Continuous Laser-Excited Photothermal Spectrometry of CdS\(_x\)Se\(_{1-x}\) Doped Glasses

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Photothermal lens measurements and finite element modeling are used to examine the physical changes taking place in optical filter glasses. Colored glass and neutral density filters are found to have a strong positive temperature-dependent refractive index change. The overall positive refractive index change is thought to be a consequence of complex counteracting factors: stress-induced birefringence, polarizability, structural network, and temperature-dependent carrier density changes in the CdS$_x$Se$_{1-x}$ microcrystals that produce optical properties of these glasses. Finite element analysis (FEA) modeling is used to examine the temperature profiles and the goodness of the semi-infinite thermal diffusion solution normally used for thermal lens experiments. The results of FEA were used to optimize experimental parameters and calculate values of $dn/dT$ for the glass by comparison with standard liquid samples.

Index Headings: CdS$_x$Se$_{1-x}$ Doped glasses; Photothermal; Semiconductor; Finite element.

INTRODUCTION

A couple of years ago our laboratory started searching for standard materials that could be used to calibrate a photothermal lens apparatus without having to make up liquid samples. It was thought that colored glass filters would serve as such a standard. Colored glass or volume-absorbing neutral density filters would be stable over time, could be easy to use, and the equivalent glass might be available to a number of researchers due to their wide-spread availability. If all researchers shared the same calibration, then measurements could be compared from laboratory to laboratory.

Two problems with using the glass optical filters were soon discovered. First, the colored glass and neutral density filters that we examined had anomalous physical properties. In particular, we find that these optical glasses have a positive temperature-dependent refractive index change coefficient. Second, 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.

Nanoparticles of semiconductor materials are often responsible for the optical absorption in commercial colored glass filters. The chemical composition, size, and method of synthesis of the nanoparticles affect optical properties of the glass filters of which most are high-pass wavelength cut-off filters used in spectroscopy and other optical technologies. Commercial colored glass wavelength cutoff filters utilize semiconductor nanoparticles on the order of 10 nm. Pereira et al. reported the complexity of the solution to theoretical treatment of the thermally induced bistability in semiconductor-doped glass (SDG) due to thermal lens effect.

Photothermal lens spectrometry is based on the measurement of refractive index changes that occur upon optical excitation. When a medium absorbs electromagnetic radiation, all or a fraction of the excitation energy is converted to heat. The heat increases temperature and causes a refractive index change. A low-power probe laser is used to monitor the refractive index change. In the case of photothermal lens spectrometry, the probe laser will focus or defocus relative to the normal beam propagation due to the transient lens. The change in probe laser beam propagation allows the determination of the refractive index change. Models are used to calculate temperature changes resulting from the absorption of excitation laser power. The combination of experiment and theory, then, allows one to determine the temperature-dependent refractive index change, $dn/dT$, for the transparent sample.

Among the currently used thermo-optical techniques, thermal lens and thermal deflection have received enormous interest from many authors; the most widely known and used is thermal lens. Theoretical models of thermal lens effects in fluids are well established, although a number of approximations are commonly used to obtain tractable analytical results. Obtaining accurate theoretical descriptions of thermal diffusion in solids excited by laser beams is still an active area of research. The use of thermal lens for analysis of transparent solid materials has been reported by some authors.

We present here experimental and modeling investigations of thermal lensing in colored glass filters and ethanol solutions contained in sample cuvettes. The aim of this paper is to describe qualitatively the temperature profile and refractive index change in our sample due to absorption of laser light irradiation by the sample. Thermal lens spectrometry is modeled as simply being proportional to the inverse photothermal lens strength. The result in transmittance mode was compared with the result obtained from liquid in a conventional cuvette. Thermal lens experiments in reflection mode and thermal deflection confirmed the induced thermal expansion in the sample and the heat transfer to the coupling fluid, in this case, air. Finite element analysis (FEA) is used to investigate analytical solution to the temperature profile in solution and solid samples. FEA modeling is described and model results are compared to the usual semi-infinite cylinder approximations.

