THERMAL DIFFUSIVITY MEASUREMENTS USING OPEN PHOTOACOUSTIC CELL TECHNIQUE

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ABSTRACT

The application of open photoacoustic cell (OPC) technique is demonstrated for measuring thermal diffusivity of solid samples. It is based upon the measurement of the photoacoustic signal in the modulation frequency region where the thermal diffusion length equals to the sample thickness. The measurements were carried out at room temperature for gold alloys ($Au_{0.75}Ag_{0.25}$ and $Au_{0.50}Ag_{0.50}$); epoxidised natural rubbers [ENR 25 (75%C) and ENR 50 (75%C)]; and superconducting ceramics ($Bi_2Pb_{0.6}Sr_2Ca_{1.94}Ba_{0.06}Cu_3O_\delta$, and $Bi_2Pb_{0.6}Sr_2Ca_{1.93}Zn_{0.07}Cu_3O_\delta$). The thermal diffusivity values obtained in this measurement were in the range of 0.97 for Al down to 1.61 x 10^{-3} cm^2/s for polymer sample.

1. INTRODUCTION

Since 1975, the photoacoustic (PA) spectroscopy has been a very useful technique for spectroscopic investigation of optical and thermal properties of materials[1]. Among those properties, thermal diffusivity, α, defined as $\alpha = \frac{k}{\rho c}$, (where k is the thermal conductivity, ρ is the mass density and c is the specific heat), is one of the frequent physical parameters to be measured due to the fact that it is unique and may represent an intrinsic property of the material.

The basic method of generating photoacoustic phenomena is to place a sample in a closed cell containing a gas and a sensitive microphone. The sample, which is illuminated with chopped monochromatic light, becomes heated intermittently as a result of non-radiative transition. As the heat diffuses to the surface of the sample, it in turn heats the gas in contact in the cell. The periodic heating of the gas generates a pressure variation in the surrounding gas medium that can be detected by the sensitive microphone. In this paper, an open photoacoustic cell (OPC), as described by Da Silva *et al*[1] and Marquezini *et al*[2], was used for measuring thermal diffusivity of gold alloy, polymer and ceramic superconductor samples. As in other photoacoustic techniques, there are three main advantages for using OPC. First, the use of a minimal gas chamber that can

indirectly increase the signal to noise ratio. Secondly, no special sample preparation is required and finally no elaborate experimental procedures are needed. These are realized in the present OPC configuration by placing the sample directly on the top of a small microphone and thus, the space between sample and microphone diaphragm will serve as a small photoacoustic gas chamber.

2. THEORY

Applying the simple one-dimensional thermal diffusion model of Rosencwaig and Gersho[3], the pressure fluctuation, Pth, in the air chamber of the open photoacoustic cell detection, is given by[4,5,6]:

$$P_{th} = \frac{\gamma P_o I_o (\alpha_g \alpha_s)^{1/2}}{2\pi l_g T_o k_s f} \quad \frac{e^{j(\omega t - \pi/2)}}{\sinh(l_s \alpha_s)} \tag{1}$$

Where γ is the air specific heat ratio, P_o and T_o are respectively the ambient pressure and temperature, I_o is the absorbed light intensity, f is the modulation frequency, and l_i, k_i and α_i are the thickness, thermal conductivity and thermal diffusivity of material i, respectively. The subscript i denotes the sample (s) and gas (g) media. Besides that, $\sigma_i = (1 + j)a_i$ is the complex thermal diffusion of the material i where, the coefficient, $a_i = (\pi f/\alpha_i)^{1/2}$. According to this model, the heat generated in the sample is transferred to the gas immediately in contact with the sample. In the process, one of the important parameters involved in this work is thermal diffusion length of the sample, μ_s, which can be defined in terms of the thermal diffusivity as:

$$\mu_s = \sqrt{\frac{\alpha}{\pi f}} \tag{2}$$

Hence, at sufficiently low frequencies, the diffusion length may become very large and greater than the sample thickness. In this case of thermally thin sample whereby, $\mu_s > l_s$, Eq. (1) reduces to:

$$P_{th} \cong \frac{\gamma P_o I_o \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} l_g l_s T_o k_s} \quad \frac{e^{j(\omega t - 3\pi/4)}}{f^{3/2}} \tag{3}$$

