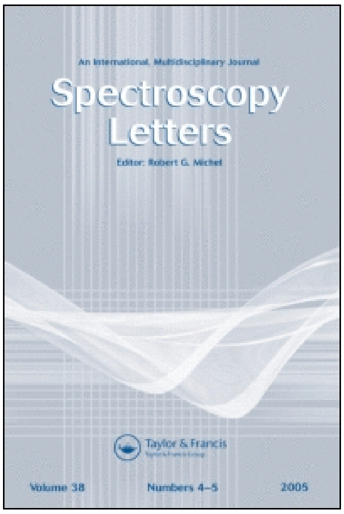

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Photopyroelectric (PPE) Phase Spectroscopy for Sensitive Optical Absorption Coefficient and Thermal Diffusivity Measurement

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PHOTOPYROELECTRIC (PPE) PHASE SPECTROSCOPY FOR SENSITIVE OPTICAL ABSORPTION COEFFICIENT AND THERMAL DIFFUSIVITY MEASUREMENT

Keywords: photothermal spectroscopy, photopyroelectric spectroscopy, absorption coefficient, thermal diffusivity.

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ABSTRACT

A novel spectroscopic method for the measurement of small relative changes of the optical absorption coefficient or thermal diffusivity is demonstrated, based on a sharp signal phase variation in PPE experiments, under well defined circumstances.

INTRODUCTION

The photopyroelctric (PPE) spectroscopy is an optical calorimetric technique[1] from the group of the photothermal methods for the optical and thermophysical caracterization of materials. In principle, it is based on the measurement of the sample temperature increase due to absorption of radiation, by using a pyroelectric sensor placed in thermal contact with the sample. Most of the spectroscopic applications of the PPE method with periodic excitation are based on the signal amplitude monitoring, but the signal phase contains useful spectroscopic information as well[2,3], due to the specific propagation character of the thermal wave. In an infinite and homogeneous medium, it is described by a complex propagation operator with the real and imaginary parts accounting for the attenuation and dephasing of the thermal wave, respectively.

While investigating the spectral properties of a protonic conductor, $H(UO_2)PO_4.4H_2O$, (HUP), we observed an unusually large PPE signal phase varation in the range 0.4-0.6μm, where this material presents a significant change of the optical absorption coefficient. According to the PPE theory[4], such an effect is the consequence of the change of the optical or thermal properties of the sample and may occur only under particular experimental conditions. The paper presents a sensitive method for the measurement of two sample-related parameters, based on this anomalous PPE phase spectrum.

THEORETICAL BACKGROUND

The general expression of the PPE signal[4] depends on several optical and thermophysical sample properties, but two independent parameters, the thermal thickness aL and the optical thickness βL are sufficient to define the specific experimental configuration, described by a special case of the general expression, out of six possibilities[5], denoted 1a-1c, 2a-2c. Here L is the sample tihckness, β is the optical absorption coefficient, and:

$$a = (\pi f/\alpha)^{1/2} \qquad (1)$$

is the diffusion length of the thermal wave, with α the thermal diffusivity and f the modulation frequency of the exciting light. A convenient way of visualizing the behavior of the PPE signal is the representation of the amplitude and phase surfaces as a function of the dimensionless parameters aL and βL, Fig.1. Our experiments on HUP were situated in the special cases 1b and 1c. The respective signals are proportional to the factor F:

$$F = \exp[-(1+i)aL] \qquad \text{if } 1<aL<\beta L \quad \text{(case 1b)}, \qquad (2)$$

$$F = \exp(-\beta L) \qquad \text{if } 1<\beta L<aL \quad \text{(case 1c)}. \qquad (3)$$

The interpretation of Eqs.(2,3) is the following: in case 1b the optical thickness is larger than the thermal thickness. Consequently, the light will be rather absorbed within the sample than transmitted to the pyroelctric sensor. The absorbed fraction is convrted into thermal waves which eventually reach the sensor with a phase lag of φ=aL rad and an attenuation of exp(-aL), Eq.(2). In case 1c, the thermal thickness is larger than the optical thickness and the information reaching the sensor is dominated by the fraction of light exp(-βL), transmitted through the sample with no dephasing, Eq.(3). It follows that at the boundary between the 1b/1c cases, defined by aL=βL on the phase surface, there is a phase jump of $\Delta\varphi$=aL rad. This effect is illustrated in Fig.1, which is a numeric simulation of the signal phase based on the exact expression for the PPE signal[4].

The anomalous phase behavior, not predicted by the special cases, consists in the local hump of this surface, centered at aL=βL=6.27. The anomaly is present also on the amplitude surface as a dip localized at aL=βL=5.28 and confirmed experimentally[6].

The regular phase jump combined with the anomalous phase overshoot shown in Fig.1, yields a sharp total phase change of nearly 270deg upon the variation of either the aL or βL parameter about the value 6.27.

EXPERIMENTAL

After chemical preparation, the HUP substance in the form of a yellow powder was pressed to a slab with a thickness of 0.35mm.

