Material characterization with top-hat cw laser induced photothermal techniques: a short review

N. G. C. Astrath¹*, J. Shen¹**, M. L. Baesso², F. B. G. Astrath¹, L. C. Malacarne², P. R. B. Pedreira², A. C. Bento², and J. Zhou¹

¹National Research Council of Canada, Institute for Fuel Cell Innovation, 4250 Wesbrook Mall, Vancouver, British Columbia V6T 1W5, Canada

²Departamento de Física, Universidade Estadual de Maringá, Av. Colombo 5790, 87020-900, Maringa PR, Brazil

* AstrathNGC@pq.cnpq.br; ** Correspondence to: Jun.Shen@nrc-cnrc.gc.ca

Abstract. In this work, we present a short review of the recent development of the theoretical models for top-hat cw laser induced spectroscopies of thermal lens and thermal mirror. With the same probe and top-hat excitation lasers, an apparatus is set up to concurrently measure both thermal lens and thermal mirror effects of transparent samples. With the theoretical models and the experimental apparatus, not only optical and thermal properties are measured, but also the fluorescence quantum coefficient and the temperature coefficient of the optical path length of a fluorescent sample are simultaneously determined with no need of any reference sample. Mechanical properties also could be measured. Opaque samples are also studied using top-hat cw laser thermal mirror and top-hat photothermal deflection techniques to determine thermal properties (e.g., thermal conductivity and unit volume specific heat). This work shows that the combined top-hat cw laser photothermal techniques are useful for non-destructive evaluation of both transparent and opaque samples with a less expensive non-TEM₀₀ Gaussian laser.

1. Introduction

Nondestructive characterization of materials is one of major application areas of photothermal (PT) techniques [1]. The common principle of these techniques consists of measuring a thermal effect in a sample as a result of the nonradiative deexcitation process that takes place following the absorption of incident excitation radiation. The thermal effect provides a detection mechanism, such as temperature rise, surface deformation, PT radiometry, and optical refractive index gradient [1]-[6]. The excitation radiation used in PT techniques is usually a TEM₀₀ Gaussian laser, probably because of the convenience for theoretical modeling, such as for the models of thermal lens (TL) and PT surface deformation [namely thermal mirror (TM)] [7]-[9]. Due to the high cost of high power TEM₀₀ Gaussian excitation lasers and their inadequate applicable wavelengths, it is desirable to use less expensive non-Gaussian excitation lasers to replace the Gaussian ones in order to expand the applicability of the PT techniques for quantitative analysis. Hence Li et al introduced pulsed [10]-[12] and modulated [13]-[14] top-hat beam excitation into PT techniques.

In this paper, we show the recent [15]-[17] development of the theoretical models for time-resolved mode-mismatched thermal mirror and thermal lens spectroscopies with top-hat excitation for
quantitative material characterization. For optically transparent samples, we build an experimental apparatus to simultaneously measure the TL and TM effects using the same probe and top-hat excitation lasers. For opaque samples, the experiments of TM and photothermal beam deflection are performed. Analyzing the experimental results with the developed theoretical models, we attain the thermal properties of all the samples. Furthermore, we obtained the fluorescence quantum coefficient and the temperature coefficient of the optical path length of a transparent fluorescent sample with no need of any reference sample. In addition, the expansion coefficients of the opaque samples are determined. Our experimental results clearly demonstrate the high value of the application of the top-hat excitation in photothermal techniques.

2. Theory

In a TM experiment, a top-hat cw excitation laser strikes on a solid sample surface, as shown in Figure 1 (a), resulting in a surface thermoelastic displacement. A weak TEM$_{00}$ Gaussian probe beam, collinear with the excitation laser and propagating in the Z-direction, is reflected from the displacement, which acts as a concave or convex mirror to the probe beam, thereby producing an additional phase shift in the electrical field and intensity profile change of the probe beam. By detecting the intensity change at the center of the probe beam, physical properties of the sample can be measured.

