JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 3, March 2007, p. 595 - 598

High accuracy photopyroelectric calorimetry. Application to liquid mixtures and composites

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A photopyroelectric (PPE) calorimetric method, based on the sample's thickness scan of the signal amplitude and phase, is proposed in order to obtain accurate values of thermal parameters of liquid samples. The accuracy of the method (about 1% for the determination of thermal diffusivity and 3% for thermal effusivity) makes it suitable for studies of processes associated with small changes in the values of thermal parameters. In order to prove the versatility of the technique, room temperature values of the thermal parameters of some vegetable oils were measured, molecular associations in water-ethylene glycol mixtures and a sedimentation process in a SiO_2 colloidal solution were detected. Due to its qualities (high accuracy, low time consuming, small quantity of sample required) the method is recommended as an alternative for thermal properties investigations of nanofluids.

(Received November 15, 2006; accepted December 21, 2006)

Keywords: Photopyroelectric colorimetry, Liquid mixture

1. Introduction

Nanofluids have been proposed as a route for surpassing the performance of heat transfer liquids currently available. Recent experiments on nanofluids have indicated significant increases in thermal conductiviycompared with liquids without nanoparticles or larger particles, strong temperature dependence of thermal conductivity, and significant increases in critical heat flux in boiling transfer. Generally, the conventional method for increasing heat dissipation is to increase the area available for exchanging heat with a heat transfer fluid. However, this approach requires an undesirable increase in the thermal management system's size. The novel concept of nanofluids - heat transfer fluids containing suspensions of nanoparticles - has been proposed as a means of meeting these challenge [1]. Nanofluids have attracted great interest because of recent reports of greatly enhanced thermal properties. For example, a small amount (<1% volume fraction) of Cu or carbon nanoparticles dispersed in ethylene glycol or oils is reported to increase the thermal conductivity of the liquid by 40% and 150%, respectively [2,3]. Conventional particle-liquid suspensions require high concentrations (>10%) of particles to achieve such enhancement. This enhancement of thermal properties are not merely of academic interest. If confirmed, it would make nanofluids promising for applications in thermal management. Furthermore, suspensions of metal nanoparticles are also being developed for purposes such as medical applications, including cancer therapy [4].

However, some of experimental results are controversial (e.g. the extent of thermal conductivity enhancement sometimes greatly exceeds the theoretical predictions) and, it seems that some accurate experimental methods for thermal parameters investigations (well adapted to fluids) are required.

During the last few decades, a new set of techniques, called photothermal (PT) methods, have been proposed for accurate calorimetric investigations [5]. All PT techniques are based on the same principle: a sample, irradiated with an optical wave, transforms a part of radiation into heat. The quantity of developed heat and its propagation through the sample are connected with sample's related optical and thermal parameters. One of the most used PT method is the photopyroelectric (PPE) technique [6,7]. In the PPE technique, the temperature variation of a sample, exposed to a modulated radiation, is measured with a pyroelectric sensor. During the last years the PPE technique has been extensively applied to the study of thermal properties of condensed matter samples. Using different experimental detection schemes and theoretical approaches, one can obtain all dynamic (thermal diffusivity, conductivity and effusivity) and static (specific heat) sample's related thermal parameters. The PPE method is a contact one, very suitable for investigating liquid samples.

In principle, a calorimetry (classical or photothermal) is able to give only global information about the thermal properties of a sample. However, when high accurate investigations are possible, intimate processes as molecular associations or sedimentation processes can be studied, and/or structural and compositional data can be obtained.

In the following, we propose a PPE detection method, able to measure with a very high accuracy the dynamic thermal parameters (thermal diffusivity and effusivity) of a liquid specimen. The remaining thermal parameters (thermal conductivity and specific heat) can be then derived. The method is based on the sample's thickness

scan of the amplitude and phase of the complex PPE signal [8]. The high accuracy of the method leads to specific applications, as, for example, low concentrations detection, or sedimentation processes studies for (nano or micro-size) powders in solutions.

