Lock-in thermography versus PPE calorimetry for accurate measurements of thermophysical properties of solid samples: a comparative study

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Abstract

The aim of this paper is to compare the measurement accuracy of photopyroelectric calorimetry in back detection configuration (BPPE) and infrared lock-in thermography (LT) for thermal diffusivity measurement of solid samples. For this purpose, the following materials with well-known thermal properties have been selected: glassy carbon (type G), $LiTaO_3$ crystal and binary II-VI semiconductors (based on CdSe and CdTe). The advantages and drawbacks of the two techniques have been analyzed both theoretically and experimentally.

Keywords: Thermal diffusivity; Lock-in thermography; PPE method; II-VI binary crystals

1 Introduction

Thermal characterization of the materials is very important due to the dissipation of the heat in projected systems e.g. miniaturized semiconducting devices. Thermal parameters are unique for each material, being strongly dependent on the composition, structural characteristics and fabrication process. From an application point of view, thermal diffusivity describes how quickly a material reacts to a change in temperature [1-5]. Thermal diffusivity of solid samples is typically measured with non-contact techniques such as flash method [6] or photothermal radiometry (PTR) [2]. In this work, the thermal diffusivity of some solid samples having well-known thermal properties was determined by means of contact (PPE calorimetry) and non-contact (IR lock-in thermography) techniques. The aim of this paper is to compare the results obtained by two techniques as well as to find out the most suitable theoretical and experimental conditions for improving the accuracy of the results.

The PPE technique has been extensively applied for the study of thermal properties of condensed matter [4,7,8]. The major advantages of this technique are its simplicity, high sensitivity, non-destructive character and adaptation on experimental restrictions for theoretical requirements. In classical BPPE method, for the investigation of solid samples, a coupling fluid must be introduced between the sample and sensor in order to ensure a good thermal contact. This always leads to an error in thermal diffusivity measurement. This fact is well known and it was previously discussed by Salazar *et al* [9-11]. They have shown that the results obtained with BPPE technique are always underestimated due to the presence of the coupling fluid between the sample and the sensor. The influence of the coupling fluid in pyroelectric measurements of solids becomes significant especially for high conductive samples and at high modulation frequency of incident radiation. Up to date many different solution have been proposed, often based on non-contact techniques such as photothermal radiometry (PTR) [2,8,12].

It has been shown that lock-in thermography allows the determination of thermal diffusivity and thermal conductivity of solid samples [13]. The procedure is fast and requires little preparation, i.e. the blackening of the investigated surface (for semi-transparent samples) and a calibration procedure for measurement of thermal conductivity. Thermal diffusivity is being estimated from the phase image obtained after lock-in detection. Infrared lock-in thermography has been also successfully applied to the determination of thermal diffusivity of thin slabs and filaments [14]. However, in the case of thin samples, experimental conditions must be chosen carefully to fulfill theoretical requirements, e. g. the sample should be kept in vacuum to suppress convective heat losses (especially for samples with low thermal diffusivity). Several conditions must be fulfilled in the case of LT technique: (i) the thickness of the blackening layer must be negligible with respect to the sample thickness, (ii) to prevent nonlinear heating effects, small laser powers must be applied, (iii) the sample under investigation should be thermally thick.

The classic BPPE calorimetry with frequency scanning procedure is used for thermal diffusivity measurements of solid samples. The influence of different coupling fluids on the accuracy of the results has been analyzed. The experimental set-up was improved in order to minimize the measurement errors. The parallelism between the sample/camera objective and the influence of the excitation frequency on the results have been also analyzed. The results obtained by two techniques were compared.

2 Material and methods

Several different solid materials were investigated in this work: (i) a glass-like carbon plate (GC) type G [15] having a square shape (thickness 1 mm), (ii) a LiTaO$_3$ crystal with Cr+Au electrodes (thickness 0.4 mm), (iii) a binary II-VI crystal based on CdSe (thickness 1.15 mm) (iv) and a binary II-VI crystal based on CdTe (thickness 1.04 mm). The binary II-VI crystals under investigation were grown from the melt by the high-pressure (150 atm of Argon) modified vertical Bridgman method using high purity (99.995%) powders in a graphite crucible. The crystal rods (1 cm in diameter) were cut into about 1.5 mm thick plates. To provide a good thermal contact with the pyroelectric sensor, the surface of the sample was polished in order to be as flat as possible. The samples were first grounded by using a grinding powder (Al$_2$O$_3$ with 10 µm diameter) and next polished with the diamond paste (1 µm diameter). During the polishing procedure the thickness of the specimens was controlled at several points to assure the parallelism of the two sides of the samples. The thickness of all specimens was measured with a micrometer with an accuracy of 10 µm.

