Chapter 5

EVALUATION OF THE THERMAL DIFFUSIVITY OF POLYANILINE -TiO₂ COMPOSITE USING LASER INDUCED THERMAL LENS TECHNIQUE

5.1. Introduction

Photothermal spectrometric techniques such as thermal lens spectrometry (TLS) are characterized by high sensitivity, which enables measurement of absorption as low as 10⁻⁷. The thermal lens technique is based on measurement of the temperature rise that is produced in an illuminated sample as a result of nonradiative relaxation of the energy absorbed from a laser. Because the technique is based on direct measurement of the absorbed optical energy, its sensitivity is higher than conventional absorption techniques. In this chapter the thermal diffusivity measurements of polyaniline modified TiO₂ samples were studied using laser induced thermal lens technique.

5.1. Introduction

The knowledge of the thermal conductivity and/or the thermal diffusivity is more and more required in many industrial fields. As a matter of fact, these are the most important parameters when heat transfer processes are involved. In the power generation industries, materials are selected primarily considering...
their thermal properties [1-4]. In the automotive and aeronautical industries, CMC (ceramic matrix composite) materials for high performance brakes and heat shields are under development and manufacturers require, as essential information the thermal diffusivity [5].

Photothermal spectroscopy is a group of high sensitivity spectroscopy techniques used to measure optical absorption and thermal characteristics of a sample. The basis of photothermal spectroscopy is the change in thermal state of the sample resulting from the absorption of radiation. Light absorbed and not lost by emission results in heating. The heat raises temperature thereby influencing the thermodynamic properties of the sample or of a suitable material adjacent to it.

The thermal lens technique is based on measurement of the temperature rise that is produced in an illuminated sample as a result of nonradiative relaxation of the energy absorbed from a laser. Because the technique is based on direct measurement of the absorbed optical energy, its sensitivity is higher than conventional absorption techniques. However, advantages of the thermal lens technique are not only limited to its ultrasensitivity but also include other unique characteristics including small volume sample capability and dependency on thermo optical properties of solvents [6]. The availability of lasers makes it possible to observe and measure a variety of phenomena, which would not otherwise be feasible using other light sources. One such phenomenon is the photothermal effect [7]. In the case of the thermal lens which is a type of photothermal effect, a sample is excited by a laser beam, which has a symmetrical intensity distribution [6]. The nonradiative relaxation releases the absorbed energy in the form of heat. The heat generated is strongest at the center of the beam because the beam intensity is strongest at that point.
Consequently, a lens like optical element is formed in the sample owing to the temperature gradient between the center of the beam and the bulk material. The thermal lens effect is observable for laser beams in the power range of only microwatts in samples normally thought to be transparent, and is thus suitable for the low absorption measurement of nonfluorescent samples. Its sensitivity is relatively higher than that of the conventional transmission or reflection measurements because, in this technique, the absorbed energy is measured directly. The first measurement of the thermal lens effect was performed by Gordon et al. in 1965 using a simple single-beam apparatus [7].

The unique characteristics of lasers, namely low-beam divergence, pure polarization, high spectral and spatial resolution, and its ability to be focussed to a diffraction-limited spot, have been fully exploited to use the thermal lens as a detection technique for micro fluidic devices. As a consequence of these developments, the thermal lens technique has been established as a highly sensitive technique for trace chemical characterization, including single molecule detection. In addition to its ultrasensitive and small-volume capabilities, the thermal lens technique has other features such as the thermal lens signal is dependent not only on sample concentration and excitation laser power but also on the position and thermo physical properties of the sample. These unique features have been exploited either to further increase its sensitivity or to use it for sensitive and accurate determination of thermal physical properties of a variety of substances including solids, liquids, and gases.

Polyaniline (PANI) is one of the typical conducting polymers of the first generation. Much of the work was focused on tailoring its electrical conductivity. Heat diffusion in this material remains practically unexplored. Its use in diverse fields such as molecular electronics and sensor technology
makes proper thermal design of the devices employing conducting polymers essential [8-14]. Poor thermal management of devices employing conducting polymers may lead to device failure. An estimate of heat diffusion in a material can be obtained from its thermal diffusivity value. It is the ratio of thermal conductivity to the thermal capacity per unit volume, given by \( \alpha = k/\rho C \); where \( k, \rho \) and \( C \) are the respective values of thermal conductivity, density and specific heat capacity of the material.

