ABSTRACT

Aranmula mirror is a metallic mirror prepared by ethanometallurgical process by a group of families at Aranmula, a village in Kerala, south India. Recently there has been an interest in investigating the properties of Aranmula Mirror using modern scientific techniques. The present work describes the evaluation of thermal diffusivity and reflection coefficient using photoacoustic technique.

APPENDIX 1

PHOTOACOUSTIC STUDY IN ARANMULA MIRROR
ABSTRACT

Aranmula mirror is a metallic mirror prepared by ethanometallurgical process by a group of families at Aramula, a village in Kerala, south India. Recently there has been an interest in investigating the properties of Aramula Mirror using modern scientific techniques. The present work describes the evaluation of thermal diffusivity and reflection coefficient using photoacoustic technique.
The art of making metal mirrors has been practiced in various parts of the world even before 1400 BC, for distortion free images. By 1400 BC people created a metal mirror of bronzes containing 30-weight percent tin. Although brittle, high-tin bronzes yielded a highly reflecting surface. The art of making metal mirrors from copper-tin bronzes was known in India. This ancient art of metal mirror making is still practiced by only a small number of families at Aranmula, a small village in Kerala, South India. The properties and method of casting of these mirrors have recently been studied by Pillai et al [1]. The mirror is found to be an alloy of Cu-70.4%, Sn-29.4%, Zn-0.06%, P-0.02%, & Fe-0.034% and Ni-0.052%. The present work deals with the determination of thermal diffusivity and reflection coefficient of Aranmula mirror using photoacoustic effect.

By studying the chopping frequency dependence of the acoustic signal generated in the coupling gas at a fixed optical wavelength, the thermal diffusivity of the sample can be evaluated [8,14,15]. By noting down the PA signal for the mirror and carbon black the reflection coefficient can be calculated.
To determine the reflection coefficient of the mirror by PA technique carbon black is used as the reference sample. If $S_c$ and $S_m$ are the PA signal amplitudes and $A_c$ and $A_m$ are the absorption coefficients for carbon black and the mirror respectively, for the incident beam of intensity $I_1$ we can write,

$$\frac{S_m}{S_c} = \frac{A_m I_1}{A_c I_1} = A_m$$  

(1)

(where $A_c=1$) and reflection coefficient

$$R = 1 - A_m$$  

(2)

To determine the reflection coefficient of the Aranmula mirror PA signal for the mirror and carbon black are noted for a given chopping frequency and laser power. The reflection coefficient is calculated from equations 1 and 2.

To determine the thermal diffusivity of the metal mirror a small piece of the sample is kept in the PA cell and the frequency dependence the acoustic signal is studied. Knowing the thickness ($l_s$) of the sample and characteristic frequency ($f_c$) from the log-log plot, the thermal diffusivity can be calculated using the relation...
α = l s^2 f_c [2-9]. The details of thermal diffusivity measurements are given in chapter 3.

The Aranmula mirror used for the present study has a thickness of 1.24 mm. From the log-log plot it is found that the characteristic frequency is at 68.79 Hz. The thermal diffusivity thus calculated gives the value $1.058 \pm 0.001$ cm$^2$/s, which differs much from the value of copper (1.18 cm$^2$/s) which is the major constituent (70.4%) of the sample [10].

The reflection coefficient of the Aranmula mirror used for the present study, calculated from equations 1 and 2 yielded the value to be 0.92.

References


REFERENCES


Mirage effect or photothermal deflection effect is another thermooptic effect that can be used to characterize thermal and optical properties of materials. The use of mirage technique in material studies is described by taking specific example of phthalocyanines, which have importance in photonic applications.

APPENDIX II

THERMAL DIFFUSIVITY MEASUREMENTS ON SOME METAL PHTHALOCYANINES USING MIRAGE EFFECT
The "mirage" technique (optical beam deflection) first introduced by Boccarà, Fournier and Badoz [1] in early 1980s, has recently been revived as an elegant method for measuring the optical and thermal properties of materials [2-4] because of its high sensitivity and non-destructive nature [5]. The basic principle of the photothermal technique is that the specimen irradiated by an intensity modulated (chopped) laser beam (pump) undergoes optical absorption and is heated up by non-radiative transitions, the heat, which is periodically deposited in the sample, is transferred to the coupling medium by thermal conduction and this sets up a refractive index gradient (RIG) in the coupling medium. A second laser beam (probe) scanning the sample surface gets deflected due to the RIG produced by the beam. The deflection of the probe beam is detected by an optical fibre based position sensitive detector (PSD).

The technique can be performed in two ways. (1) Transverse PTD - where we assume that the pump beam propagates through the medium in the z direction and the probe beam propagating perpendicular to the pump beam i.e. along y direction (2). Collinear PTD - where the probe beam propagates along the z direction itself or makes an angle with respect to the pump beam direction [6-11].
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The technique finds profound applications in fields like spectroscopy, imaging, thermal studies, ablation studies, thermodynamic transport properties etc. In the present chapter we have employed PTD technique to determine the thermal diffusivity of some metal phthalocyanines, organic semiconductors.