For the PPE investigations, a modified experimental setup in the back configuration was used (Fig. 1). It consisted of a 300 mW power blue diode laser (λ=405 nm), a 0.4 mm thick LiTaO$_3$ detector, provided with CrAu electrodes and a SR850 dual-phase lock-in amplifier. The reference signal provided from the internal oscillator of the lock-in was used for the modulation of the incident radiation. In standard BPPE configuration the sample (placed onto the sensor) is directly excited with a modulated radiation. A thin layer of ethylene glycol served as coupling fluid between the sample and the sensor. To improve the thermal contact between the sample and the sensor, a textolite disc was mechanically pressed to the sample. This also prevented the sensor from direct illumination. The modulation frequency of the excitation source was changed in the frequency range 1 to15 Hz.
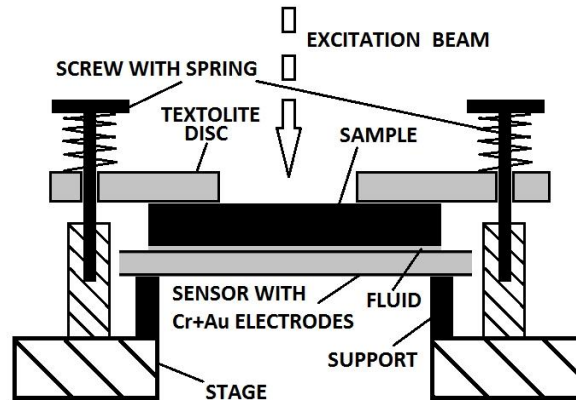

Fig. 1 Modified experimental setup for the BPPE method

The experimental IR setup included a heat source, a waveform generator, an infrared camera and a computer for data acquisition (Fig. 2). The intensity-modulated optical stimulation was delivered by an Nd:YAG laser (Laser Quantum OPUS, with λ=532 nm and P=0.5 W). The IR camera (FLIR 7200 series, with a 256x320 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 in the surface temperature of the specimens. 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.
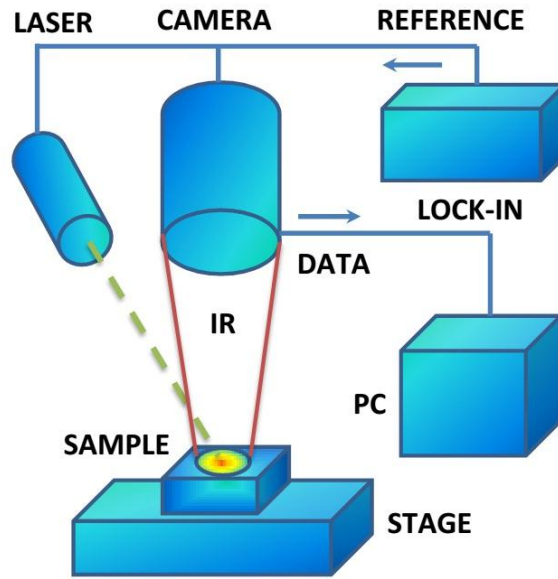

Fig. 2 Experimental setup for the lock-in thermography technique

In order to ensure the optical opacity of the transparent samples and to avoid the influence of optical excited -states of the semiconductor on its thermal properties CdSe and CdTe samples have been blackened with a very thin carbon layer. Because the deposited carbon layer is less than 10 μm and has a high thermal conductivity, one can neglect its influence on the signal.
All the measurements have been performed at room temperature and were computer-controlled.