2. Theory

We will use the "back" PPE (BPPE) configuration [9, 10] with the following restrictions: (i) a one dimensional propagation of heat is considered (the diameter of the laser beam is larger than the thermal diffusion length in the sample); (ii) the heat transport is due only to the conduction; (iii) the sample is thermally thick; (iv) the sensor is optically opaque.

In this particular case, the PPE complex signal is given by:

$$V(L_m, \alpha_m, \omega) = 2V_0(b_{qm} + 1)^{-1}(b_{mp}+1)^{-1}\exp(-\sigma_m L_m)[1-R\exp(-2\sigma_m L_m)]^{-1} \quad (1)$$

where: $R_{jk} = (b_{jk}-1)/(b_{jk}+1)$; $b_{jk}=e_j/e_k$;

$$\sigma_j= (1+i)\, a_j \; ; \; R = R_{mq}R_{mp}; \quad (2)$$

and where *p, q* and *m* refer to pyroelectric sensor, window (quartz) and sample (material). (See Fig. 1 for the geometry of the detection cell). V_0 is an instrumental factor. L_m represents the geometrical thickness of the sample (cell), e_j the effusivity of the layer '*j*', and a_j is the reciprocal of the thermal diffusion length

($a_j = 1/\mu_j$). $\mu = (\alpha/\pi f)^{1/2}$ with α thermal diffusivity and f chopping frequency.

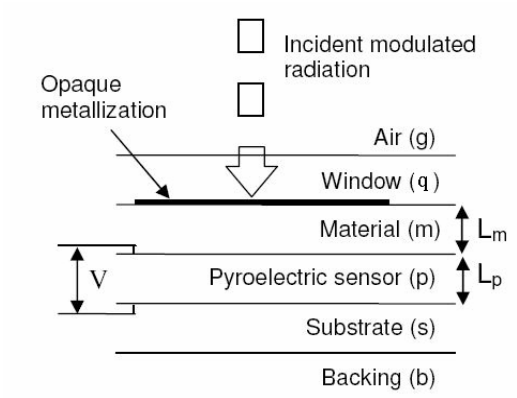

Fig. 1. The geometry of the detection cell.

A simple algebra leads to the following expression for the phase of the PPE signal:

$$tg\Theta=-\{\sin(a_mL_m)-R\exp(-2a_mL_m)[\sin(a_mL_m)\cos(2a_mL_m)-\cos(a_mL_m)\sin(2a_mL_m]\}\{\cos(a_mL_m)-R\exp(-2a_mL_m)[\sin(a_mL_m)\sin(2a_mL_m)+\cos(a_mL_m)\cos(2a_mL_m)]\}^{-1} \quad (3)$$

A simulation of Eq.(3), for different values of R, in the [–1, 1] range, is presented in Fig. 2. It indicates that the phase of the PPE signal behaves linearly as a function of the sample's thickness for $a_mL_m > 1.5$. From the linear part of the graph, one can obtain the sample's thermal diffusivity.

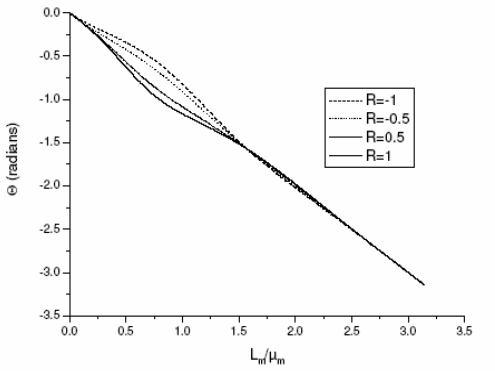

Fig. 2. The phase of the signal versus the thickness of the sample.

