of the temporal evolution of the sample temperature profile $\Delta T(r,t)$, caused by a Gaussian beam. The TL transient signal amplitude is proportional to its phase shift given by [3]:

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

where P is the excitation laser power, K the thermal conductivity, λ_p the probe beam wavelength, L the sample thickness, ds/dT the optical path temperature coefficient, A is the absorption coefficient and $\varphi = 1 - \eta\lambda_e/ < \lambda_{em} >$ is the fraction of absorbed energy converted into heat per photon, where η is the sample radiative quantum efficiency, λ_e is the excitation beam wavelength, $< \lambda_{em} >$ is the average wavelength of the fluorescence. In the case of CoF_2 doped samples, we supposed that all absorbed energy is converted into heat so $\eta = 0$ and $\varphi = 1$.

The optical path change with temperature is given by:

$$\frac{ds}{dT} = (n-1)(1+\nu)\gamma + \frac{dn}{dT} \quad (4)$$

where n is the refractive index, ν is the Poisson's ratio, γ is the linear temperature expansion coefficient.

The characteristic TL signal response time t_c is given by:

$$t_c = \frac{\omega_{oe}^2}{4D} \quad (5)$$

where $D = K/\rho C$ is the thermal diffusivity, ρ is the density, C is the specific heat and K is the thermal conductivity.

We performed time-resolved TL experiments in several fluoride glasses, using the two-beams mode mismatched TL configuration. The parameters θ and t_c can be determined by proper fitting of the transient TL signal and then the thermal diffusivity D and conductivity K and the optical path change with temperature ds/dT can be obtain.

III. Experiment

The starting materials used for preparation of the glasses are fluorides (BDH and Strem products), and oxides as In_2O_3 and Ga_2O_3 (MetalEurop). The ammonium bifluoride is used to transform oxides in fluorides crucible the mixture is heated for melting and refining. Finally, the melt is poured into a brass mold preheated few degrees below the T_g temperature to prepare samples with a 4mm thickness. All these operations were made in gloves boxes with controlled inert atmosphere which relative moisture is below 10ppmv.

Table 1 shows the concentration used in glasses preparation.

The mode-mismatched thermal lens experimental setup used is showed in Fig. 1. In this method, use one Ar^+ laser (excitation beam) and one HeNe laser (probe beam) and the sample is positioned at the waist of the excitation laser beam, where the power density is maximum.

Acronym	ZrF_4	YF_3	LaF_3	AlF_3	GaF_3	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					*2GdF3*	*40*		*20*	*16*	*20*		*2*

Table 1: *Concentration of glasses* mol%.

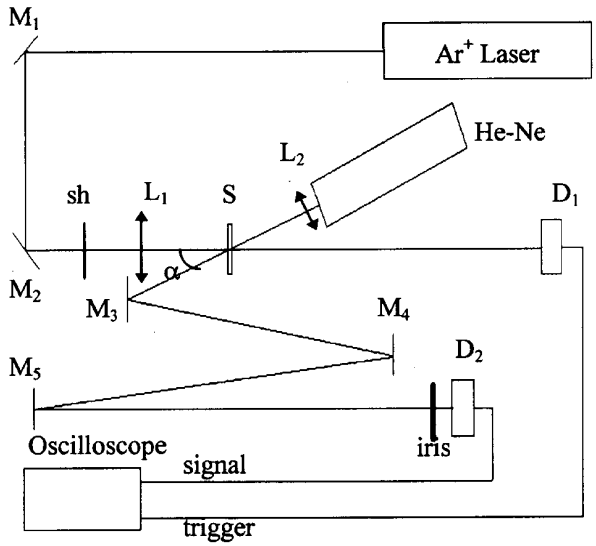

Figure 1. A schematic diagram of the mode-mismatched thermal lens experimental apparatus, where M_1, M_2, M_3, M_4 and M_5 are mirrors, sh is the shutter, D_1 and D_2 are photodiode, a is the angle between the probe beam and the excitation beam L_1 and L_2 are lens and S is the sample.

The scheme of the geometric position of the beams in a mode-mismatched is showed in the Fig. 2, where ω_{op} is the probe beam spot size.

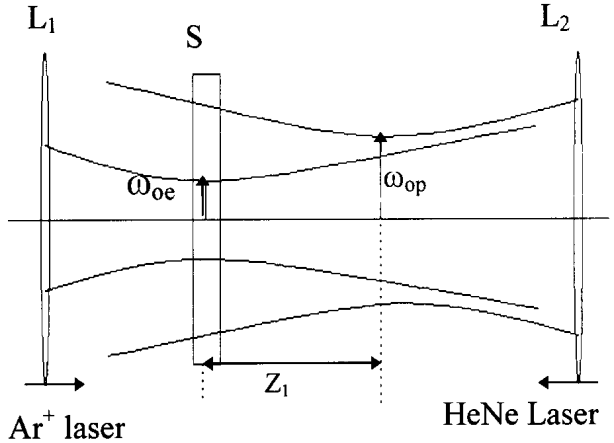

Figure 2. Scheme of the geometric position of the excitation and probe beam.