3 Theory

The BPPE configuration cell consists of four-layers disposed as follows: air/opaque sample/pyroelectric sensor/air. Assuming a perfect thermal contact between the sample and the sensor and the one-dimensional model of the heat propagation through the sandwich-type system, the complex PPE signal is given by [16,17]:

$$V = \frac{2V_0 e^{-\sigma_s L_s}}{b_{sp}+1} \frac{1-e^{-2\sigma_p L_p}}{1+R_{sp}e^{-2\sigma_p L_p}-(R_{sp}+e^{-2\sigma_p L_p})e^{-2\sigma_s L_s}} \tag{1}$$

In Eq. (1) V_0 is an instrumental factor, ij represents s and p layers of the detection cell, respectively, $R_{ij}=(b_{ij}-1)/(b_{ij}+1)$ is the reflection coefficient of the thermal wave at ij interface, $b_{ij}=e_i/e_j$ and e is thermal effusivity, $\sigma_i=(1+i)a_i$ is the complex diffusion coefficient, a_i is the reciprocal of the thermal diffusion length μ_i, $a_i=1/\mu_i$, $\mu_i=(2\alpha_i/\omega)^{1/2}$, ω is the angular modulation frequency and L_i is the thickness of the layer i. In order to eliminate the instrumental factor V_0, the useful signal is normalized with respect to the signal obtained with the empty sensor [18]. After the normalization procedure and assuming the thermally thick regime for both the detector and the sample ($\mu_i < L_i$), one can calculate the thermal diffusivity by using the amplitude (Eq. (2)) and/or the phase (Eq. (3)) of the complex signal [18]:

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$$\ln|V_n| = \ln\frac{2}{b_{sp}+1} - a_s L_s \qquad (2)$$

$$\Theta = \Theta_0 - L_s\left(\frac{\omega}{2\alpha_s}\right)^{1/2} \qquad (3)$$

The amplitude is affected by external factors such as laser-intensity fluctuations and the roughness of the surface, whereas the phase provides more accurate results, being independent on these external factors. For this reason, the thermal diffusivity was calculated according to Eq. (3), the excitation frequency being used as scanning parameter.

The theoretical model for thermal diffusivity measurement of solid samples by lock-in thermography is presented below. The heat wave equation generated by a time-periodic punctual heat source in an isotropic and homogeneous medium with thermal diffusivity α, can be written as [13]:

$$T(x,t) = T_o e^{j(2\pi ft - kx)} \qquad (4)$$

where x is the thermal wave propagation direction, T_0 is the surface temperature, f is the excitation frequency, t is the time and k is the wave vector. The 1-D thermal diffusion equation is given by:

$$\alpha\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{\partial T(x,t)}{\partial t} \qquad (5)$$

where:

$$k = \pm(1-j)\sqrt{\frac{\pi f}{\alpha}} \qquad (6)$$

For physical reasons, the thermal wave must converge at infinity, which requires:

$$k = (1-j)\sqrt{\frac{\pi f}{\alpha}} \qquad (7)$$

The thermal wave can be written as follows:

$$T(x,t) = T_o e^{-\sqrt{\frac{\pi f}{\alpha}}x}\, e^{j\left(2\pi ft - \sqrt{\frac{\pi f}{\alpha}}x\right)} \qquad (8)$$

The propagation of a plane thermal wave through a medium of the thickness x and the thermal diffusivity α, trains a phase shift $\Delta\varphi$ having the following expression:

$$\Delta\phi = -\sqrt{\frac{\pi f}{\alpha}}x = ax \qquad (9)$$

where a is the slope of the phase-distance graph. The thermal diffusion length is expressed by:

$$\mu = \frac{1}{a} = \sqrt{\frac{\alpha}{\pi f}} \qquad (10)$$

The thermal diffusivity can be calculated according to Eq. (10).