The amplitude of the PPE signal can be also used for calorimetric purposes (measurement of thermal effusivity), if one performs, in the same configuration, two measurements: with sample and with a calibration liquid (water in our case – symbol 'w'). In such a case, the normalized signal is given by:

$$V_n = 2(b_{wp}+1)\,(b_{qp}+1)^{-1}\,(b_{mp}+1)^{-1}\exp[-L_m(a_w-a_m)]\,\exp[-iL_m(a_w-a_m)] \quad (4)$$

Consequently, the amplitude of the signal has the following dependence on the sample's thickness:

$$\mathrm{Ln}|(V_n)| = -L_m(a_w-a_m) + \ln\,[2(b_{wp}+1)\,(b_{qp}+1)^{-1}\,(b_{mp}+1)^{-1}] \quad (5)$$

If we denote by y_0 the value of the free term in Eq. (5), we obtain for the sample's thermal effusivity e_m the following equation:

$$e_p^{-1}e_m^{\,2} + [(1+e_qe_p^{-1}) - 2(1+e_qe_p^{-1})\exp(-y_0)]e_m + e_q=0 \quad (6)$$

In conclusion, one can obtain sample's thermal effusivity, by performing a thickness scan of the amplitude of the signal, provided the absolute thickness of the sample in Eq. (5) is known.

3. Experiment

The experimental setup was a standard one for back detection configuration [10]. An Ar^+ laser (Spectra Physics) with stabilized power output at λ = 514 nm, modulated with an acousto-optical modulator (Intra Action), was used as radiation source. The pyroelectric sensor, a 510 μm thick $LiTaO_3$ single crystal, provided with Cr-Au electrodes on both faces, was glued on a micrometric table. The backing material for the sensor was air. The modulated radiation passed through a 1.2 mm thick quartz window (Hellma Co.) situated on a rotating

table, and was absorbed by an opaque 0.1 μm thick titanium layer, deposited on the rear side of the window. The liquid sample accommodated the space between the sensor and the titanium layer. The sample's thickness variation was performed with a step of 0.1 μm, and with a rate of 0.2 μm/s (ITL09 micro-controller). The PPE signal was processed with a digital lock-in amplifier (Stanford SR830). The sample's thickness control and data acquisition were performed with adequate software.

Tacking into account the fact that the nanoparticles are usually dispersed in oils or ethylene glycol, two vegetable oils with rather close values of thermal parameters, binary mixtures of water-ethylene glycol and some SiO_2 colloidal solution were selected as testing materials. When necessary, water was used as calibration liquid.

The thermal parameters of the components of the detection cell were [10]: $e_p = 3750 Ws^{1/2}/m^2K$; $e_q = 1531 Ws^{1/2}/m^2K$; $e_w = 1582 Ws^{1/2}/m^2K$. Several chopping frequencies were tested and the 1-10 Hz range was finally selected as a suitable interval for the experiment.

4. Results and conclusions

Fig. 3 contains the behaviour of the thermal diffusivity of olive and sunflower oils as a function of the cell's thickness, as deduced from the phase of the PPE signal (Eq.(3)). The room temperature value of the thermal diffusivity is represented by the points situated on the horizontal portion of the curve (170-250 μm).

Fig. 4 represents the behaviour of the amplitude of the PPE signal as a function of cell's thickness. The obtained values for the thermal effusivity of the same oil samples are almost the same.

Using the well known relationships connecting the four thermal parameters ($\alpha=k/C$ and $e=(Ck)^{1/2}$) [6,7], the remaining two (volume specific heat and thermal conductivity) can be calculated. We obtained for the investigated samples:

$C=1.62*10^6 J/m^3K$, $k=1.49*10^{-1}$ W/mK for olive oil, and $C=1.62*10^6 J/m^3K$, $k=1.5*10^{-1}$W/mK for sunflower oil;

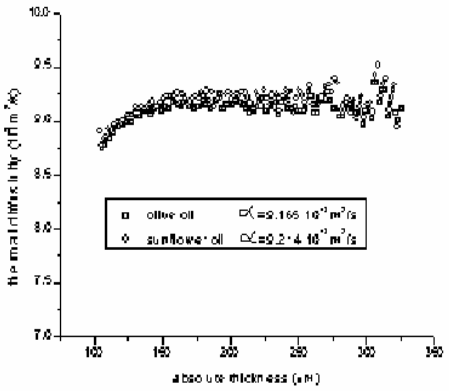

Fig. 3. The thermal diffusivity versus the absolute sample thickness.