THEORY

The photothermal lens signal is dependent on the spatially dependent refractive index change produced when energy deposited in the absorbing sample produces a temperature change. The time- and space-dependent temperature change is described by the differential equation for thermal diffusion. In radial symmetry, using appropriate lasers for sample excitation,
the equation describing heat diffusion is

\[
\frac{\partial}{\partial t} \delta T(r, z) - D_T \nabla^2 \delta T(r, z) = \frac{U(r, z)}{\rho C_p}
\]  

(1)

In this equation, \( \delta T(r, z) \) (K) is the spatially dependent temperature change. The radial coordinate is \( r \) (m), while the linear cylinder coordinate is \( z \) (m). The time, \( t \) (s), dependence is implicit. The rate of heat transfer is governed by the thermal diffusion coefficient, \( D_T \) (m\(^2\) s\(^{-1}\)). The right-hand side of this equation is the temperature change source. \( U(r, z) \) (W m\(^{-3}\)) is the spatially dependent energy density, \( \rho \) (kg m\(^{-3}\)) is density, and \( C_p \) (J kg\(^{-1}\) K\(^{-1}\)) is heat capacity of the sample.

Optical absorption within the sample results in sample heating at a rate that mimics the excitation laser beam profile. The absorbed power density for collimated continuous Gaussian profile laser irradiation propagating on the \( z \)-axis is

\[
U(r, z) = 2\pi \frac{\Phi_0}{\lambda^2} e^{-2r^2/\omega^2}
\]  

(2)

where \( \Phi_0 \) (W) is the incident laser power, \( \alpha \) (m\(^{-1}\)) is the exponential absorption coefficient, and \( \omega \) (m) is the excitation beam waist at the sample position. The \( z \)-axis origin is taken to be at the entrance interface of the sample.

The strength of the photothermal lens element is found from the second radial derivative, evaluated on-axis. Integration over path length results in the inverse lens strength:

\[
\frac{1}{f(t)} = \left( \frac{dn}{dT} \right) \int_{z=0}^{z=1} \left| \frac{d}{dz} \delta T(r, z; t) \right|_r dz
\]  

(3)

dn/dT (K\(^{-1}\)) is the temperature-dependent refractive index change, also known as the thermal-optical coefficient. This equation is strictly valid for parabolic temperature change distributions. However, the temperature change is not necessarily parabolic. So the probe laser should have a smaller diameter than the temperature change distribution for Eq. 3 to be valid. This may be true with continuous excitation since thermal diffusion broadens the temperature change relative to the region of excitation.

The photothermal lens signal is related to the inverse focal length. While it is dependent on the beam propagation characteristics of the particular apparatus, the experimental signal, \( S(t) \), calculated from

\[
S(t) = \frac{\Phi_p(t = 0)}{\Phi_p(t)} - 1
\]  

(4)
is generally proportional to the inverse focal length as \( S(t) \approx -2z'/r(t) \). In Eq. 4, \( \Phi_p(t) \) (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 \( z' \) (m) in front of the sample.

The photothermal lens strength can be found by numerical integration of the heat diffusion differential equation with appropriate boundary conditions. Analytical solutions of the lens strength can be obtained by making several approximation assumptions. First, it is assumed that there is negligible thermal diffusion through the sample cell windows, or the sample–air interface in the case of a solid (e.g., glass plate) sample. Second, it is assumed that there is no significant attenuation of the excitation laser passing through the sample. In this case the exponential term containing the optical absorption coefficient, \( \alpha \), is set equal to unity. With these assumptions, the solution to Eq. 1 using Eqs. 2 and 3 is:

\[
\frac{1}{f(t)} = \left( \frac{dn}{dT} \right) \frac{\Phi_0 z' Y_{th}}{\pi \kappa w^2 (1 + \kappa t / 2t)}
\]  

(5)

The heat yield, \( Y_{th} \), term is used to account for finite heat yield in cases where energy is lost through luminescence. \( l \) (m) is the sample path length, \( \kappa_t \) (s) is the characteristic thermal diffusion time constant defined by

\[
t_c = \frac{w^2}{4D_T}
\]  

(6)

\( D_T = k / \rho C_p \) is the thermal diffusion coefficient, and \( k \) (J K\(^{-1}\) m\(^{-1}\) s\(^{-1}\)) is the thermal conductivity.