4 Results and Discussion

Phase characteristics of selected GC sample for different coupling fluids as a function of the square root of the modulation frequency are given in Fig. 3. For each case identical experimental procedure was applied.
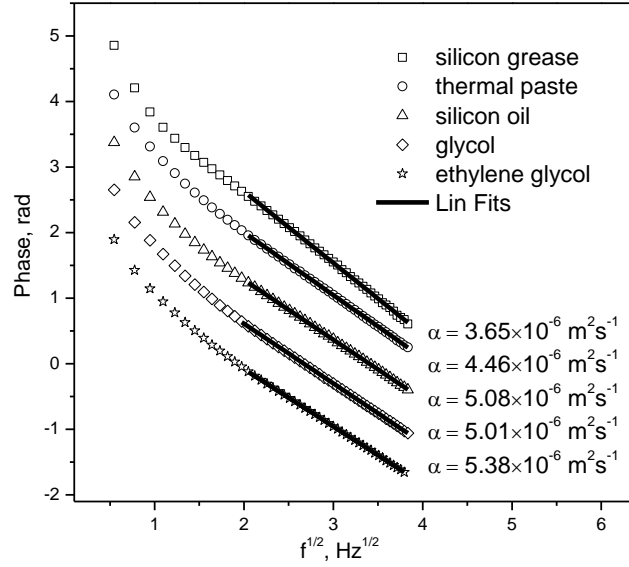
Fig. 3 Phase characteristics of glassy-like carbon for different coupling fluids as a function of the square root of the modulation frequency, points are experimental data and lines are linear fits

One can observe that obtained results strongly depend on type of the coupling medium. For silicon grease the thermal diffusivity of GC sample is underestimated more than 30 % comparing with ethylene glycol. Better coupling fluid is thermal paste, the difference is about 15 % but it is still not acceptable. The best solution seems to be more liquid fluids like silicon oil, glycol or ethylene glycol. Another advantage of this kind of couplers is they can be very easily removed from the surface of the sensor comparing with more solid grease based coupling substances. Considering the thermal conductivity of different coupling fluids one can assume the best one has the thermal paste. On the other hand, chosen in this work ethylene glycol is rather poor thermal conductor. One can conclude that thermal properties of the coupling medium are not as important as its final thickness in the sample/sensor system. Grease based couplers are not able to create such thin layer like more fluent water or ethylene glycol. Another problem in case of grease coupling fluids can be connected with removing air bubbles from the contact layer. One can conclude that coupling medium in this type of measurement should be chosen with great care.

The curves given in Fig. 4 were obtained applying modified experimental setup described in second section and presented in Fig. 1. A comparison of experimental results obtained before and after the modification on the example of CdTe sample is shown in Fig. 4. The difference in the slopes between two curves can be clearly seen, consequently the thermal diffusivity of the specimen was calculated from the slopes as $4.244\pm0.035\times10^{-6}$ m$^2\cdot$s^{-1} for standard configuration and as $4.473\pm0.008\times10^{-6}$ m$^2\cdot$s^{-1} after applying the modification. Given thermal diffusivities were calculated as average values from three independent measurements with standard deviation as an uncertainty. One can see that thanks proposed simply solution significant reduction of the influence of the coupling fluid takes place (the final thickness of ethylene glycol is reduced). The standard deviation of the thermal diffusivity is much smaller in case of modified BPPE technique indicating more stable measurement conditions.
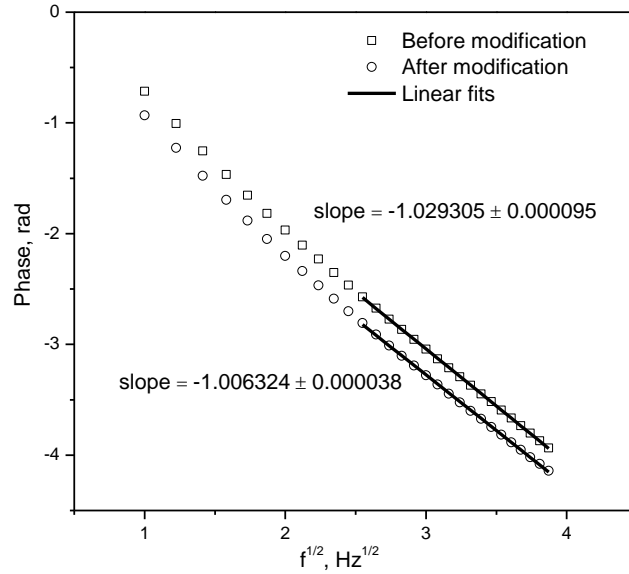
Fig. 4 Phase characteristics of CdTe sample measured before (squares) and after (circles) the modification of the experimental setup as a function of the square root of the modulation frequency, points are experimental data and lines are linear fits