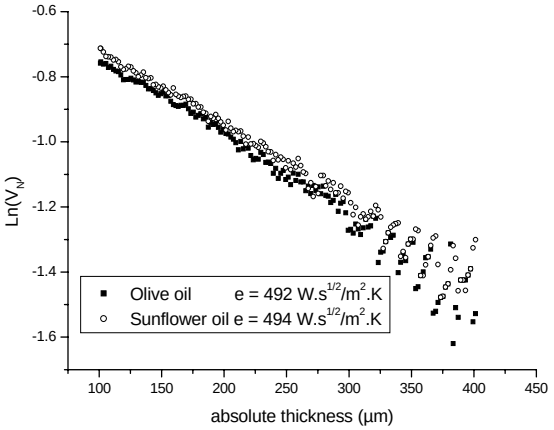

Fig. 4. The amplitude of the signal versus the absolulte sample thickness.

Fig. 5 displays the thermal diffusivity as a function of composition for binary water-ethylene glycol mixtures. The almost linear behaviour of the thermal diffusivity as a function of mass concentration of water indicates that the two liquids are non-interacting ones.

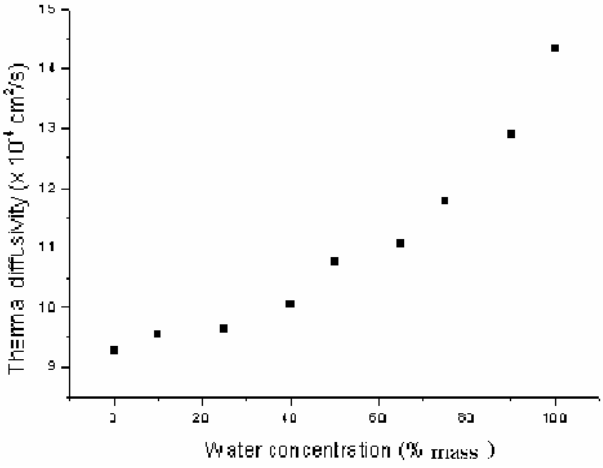

Fig. 5. The thermal diffusivity versus the water mass concentration.

Fig. 6 presents the behaviour of the phase of the PPE signal as a function of relative thickness for a SiO_2 colloidal solution kept unstired for 15 min. The observed nonlinear behaviour is associated with an increase of the diffusivity (decrease of the slope of the curve) with decreasing sample's thickness; this fact indicates that a sedimentation process occurs in the solution.

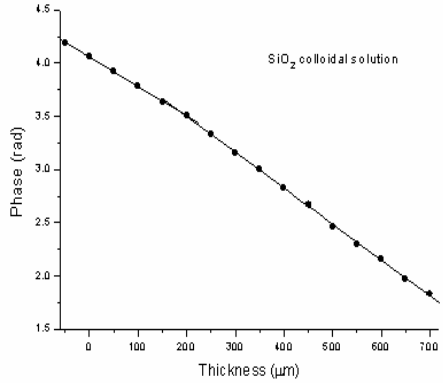

Fig. 6. The phase of the signal versus the relative thickness for a SiO_2 colloidal solution.

In conclusion, a PPE calorimetric method, based on the sample's thickness scan of the signal amplitude and phase, was used in order to obtain accurate values of thermal parameters of some liquid samples. The final accuracy of the method was about 1% for the determination of thermal diffusivity and 3% for thermal effusivity. The high accuracy of the method makes it suitable for studies of processes associated with small changes (few percents) in the values of thermal parameters (compositional changes, molecular associations, sedimentations, etc). Due to the fact that it is a contact technique that requires a sample thickness variation, the method can be applied only to liquids. The necessary sample quantity is very small; about 1μl. We recommend the method as an alternative for thermal properties investigations of nanofluids.

Aknowledgements

Work partially supported by the Romanian Ministry of Education and Research through the National Research Programs 39N/2006 and CEEX 1433/27.04.2006. One of the authors (D.D.) acknowledges the receipt of a visiting scientist grant from Region Nord Pas de Calais France, which made possible the present work. Useful conversation on the subject with drs. A.Hadj Sahraoui, S. Longuemart and S Delenclos are also acknowledged.

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