With a liquid sample, \( dn/dT \) is usually negative so that the thermal lens is negative where thermal expansion is the overriding contributing factor in \( dn/dT \). For glass, the following equation has been shown by Prod’homme:

\[
\frac{dn}{dT} = \frac{(n_0^2 - 1)(n_0^2 + 2)}{6n_0^2} \left( \frac{1}{\gamma} \frac{dY}{dT} - 3\beta \right)
\]  

(7)

where \( \beta = 1 / \sqrt{V(dV/dT)} \) (K\(^{-1}\)) is the volume expansion coefficient and \( \gamma \) is the polarizability coefficient. The form of this result implies that, depending on the glass structure, \( dn/dT \) can either be negative or positive. A structure with a high expansive network will result in a negative temperature-dependent refractive index. The later is normal for gases and liquids, and many solids as well. On the other hand, a large positive temperature-dependent polarizability term can result in an overall positive \( dn/dT \). With few exceptions, in particular, near-phase-change temperatures, most materials expand with increased temperature. But there are mechanisms for increasing refractive index with temperature. Solid phase changes, expansion induced stress, semiconductor conduction band population changes, and production of new states may result in a positive temperature-dependent refractive index change.

**EXPERIMENTAL**

The diagram in Fig. 1 illustrates the apparatus setup for the thermal lens experiment. A continuous-wave Ar\(^+\) laser (Coherent Innova 90, Model 90-6) operating at 514.5 nm is used as the excitation source and a 632.6 nm HeNe laser (Uniphase, Model 1107P) is used to probe the resulting photothermal signal. We favor collinear dual-beam geometry for our thermal lens experiments. The distance between the sample and the photodiode detector is optimized to satisfy the far-field paraxial approximation. Two lenses (10 cm and 25 cm focal length) are used to focus the excitation beam in the sample and after the HeNe beam focus.

The excitation beam is modulated with a Wavetek model 184 operated with a Newport model 845 digital shutter, and excitation source power is measured with a Scientech model 36-001 laser power monitor. The photothermal lens caused blooming or focusing of the probe laser. This is measured as a change in the power at the center of the beam. The center HeNe beam power is measured using a pinhole and a United Detector Technology (UDT) Model PIN-10DP photovoltaic photodiode detector. These detectors have large 1-cm-diameter active areas...
for easy setup. A 632.8 nm laser line bandpass filter is used to prevent the transmitted Ar+ laser beam from being detected by the photodiode detector. A small fraction of the probe beam is split off prior to the pinhole aperture and a second bandpass filter/photodiode is used to monitor the probe laser power past the sample. Changes in the probe laser power are compensated for using an operational amplifier divider, the circuit of which divides the thermal lens signal by the signal proportional to the HeNe laser power. Photodiodes are often saturated by laser light sources. The photodiode signals are checked for linearity with neutral density filters.

This probe laser power compensated thermal lens signal is amplified and electronically filtered with a Tektronix model AM-502 differential amplifier. The analog signal is subsequently digitized with a 16-bit analog-to-digital converter board and processed by multichannel analysis software. The latter averages several signal transients. Multichannel averaging was performed to improve the raw photothermal lens signal estimation precision. The photothermal lens signal was calculated from this raw data using a simple spreadsheet program.

Photothermal reflection lens experiments used an apparatus similar to that of the transmittance mode experiments. For these experiments the photothermal lens detector, consisting of the pinhole aperture, HeNe laser line filter, and PIN photodiode, is positioned at an angle of about 10° to monitor variation in the power in the center of the probe laser beam reflected from the glass surface.