Fig. 5 presents the behavior of the phase as a function of the square root of the modulation frequency of all investigated materials measured with PPE technique in back measurement configuration. For low frequencies regime the curves exhibit a non-linear dependence due to the thermally thin regime for the sample or/and the sensor. Consequently, linear fits (the least square method was applied) have been performed in different frequency ranges, according to the theoretical requirements. Thermal diffusivities were calculated according to Eq. (3). The measurements were performed using ethylene glycol as coupling fluid.
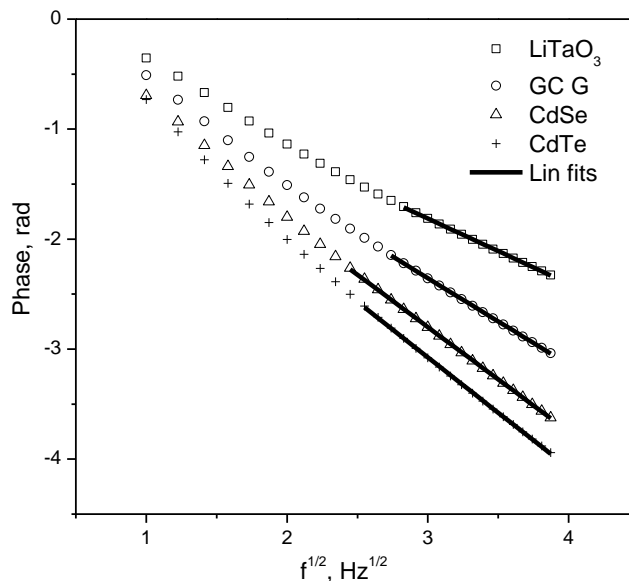

Fig. 5 The PPE phases in radians of all investigated samples as a function of the square root of the modulation frequency, points are experimental data and lines are linear fits

Phase images for glassy-like carbon sample with the corresponding profiles are shown in Fig. 6 (a) and (b), respectively.
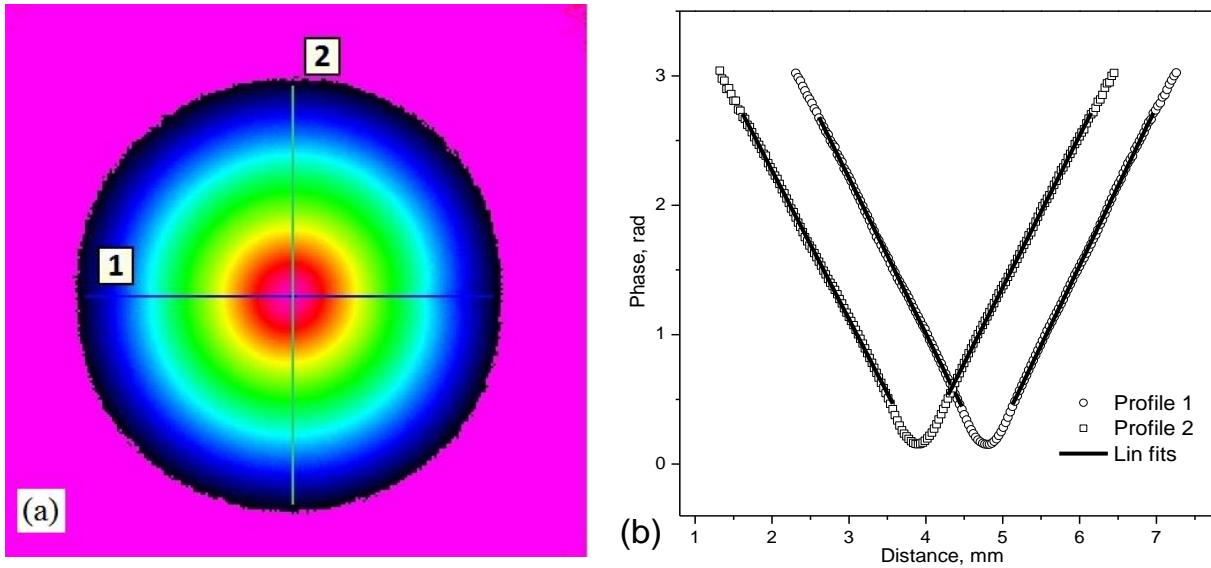