The distribution of the temperature rise, $T(r, z, t)$, in an isotropic sample can be found by solving heat conduction differential equation [18]

$$c \rho \frac{\partial T(r,z,t)}{\partial t} - k \nabla^2 T(r,z,t) = Q(r,z)$$

with the initial condition $T(r,z,0) = 0$ and the boundary conditions $T(\infty, z, t) = 0$ and $\partial T(r,z,t)/\partial z |_{z=0} = 0$. The top-hat excitation intensity $I_{th}(r)$ can be expressed as

$$I_{th} = \frac{P}{\pi a_0^2} U(a_0^2 - r^2),$$

in which $P$ is the excitation laser power. The Unit-step function, $U(x)$, is zero for a negative argument and one for a positive one. The top-hat heat source can be written as
\[ Q(r, z) = Q_0 U(\omega_0 - r) Q(z) \]  

with \( Q_0 = P A \phi / \rho c \omega_0 \) and \( Q(z) = \exp(-A \zeta) \). \( A \) is the optical absorption coefficient of the sample at the excitation laser wavelength; \( \phi = 1 - \eta \lambda_e / <\lambda_m> \). \( \lambda_e \) is the excitation beam wavelength, \( <\lambda_m> \) the average wavelength of the fluorescence emission, and \( \eta \) is the fluorescence quantum efficiency. The solution of heat conduction differential equation is

\[ T_{R,M}(r, z) = \frac{T_0 A_0}{2} \int_0^\infty f_{R,M}(\alpha, z, t) J_0(\omega_0 \alpha) \, d\alpha \]  

with

\[ f_{R,M}(\alpha, z, t) = \int_0^\infty \exp \left[ \frac{(A_0 - \alpha)(A_0 + \alpha) \tau_0 / \omega_0 - z \alpha}{4t_2} \right] \times \]

\[ \times \left[ 1 + \text{Erfc} \left( \frac{\alpha - A_0 \tau_0 / \omega_0}{\sqrt{\pi t_2}} \right) + \text{exp}(2zA) \text{Erfc} \left( \frac{\alpha + A_0 \tau_0 / \omega_0}{\sqrt{\pi t_2}} \right) \right] \, d\alpha \]  

Here \( T_0 = P \phi / (4\pi k t_c) \). \text{Erfc}(x) is the complementary error function, and \( J_n(x) \) is the n-order Bessel function of the first kind. \( t_c = \omega_0^2 / 4D \) is the characteristic thermal time constant, and \( D = k / \rho c \) the thermal diffusivity of the sample. In a quasi-static approximation, the surface thermoelastic deformation can be attained by introducing the scalar displacement potential \( \psi \) and the Love function \( \Phi \) [19]. By using the temperature rise distribution Eq. (4) and the boundary condition over the stress [19], the \( z \) component of the surface thermoelastic displacement vector \( u_z(r, 0, t) \) takes the form

\[ u_z(r, 0, t) = -\frac{\kappa_0}{4 \omega_0 t} \int_0^\infty h(\alpha, t) J_0(\omega_0 \alpha) \, d\alpha \].  

Here

\[ h_{R,M}(\alpha, t) = A_0 \omega_0 \omega_0 \text{Erfc} \left( \frac{-c A_0}{2 \omega_0 \sqrt{t_c / t}} \right) + \frac{\sqrt{\pi \omega_0 A_0}}{2 \alpha^2} \exp \left( -\frac{\alpha^2}{4t_2} \right) \]  

\[ + \frac{2A_t}{\alpha^2 \left[ \alpha^2 - A_0^2 \right] \text{Erfc} \left( \frac{c A_0}{2 \omega_0 \sqrt{t_c / t}} + 2 \alpha \right) \text{Erfc} \left( \frac{c A_0}{2 \omega_0 \sqrt{t_c / t}} \right) \text{Erfc} \left( \frac{A_t \omega_0}{2 \omega_0 \sqrt{t_c / t}} \right) \text{Erfc} \left( \frac{A_t \omega_0}{2 \omega_0 \sqrt{t_c / t}} \right) \].  

In Figure 1 (b), a cw top-hat beam (excitation laser) excites a weakly absorbing sample of thickness \( l \). As a result, a transverse temperature gradient and then a refractive index gradient that behaves like an optical lens are produced, thus causing a TL. Collinear with the excitation beam, a weak TEM00 Gaussian beam travels through and probes the TL, resulting in an additional phase shift in its electrical field and a change in its intensity profile. It is assumed that the absorbed excitation laser energy by the sample is low so that the excitation laser can be considered to be uniform along the \( Z \)-direction. The temperature rise in the weakly absorbing sample is given by

\[ T(r, z, t) = 4T_0 \int_0^\infty \frac{1 - e^{-\omega_0 \omega_0 / \alpha^2 \omega_0}}{\alpha^2 \omega_0} J_0(\omega_0 \alpha) \, d\alpha \].
The additional phase shift in the electrical field of the probe beam caused by the TL and TM, respectively, is

\[
\Phi_{\text{TL}}(g, t) = \theta_{\text{TL}} \int_0^\infty \left[ \frac{1 - e^{-\frac{\omega_0^2 t}{\alpha^2 \omega_n^2}}} {\alpha^2 \omega_n^2} \right] \left[ 1 - J_0 \left( \sqrt{mg \omega_n \alpha} \right) J_1 \left( \omega_n \alpha \right) \right] d\alpha,
\]

\[
\Phi_{\text{TM}}(g, t) = \theta_{\text{TM}} \int_0^\infty \alpha^2 f(\alpha, t) J_0 \left( \sqrt{mg \omega_n \alpha} \right) d\alpha.
\]

