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Agustín Salazar and Alberto Oleaga

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Overcoming the influence of the coupling fluid in photopyroelectric measurements of solid samples

Agustín Salazar^{a)} and Alberto Oleaga

Departamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería, Universidad del País Vasco, Alameda Urquijo s/n, 48013 Bilbao, Spain

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The thermal diffusivity of solid samples is systematically underestimated in a photopyroelectric technique used in the standard back configuration due to the presence of the coupling fluid between sample and detector. In this work, we propose a new method to overcome the undesired effect of the coupling fluid. It relies on the use of a transparent pyroelectric sensor and a transparent coupling fluid, together with a self-normalization procedure. In this way, we are able to measure accurately (a) the thermal diffusivity of opaque solid samples, and (b) the thermal diffusivity and the optical absorption coefficient of semitransparent solid samples. © 2012 American Institute of Physics. [doi:10.1063/1.3680113]

I. INTRODUCTION

Since the pioneering work by Mandelis and Zver,¹ the photopyroelectric (PPE) technique has been widely used to measure the thermal diffusivity of solids and liquids (see Ref. 2 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, thermal diffusivity (D) and thermal effusivity ($e = \sqrt{\rho c K}$) are obtained, respectively.^{3,4} Then, from the constitutive relation ($K = \rho c D$, where ρ is the density), thermal conductivity (K), and specific heat (c) can be retrieved. However, in the case of solid samples, a thin layer of coupling fluid must be added to guarantee the thermal contact between sample and pyroelectric detector. Although being extremely thin (only a few μm) it increases the slopes of the above-mentioned linear relations and, therefore, the thermal diffusivity of the solid under study is always undervalued.^{5,6} 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. In the past, the use of air with controlled thickness as coupling fluid was proposed.⁷ However, this air gap reduces the PPE signal while complicating the data processing. 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 work, we propose a new photopyroelectric method to measure (a) the thermal diffusivity of opaque solids and (b) the thermal diffusivity and the optical absorption coefficient of semitransparent 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,⁸ i.e., the ratio of the PPE signal when illuminating the sample (back configuration) and when illuminating the pyroelectric sensor (front illumination), as it is shown in Fig. 1.

II. THEORY

Let us start with the most general case of a semitransparent 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 wavelength λ whose intensity I_o is modulated at a frequency f ($\omega = 2\pi f$). The geometry of the problem is shown in Fig. 1. Both pyroelectric plate and coupling fluid are transparent, while the light intensity inside the sample decreases according to the exponential Beer-Lambert law (no light diffusion effects are considered). The PPE signal (S) is proportional to the spatially averaged temperature of the pyroelectric plate ($\langle T_p \rangle$),⁹

$$S = ab \langle T_p \rangle = ab \frac{1}{L_p} \int_{-(L_s+L_f+L_p)}^{-(L_s+L_f)} T_p(z) dz, \quad (1)$$

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.

A. 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

$$T_s(z) = A_o e^{q_s z} + B_o e^{-q_s z} + C e^{\alpha z}, \quad (1a)$$

^{a)}Electronic mail: agustin.salazar@ehu.es.

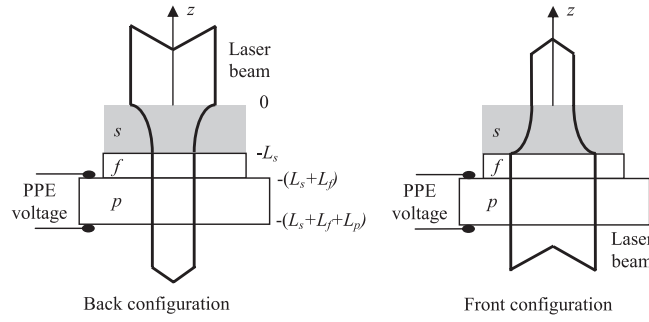


FIG. 1. Diagram of the PPE setup for a three-layer system with a semitransparent sample (s) and completely transparent coupling fluid (f), and pyroelectric sensor (p). In the back configuration the laser beam hits first the sample, while in the front configuration the laser beam hits first the pyroelectric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

