

A New Method to Overcome the Underestimation of the Thermal Diffusivity of Solid Samples Induced by the Coupling Fluid in Photopyroelectric Measurements

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Abstract The thermal diffusivity of solid samples is systematically underestimated when using the photopyroelectric technique in the standard back configuration, due to the presence of the coupling fluid between the sample and detector. In this study, a new method is proposed to overcome this issue. It relies on the use of (a) a transparent pyroelectric sensor, (b) a transparent coupling fluid, and (c) a self-normalization procedure. In this way, the thermal diffusivity of opaque solid samples can be measured accurately.

Keywords Photopyroelectric · Thermal diffusivity · Photothermal techniques · Thermal effusivity

1 Introduction

The photopyroelectric (PPE) technique has been widely used to measure the thermal diffusivity of solids and liquids (see [1] and references therein). In the standard back configuration, an opaque sample is periodically illuminated on one side while the other side is in contact with the pyroelectric detector. For normalization purposes (to avoid the frequency dependence of the detection electronics), this signal is divided by the signal provided by the bare detector. It was demonstrated that for thermally thick samples, the natural logarithm of the amplitude and the phase of the normalized PPE signal are parallel straight lines when represented as a function of the square root of the modulation frequency. From their slope and from the vertical separation, the thermal diffusivity (D) and thermal effusivity ($e = \sqrt{\rho c K}$) are obtained, respectively [2,3].

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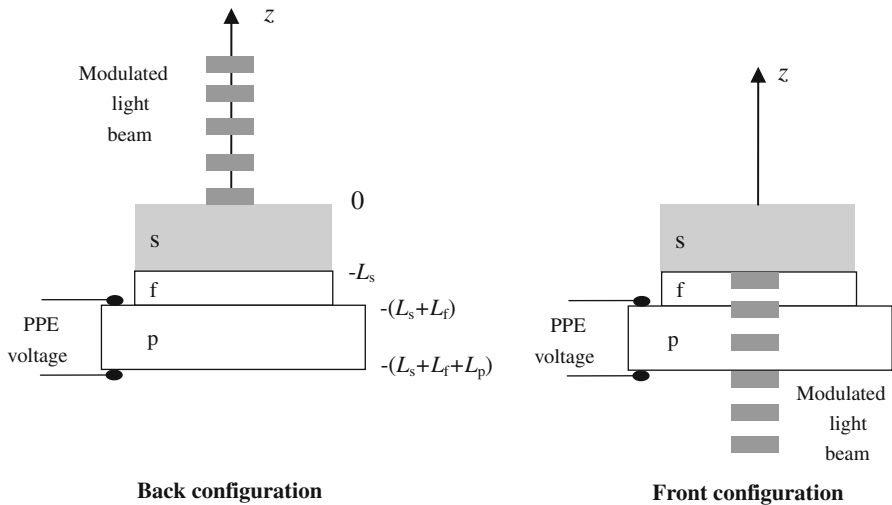


Fig. 1 Diagram of the PPE setup for a three-layer system with an opaque sample (s) and completely transparent coupling fluid (f) and pyroelectric sensor (p). In the back configuration the laser beam hits first the sample, while in the front configuration the laser beam hits first the pyroelectric sensor

However, in the case of solid samples, a thin layer of coupling fluid must be added to guarantee the thermal contact between the sample and pyroelectric detector. Although being extremely thin (only a few microns), it increases the slopes of the above mentioned straight lines, and therefore, the thermal diffusivity of the solid under study is always undervalued [4]. Due to the low thermal diffusivity of the coupling fluids (silicone grease, oils, or similar), this underestimation of D is worse for high thermal conducting samples. The disturbing effect of the coupling fluid explains why the PPE technique has been extensively used to characterize the thermal properties of liquids (liquid crystals, oils, organic liquids, pasty materials, etc.), but it has been less used with solid samples.

In this study, we propose a new PPE method to measure accurately the thermal diffusivity of opaque solids, while avoiding the undesired effect of the coupling fluid layer. The new method is based on the use of a transparent pyroelectric transducer (LiTaO_3) with transparent electrodes made of indium tin oxide (ITO), and a transparent coupling fluid (silicone grease). Moreover, self-normalization is used [5], i.e., the ratio of the PPE signal when illuminating the sample (back configuration) and when illuminating the pyroelectric sensor (front illumination), as is shown in Fig. 1.

2 Theory

Let us start with the most general case of an opaque slab of thickness L_s , placed on top of a pyroelectric plate of thickness L_p , with a fluid layer between them to guarantee the thermal contact. This three-layer structure is illuminated by a laser beam of intensity I_0 modulated at a frequency f ($\omega = 2\pi f$). The geometry of the problem is shown in

Fig. 1. Both the pyroelectric plate and coupling fluid are transparent. The PPE signal (S) is proportional to the spatially averaged temperature of the pyroelectric plate $\langle T_p \rangle$ [6],

$$S = ab \langle T_p \rangle = ab \frac{1}{L_p} \int_0^{L_p} T_p(z) dz, \tag{1}$$

where a is a frequency-independent factor that depends on the physical properties of the detector (pyroelectric coefficient, dielectric constant, and permittivity) and b is a frequency-dependent factor that accounts for the influence of the detection electronics.