The transverse photothermal deflection (PDS) apparatus used in these studies is similar to those described by Boccara et al.\textsuperscript{15,16} The excitation and probe lasers are the same as those used in the thermal lens experiment apparatus described above. Beam deflection angle is measured by a segmented position-sensing bi-cell detector (United Detector Technology PIN bi-cell detector with a Model 301-DIV analog processor). The resulting signal was also amplified with a Tektronix AM-502 differential amplifier and subsequently digitized with a 16-bit analog-to-digital converter board with multichannel averaging software written in the C++ computer language. Further data processing is performed on a PC with a spreadsheet program.

**Finite Element Analysis.** Finite element analysis software provides numerical solutions to the heat transfer equations with the realistic boundary conditions imposed by the complicated experimental geometries. To better understand the transient temperature profile in the samples, finite element analysis is used to model stationary temperature changes. The result of the finite element analysis is then compared to conventional analytical solutions to gauge the error. The experimental setup and the apparatus constraints are guided by the error analysis. Analysis based on Comsol Femlab V3.1 is carried out on a personal computer (Compaq Presario SR1330x, AMD Athlon XP 3200 processor).

Analysis follows the steps below:

1. Define sample geometry and specify materials, boundary conditions, heat sources, and sinks.
2. First solve problems with rough finite element definition and further refine elements and domain.
3. Get $dT$ either at single time, a time series, or at steady state.

The relative photothermal lens signal strength is found from Eq. 3. However, the $dn/dT$ is not known and so is taken as being unity. The path integral of the second radial derivative was found by either (1) exporting two temperature change rays into a text file, reading the text file into a MS Excel spreadsheet, and calculating the second derivative from the ray data, or (2) using the Comsol Integration coupling variable to integrate the 2nd-derivative function of the temperature change ray.

To find the $d^2\delta T/dr^2$ using the first method, the temperature change is taken along two rays, one at $r = 0$, $\delta T(0)$ and the other at a small radius, $\delta T(r)$. The temperature change is assumed to be parabolic near the optical axis so that $\delta T(r) = a + br^2$, where $a$ and $b$ are constants. With the parabolic approximation $d^2\delta T/dr^2 = 2b$, it is easy to show that $b = [\delta T(0) - \delta T(r)]/2r^2$ and thus $d^2\delta T/dr^2 = 2(\delta T(0) - \delta T(r))/r^2$. The only caveat is that the radius must be small.

Small square glasses (5 cm × 5 cm × 0.5 cm and 5 cm × 5 cm × 0.1 cm) were modeled using Comsol Multiphysics to represent the actual glass sample used in the experiment. For convenience, the glass was modeled with the origin at the center of one of the square faces so that the $z$-axis runs along the path length of the excitation and probe beams. The temperature profile of the glass square was obtained by having the FEA software solve the heat equation with the boundaries set at zero degrees (assuming no convectional heat transfer at the surfaces) and heat input along the $z$-axis defined by Eq. 2. This way, the temperature solution represents $\delta T$. The model was solved using steady-state conditions, not considering convection because the sample is solid. The values of $\alpha$, $\Phi_0$, and $w$ used were 29.7 $(\text{m}^{-1})$, 75 mW, and 160 $\mu$m, respectively.

**Samples.** A commercial standard 5 cm × 5 cm colored glass wavelength cutoff made with CdS,Se$_{1-x}$, microcrystal on the order of 10 nm is investigated as an absorbing solid material. Corning 3750 (CS3-79, 5 mm thickness) and Schott NG 11 (1 mm thickness) glass filters were used. Solutions of iron (II) dicylopentadiene $(\text{FeCp}_2)$ in ethanol were used as the liquid standards. Linear dilution is used to obtain lower absorbance from stock solutions of high enough absorbance to measure using a spectrophotometer in a conventional 1 cm path length liquid cuvette. Cuvettes from NSG Precision Cells, Inc., 10 × 5 mm and 10 × 2 mm, were used to approximate the path length in the solid samples. The sample is positioned at the focus of
the excitation beam for maximum temperature gradient, and the solid versus liquid experiment is carried out separately at room temperature under the same conditions. Sample absorbances were recorded with a Shimadzu UV-2401 spectrophotometer.

