Pulsed laser excited photothermal lens spectrometry of cadmium sulfoselenide doped silica glasses

Prakash R. Joshi, Oluwatosin O. Dada and Stephen E. Bialkowski*
Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300 USA
*stephen.bialkowski@usu.edu

Abstract. Experimental results for photothermal lens measurements are compared to finite elemental analysis models for commercial colored glass filters. Finite elemental analysis software is used to model the photothermal effect by simulating the coupling of heat both within the sample and out to the surroundings. Modeling shows that heat transfer between the glass surface and the air coupling fluid has a significant effect on the predicted time dependent photothermal lens signals. For comparison with experimental signals, a simple equation based on the finite element analysis result is proposed for accounting for the variance of experimental data where this type of heat coupling situation occurs. The colored glass filters are found to have positive thermo-optical coefficient. Finite element analysis modeling results are also used to correlate experimental measurements of different sample geometries. In particular, the glass samples are compared to ethanol solutions of iron (II) dicyclopentadiene in a sample cuvette even though heat transfer is different for these two samples.

1. Introduction
Thermal lens spectrometry (TLS) can measure very low optical absorption coefficients of transparent samples.1 Time-resolved TLS has been shown to be a useful method to measure the thermal diffusivity of transparent samples as well as the temperature coefficient of the optical pathlength, s, change, ds/dT.2-5 The knowledge of the thermo-optical properties is essential for evaluating the figures of merit of optical glasses. They can readily be used to determine the working glass conditions such as thermal shock, thermal stress resistance, and thermal lens effect.6 Semiconductor Doped Glass are candidates for resonant nonlinear optical materials. Commercial colored glass wavelength cutoff filters utilize semiconductor nanoparticles (NP) on the order of 10 nm (CdS,Se1-x).NP of semiconductor materials is often responsible for the optical absorption in colored glass filters.

Therefore, considering the importance of determining the thermo-optical properties of laser glass materials, a simple and accurate method to determine these properties quantitatively is of utmost importance. Optical glasses have a positive temperature-dependent refractive index change coefficient. Heat transfer from a glass plate excited with a laser is far from the ideal situation described by the semi-infinite cylinder approximate models that are most often used to describe the photothermal lens experiments.

The aim of this paper is to use the thermal lens method to obtain accurate measurements of the thermo-optical properties of glasses; first by using pulsed laser excitation which creates a temperature changes on timescales short compared to heat transfer and second by using Finite Element Analysis (FEA) to model heat transfer to the surroundings. In pulsed laser excitation, the temperature change is produced almost instantly or at least in a time when little heat has diffused
to the surroundings. In this regard, pulsed laser excitation can be advantageous for measuring absorbance.

2. Theory
The thermal lens effect is caused by the deposition of heat via non-radiative decay processes after the laser beam with Gaussian profile has been absorbed by the sample. For pulsed laser excitation, the experimental photothermal signal, $S(t)$, is defined by

$$S(t) = \frac{\Phi(\infty) - \Phi(t)}{\Phi(t)}$$

Where $\Phi$ (W) is the irradiance of the probe laser passing through a pinhole aperture placed far away from the sample and the probe laser is focused a distance $z_0$ (m) in front of the sample which is proportional to the inverse focal length of the thin lens produced in the sample due to laser heating,

$$S(t) \sim \frac{1}{f(t)}$$

$Q$ (J) is laser energy, the $Y_{hl}$ is a heat yield parameter accounting for energy loss due to luminescence during sample excitation and $w$ (m) is excitation laser beam electric field width. $\rho$ (kg m$^{-3}$), $C_p$ (J kg$^{-1}$), $\alpha$ (m$^{-1}$) and $l$ (m) are density, specific heat capacity, absorption coefficient and pathlength respectively. $\frac{ds}{dT}$ (K$^{-1}$) is the thermo-optical coefficient allowing for pathlength expansion.

3. Materials and Methods
Photothermal signals are modelled for heat transfer from glass to air after laser excitation and the FEA model results are subsequently compared to the experimental signals. FEA model results for coloured glass filter with and without boundary condition and the experimental investigations of thermal lens in coloured glass filters and liquid sample cells are presented.

FEA is a tool for numerical solutions to complex differential equations The Comsol Multiphysics software (v.3.5a) in conduction and convection mode solves the heat diffusion equation given as

$$\rho C_p \frac{\partial T(r,z,t)}{\partial t} - k V^2 \delta T(r,z,t) = q_{in}(r,z,t) - \rho C_p \alpha \cdot V \delta T(r,z,t)$$

FEA modeling consists of the drawing the sample geometry; specify material boundary conditions, heat sources, and sinks. And then the problems are solved with rough finite element definition and further refinement of elements and domain are made. Finally, $\delta T$ can be obtained either at single time, a time series or at steady state. The path integral of the second radial derivative was found by using the Comsol integration coupling variable to integrate the second derivative function of the temperature change.

