Thermochimica Acta 614 (2015) 232–238

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

On the optimization of experimental parameters in photopyroelectric investigation of thermal diffusivity of solids

K. Strzałkowski[a,*], D. Dadarlat[b], M. Streza[b], F. Firszt[a]

[a] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[b] National R&D Institute for Isotopic and Molecular Technologies, Donath Str. 65-103, POB-700, 400293 Cluj-Napoca, Romania

ARTICLE INFO

Article history:
Received 14 April 2015
Received in revised form 7 June 2015
Accepted 19 June 2015
Available online 26 June 2015

Keywords:
Coupling fluid
Lock-in thermography
Photopyroelectric calorimetry
Thermal diffusivity

ABSTRACT

In this paper, the possibility of optimizing the experimental conditions for a correct photopyroelectric evaluation of the thermal diffusivity of solid samples is studied. For this purpose, a glassy carbon sample, with known thermal properties, was selected as test material and two types of techniques were applied in order to get the value of its thermal diffusivity: (i) the photopyroelectric calorimetry in back detection configuration and (ii) the infrared thermography. Assuming that the values of thermal diffusivity obtained by thermography are correct (a non-contact technique), we studied how to eliminate the underestimation (due to the presence of the coupling fluid) of the results in the back photopyroelectric calorimetry investigations. Experiments with different types of coupling fluids and numerical simulations were performed in order to evaluate the influence of the coupling fluid on the value of the thermal diffusivity. The conclusion is that a proper choice of the type of coupling fluid and some improvements performed in the experimental design of the photopyroelectric calorimetry detection cell (with the purpose of reducing the coupling fluid's thickness), can eliminate the difference between the results obtained with the two photothermal (contact and non-contact) techniques.

1. Introduction

The photopyroelectric method (PPE), in various detection configurations, has been extensively applied to study the thermal properties of condensed matter samples; see for example [1–4] among others. The major advantages of this technique are its simplicity, high sensitivity, non-destructive character and its easy adaptation to the experimental restrictions imposed by the theoretical requirements. It is now well-known that using the two detection configurations, "back" (BPPE) and "front" (FPPE), and the information contained in the amplitude and/or phase of the PPE signal, one can directly measure two dynamic sample's related thermal parameters, thermal diffusivity and effusivity. The remaining thermal parameters can be then calculated and so, PPE is able to offer a complete thermal description of the investigated material. Concerning the investigated materials, the liquids are the most suitable samples due to the perfect sample–sensor thermal contact. For solid samples, a coupling fluid is always necessary between the sensor and the sample and, unfortunately, this coupling fluid influences the quantitative results. When accurate results are required, people try to eliminate or, at least, to reduce the influence of coupling fluid on the measurement's accuracy [5–8].

During the last decades, the thermal-wave resonator cavity (TWRC) method [9] was probably the most successful in controlling the influence of coupling fluid on the values of the investigated thermal parameters. However, sometimes this method cannot be used and, in such cases, one has to act on other experimental parameters as type of coupling fluid, chopping frequency, etc. The TWRC method was used mainly to characterize liquid samples. It was used to increase the accuracy for both thermal diffusivity (back PPE configuration) and effusivity (front PPE configuration) investigations. The main reason was that in the frequency scanning procedures the exact thickness of the liquid under investigation was not known [10].

In the case of solid samples the TWRC method can be applied only in the front configuration and it is only the thermal effusivity coming out from the measurement (the solid under investigation is in a back position). At the same time, even in this configuration, TWRC cannot be applied if the solid sample is porous, pressed powder or very thin [11]. Consequently the TWRC method cannot be applied for thermal diffusivity investigations of solids and this is the reason for which we propose in the paper to optimize the frequency scanning procedure.

---

* Corresponding author.
E-mail address: skaroll@fizyka.umk.pl (K. Strzałkowski).

http://dx.doi.org/10.1016/j.tca.2015.06.027
0040-6031/

In this paper we will focus only on solid samples, on one thermal parameter, thermal diffusivity [12–16] and on one detection configuration BPPE (associated with the chopping frequency as scanning procedure) [11]. This is a simplified classical and largely used configuration, composed by 4 layers (air/sample/sensor/air) in which, if we assume optical opacity for the sample and thermally thick regime for the sample and sensor, we can obtain the value of the sample's thermal diffusivity from the slope of the amplitude and/or phase of the signal as a function of square root of the chopping frequency (see Eqs. (1) and (2)) [11]:

$$\ln|V_n| = \ln\frac{2}{b_{sp}+1} - L_s\left(\frac{\omega}{2\alpha_s}\right)^{1/2} \tag{1}$$

$$\Theta = \Theta_0 - L_s\left(\frac{\omega}{2\alpha_s}\right)^{1/2} \tag{2}$$

In Eqs. (1) and (2) the standard notations have been used: s and p represent the sample and pyroelectric sensor, respectively, $b_{sp} = e_s/e_p$ where e is the thermal effusivity, α is the thermal diffusivity, ω is the angular modulation frequency and L_s is the thickness of the sample (the sensor is considered semi-infinite). Θ is the phase of the signal (Θ_0 is a frequency independent offset) and V_n is the normalized amplitude of the BPPE signal (the normalization was performed with the signal obtained with empty sensor).