This means that the amplitude of the PA signals decreases as $f^{1.5}$, as one increases the modulation frequency. On the other hand, at high modulation frequencies, the sample may become thermally thick whereby the thermal diffusion length is less than the sample thickness ($\mu_s < l_s$), Eq. (1) becomes:

$$P_{th} \cong \frac{\gamma P_o I_o (\alpha_g \alpha_s)^{1/2}}{\pi l_g T_o k_s} \quad \frac{e^{-l_s\sqrt{\pi f/\alpha_s}}}{f} \times e^{j(\omega t - \pi/2 - l_s a_s)} \tag{4}$$

From Eq. (4), the amplitude of PA signal decreases with the modulation frequency as, $(1/f)\exp(-a\sqrt{f})$ where a, is a parameter defined as $a = l_s\sqrt{\pi/\alpha_s}$. However, for a plate shaped solid sample surrounded by the air as in this work, the effect of thermoelastic bending of the sample may not be neglected. This effect is essentially due to the temperature gradient inside the sample along the thickness axis. This temperature gradient caused displacement along the radial direction of the sample and induced a bending along the sample thickness axis (drum effect). Perondi and Miranda[7] had studied the drum effect and they found that the PA signal varied as f^{-1} for thermally thick sample. The drum effect was also reported by Rousset *et al*[8] who found that the thermoelastic signal contribution was dominant at frequencies above the characteristic frequency and became constant at frequencies below the characteristic frequency (frequency at which the sample changes its behavior from thermally thin to thermally thick).

Although the drum effect may interfere during the measurements, a turning point still occurs at a characteristic frequency, say $f=f_c$ when the diffusion length becomes equal to sample thickness. Applying the Eq. (2), for the case of $l_s = \mu_s$, the thermal diffusivity of the sample can be expressed as:

$$\alpha_s = \pi f_c l_s^2 \tag{5}$$

3. EXPERIMENT

The superconductor samples of $Bi_2Pb_{0.6}Sr_2Ca_{2-x}Ba_xCu_3O_\delta$ (x=0.06) and $Bi_2Pb_{0.6}Sr_2Ca_{2-x}Zn_xCu_3O_\delta$ (x=0.07) were prepared according to a set of procedures starting from powder milling to calcination, pelletization and finally sintering. The synthesis of the Ag_xAu_{1-x}(x=0.50, 0.75) alloy samples also underwent the powder mixing process, pelletization and sintering. After polishing, the thickness of the samples are between 0.41 mm and 0.75 mm. However, the samples of epoxidised natural rubber 25 and 50 (ENR 25 and ENR 50) with 75% carbon were separately prepared by the Rubber Research Institute of Malaysia (RRIM). Each RRIM sample was sliced to (0.03-0.04) mm thickness using a special cutter (Spencer Microtome 820).

The OPC experimental arrangement is schematically shown in Figure 1. The sample was directly mounted onto an electret microphone (Cirkit) by employing silicon grease. The typical design of the electret microphone which consists of a metalized diaphragm and a metal backplate separated from the diaphragm by an air gap is shown in Figure 2. The opening of this microphone is a circular hole of 2.5 mm diameter, where the sample and the metallized diaphragm form a photoacoustic cell with the air volume of about 7.85 mm^2. The argon ion laser (Omnichrome 543) beam with λ = 529 nm, which after being mechanically chopped by an optical chopper (SR540), was focused onto the sample. As a result of the periodic heating, the heat generated in the sample that is transferred to the gas in immediate contact with the sample causes the pressure in the air chamber to

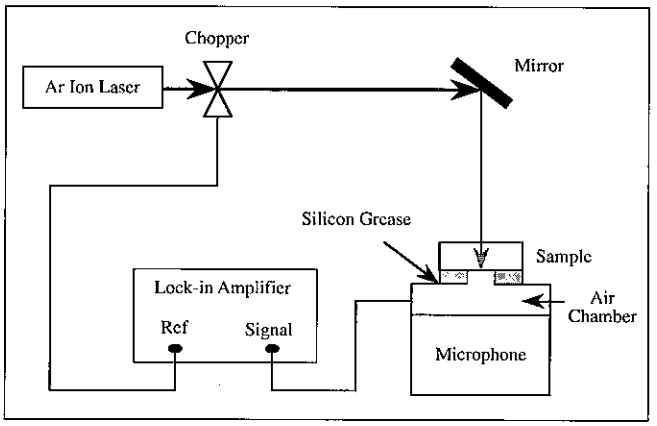

Figure 1: Experimental set-up of open photoacoustic cell technique.