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

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

where $C = I_o \alpha / 2K_s (q_s^2 - \alpha^2)$, being α the optical absorption coefficient of the sample to the laser wavelength and $q = \sqrt{i\omega/D}$. 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,

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

- (b) Heat flux continuity at the same interfaces,

$$\begin{aligned} K_s \left. \frac{dT_s}{dz} \right|_{z=-L_s} &= K_f \left. \frac{dT_f}{dz} \right|_{z=-L_s} \\ K_f \left. \frac{dT_f}{dz} \right|_{z=-(L_s+L_f)} &= K_p \left. \frac{dT_p}{dz} \right|_{z=-(L_s+L_f)}. \end{aligned} \quad (2b)$$

- (c) Adiabatic boundary conditions at the external surfaces, i.e., absence of heat losses,

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

By substituting Eqs. (1) into Eqs. (2), the temperature of the pyroelectric plate is obtained. Its average value is given by

$$\begin{aligned} \langle T_p \rangle_{back} &= \frac{1}{L_p} \int_{-(L_s+L_f+L_p)}^{-(L_s+L_f)} T_p(z) dz = -F_o [q_s (e^{2q_s L_s} - 1) \\ &\quad + \alpha (1 + e^{2q_s L_s} - 2e^{(\alpha+q_s)L_s})], \end{aligned} \quad (3)$$

where F_o is a factor depending on the optical, thermal, and geometrical properties of the three layers.

B. 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

$$T_s(z) = A_1 e^{q_s z} + B_1 e^{-q_s z} + C e^{-\alpha(z+L_s)}, \quad (4a)$$

$$T_f(z) = D_1 e^{q_f(z+L_s)} + E_1 e^{-q_f(z+L_s)}, \quad (4b)$$

$$T_p(z) = F_1 e^{q_p(z+L_s+L_f)} + G_1 e^{-q_p(z+L_s+L_f)}. \quad (4c)$$

Constants A_1 , B_1 , D_1 , E_1 , F_1 , and G_1 are obtained from the boundary conditions at the interfaces, which are the same as in the back configuration (Eqs. (2)). By substituting Eqs. (4) in to Eqs. (2), the temperature of the pyroelectric plate in the front configuration is obtained. Its average value is given by

$$\begin{aligned} \langle T_p \rangle_{front} &= \frac{1}{L_p} \int_{-(L_s+L_f+L_p)}^{-(L_s+L_f)} T_p(z) dz \\ &= F_o [-2\alpha e^{q_s L_s} + (\alpha - q_s) e^{(\alpha+2q_s)L_s} \\ &\quad + (\alpha + q_s) e^{\alpha L_s}]. \end{aligned} \quad (5)$$

Note that the factor F_o is the same as in the expression for the back configuration (see Eq. (3)).

C. 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 writes as

$$\begin{aligned} S_n &= \frac{S_{back}}{S_{front}} = \frac{ab \langle T_p \rangle_{back}}{ab \langle T_p \rangle_{front}} \\ &= \frac{F_o [-q_s (e^{2q_s L_s} - 1) - \alpha (1 + e^{2q_s L_s} - 2e^{(\alpha+q_s)L_s})]}{F_o [-2\alpha e^{q_s L_s} + (\alpha - q_s) e^{(\alpha+2q_s)L_s} + (\alpha + q_s) e^{\alpha L_s}]} \\ &= \frac{\alpha - e^{-\alpha L_s} [\alpha \text{Cosh}(q_s L_s) + q_s \text{Sinh}(q_s L_s)]}{\alpha \text{Cosh}(q_s L_s) - q_s \text{Sinh}(q_s L_s) - \alpha e^{-\alpha L_s}}. \end{aligned} \quad (6)$$

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 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 , and L_s), i.e., it depends neither on the properties of the pyroelectric sensor nor on the properties of the coupling fluid, because they are included within the multiplying factor F_o . 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. Accordingly, the self-normalized PPE technique with a transparent detector can be used to retrieve α and D of semitransparent samples simultaneously and accurately.