Fig. 6 Thermal image of the phase of the glassy-like carbon (a) sample measured at 4 Hz and corresponding phase profiles (b,c) taken from the thermal images, circles correspond to measured data and lines are linear fits

The impact zone of the laser is represented by the constant phase zones. The diameter of the laser is about 300μm (1px=30μm), being considered a punctual excitation source. This method is sensitive to the parallelism of the measured sample surface to the detector of the camera. In case of non-parallel alignment of the sample/camera system, one can measure the projection of the temperature field of the specimen. To calculate the relative error in thermal diffusivity arising from non-parallel alignment simple calculation were performed with respect to the sample with the thermal diffusivity of the order 6 m^2·s^{-1} ×10^{-6}. The slope a from the phase-distance graph presented in Fig. 6 (b) is given by simple relation: $a=y/x$. An effective distance seeing by camera can be written as follows: $a=y/(x \cdot \cos\theta)$, where θ represents the angle between optical axis of the camera-sample system and the normal vector of the specimen surface (see inset in Fig. 7).

Obtained results given in Fig. 7 were calculated according to Eq. (10). The dependence of the relative error as the function of the angle exhibit non-linear character. For 5 degree the error is of the order of 1%, for 10 is three times larger and for higher values of θ continues to grow very quickly. In this work the proper alignment was assured by manipulating the sample/camera system until the image of the specimens seeing by camera was symmetrical (all samples investigated in this work were of regular shape). Proper applying of LT technique requires working with the sample in its thermal thick regime. Failing to accomplish this condition leads to underestimation of the thermal diffusivity of the order 20 or even 30 % [13]. Choosing proper modulation frequency for completely new sample is not easy task. If the frequency will be to low, one can get the underestimated value of the thermal diffusivity. On the other hand, for higher frequencies the blackening layer can influence the results. For glassy-like carbon the measurements of the thermal diffusivity were performed in the range of frequency 0.05 – 4 Hz. The final results were calculated according to Eq. (10) as average values from three independent experiments with standard deviation as error bars. Obtained results are presented in Fig. 8.
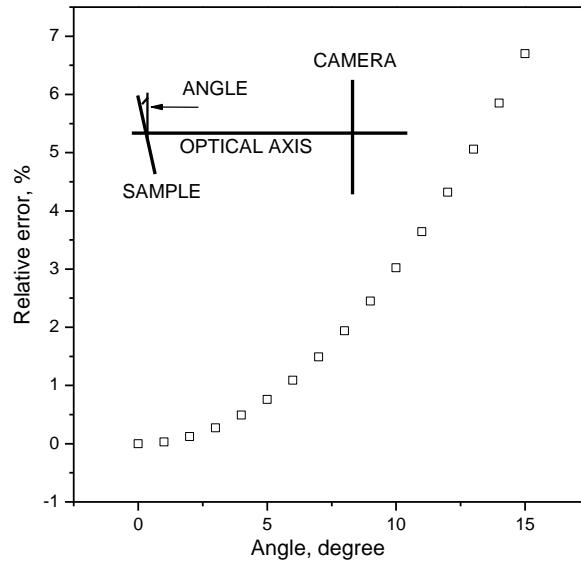
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Fig. 7 Relative error of the thermal diffusivity calculated from the slope of the phase profile as a function of angle, the angle represents non-parallel alignment of the sample surface to the face of the camera