The excitation laser beam was a Ar^+ laser at 514nm. It was focused by a converging lens (L_1) with focal length f_1= 15cm, and the sample was put at its focal plane. Exposure of the sample to the excitation beam was controlled by means of a shutter. The probe laser beam was a HeNe laser at 632.8nm. It was focused by a converging lens (L_2) with focal length f_2= 25cm 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, after passing through the sample, was incident on a photodiode (D_1) and used as a trigger. These adjustable mirrors M_3, M_4 and M_5 were used to get a long optical length (~2m) from the sample to a pinhole mounted before the photodiode (D_2). An iris was put in front of the detector in order to select the beam central part.

The optical absorption coefficients were determined using the same experimental configuration applied for the TL measurements. The transmitted light of the Ar^+ laser at 515.5nm was recorded for different incident power.

The experiment parameters used are summarized in the Table 2.

Fig. 3 shows the absorption spectra of 0,2% CoF_2 ZBLAN sample measured in the CARY 17 Spectrophotometer.

We used the sample soda lime like model in our measurements. Supposed that we can have region of sample non-homogeneous, made measurements with the same sample in three areas different, and calculated the media.

λ_p	632.8 x 10^{-7} cm
Z_{op}	21.6 ± 0.04 cm
Z_{cp}	4.27 ± 0.07 cm
λ_e	514.5 x 10^{-7} cm
Z_{oe}	14.47 ± 0.002 cm
Z_{ce}	0.34 ± 0.003 cm
ω_{oe}	2.35 x 10^{-3}cm
Z_1	4 cm
ω_p	12.7 x 10^{-3} cm
$m = (\omega_p / \omega_{oe})^2$	29.22
$V = (Z_1 / Z_{cp})$	0.937

Table 2: *The experimental parameters for TL measurements.*

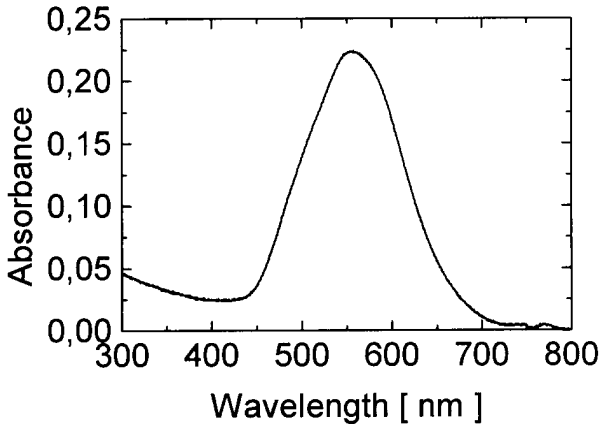

Figure 3. Absorption spectrum of ZBLAN with 0.2% CoF_2.

IV. Results and discusion

Fig. 4 shows a typical TL signal, for the ZBLAN with 0,3% CoF_2. We fit the experimental data with Eq. (1) and obtained $\theta = 0.23 \pm 0.0004$ and $t_c = 0,52 \pm 0.004$ms. Using Eq. (5) from t_c and ω_{oe} (Table 2) we calculated $D = 2.6 \times 10^{-3}$cm^2/s.

We studied 4 ZBLAN samples doped with 0.1, 0.2, 0.3 and 0.375 wt% CoF_2. Fig. 5 shows that, in this CoF_2 concentration range, the thermal diffusivity is practically constant (within the our experimental uncertainty) $D = (2.6 \pm 0.14) \times 10^{-3}$cm^2/s. From this D value, we calculated $K = (7.4 \pm 0.4) \times 10^{-3}$W/kcm using the ρC value for ZBLAN from ref. [9].

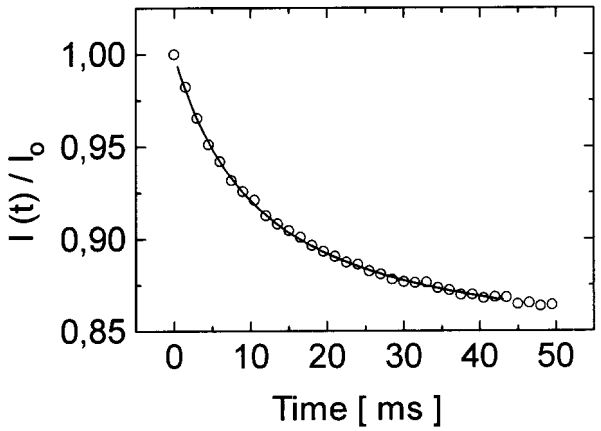

Figure 4. Transient Thermal Lens signal for the 0.3% CoF_2 ZBLAN sample in a $P = 42.2$mW ($\lambda = 515.5$nm). The line indicates the fit made with Eq. (1) with $\theta = 0.23 \pm 0.0004$ and $t_c = 0.52 \pm 0.004$ms.