RESULTS AND DISCUSSION

Thermal lens theories were developed mainly with consideration of the liquid-phase experiment, in which \( dn/dT \) is negative. For glasses, \( dn/dT \) can either be negative or positive due to many counteracting effects.\(^{17,18}\) Lima et al.\(^{19}\) gave insight into different factors that can lead to a positive refractive index gradient in solids.

Glasses are reported to exhibit high \( \chi^{(3)} \) and photo-darkening effects, giving rise to optical phase conjugates. The nonlinear absorption coefficient and the index of refraction change in SDG are due to the photo-darkening effect. The latter is attributed to a photochemical process in the semiconductor microcrystallite.\(^{20}\)

Trends in the nonlinear properties of SDG may also depend on the band-gap wavelength. Band-gap wavelengths of 490.1 nm and 713.9 nm at room temperature have been reported for CdS and CdSe, respectively, and linear interpolation between the two wavelengths can be used to estimate the band-gap wavelength for CdS\(_x\)Se\(_{1-x}\).\(^{21,22}\) The nonlinear refractive index change is expected to be positive in the SDG at excitation wavelengths below the band-gap wavelength and negative at wavelengths above the band-gap wavelength.

We have presented thermal lens experiments and finite element modeling to investigate the temperature profile and change in refractive index of CdS\(_x\)Se\(_{1-x}\)-doped glass. Figures 2a, 2b, and 2c show the experimental thermal lens signal for commercial colored glasses and FeCp\(_2\) in transmittance mode with the excitation beam operated at 514.5 nm and an excitation power of 75 mW. Conventional thermal lens signal is expected to correspond with a negative change in refractive index induced by a temperature gradient perturbation as a result of absorption of the excitation energy by the sample. The thermal lens signal (arbitrary unit) for an FeCp\(_2\) solution with a measured absorbance of 0.000 375 AU for 5 mm path length (Fig. 2a) indicates a decrease in refractive index of the sample. The thermal lens signals of Corning and Schott commercial glass filters, which have lower molar absorption compared to the liquid (Figs. 2b and 2c) are inverted contrarily, which indicates an increase in refractive index.

We observed the same trend in the signal for glass filters that are doped with other materials rather than the semiconductor microcrystals, for example, the Schott’s neutral density filters. This shows that positive \( dn/dT \) cannot only be a result of semiconductor microcrystal. Lima et al.\(^{19}\) has reported positive \( dn/dT \) in their experiment due to counteracting induced stress in the glass material. The experimental FeCp\(_2\) signal magnitude is large compared to glass at the same absorbance, while the time constant for the glass signal is shorter than that of the FeCp\(_2\) solution due to the microcrystallites and thermal heat coupling with the surrounding fluid. The signal output in this experiment is consistent with previous methods reported.\(^{21}\) The excitation beam wavelength falls below the CdS\(_x\)Se\(_{1-x}\) band-gap wavelength, which produces a positive refractive index change due to increased carrier density.

A photothermal reflection experiment measuring the variation in the reflected beam due to “photothermal bump” on the surface of the glass confirmed induced thermal expansion within the glass. Indirect photothermal refractive index gradient measurements, popularly known as photothermal deflection, also confirm thermal heat transfer between the glass surface and the coupling fluid, which shows another weakness in semi-infinite boundary conditions normally assumed in thermal lens experiments that is not considered in this experiment. The signal versus time curve in the thermal reflection and thermal deflection measurements are inverted compared to the glass thermal lens signal in transmittance mode, indicating expansion
in the glass due to the temperature gradient and heat coupling to the surroundings.

The FEA thermal lens signals (Figs. 3a and 3b) 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 values of \( \frac{dn}{dT} \) for the glasses were estimated by comparing data obtained from the thermal lens signals for the glasses and the well-established photothermal properties of ethanol. At steady-state conditions, Eq. 3 indicates that the thermal lens signal is proportional to the integral of the second derivative of the radial temperature profile. The integration term from Eq. 3 may be obtained directly from finite element analysis modeling solution.