If the sample is opaque ($\alpha L_s \rightarrow \infty$) and thermally thick ($\text{Re}(q_s) \times L_s = \text{Im}(q_s) \times L_s \rightarrow \infty$), 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, $\text{Ln}(S_n)$, 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.^{5,6} 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).

III. EXPERIMENTAL RESULTS AND DISCUSSION

In order to verify the validity of the model we have performed self-normalized PPE measurements on both opaque and semitransparent samples. These slabs, with thicknesses ranging from 0.3 to 3 mm, 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.

In Table I, we show the results of the thermal diffusivity of the following opaque samples using this new method (self-normalization + transparent detector): Rigid graphite, Ni, SiC (38% porosity), vitreous carbon (Sigradur G), Cr₂O₃ single crystal, and carbon fiber reinforced (CFR) composite. These materials have been selected to cover a wide range of diffusivities. For comparison, the results obtained using a standard back configuration with an opaque detector (LiTaO₃ with opaque electrodes) are also shown. As predicted, the thermal diffusivities obtained with the standard method are systematically underestimated. This underestimation is overcome by using the new method proposed in this work.

We have also studied four optical filters of different optical absorption coefficients: a neutral density (ND) filter from

TABLE I. Thermal diffusivity of opaque materials. The uncertainty is 5%.

Material	D (mm ² /s)	D (mm ² /s)	D (mm ² /s)
	Opaque pyro (Standard method)	Transparent pyro (New method)	
Graphite	71	85	87
Ni	18	21	22
Porous SiC	6.0	6.8	7.0
Vitreous C	5.4	6.0	6.0
Cr ₂ O ₃	3.4	3.8	3.8
CFR composite	0.48	0.51	0.50

^aReference 10.

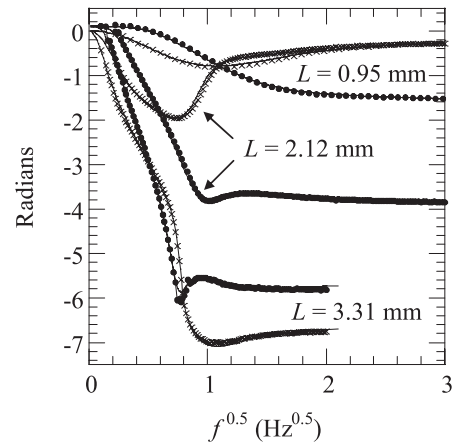


FIG. 2. Experimental values of $\text{Ln}(S_n)$ (dots) and $\Psi(S_n)$ (crosses) for three samples of the same neutral density filter but of different thickness. Continuous lines are the fittings to Eq. (2).

Edmund Optics, a neutral density filter from Schott (NG 1), and two dark red filters from Schott (RG 695 and RG 715). For each of them we have measured samples of different thickness in order to verify the self-consistency of the retrieved values. As an example, we show in Fig. 2 the experimental PPE data for three samples of the same ND filter but having different thicknesses. Dots correspond to the natural logarithm of the amplitude $\text{Ln}(S_n)$ and crosses for the phase $\Psi(S_n)$. The continuous lines are the fittings to Eq. (6). A summary of the retrieved values of D and α is shown in Table II. For each filter, the same D and α values are obtained inside the experimental uncertainty (5%) regardless of their thickness, indicating the reproducibility of the method. The retrieved α value of each filter agrees with that measured with a Cary spectrometer. Regarding the thermal diffusivity values, all of them fall in the typical range of optical glasses (0.5–0.6 mm²/s). As far as we know, there are no thermal diffusivity data on the RG 695 and RG 715 filters. However, the two neutral density filters were recently measured by the authors using a photothermal radiometry (PTR) setup and the results are in agreement with the values obtained in this work (see Table I in Ref. 10).

TABLE II. Thermal diffusivity (D) and optical absorption coefficient (α) of semitransparent materials. The uncertainty in D and α is 5%.