![Fig.1: Structure of Phthalocyanines.](image)

Phthalocyanines, the organic semiconductors, have attracted a great deal of attention in recent years due to their potential application in various fields like imaging, microelectronics, catalysis, photochemistry, sensors
Phthalocyanines are macrocyclic compounds containing four pyrrole units, which are fused to an aromatic structure [Fig.1]. The compounds usually referred to under phthalocyanine class consist of metal derivatives of phthalocyanines. Two hydrogen atoms attached to the two-isoindole group can be replaced by atoms from every group in the periodic table to form the metal phthalocyanines. Also, each of the sixteen peripheral hydrogen atoms on the four benzene rings can be substituted by a variety of atoms and groups. In metal phthalocyanines, for example, the metal atom supplies one electron each to the nitrogen atoms of the isoindole groups and these isoindole nitrogen atoms in turn supplies an electron to the metal atom, forming a covalent bond. The unshared pairs of electrons in the remaining two isoindole nitrogen atoms presumably from coordinate covalent bonds with the metal atom.

PTD technique has been proved to be a useful, elegant and sensitive tool for the measurement of thermal diffusivity [2,20-24]. The schematic of the PTD process (transverse geometry) is shown in figure 2.
Fig. 2: Schematic of the PTD method showing the two deflection components (transverse configuration)

Let y and z be the transverse and vertical offset of the probe beam with respect to the pump beam axis [2, 20, 199].
Resolving the deflected beam, the transverse ($\phi_t$) and normal ($\phi_n$) components can be estimated as

\[
\phi_t = \frac{1}{n} \left( \frac{\partial n}{\partial t} \right) \int \left( \frac{\partial T}{\partial y} \right) \, dx
\]

In order to determine the thermal diffusivity, the sample is illuminated by an intensity modulated laser beam (pump beam). The subsequent non-radiative de-excitation process occurring inside the sample results in the heating of the sample. The thermal waves generated from the sample sets a refractive index gradient with respect to the medium and $T$ is the temperature near the heated sample at time $t$. The total deflection is given by

\[
M = |\phi_n|^2 + |\phi_t|^2
\]

where $n$ is the refractive index of the medium and $T$ is the temperature near the heated sample at time $t$. The total deflection is given by

\[
\phi_n = \frac{1}{n} \left( \frac{\partial n}{\partial t} \right) \int \left( \frac{\partial T}{\partial z} \right) \, dx
\]

Since \( (\partial n/\partial t)_\text{sample} \gg (\partial n/\partial t)_\text{gas} \), \( \nabla T_s > \nabla T_g \).

Hence \( |\phi_s| >> |\phi_g| \), which is true for both normal and transverse components. 's' and 'g' stands for the sample relative to the central position. The distance of separation between \( x_0 \) these points can be used to study the thermal wavelength as a function of frequency (thermal wavelength is given by \( \lambda = 2(\pi/\lambda)^{1/2} \)). The slope of the frequency axis gives the thermal diffusivity of the solid and changes the phase by 180 at the origin. The effect of
\( \phi_t \) dominates over the normal component near the interface along the source, while \( \phi_n \) dominates near the interface away from the source [25].

In order to determine the thermal diffusivity, the sample is illuminated by an intensity modulated laser beam (pump beam). The excitation and subsequent non-radiative de-excitation process occurring inside the sample result in the heating of the sample. The thermal waves generated from the sample sets a refractive index gradient within the sample or in the adjacent coupling medium. If a second laser beam (probe beam) is allowed to graze the sample surface at a finite height \( h \), the beam gets deflected. The in phase component of the deflected signal is measured at different positions \( \langle x \rangle \) of the probe beam across the pump beam spot on the sample surface. From the plot of \( x \) Vs phase, the zero crossing points on either side of the central zero at which the signal are shifted in phase by \( \pm 90 \) relative to the central position. The distance of separation between \( \langle x_0 \rangle \) these points can be used to determine the thermal wavelength as a function of frequency (thermal wavelength is given by \( \lambda_t = 2(\pi \alpha / f)^{1/2} \)). The slope of thermal wavelength Vs the reciprocal of the square root of the frequency gives the thermal diffusivity of the solid.
Numerical analysis shows that [26] the distance \( x_0 \) is given by

\[
x_0 = d + (\frac{\gamma \pi \alpha}{f})^{1/2}
\]  
(4)

where \( d \) is the intercept that is of the order of the pump beam diameter and \( f \) is the chopping frequency \( (\frac{\gamma \pi \alpha}{f})^{1/2} \) is the slope of \( x_0 \) Vs \( (1/f)^{1/2} \) plot. \( \gamma \) is a parameter, which depends on the bulk thermo-optical properties of the material [27]. It has been proved that \( \gamma = 1.44 \) for optically opaque and thermally thick samples [28] but \( \gamma = 1 \) for all other cases. As the thermal wavelength decreases with the increase of chopping frequency, the low frequency portion of the graph should be given greater importance in the determination of thermal diffusivity.