5.2. Theory

Thermal lens spectrometry (TLS) is one of precise photo-thermal techniques based on temperature gradient which is caused by absorption of optical radiation and non-radiative relaxation of the excited molecules. Photothermal lens spectroscopy (PTS or TLS) measures the thermal blooming that occurs when a beam of light heats a transparent sample. It is typically applied for measuring minute quantities of substances in homogeneous gas and liquid solutions [15]. The thermal lens effect originates from nonradiative relaxation of excited species in a sample irradiated by a laser beam with a Gaussian intensity profile. So when sample absorb the beam with Gaussian distributed intensity the temperature distribution has radially dependence. During such radiation less relaxation processes, which include vibrational relaxation, intersystem crossing, and external conversion, the absorbed energy from the excitation light is converted to heat. As a result, the temperature of the irradiated sample changes and a refractive index gradient is formed in the sample, resulting in a change in the laser beam radius, and a related change in the intensity of the beam on its axis. This gradient of temperature can create a refractive index gradient which behaves similarly to a converging or diverging lens depending on whether the change rate of refractive index with respect to
Evaluation of the thermal diffusivity of polyaniline-TiO$_2$ composite using laser induced thermal lens technique

temperature, is positive or negative [16,17]. This technique has very important properties such as “high sensitivity” that makes it appropriate for measuring the thermal diffusivity of samples rely on physical changes that arise in the sample. The magnitude of the thermal lens effect is proportional to the amount of heat generated in the irradiated sample, and is consequently dependent on the power $P$ of the excitation light, absorbance $A$ of the sample, as well as on the fluorescence efficiency of absorbing species, which decreases the thermal lens effect.

5.3. Thermal lens technique

In a simplified form, the essence of this technique is as follows. Irradiation of an absorbing medium by a laser beam with a Gaussian intensity distribution in the transverse cross section induces a temperature gradient in it due to non uniform heating. In turn, a change in temperature causes local changes in the refractive index of the medium, in correspondence with the laser beam intensity distribution. The occurrence of the refractive index gradient in the medium leads to the formation of an optical element, which acts as a scattering/collecting lens; this element was referred to as a thermal lens. Since the refractive index of most materials in the transparency range decreases with an increase in the temperature, the thermal lens is generally scattering; i.e., the transverse laser-beam size increases when the medium is heated. Fig.5.1. shows the thermal lens formation of a sample.
Variations in the refractive index of the medium can be caused by changes in both the temperature $T$ and density $\rho$ of the medium

$$\Delta n = \left( \frac{\partial n}{\partial T} \right)_p \Delta T + \left( \frac{\partial n}{\partial \rho} \right)_T \Delta \rho.$$ 

The thermal lens technique can be implemented using both single- and double-beam measurement schemes. In the single-beam scheme radiation of one laser is simultaneously used for excitation (generation of a thermal lens) and probing. Being absorbed, laser radiation heats the sample, and the change in its intensity yields information about absorption in the medium. The measurement technique generally implies recording the temporal shape of photothermal signal from a photodetector with a diaphragm, located in the far-field zone [18].

The double-beam scheme is more universal. Here, a thermal lens induced by excitation (pump) radiation is recorded by measuring defocusing of an additional probe beam. Its main advantage is that it allows one to study the spectral dependence of the absorption of materials; this cannot be done within the single-beam scheme. One of configurations of the classical double-beam measurement scheme is shown in Fig.5.2.
Fig. 5.2. Thermal lens technique (longitudinal version): double-beam measurement scheme; the pump and probe beams propagate coaxially

The double-beam scheme is implemented in either longitudinal (Fig. 5.2.) or transverse [19, 20] configurations; in the latter case, the excitation beam is focused into the sample perpendicularly to the probe beam. In most cases the longitudinal (collinear) version is used. In this case, applying a dichroic mirror, one makes both beams propagate coaxially in the sample, due to which the maximum interaction length is provided. Here, the so-called mode-matched and mode-mismatched configurations are distinguished. In the former case the waists of both beams coincide in the measurement cell (sample), whereas in the latter version they are spatially separated (Fig. 5.3.).