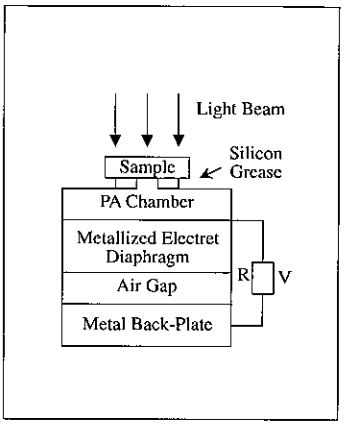

Figure 2: Cross section of the open photoacoustic cell detector.

oscillate at the chopping frequency. This, in turn, causes diaphragm periodic deflection, which generates a voltage across the load resistor, R. The generated PA signal was then analyzed by using a lock-in amplifier (SR530). All the measurements were carried out at room temperature (~20°C).

4. RESULTS AND DISCUSSION

Prior to thermal diffusivity measurement of gold alloy, epoxidised natural rubber and ceramic superconductor samples, the experiment set up and the detection system have been tested for measurements on Al and Sn standard samples of thickness 1.04 mm and 0.45 mm respectively. Both samples, with purity as high as 99.99% for Al and 99.9985% for Sn, were supplied by Alfa Aesar (Johnson Matthey Co.). For both samples, the OPC signal was monitored as a function of chopping frequency in the range of (10 – 90) Hz. Using the same technique proposed by Da Costa and Siqueira[4], the values of the characteristic frequency, f_c was determined by plotting the graph *ln* (PA signal) versus *ln* ($\sqrt{f}$). By substituting the relevant f_c into the Eq. (5), the thermal diffusivity of Al and Sn was found as 0.97 cm^2/s and 0.35 cm^2/s respectively. These values are in a good agreement to the values that were previously reported by Busse and Walther[9].

In our further work, gold alloys [$Au_{0.75}Ag_{0.25}$ and $Au_{0.50}Ag_{0.50}$]; epoxidised natural rubber [ENR 25 (75%C) and ENR 50 (75%C)] and superconducting ceramics [$Bi_2Pb_{0.6}Sr_2Ca_{1.94}Ba_{0.06}Cu_3O_\delta$ and $Bi_2Pb_{0.6}Sr_2Ca_{1.93}Zn_{0.07}Cu_3O_\delta$] doped with Ba and Zn were chosen with the sample thickness as shown in Table 1.

Figures 3(a) and 4(a) show the example of the dependent of PA signal on modulation frequency for ENR 25 (75%C) and $Au_{0.75}Ag_{0.25}$. The curves represent the two characteristics of the samples, which are thermally thin (at low frequency range) and thermally thick (at high frequency range). From the plots of *ln*(PA signal) versus *ln* ($\sqrt{f}$) in Figures 3(b) and 4(b), the characteristic frequency, f_c for ENR 25 (75%C) and $Au_{0.75}Ag_{0.25}$ are 34.95 Hz and 66.02 Hz respectively. The corresponding values of

Table 1: Thermal diffusivity of our samples.

Sample	Thickness (mm)	Thermal diffusivity (cm^2/s)	Literature values (cm^2/s)	Synthesis conditions
Al	1.04	0.97	0.98	Supplied by Alfa Aesar
Sn	0.45	0.35	0.37	Supplied by Alfa Aesar
$Au_{0.75}Ag_{0.25}$	0.52	0.56	-	Pelletization & Sintering
$Au_{0.50}Ag_{0.50}$	0.50	0.75	-	Pelletization & Sintering
ENR 25 (75%C)	0.04	1.76 x 10-3	-	Melt & Molding
ENR 50 (75%C)	0.03	1.61 x 10-3	-	Melt & Molding
$Bi_2Pb_{0.6}Sr_2Ca_{1.94}Ba_{0.06}Cu_3O_\delta$	0.91	0.68	-	Pelletization & Sintering
$Bi_2Pb_{0.6}Sr_2Ca_{1.93}Zn_{0.07}Cu_3O_\delta$	0.72	0.41	-	Pelletization & Sintering