The schematic of the experimental set-up arranged for the present investigation is shown in figure 3. The 488 nm line of an Argon-ion laser [LiCoNiX 5302A] is used as the pump source whereas a He-Ne laser at 632 nm wavelength and power 5mW [Spectra Physics] is used as the probe beam. In order to reduce the probe beam diameter, it is passed through a fine aperture, without diffraction. An electromechanical chopper is used to modulate the pump beam. This modulated pump beam is focused into the sample.
The sample is taken in the form of pellets and mounted on a xyz translator. The probe laser and the PSD are also arranged on a xyz translator. The inphase component of the deflected signal is measured for various values of $x$. Determining $x_0$, the distance between the zero crossing points separated by a phase $180^\circ$, from the $x$ Vs phase graph another graph $x_0$ Vs $(f)^{-1/2}$ is drawn. From the slope of $x_0$ Vs $(f)^{-1/2}$ graph, thermal diffusivity can be calculated.

Thermogravimetric analysis shows that the samples do not decompose at temperatures higher than 300 °C. Hence the modulated laser beam of power (-100 mW) does not decompose the samples.

Fig. 3: Schematic of the experimental set-up for PTD studies

The deflection is measured using a position sensitive detector and its output is amplified by a differential pre-amplifier and analysed using a lock-in amplifier [EG & G 5208].
The sample is taken in the form of pellets and mounted on a xyz translator. The probe laser and the PBD are also arranged on a xyz translator. The inphase component of the deflected signal is measured for various values of x. Determining $x_0$, the distance between the zero crossing points separated by a phase 180°, from the x Vs phase graph another graph $x_0$ Vs $(f)^{-1/2}$ is drawn. From the slope of $x_0$ Vs $(f)^{-1/2}$ graph, thermal diffusivity can be calculated.

The experimental set-up is standardised by determining the thermal diffusivity of copper (1.14 cm²/s). Thermogravimetric analysis shows that the samples do not decompose at temperatures lower than 300 °C. Hence the exposure to the intensity modulated laser beam of power levels used in the present investigation (~100mW) does not decompose the samples.

Variation of the phase of the PTD signal with distance from the heating beam spot for FePc for three different chopping frequencies is shown in figure 4. From the slope of the $(1/f)^{1/2}$ Vs $x_0$ graph (Fig. 5) the thermal diffusivity ($\alpha$) can be calculated using the relation

$$\text{Slope of } (1/f)^{1/2} \text{ Vs } x_0 \text{ graph } = (\pi \alpha)^{1/2}$$
Fig. 4: Variation of the phase of the PTD signal with distance (mm) from the heating beam spot for FePc for three different chopping frequencies.

Phthalocyanines are inorganic semiconductors with the carriers, conjugate π electrons. When the samples are iodinated, they act as I⁻ in the inter cavity of the quasi one-dimensional lattice of Phthalocyanines [19]. The presence of I⁻ in the cavities may alter the natural vibrational frequency of the lattice along with other factors which depend on lattice parameters. Thermal diffusivity of such materials is often dependent on the lattice. The observed increase in the thermal diffusivity of these metal Phthalocyanines can thus be attributed to the I⁻ ions of Phthalocyanines.

Fig. 5: $x_0$ (cm) vs. $f^{-1/2}$ plot for FePc.
The values of thermal diffusivities of FePc and EuPc and their iodinated samples are given in Table 1. It is found that the thermal diffusivity increases on iodination.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Thermal diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc</td>
<td>0.380</td>
</tr>
<tr>
<td>FePc(I)</td>
<td>0.630</td>
</tr>
<tr>
<td>EuPc</td>
<td>0.717</td>
</tr>
<tr>
<td>EuPc(I)</td>
<td>0.820</td>
</tr>
</tbody>
</table>

Phthalocyanines are inorganic semiconductors with the carriers, conjugate π electrons. When the samples are iodinated, I⁻¹ exists as I₃⁻ in the inter cavities of the quasi one-dimensional lattice of Phthalocyanines [29]. The presence of I₃⁻ in the cavities may alter the natural vibrational frequency of the lattice along with other factors which depends on lattice parameters. Thermal diffusivity is one such parameter, which depends on the lattice. The observed increase in the thermal diffusivity of these metal Phthalocyanines can thus be attributed to the incorporation of I₃⁻ in the cavities of Phthalocyanines.
The PTD technique is effectively employed in the determination of thermal diffusivities of some metal Phthalocyanines, organic semiconductors. The effect of iodination on the thermal diffusivity of FePc and EuPc are also studied.