Samples of standard 5 cm x 5 cm coloured glass wavelength cut-off filters, Corning 3389 in CS3-73-3.05 mm, and Corning 3389 in CS3-73-1.45 mm format (CdS$_x$Se$_{1-x}$ doped) were taken for the investigation. Conventional two-colour photothermal lens apparatus, with probe laser 632.6 nm HeNe, and excitation source XeCl excimer dye pulsed laser operating at 490 nm was used.

4. Results and Discussion
The FEA models of the photothermal heating of the glass samples showed significant heat transfer between the glass and air. Boundary conditions normally assumed in thermal lens is that this heat transfer is negligible. The thermo-optical coefficient, $\frac{ds}{dT}$, is negative for liquid samples for solids and glasses it may be positive or negative due to many counteracting effects. The time constant for the glass signal is shorter than that of the iron (II) diphenylpentadine (FeCp$_2$) solution due to the microcrystallites and thermal heat coupling with the surrounding fluid. Thicker glass has bigger signal.
The FEA thermal lens signals show a negative refractive index change in both liquid and glass which indicates ideal situations because those factors that contribute to positive refractive index change in glasses were not taken into consideration in the models. The photothermal signal in air is due to the diffused heat from the glass. If we compare the magnitude of photothermal signal in glass and the surrounding air, the signal in glass is about 4 orders more than that of in air. This is because the temperature change with pulsed laser excitation is very much faster than the heat diffusion to the surroundings.

The signal reaches maximum in glass within no time but in air it takes some time to reach highest value. This is due to the fact that the diffusion of heat from glass to air is relatively slow process in comparison to the excitation process. The FEA modeling of glass with (no transfer of heat from glass to air) and without (transfer of heat from glass to air) boundary condition clearly shows that the heat transfer from glass to the air is not critical. Therefore, semi-infinite cylinder approximation model should be a valid assumption for the maximum photothermal lens signal.

Comparing the inverse focal length equation at zero time for glass and standard solution we get the following equation to calculate the $\frac{ds}{dT}$ of glass.

$$\frac{ds}{dT} = \frac{S_g \rho_g \alpha_g C_{p,g}}{S_s \rho_s \alpha_g C_{p,s}}$$

The subscripts $g$ and $s$ are referred to glass and standard respectively. The liquid sample is contained in a cuvette and $\frac{ds}{dT}$, is taken to be the $(dn/dT)$ of the ethanol solvent. In other words, there is no thermal longitudinal thermal expansion.

The experimental thermal diffusion constant calculated for glass agrees with the theoretical value obtained from the given values of density, specific heat capacity and the corrected time constant obtained from experiment and modeling.

The $\frac{ds}{dT}$ term, which can be positive or negative since it is affected by counteracting factors. An increase in the specific volume (m$^3$ kg$^{-1}$) due to thermal expansion decreases the refractive index, due to the greater inter-molecular spacing. Secondly, an increase in the electronic polarizability causes the refractive index to gradually increase. In glasses, this effect is associated with the shift for longer wavelength of the UV absorption edge. Using Prod’homme equation and calculated value of $\frac{ds}{dT}$, the temperature coefficient of electronic polarizability is found to be $5.2 \times 10^{-5}$ K$^{-1}$ which is similar to the values found in literature.
We previously reported the photothermal lens signal for similar glasses using continuous laser excited photothermal spectrometry. The one of the problem realized at that time was that the heat transfer from a glass plate excited with a laser is far from the ideal situation described by the semi-infinite cylinder approximate models that are most often used to describe the photothermal lens experiment.

Here we have resolved the problem using: (a) pulsed laser excitation where the signal decay is faster than the heat diffusion to the surrounding, and (b) FEA modeling to take account the likely deviation from semi-infinite cylinder approximate models that are most often used to describe the photothermal lens experiment.

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**Figure 2.** Semi-infinite cylinder (dotted line) and FEA modelling of glass with (dashed line) and without (solid line) air boundary.

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**Figure 3.** FEA modelling of photothermal lens signal of air around the glass filter.

5. Conclusions
FEA modeling can be used to better understand the pulsed laser excited photothermal spectroscopy signals by correctly accounting for the heat transfer of the sample to the surroundings. FEA modeling is particularly useful to account for surface heat transfer that will occur in glasses and other samples where the absorbing material is in direct contact with the coupling fluid surroundings. The cylindrical approximation is not a valid in these cases. Anomalous \( \frac{ds}{dT} \)
behavior of these glass filters is thought to be due to the counteracting effects: optical nonlinearity, stress-induced birefringence, and the structural network in the glass structure. Further investigation using FEA modeling to take into account physical effects such as surface deformation due to thermal expansion, is will be required to understand the thermo-optical phenomenon.

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