Corrected signal for each material was obtained by comparing the FEA signal with the experimental signal, \( \frac{dn}{dT} \) for the glasses was estimated by comparing the corrected signals of the glasses with those of ethanol. The \( \frac{dn}{dT} \) was estimated using Eq. 8 with corrected signals:

\[
\frac{dn}{dT_g} = \frac{dn}{dT_e} \frac{S_g}{S_e} k_e \frac{\sigma_e}{\sigma_g}
\]

\( S \) is the corrected signal and the subscripts \( e \) and \( g \) stand for ethanol and glass, respectively. Other variables are as defined above. Table I shows the calculated \( \frac{dn}{dT} \) and the coefficient of electronic polarization, \( \sigma \), for the glasses. Given \( \beta \) and \( n \), from Eq. 7, the electronic polarization coefficient, \( \sigma \), was calculated using estimated \( \frac{dn}{dT} \). The values of the polarization coefficient are in agreement with Prod’homme’s report on silica glasses with low expansivity. This accounts for the fact that electronic polarization is the dominant factor contributing to refractive index variation. An increase in electronic polarization causes the refractive index to increase in silica glasses.

One of the key challenges of photothermal spectroscopy is obtaining the temperature change produced within the sample. The problem is complicated if the refractive index change dissipates faster than the change in temperature. Finite elemental analysis modeling also helps in understanding the dynamics of the temperature distribution with experimental parameters such as beam waist, path length, and geometry. The results of inverse focal length as a function of excitation beam waist calculated using finite element modeling are shown in Fig. 4. The results showed that glasses exhibit larger deviations from conventional analytical solutions due to direct sample-to-air contact. It is also shown that the approximation improves with increasing path length-to-radius ratio.

### TABLE I. Thermo-optical constants for glass filters.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \frac{dn}{dT} \times 10^4 ) (K(^{-1}))</th>
<th>( \beta \times 10^6 ) (K(^{-1}))</th>
<th>Refractive index (( n ))</th>
<th>( \sigma \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>-4</td>
<td>990</td>
<td>1.361</td>
<td>18.1</td>
</tr>
<tr>
<td>Corning CS-3-79</td>
<td>1.02</td>
<td>12</td>
<td>1.509</td>
<td>3.16</td>
</tr>
<tr>
<td>Schott NG 11</td>
<td>0.145</td>
<td>7</td>
<td>1.38</td>
<td>29.68</td>
</tr>
</tbody>
</table>

\( \frac{dn}{dT} = -4 \times 10^{-4} \) (K\(^{-1}\)), \( \kappa_e = 1.38 \) (W m\(^{-1}\)K\(^{-1}\)), \( \kappa_e = 0.167 \) (W m\(^{-1}\)K\(^{-1}\)), \( \sigma_e = 0.075 \) (m\(^{-1}\)), \( \sigma_g \) (Corning) = 29.68 (m\(^{-1}\)) and \( \sigma_g \) (Schott) = 148.7 (m\(^{-1}\)).

### CONCLUSION

A method for understanding the thermo-optical phenomenon in thermal lens measurements of colored glass filters by applying finite element analysis has been presented. FEA proved useful in understanding the physics of photothermal...
spectroscopy and the validity of the conventional analytical solution used in thermal lens experiments. It was found that the conventional theoretical model used was not adequate to account for the aberrant nature of the results observed in glasses. Photothermal reflection measurements confirm a positive thermal expansion when the glass is heated. Counterintuitively, the refractive index increases with temperature due to counteracting effects in the glass filters. Positive refractive index changes in non-semiconductor-doped glass filters can be attributed to stress-induced birefringence, structural components, and electronic polarizability, but the effect is complicated with semiconductor-doped glass filters due to additional factors attributed to the increase in the carrier density of semiconductor microcrystals. “Long-lived trap states” have been proposed to account for photo-darkening in CdS\textsubscript{x}Se\textsubscript{1−x}-microcrystal glasses. There is ongoing research in our laboratory on using finite-element models to further investigate the infinite cylinder approximation commonly used in thermal lensing results. It has been difficult to fully understand the thermo-optical phenomena in the glasses without prior knowledge of the properties and structural composition of the material.

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