Here \( g = \left( r/\omega_n \right)^2 \) and \( m = \omega_n^2 / \omega_0^2 \).

\[
\theta_{\text{TL}} = \frac{P_{\text{TL}} \int (ds/dT) \phi}{\lambda_p k}, \quad \theta_{\text{TM}} = -\frac{2P_{\text{TM}} (1 + \nu)}{\lambda_p k} \phi,
\]

The complex electric field of the TEM\(_{00}\) Gaussian probe beam through the TL or reflected by the TM is given by

\[
U_i(r, Z_i) = B \exp \left[ - \left( \frac{\pi}{\lambda_p R_{\text{TM}}} \right) - \frac{r^2}{\lambda_p R_{\text{TM}}} \right],
\]

with \( B = \omega_n^2 (2P/L)^{1/2} \exp(-i2\pi Z_i/\lambda_p) \). \( P \) and \( R_{\text{TM}} \) are transmitted (for TL) or the reflected (for TM) probe beam power and the radius of curvature of the probe beam at \( Z_i \), respectively. The propagation of the probe beam to a detector plane can be treated as diffraction. In this paper only the centre of the probe beam spot at the detector plane is considered. By using Fresnel diffraction theory, the complex amplitude of the probe beam at the detector plane is \( U_i(Z_1 + Z_2, t) \). The intensity at the detector plane \( I(t) \) then can be calculated as \( I(t) = |U_i(Z_1 + Z_2, t)|^2 \).

In the foregoing calculation of thermal mirror, the contribution from the light reflected from the reflectivity change \( \Delta R/R \) is ignored. Using the Eq. (21) of Ref. [20],

\[
\frac{\Delta R}{R_0} = \frac{4}{n_0^2 - 1} \frac{dn}{dT} \Delta T,
\]

and taking values of a transparent soda lime glass \( n_0 \approx 1.5, dn/dT \approx 4 \times 10^{-6} \text{ K}^{-1} \), and \( \Delta T \approx 10^4 \text{ K} \), the \( \Delta R/R \) is about \( 6.4 \times 10^{-7} \), which is negligible. In the solution of the thermo-elastic equation, we use the quasi-static approximation, in which the second time derivative term is neglected. As shown in Ref. [21], the dynamic wave behavior becomes apparent for shot pulse (ns scale). Our time-resolved experiments are in the scale of \( \sim 80 \text{ ms} \), not a short pulsed one, and therefore there is no need to consider the contribution from the dynamic wave.

3. Experiment

The left figure of Figure 2 shows a schematic diagram of the experimental apparatus used for the combined TL and TM experiments. A multi-mode diode-pumped solid-state laser (Melles Griot, Model 85 GLS 309, 532.0 nm) was employed to provide the top-hat beam excitation. The excitation beam was expanded using a set of lenses and an aperture to select a nearly homogeneous area of the excitation beam profile, thereby producing a top-hat intensity profile in the sample. Exposure of the sample to the excitation beam was controlled by means of a shutter (ThorLabs, Model SH05), and the
signal from a photodiode \( P_1 \) was used to trigger a digital oscilloscope (Tektronics, Model TDS 3052) to record the TL and TM signals. A weak TEM\(_{00}\) Gaussian He-Ne laser at 632.8 nm (Melles Griot, Model 05LHP151), almost collinear to the excitation beam \((\alpha<1.5^\circ)\), probed the TL by analyzing the transmitted beam, or probed the TM by examining the reflected one. The probe beam was focused by lens \( L_4 \) \((f = 20\text{cm})\), and the sample was positioned near its confocal plane. After passing through the TL or reflected by the TM, the probe beam propagated to a photodiode \( P_2 \) for TL detection and \( P_3 \) for TM detection positioned in a far field \((Z_f \approx 5\text{ m})\). Pinholes were put in front of the photodiodes \( P_2 \) and \( P_3 \), and only the central part of the probe beams were detected by the photodiodes and then recorded by a digital oscilloscope. The right figure in Figure 2 presents the TM experimental setup for opaque samples with the same equipment above.