It is to mention that, in the theoretical development of this particular detection case, the layer of coupling fluid was neglected. Experimentally, the presence of a thin (but uncontrolled in thickness) layer of coupling fluid cannot be avoided; this additional layer changes the slope of the phase (amplitude) curve and, consequently, the obtained value of thermal diffusivity is always underestimated [5–8]. The influence of the coupling medium in pyroelectric measurements of solids becomes significant especially for high conductive samples and at high modulation frequency of the incident radiation. Different solutions have been proposed in order to obtain correct values of thermal diffusivity. Some are based on non-contact techniques as photothermal radiometry (PTR) [17–19], others try to modify the experimental set-up of the PPE technique itself. Salazar et al. [5–7], for instance, used transparent electrodes (ITO) deposited on the sensor ($LiTaO_3$) surface, and introduced a self-normalization procedure [6,7]. In doing so, the thermal diffusivity of opaque solid samples could be measured with high accuracy. However, by using the proposed technique, each sample has to be measured in both, back and front configurations.The research performed in this work is focused on finding a different solution in order to minimize the undesired effect of the coupling fluid by a proper selection of the coupling fluid and by performing a simple experimental modification of the detection cell (reduction of the coupling fluid thickness). The final goal is to obtain similar results with both photopyroelectric calorimetry and infrared lock-in thermography (IRT) techniques.

2. Material preparation and experimental methods

A glassy-like square shape carbon sample (GC) with known thermal properties [20] was used as test solid sample. The thickness of the GC sample (1 mm) and the other geometrical parameters were measured with a micrometer with an accuracy of 10 μm. The sample was weighted with a Discovery OHAUS laboratory analytical balance (DV215CDM model) of sensitivity of 0.1 mg.

The experimental setup for the BPPE measurement [11] consisted of a green, current-modulated DPSS (Diode Pumped Solid State) laser (532 nm) with the output power of about 50 mW, a $LiTaO_3$ detector (0.54 mm thick) provided with Cr + Au electrodes and a SR830 lock-in nanovoltmeter for signal processing. In this configuration the sample is placed onto the sensor and is directly excited by the incident radiation. A thin layer of different fluids served as a coupling medium between the sample and the sensor. The following coupling fluids were tested: standard silicon grease, commercial ceramic thermal paste used in computers, silicon oil, glycol, ethylene glycol and distilled water. Some typical values of the dynamic thermal parameters of these coupling fluids found in literature [21,22] are presented in Table 1.

The sample under investigation was stick to the sensor with a small amount of coupling fluid. Once the sample was placed onto the detector, some pushing force together with some gentle movements was applied. A black diaphragm was used in order to protect the detector from the scattered light. Frequency scans were performed in the range 0.3–15 Hz with 0.3 Hz or 0.5 Hz single step. Standard normalization procedure with empty sensor was applied.

The experimental IRT setup included a heat source, a waveform generator, an infrared camera and a computer for data acquisition (see Fig. 1). The intensity-modulated optical stimulation ($f_0 = 2$ Hz) was delivered by a Nd:YAG laser (Laser Quantum OPUS, with $\lambda = 532$ nm and $P = 0.5$ W). The IR camera (FLIR 7200 series, with a 256 × 320 pixel array of InSb detectors sensitive in the 1.5–5.1 μm wavelength range, working at a sampling frequency of 100 Hz) recorded the changes of the surface temperature of the specimen. The noise equivalent temperature difference (NETD) of this camera is lower than 20 mK. The signals delivered by the infrared camera and the reference frequency f_0 were sent to the lock-in detection module incorporated into the camera, which outputs the continuous component image ($f = 0$) as well as the amplitude and phase images of the f-component to a PC. The optical axis of the camera was set perpendicular to the investigated surface,

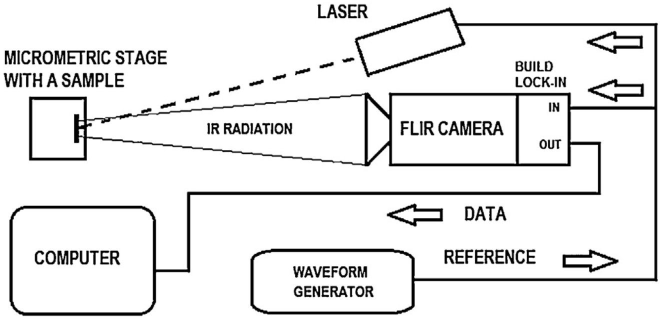

Fig. 1. Experimental setup for the lock-in thermography technique.

Table 1
Values of the dynamic thermal parameters of tested coupling fluids [21,22].

The thermal parameter	Silicon grease	Thermal paste	Silicon oil	Glycol	Ethylene glycol	Distilled water
Th. diffusivity ($m^2\,s^{-1}$) × 10^{-6}	0.01	–	0.097	0.09	0.0936	0.143
Th. effusivity ($W\,s^{1/2}\,m^{-2}\,K^{-1}$)	720	–	–	–	890	1586
Th. conductivity ($W\,m^{-1}$ K–1)	0.23	0.5-5	0.1	0.16	0.27	0.6