Material	L (mm)	D (mm ² /s)		α (mm ⁻¹)	
		This work	Literature	This work	Cary spectrometer
ND filter	3.31	0.54	0.5–0.6	1.99	1.96
ND filter	2.12	0.56	0.5–0.6	2.03	1.96
ND filter	0.95	0.55	0.5–0.6	1.90	1.96
Schott RG 695	1.42	0.48	0.5–0.6	2.9	3.01
Schott RG 695	0.65	0.49	0.5–0.6	2.8	3.01
Schott RG 715	1.14	0.47	0.5–0.6	3.9	4.02
Schott RG 715	0.89	0.45	0.5–0.6	3.8	4.02
Schott RG 715	0.62	0.49	0.5–0.6	3.9	4.02
Schott NG 1	0.39	0.48	0.5–0.6	9.8	10.2
Schott NG 1	0.27	0.50	0.5–0.6	9.7	10.2

^aReference 10.

As a final remark, it is worth noting that Eq. (6) is the same as the self-normalized PTR signal for semitransparent materials (see Eq. (2) in Ref. 10). This equivalence raises the question on which of them is the most appropriate technique to measure the thermo-optical properties of solid samples. The main advantage of the PPE technique is its high signal-to-noise ratio. In this way, power excitations of a few mW provide noise free signals while power excitations of the order of watts are needed in PTR measurements. Low power excitation means small thermal gradients inside the sample and, therefore, PPE is specially suited to characterize the thermal properties of phase transitions.¹¹ On the other hand, the transparency of the sample to IR radiation complicates the analysis of the PTR signal in such a way that Eq. (6) is no longer valid for materials that are semitransparent to IR wavelengths (Si, Ge, metallic oxides, polymers, most glasses, etc.).¹⁰ The main drawback of the PPE method is that it is a contact technique while PTR is a contactless technique allowing *in situ* measurements of big samples in industrial environments.

According to the results of this work, the self-normalized PPE technique together with the use of transparent detector and coupling fluid provides a new tool to measure accurately (a) the thermal diffusivity of opaque solids and (b) the thermal diffusivity and the optical absorption coefficient of semitransparent 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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- ¹A. Mandelis and M. M. Zver, *J. Appl. Phys.* **57**, 4421 (1985).
- ²M. Chirtoc, D. Dadarlat, D. Bicanic, J. S. Antoniow, and M. Egée, in *Progress in Photothermal and Photoacoustic Science and Technology*, edited by A. Mandelis and P. Hess (SPIE, Bellingham, Washington, 1997), Vol. 3.
- ³M. Marinelli, F. Murtas, M. G. Mecozzi, U. Zammit, R. Pizzoferrato, F. Scudieri, S. Martellucci, and M. Marinelli, *Appl. Phys. A* **51**, 387 (1990).
- ⁴S. Delenclos, M. Chirtoc, A. H. Sahaoui, C. Kolinski, and J. M. Buisine, *Rev. Sci. Instrum.* **73**, 2773 (2002).
- ⁵P. K. John, L. C. M. Miranda, and A. C. Rastogi, *Phys. Rev. B* **34**, 4342 (1986).
- ⁶A. Salazar, *Rev. Sci. Instrum.* **74**, 825 (2003).
- ⁷A. Mandelis and C. A. Da Silva, *Ferroelectrics* **165**, 1 (1995).
- ⁸J. A. Balderas-López and A. Mandelis, *Rev. Sci. Instrum.* **74**, 5219 (2003).
- ⁹M. Chirtoc and G. Mihailescu, *Phys. Rev. B* **40**, 9606 (1989).
- ¹⁰R. Fuente, E. Apiñaniz, A. Mendioroz, and A. Salazar, *J. Appl. Phys.* **110**, 033515 (2011).
- ¹¹M. Marinelli, U. Zammit, F. Mercuri, and R. Pizzoferrato, *J. Appl. Phys.* **72**, 1096 (1992).