2.1 Back Configuration

First, we look for the solution of the temperature of the pyroelectric plate in the back configuration (left side of Fig. 1). By solving the heat diffusion equation for the three-layer system (sample, fluid layer, and pyroelectric sensor), the temperature at each layer is given by

$$T_s(z) = A_o e^{q_s z} + B_o e^{-q_s z} \tag{1a}$$

$$T_f(z) = D_o e^{q_f(z+L_s)} + E_o e^{-q_f(z+L_s)} \tag{1b}$$

$$T_p(z) = F_o e^{q_p(z+L_s+L_f)} + G_o e^{-q_p(z+L_s+L_f)}, \tag{1c}$$

where $q = \sqrt{i\omega/D}$. Subindexes s, f, and p stand for solid, coupling fluid, and pyroelectric detector, respectively. Constants $A_o, B_o, D_o, E_o, F_o,$ and G_o are obtained from the boundary conditions at the interfaces:

- (a) Temperature continuity at the interfaces sample-fluid and fluid-pyroelectric

$$T_s|_{z=-L_s} = T_f|_{z=-L_s} \quad T_f|_{z=-(L_s+L_f)} = T_p|_{z=-(L_s+L_f)}. \tag{2a}$$

- (b) Heat flux continuity at the same interfaces

$$K_s \frac{dT_s}{dz} \Big|_{z=-L_s} = K_f \frac{dT_f}{dz} \Big|_{z=-L_s} \quad K_f \frac{dT_f}{dz} \Big|_{z=-(L_s+L_f)} = K_p \frac{dT_p}{dz} \Big|_{z=-(L_s+L_f)} \tag{2b}$$

- (c) Absence of heat losses at the external surfaces together with the light absorption at $z = 0$

$$K_s \frac{dT_s}{dz} \Big|_{z=0} = \frac{I_o}{2} \quad K_p \frac{dT_p}{dz} \Big|_{z=-(L_s+L_f+L_p)} = 0. \tag{2c}$$

By substituting Eq. 1 into 2a–2c, the temperature of the pyroelectric plate is obtained. Its average value is given by

$$\langle T_p \rangle_{\text{back}} = \frac{1}{L_p} \int_0^{L_p} T_p(z) dz = 2I_o \left(1 - e^{-2q_p L_p} \right) K_s K_f K_p q_s q_f q_p. \quad (3)$$

2.2 Front Configuration

Now, we look for the solution of the temperature of the pyroelectric plate in the front configuration (right side of Fig. 1). The temperature at each layer is given by the same expressions as in Eqs. 1, with the same boundary conditions except the two following ones:

$$K_s \left. \frac{dT_s}{dz} \right|_{z=-L_s} = K_f \left. \frac{dT_f}{dz} \right|_{z=-L_s} - \frac{I_o}{2} \quad (4a)$$

$$K_s \left. \frac{dT_s}{dz} \right|_{z=0} = 0, \quad (4b)$$

to take into account the absorption of the laser beam at $z = -L_s$. By substituting Eqs. 1 into the new boundary conditions, the temperature of the pyroelectric plate in the front configuration is obtained. Its average value is given by

$$\langle T_p \rangle_{\text{front}} = \frac{1}{L_p} \int_0^{L_p} T_p(z) dz = 2I_o \left(1 - e^{-2q_p L_p} \right) K_s K_f K_p q_s q_f q_p \cosh(q_s L_s). \quad (5)$$

2.3 Self-Normalized PPE Signal

The self-normalized PPE signal (S_n) is the ratio between the PPE signal using the back configuration and the PPE signal using the front configuration (see Fig. 1), and is expressed as

$$S_n = \frac{S_{\text{back}}}{S_{\text{front}}} = \frac{ab \langle T_p \rangle_{\text{back}}}{ab \langle T_p \rangle_{\text{front}}} = \frac{1}{\cosh(q_s L_s)}. \quad (6)$$

Note that the self-normalized signal does not depend on a or b , indicating that the frequency dependence of the detection electronics is removed. It is worth mentioning that Eq. 6 is of general validity in the sense that no assumptions on the thermal thicknesses of the coupling fluid and pyroelectric plate have been used, i.e., there is no restriction in the frequency range of application.

Equation 6 indicates that S_n only depends on the physical properties of the sample (D_s , α , L_s), i.e., it depends neither on the properties of the pyroelectric sensor nor on the properties of the coupling fluid. This means that the disturbing effect introduced by the coupling fluid (when using the standard configuration with opaque electrodes covering both sides of the pyroelectric detector) disappears provided it is transparent to the laser wavelength.

If the sample is thermally thick ($\text{Re}(q_s) \times L_s \rightarrow \infty$), Eq. 6 reduces to

$$S_n \approx 2e^{-q_s L_s}, \quad (7)$$

indicating that both the natural logarithm of the self-normalized PPE signal amplitude, $\ln(S_n)$, and its phase, $\Psi(S_n)$, are parallel straight lines when plotted against \sqrt{f} , with a common slope $m = -L_s \sqrt{\pi/D_s}$. This equation provides a straightforward method to measure the thermal diffusivity of opaque slabs, *overcoming the underestimation induced by the coupling fluid when using opaque detectors* [4]. The price to be paid is the lack of information on the thermal conductivity of the sample, which has been simplified in Eqs. 6 and 7.