![Diagram](image)

**Figure 2.** Schematic diagrams of the time-resolved experimental apparatus. \( M_i, L_i, \) and \( P_i \) are mirrors, lenses and photodiodes, respectively. Left: the apparatus of the combined TL and TM experiment for transparent samples; right: a TM experimental setup for opaque samples.

4. Results

Three transparent glass samples were measured with the combined TL and TM experimental apparatus: 2wt\% \( \text{Nd}_2\text{O}_3 \) doped low silica calcium aluminosilicate glass (LSCAS-2), 0.1wt\% \( \text{CoF}_2 \) doped ZBLAN glass, and 2wt\% \( \text{Fe}_2\text{O}_3 \) doped Soda-Lime glass.

| Samples       | \( D_{TL} \) (Measured) \((10^{-7}\text{ m}^2\text{s}^{-1})\) | \( D_{TM} \) (Measured) \((10^{-7}\text{ m}^2\text{s}^{-1})\) | \( ds/dT \) (Measured) \((10^{-6}\text{ K}^{-1})\) | \( A_r \) (Measured) \((10^2\text{ m}^2\text{K}^{-1})\) | \( \nu \) (Literature) | \( \alpha_t \) (Literature) \((10^6\text{ K}^{-1})\) | \( k \) (Literature) \((\text{Wm}^{-1}\text{K}^{-1})\) |
|---------------|-------------------------------------------------|-------------------------------------------------|---------------------------------|-----------------|----------------|-----------------|----------------|
| LSCAS-2       | 5.7\pm0.2                                        | 5.9\pm0.3                                        | 12.1\pm0.5                      | 1.70\pm0.03     | 0.29           | 7.5             | 1.50           |
| ZBLAN         | 3.0\pm0.2                                        | 3.1\pm0.3                                        | -(5.8\pm0.3)                    | 0.35\pm0.01     | 0.25           | 14.0            | 0.77           |
| Soda-lime     | 5.0\pm0.1                                        | 5.1\pm0.3                                        | 5.2\pm0.3                      | 1.00\pm0.03     | 0.21           | 5.2             | 1.20           |

Table 1 shows the experimental results of the combined TL and TM measurements. As expected, the thermal diffusivities of these glasses measured by TL and TM, respectively, are well consistent. In addition to the \( D, \theta_{NL} \) and \( \theta_{TM} \) can also be measured. Referring to Eq. (10), for a fluorescent sample, the combined measurements can be used to determine \( \eta \) with no requirement of a reference sample, providing the \( \alpha_t \) and \( \nu \) are known. Using the listed parameters in the Tables 1 plus \( \lambda_{\text{em}} = 1064\text{ nm} \) [22] for the LSCAS-2, we found \( \eta = 0.84 \), consistent with the literature value [22] measured with a reference. Besides the \( k, A_v, \) and \( \eta \), the thermal lens phase shift \( \theta_{TL} \) is also related to the temperature.
coefficient of the optical path length $ds/dT$, an important thermo-optical parameter of optical materials, such as a solid state laser material, correlated to light waveform distortion induced by a temperature variation. For a fluorescent sample, it is usually difficult to determine the $ds/dT$ and $\eta$ simultaneously using the TL. Combining the $\theta_T$ and $\theta_M$, one can calculate the $ds/dT$ with

$$ \frac{ds}{dT} = \frac{1}{2} \left( \frac{\theta_T}{L_T} + \frac{\theta_M}{L_M} \right) $$

without the knowledge of the $k$, $A_r$, and $\eta$. Thus, the combination of the TL and TM with the same top-hat excitation and Gaussian probe lasers provides a novel approach to measure the $ds/dT$, the experimental results are shown in Table 1.

Using the apparatus shown in the right figure of Figure 2, we performed measurements of $D_{TM}$ of opaque samples: manganese metal (99.9% from Sigma-Aldrich), glassy carbon, and BBP4 graphite plate (an anisotropic sample). Additional measurements were performed using photothermal deflection method (PD) to determine the thermal effusivities $E$ of these samples with top-hat cw laser excitation. Table 2 presents the experimental results of the thermal properties of the opaque samples. Referring to Eq. (10) for the $\theta_M$, and using the measured $\theta_M/dP$, $k$ and the literature value of $\nu$, the expansion coefficient can be determined as

$$ \alpha_r = -\frac{d\theta_M}{dP} \frac{\lambda}{\phi(1+\nu)} \left[ 1 - \eta \frac{\lambda}{\lambda_0} \right], $$

as shown in Table 2. As shown in Eq. (10), one can see that TL and TM measurements do not need any calibration and the slopes of $\theta_T/P$ and $\theta_M/P$ determine the sensitivities of TL and TM experiments, respectively.