Fig. 5.3. Mode-mismatched configuration (measurement scheme with shifted waists [20].
Thermal diffusivity $D$ of the sample can be calculated from the equation $t_c = \omega^2 / 4D$, where $\omega$ is the beam radius at the sample position (.225mm/2) and $t_c$, the time response to attain the steady state focal length. The time dependent probe beam intensity follows the expression, which used for fitting the data

$$I(t) = \frac{I_0}{\left[1 - \theta \left( 1 + \frac{t_c}{2t} \right)^{-1} + \left( \frac{1}{2} \right) \theta^2 \left( 1 + \frac{t_c}{2t} \right)^{-2} \right]}$$

5.4. Experiment

The excitation source is a continuous wave (cw), 532 nm diode pumped solid state laser, (DPSS) with a maximum power of 150 mW. The power at the sample is suitably adjusted using attenuators so that the probe beam spot is free from aberrations. A 2mW He–Ne laser used as the probe is arranged to be collinear with the pump, using a dichroic beam splitter. The two beams are focused into the sample cell such that the beam area at the sample plane is the same for both pump and probe resulting in a mode matched TL configuration. Sample was taken in cuvettes of 1 cm and 5 mm path lengths for various sets of measurements. A low frequency mechanical chopper and a shutter are used as required, either to quickly block the pump or to intensity modulate it, depending on the type of data recorded. For example if the aim is to optimize the TL experiment, it is desirable to use the chopper, and adjust the sample position, aperture position, etc. until the TL peak-to-peak signal is maximum. This also enables one to determine the thermal recovery of the sample. On the other hand, when a time dependent TL signal is required; one should replace the chopper with a shutter. The TL signal was collected using an optical fiber, positioned at the center of the probe beam spot and connected to a photodetector--
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DSO system. A filter for 532 nm was used before the detector to remove the residual pump. Fig. 5.4. shows the pulsed thermal lens experimental set-up.

![Fig. 5.4. Pulsed thermal lens experimental set-up](image)

### 5.5. Thermal diffusivity studies

Pure TiO$_2$ does not show thermal lens effect due to lack of optical absorption. However, pure polyaniline shows a thermal diffusivity of 0.0201 cm$^2$/s. On blending with TiO$_2$, the thermal diffusivity of the composite is found to increase. As the amount of polyaniline content increases, thermal diffusivity increases drastically. Table 5.1 shows the thermal diffusivity values.

Table 5.1. Thermal diffusivity values of PANI-TiO$_2$ composites for various fraction of PANI in the composites

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\theta$</th>
<th>$t_c$ (s)</th>
<th>$D \times 10^{-3}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>-19.04</td>
<td>1.57</td>
<td>0.02</td>
</tr>
<tr>
<td>TP1</td>
<td>-9.46</td>
<td>0.79</td>
<td>0.04</td>
</tr>
<tr>
<td>TP2</td>
<td>-9.90</td>
<td>0.77</td>
<td>0.041</td>
</tr>
<tr>
<td>TP3</td>
<td>-5.46</td>
<td>0.34</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Chapter 5

The best interpretation for this phenomenon is that, absorption of exciting laser light by the conducting polymer generates oscillating electron which are called hot electron. These hot electrons rapidly transfer their energy to the TiO$_2$ particle through electron-phonon scattering. This thermal energy is finally get transferred to surrounding liquid by phonon scattering with particles as scattering centres [21]. Fig.5.6. & 5.7. show the TL decay and the normalized TL time evolution signal for sample dispersed in water.

![Figure 5.6. TL decay of representative sample](image)

**Fig.5.6. TL decay of representative sample**

![Figure 5.7. The normalized TL time evolution](image)

**Fig.5.7. The normalized TL time evolution**

Signal for sample dispersed in water. The circles are experimental data and solid lines are theoretical fit.
Fig. 5.8. Photograph showing (a) Probe beam without pump laser and (b) thermal blooming of the probe beam in presence of pump laser for the representative sample dispersed in water.

The fact that the PANI- TiO$_2$ composite has enhanced thermal diffusivity in comparison with PANI, can find practical uses as efficient coolants in various industrial applications.

5.6. Conclusions

Polyaniline is known to possess a conjugated structure and samples obtained by chemical synthesis do not show any cross linking or side reactions. The local order in such a sample will be relatively high. This can lead to reduced scattering of phonons in a chemically synthesized sample. By acid doping, a three-fold increase in the value of thermal diffusivity is observed. This increase can be related to the increase in carrier concentration upon doping. In the undoped state there is a phonon-assisted heat transport. In doped samples there is a carrier contribution to heat transport and a consequent higher diffusivity [22]. Polyaniline blending modifies the thermal properties of TiO$_2$. There is an increase in thermal diffusivity with increase in amount of polyaniline content in the composites. This means that the composite material can be used as a good coolant material which will diffuse
heat from the medium at faster rate as polyaniline component increases in the composite material.

References


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