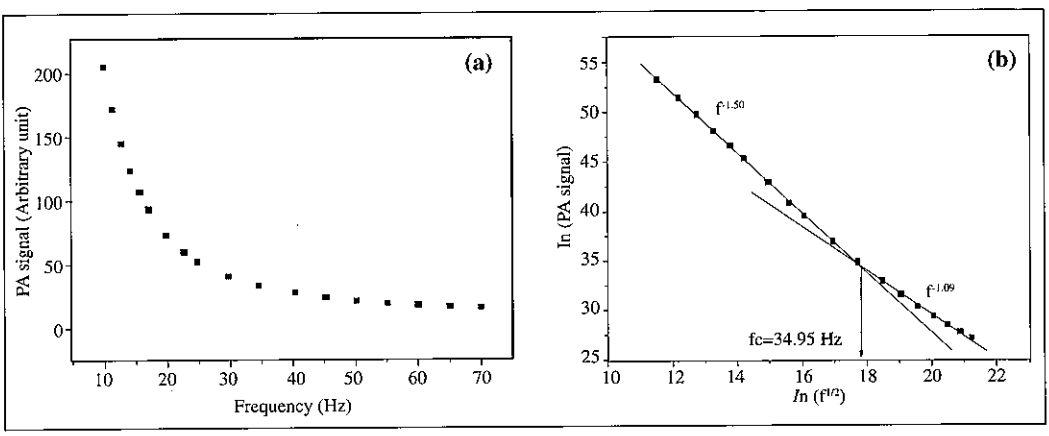

Figure 3: (a) PA signal versus frequency and (b) ln (PA signal) against ln ($f^{1/2}$) for ENR 25 (75% carbon) sample.

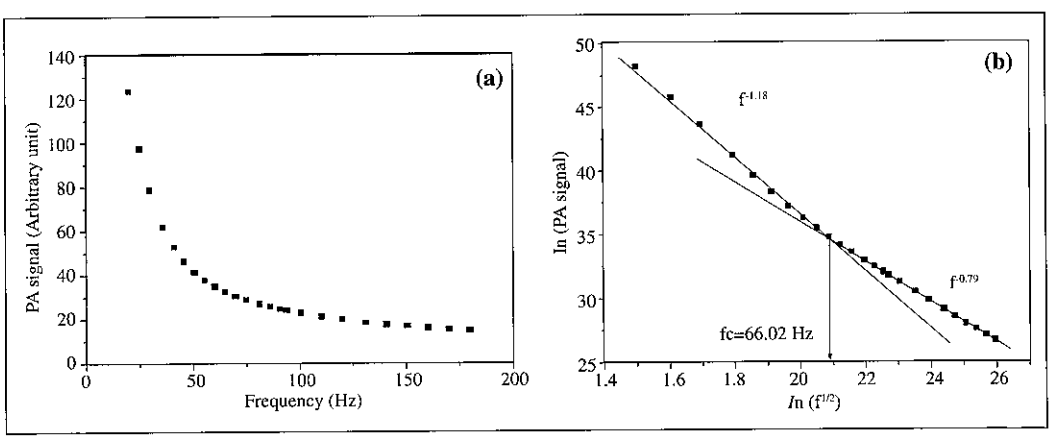

Figure 4: (a) PA signal versus frequency and (b) ln (PA signal) against ln ($f^{1/2}$) for $Au_{0.75}Ag_{0.25}$ gold alloy sample.

thermal diffusivity are 1.757 x 10^{-3} and 0.56 cm^2/s. Similar plots also observed for all of our samples. The values of thermal diffusivity of our samples are listed in Table 1. Except for polymer sample (Figure 3b), the dependence of photoacoustic signal on the chopping frequency of our samples did not agree with Eqs. (3) and (4). This may be attributed to dominating PA signal from an unknown thermoelastic effect occurred in the samples and may be due to unaccounted substantial three-dimensional heat flow in the theoretical description especially at low frequencies whereby thermal diffusion length is larger as reported by Quimby and Yen[10].

5. CONCLUSION

In this paper, we have described OPC detection of the PA signal as a function of modulation frequency. Thermal diffusivity values were obtained for Al, Sn, epoxidised natural rubber, gold alloys and superconducting ceramics samples by plotting the ln (PA amplitude) versus $ln\sqrt{f}$. The technique is simple and reasonably accurate for measuring thermal diffusivity of the solid samples. The thermal diffusivity value of gold alloys and superconducting ceramics were between 0.41 and 0.75 cm^2/s. For polymer samples (ENR25 and ENR50 with 75% carbon content) the value of thermal diffusivity were determined as 1.76 x 10^{-3} and 1.61 x 10^{-3} cm^2/s respectively.

6. ACKNOWLEDGEMENT

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7. REFERENCES

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