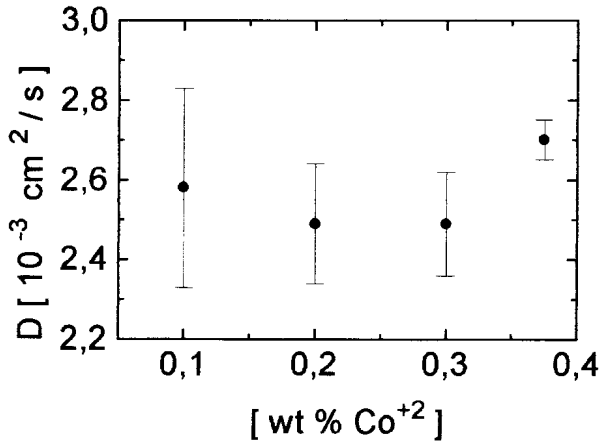

Figure 5. Thermal diffusivity versus Cobalt concentration in ZBLAN.

Fig. 6 shows that $\theta P/L$ increase linearly with the absorption coefficient A, so by Eq. (3) this behavior indicates that product $K^{-1}ds/dT$ remains constant in the CoF_2 concentration range studied. Therefore, from the linear fit of Fig. 6 and using our K media value, we calculated $ds/dT = (-5.7 \pm 0.41) \times 10^{-6}$K^{-1}.

The same procedure was adopted for the other samples. For these glasses we don't have the ρC value. However, Bruce [11] analyzed 12 kinds of fluoride glasses and concluded that, at 300K, the molar specific heat is almost constant ~ 21.3JK^{-1}mol^{-1} (86% of the Dulong-Petit value). For instance, using this value for ZBLAN we obtained $\rho C = 2.7$Ws/kcm^3 in a good agreement with the experimental value $\rho C = 2.8$Ws/kcm^3. We estimated ρC for all the samples and calculated K from our experimental D datas as shows in the Table 3.

Samples	A (cm^{-1})	D (10^{-3} cm^2/s)	K (10^{-3} W/kcm)	ds/dT (10^{-6} k^{-1})
IGPZ 0,2% CoF_2	0.9 ± 0.04	2.9 ± 0.14	8.0 ± 0.39	-1.8 ± 0.14
ISZn 0,2% CoF_2	1.0 ± 0.10	3.1 ± 0.06	8.4 ± 0.16	-1.2 ± 0.20
InSBZnGdN 0,29% CoF_2	0.8 ± 0.02	3.2 ± 0.07	8.6 ± 0.19	-1.7 ± 0.14
YABC 0,377% CoF_2	1.8 ± 0.03	3.3 ± 0.06	8.1 ± 0.15	-1.9 ± 0.13
ZBLAN 0,1% CoF_2	0.4 ± 0.09	2.6 ± 0.25	7.4 ± 0.71	-6.1 ± 1.79
ZBLAN 0,2% CoF_2	0.7 ± 0.003	2.5 ± 0.15	7.1 ± 0.43	-5.5 ± 0.43
ZBLAN 0,3% CoF_2	1.5 ± 0.02	2.5 ± 0.13	7.1 ± 0.37	-5.6 ± 0.37
ZBLAN 0,375% CoF_2	2.2 ± 0.10	2.7 ± 0.05	7.6 ± 0.14	-6.0 ± 0.52

Table 3: *Results of thermal diffusivity and conductivity and the optical path change with temperature ds/dT .*

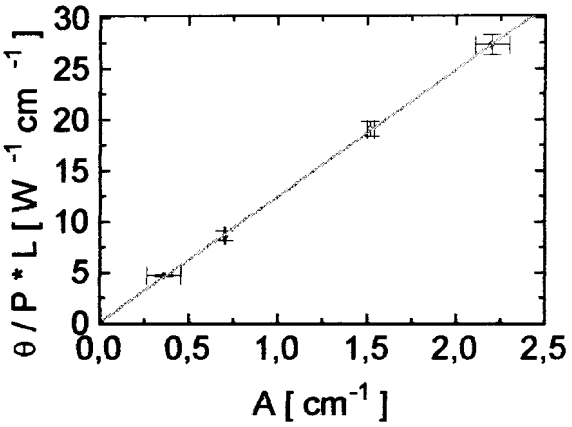

Figure 6. This graphic shows the linear comportment of product $K^{-1}ds/dT$.

V. Conclusion

All fluorides we have studied presented negative ds/dT values where $ds/dT\alpha[\phi - b\beta]$, where ϕ and β are the temperature coefficients of the electronic polarizability and volume expansion respectively, and b is a constant that depends on the glass refractive index and the Poisson's ratio ν.

For laser applications, the thermal parameters are very important. It is desired to have high thermal conductivity to dissipate the heat from the laser action region. It is well known that fluoride glasses do not have thermo-optical properties suitable for high power laser applications. However we observed that fluoroindate glasses, which have very good optical properties, presented thermal conductivity ~18% and diffusivity ~23% greater than that of ZBLAN.

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