| Samples          | $D_{TM}$ (Measured) ($10^{-8}$ m$^2$/s) | $D$ (Literature) ($10^{-8}$ m$^2$/s) | $E$ (Measured) ($10^3$ W$m^{-1/2}$s$^{-1}$m$^{-2}$K$^{-1}$) | $k = E\sqrt{D}$ (Measured) (W/mK) | $k = E\sqrt{D}$ (Literature) (W/mK) | $\alpha_r$ (Measured) ($10^{-6}$ K$^{-1}$) |
|------------------|----------------------------------------|-------------------------------------|-------------------------------------------------|----------------------------------|------------------------------------|----------------------------------|
| Glassy carbon    | 5.20±0.03                               | 5.0                                 | 3.60±0.02                                       | 8.20±0.09                        | 8                                  | 2.0±0.1                          |
| BBP4 graphite plate | 8.93±0.08                              | 8.8                                 | 7.0±0.3                                         | 20.9±0.2                         | 21                                 | 1.40±0.05                        |
| Manganese        | 2.07±0.04                               | 2.3                                 | 5.3                                             | 7.60±0.07                        | 8                                  | 21.1±0.6                         |

5. Conclusions

Theoretical models of Top-hat cw laser induced TL and TM have been derived. A combined TL and TM experimental apparatus has been developed to quantitatively measure thermal properties of three transparent samples. Furthermore, $\eta$ and $ds/dT$ could be determined at once without any reference by using the combined TL and TM apparatus. Combined with PD experiment, we also measured thermo properties as well as the expansion coefficients of the opaque samples. The theoretical model and experimental apparatus developed in this work make it promising to use a top-hat laser in photothermal experiments and to expand the applicability of photothermal science and techniques with a less expensive non-Gaussian excitation laser.

References

[1] Mandelis A 1991 *Progress in Photoacoustic and Photothermal Science and Technology* (New York: Elsevier)

[2] Almond D P 1996 *Photothermal Science and Techniques* (London: Chapman & Hall)

[3] Bialkowski S E 1996 *Photo thermal Spectroscopy Methods for Chemical Analysis* (New York: Wiley)

[4] Olmstead M A, Amer N M, Kohn S, Fournier D, and Boccara A C 1983 *Appl. Phys. A* 32 141

[5] Kuo P and Munidasa M 1990 *Appl. Opt.* 29, 5326

[6] Gordon J P, Leite R C C, Moore R S, Porto S P S and Whinnery JR 1965, *J. Appl. Phys.* 36 3

[7] Li B C 1990 *J. Appl. Phys.* 68 482
[8] Shen J, Lowe R D and Snook R D 1992 Chem Phys. 165 385
[9] Sato F, Malacarne L C, Pedreira P R B, Belancon M P, Mendes R S, Baesso M L, Astrath N G C and Shen J 2008 J. Appl. Phys. 104 053520
[10] Li B and Welsch E 1999 Appl. Opt. 38 5241
[11] Li B, Martin S, Welsch E 1999 Opt. Lett. 24 1398
[12] Li B, Martin S and Welsch E 2000 Appl. Opt. 39 4690
[13] Li B, Xiong S and Zhang Y 2005 Appl. Phys. B 80, 527
[14] Li B, Chen X and Gong Y, 2008 J. Appl. Phys. 103, 033518
[15] Astrath N G C, Astrath F B G, Shen J, Zhou J, Pedreira P R B, Malacarne L C, Bento A C and Baesso M L 2008 Opt. Lett. 33 1464
[16] Astrath F B G, Astrath N G C, Shen J, Zhou J, Malacarne L C, Pedreira P R B and Baesso M L 2008 Opt. Express 16 12214
[17] Astrath N G C, Astrath F B G, Shen J, Zhou J, Gu C E, Pedreira P R B, Malacarne L C, Bento A C and Baesso M L 2009 Appl Phys B 94 473–481
[18] Carslaw H S and Jaeger J C 1959 Conduction of Heat in Solid (Oxford: Clarendon)
[19] Nowacki W 1982 Thermoelasticity (Oxford: Pergamon)
[20] Miranda L C M 1983 Appl. Phys. A 32 87
[21] Chen J C, Wu L, and Zhang S Y’ 1994 J. Appl. Phys. 76, 716
[22] Pelicon E, Rohling J H, Medina A N, Bento A C, Baesso M L, Souza D F, Oliveira S L, Sampaio J A, Lima S M, Nunes L A O and Catunda T 2002 J. Non-Cryst. Solids 304 244