3 Experimental Results and Discussion

In order to verify the validity of the model, we have performed self-normalized PPE measurements on opaque samples with known thermal diffusivity values. These slabs are placed on top of a LiTaO₃ pyroelectric crystal 0.5 mm thick. ITO electrodes are sputtered on both sides of the pyroelectric crystal. A very thin silicone grease, which is transparent to visible light, is used to assure the thermal contact. A diode laser ($\lambda = 656$ nm) of 50 mW has been used as the heating source. Its intensity is modulated by a periodic current governed by the computer and serving as the lock-in reference. Using a beam splitter, the laser beam is directed to the sample (back configuration) or to the pyroelectric crystal (front configuration). The PPE current produced by the detector has been fed into a digital lock-in amplifier.

To verify the robustness of the method, we have measured materials covering a wide range of diffusivities: rigid graphite, Ni, SiC with different porosity, vitreous carbon (Sigradur G), Cr₂O₃ single crystal, LaMnO₃ single crystal, and carbon fiber reinforced (CFR) composite. First, we have measured them using the new method (self-normalization + transparent detector) and then, for comparison, using a standard back configuration with an opaque detector (LiTaO₃ with opaque electrodes). As an example, the results for a vitreous carbon slab 1.33 mm thick are shown in Fig. 2. For frequencies lower than 4 Hz, the sample is thermally thin, whereas for frequencies higher than 50 Hz, the signal is so small that it is affected by the electronic noise. Between both frequencies, $\ln(S_n)$ and $\Psi(S_n)$ behave linearly as a function of \sqrt{f} . However, the slopes obtained with the new method (black dots) are slightly smaller than those obtained with the standard method (open circles). Therefore, the thermal diffusivities obtained from the expression $m = -L_s \sqrt{\pi/D_s}$ are higher for the new method ($6.0 \text{ mm}^2 \cdot \text{s}^{-1}$, the nominal value) than for the standard one ($5.4 \text{ mm}^2 \cdot \text{s}^{-1}$, underestimated value).

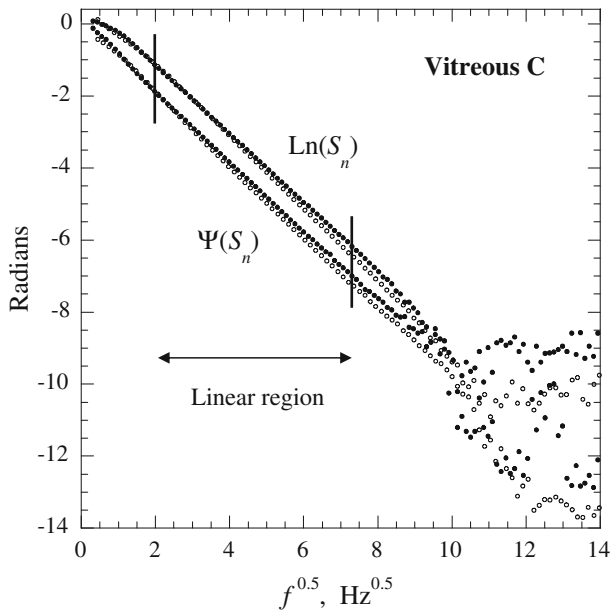


Fig. 2 Experimental values of $\ln(S_n)$ and $\Psi(S_n)$ for a vitreous carbon slab 1.33 mm thick. *Black dots* correspond to the values obtained with the new method, while *open circles* correspond to those obtained with the standard method

Table 1 Thermal diffusivity of opaque materials

Material	Opaque pyro standard method D ($\text{mm}^2 \cdot \text{s}^{-1}$)	Transparent pyro new method D ($\text{mm}^2 \cdot \text{s}^{-1}$)	Literature ^a D ($\text{mm}^2 \cdot \text{s}^{-1}$)
Graphite	71	85	87
Ni	18	21	22
SiC (0 % porosity)	45	56	57
SiC (25 % porosity)	20	26	25
SiC (38 % porosity)	6.0	6.8	7.0
Vitreous C	5.4	6.0	6.0
Cr_2O_3	3.4	3.8	3.8
LaMnO_3	1.27	1.37	1.38
CFR composite	0.48	0.51	0.50

The uncertainty is 5 %

^a From Refs. [7,8]

In Table 1, we summarize the thermal-diffusivity values for the complete set of samples we have measured. As can be seen, the thermal diffusivities obtained with the standard method are systematically underestimated, while the new method gives the right value inside the experimental uncertainty.

According to the results of this study, the self-normalized PPE technique together with the use of a transparent detector and coupling fluid provides a new method to

measure accurately the thermal diffusivity of opaque solids. This is possible since the self-normalized PPE signal is independent of the physical properties of both the coupling fluid and the pyroelectric sensor itself.

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