For very low frequencies, below 1 Hz, effects connected with convection cannot be neglected and the sample is mainly thermally thin. Obtained thermal diffusivity is too low. Thermal diffusion length for GC sample for 2 Hz is about 0.97 mm; the specimen starts to be thermally thick. However, the proper frequency should be chosen higher [13]. In this work for glassy-like sample 4 Hz were applied to get the value of the thermal diffusivity. If thermal parameters of the sample under investigation would be completely unknown, PPE technique could be useful to estimate its thermal diffusivity, and consequently proper modulation frequency for LT.
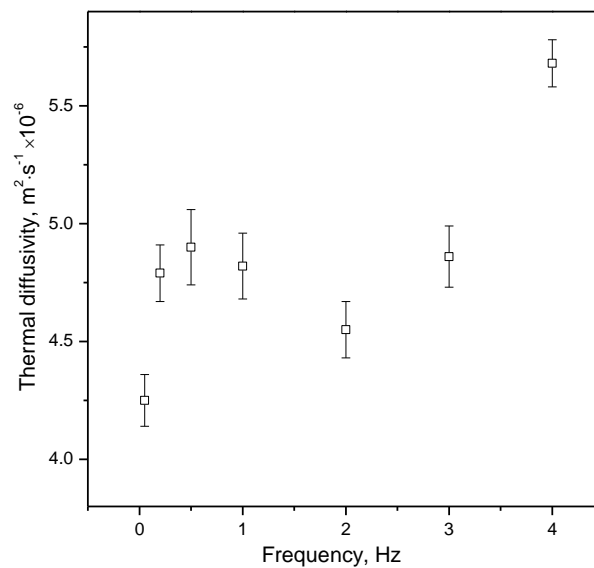

Fig. 8 Measurements of the thermal diffusivity for glassy-like carbon were performed in the frequency range of $0.05 - 4$ Hz, points refer to experimental data and error bars to the standard deviation

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The thermal diffusivities of all measured specimens are given in Table 1. The values obtained from PPE and LT techniques are listed in separate columns with standard deviation as the uncertainty. They remain in good agreement with literature data given in third column and confirm an ability of applied techniques for proper thermal characterization of solid materials.

Table 1 Thermal diffusivity ($m^2 \cdot s^{-1} \times 10^{-6}$) of the investigated materials

Material	PPE	LT	Literature
GC type G	5.378±0.021	5.601±0.135	5.4-6, [10,11]
CdSe	4.602±0.016	4.615±0.169	4.5, [7]
CdTe	4.473±0.008	4.485±0.135	4.78, [20]
LiTaO$_3$	1.362±0.005	1.36±0.085	1.22-1.54, [19]

For CdSe, CdTe and LiTaO3 samples there is a very good agreement between PPE and LT methods, obtained values lie within error bars. Some discrepancy of about 4% for glassy-like carbon can be found, however the difference is not too large. Considering standard deviation, the BPPE technique together with proposed modification is much more stable and accurate than LT method. However, the photopyroelectric calorimetry is well established technique, in contrast to infrared lock-in thermography, which is quite new technique still under development. From the experimental point of view, infrared lock-in thermography being non-contact method, seems to be an interesting alternative because the measurements are fast and no coupling medium is required.

5 Conclusions

In this paper thermal diffusivity of the investigated samples was obtained by two experimental methods: BPPE technique and IR lock-in thermography. Obtained values of the thermal diffusivity were consistent with literature data. In case of solid samples a coupling medium in back PPE configuration is required; it always introduces some additional uncertainty to the system. The values of the thermal diffusivity of the GC sample derived from BPPE measurements for different coupling substances were underestimated in comparison with LT results. The difference was especially large for grease based couplers. As stable and giving good results ethylene glycol has been chosen as coupling fluid.

From experimental results concluded that the most important role in the reduction of the influence of the coupling fluid plays its thickness. To overcome this undesired effect the experimental set-up was improved in order to minimize the measurement errors. After the modification both, contact (PPE) and non-contact (LT) methods, lead to similar results, lying within error bars. Only for glassy-like carbon the discrepancy of about 4% has been observed.

The parallelism between the sample/camera objective and the influence of the excitation frequency on the results were also analyzed. Infrared lock-in thermography turned out to be sensitive on sample/camera alignment. In case of non-parallel arrangement one can expect increasing relative error in the thermal diffusivity. For this purpose standard deviation for LT method was about one order in magnitude larger comparing with PPE. In the future additional procedure to assure proper alignment of the sample/camera system will be introduced.

For completely new materials with unknown thermal properties very important is choosing proper modulation frequency. For such a case LT and PPE techniques may be complementary. The PPE method could be used to estimate thermal diffusivity of the sample. One can conclude that infrared

lock-in thermography is very interesting as non-contact, fast and convenient method, however experimental conditions must be chosen very carefully. On the other hand, PPE technique with frequency scanning procedure remains still simple and important method in thermal inspection of solid materials.

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