The experimental setup is common for PPE spectroscopic investigations and was described in other works[7]. The source is a 12V/100W tungsten-halogen lamp. The radiation is modulated with a mechanical chopper driven by a synchronous motor and then focused with a quartz lens onto the 4x0.5mm^2 entrance slit of a Carl Zeiss Jena monochromator type SPM-2. The PPE cell attached to the exit slit consists of a 4x3x0.2mm^3 PZT pyroelectric ceramic sensor provided with gold electrodes. One of its sides is blackened with china ink and is placed in thermal contact with the back of the

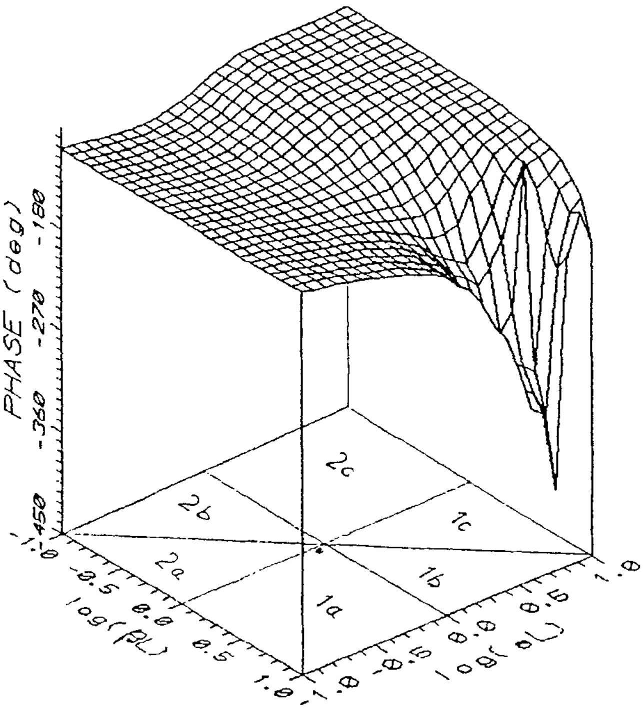

FIG.1. PPE signal phase surface vs. the optical and thermal thicknesses of the sample, (theory). Note the anomalous phase increase between $\log_{10}(aL)=\log_{10}(\beta L)=0.75$–$0.85$ superposed on the general phase decrease in case 1b.

sample slab, via a small quantity of silicone grease. The radiation having a spectral width of 0.005µm impinges on the sample front side. The signal from the detector having a capacity of 175pF is fed into an 100Mohm low noise preamplifier type Unipan 233.7 and then is processed by two lock-in amplifiers type Unipan 232 (Poland) in parallel, with the phase settings adjusted in quadrature one to the other. The spectral range 0.4-0.6µm was swept at the chopping frequencies f=2, 4, 8, 16 and 32Hz. The angle of the complex signal vector recorded on a X-Y plotter connected with

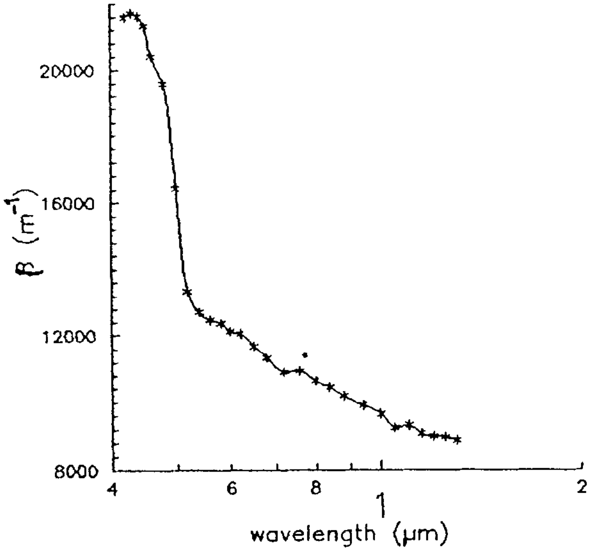

FIG.2. Optical absorption spectrum of $H(UO_2)PO_4.4H_2O$ calculated from the experimental transmittance data.

the two lock-in instruments, yielded directly the phase spectrum which was subsequently corrected for the frequency dependent contribution of the electronics to the total phase.

The transmittance spectrum of the HUP sample was obtained with the same setup, with the difference that it was placed in front of the sensor, at a distance of 2mm. In this way the sample is thermally decoupled from the sensor and the signal amplitude, normalized to the spectrum of the bare detector, is proportional only to the fraction of the transmitted light. Due to the fact that the sample-sensor distance is small, the partial diffusion of light by the pressed powder does not affect the results.

RESULTS AND DISCUSSION

The optical transmittance data were used for the calculation of the absorption coefficient spectrum presented in Fig.2, showing

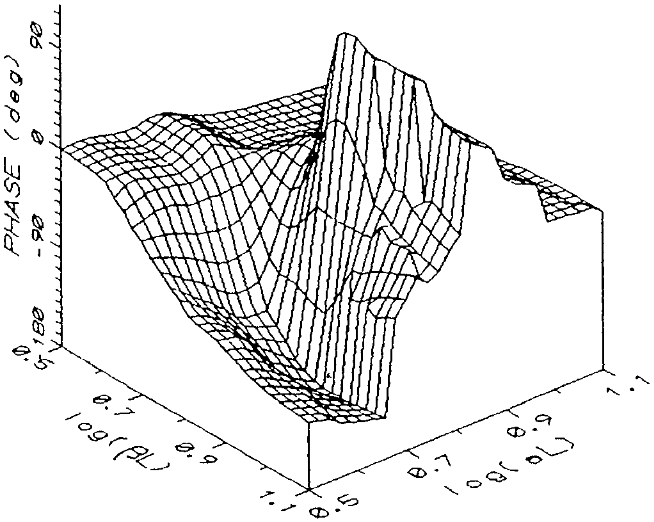

FIG.3. Same as in Fig.1, (experimental results).

a sharp increase below 0.5μm due to the strong absorption band of the uranyl ion.

The two parameters of the phase measurements, the radiation wavelength and the modulation frequency, had to be transformed into the coordinates aL and βL to allow for comparison with the theory. The data in Fig.2 were used for the transformation from the radiation wavelength to βL. The transformation from f to aL is based on Eq.(1) and on the assumption that the highest experimental phase value corresponds to the theoretical peak anomaly situated at aL=6.27.

The Fig.3 shows the experimental phase surface, plotted versus the dimensionless coordinates. Obviously, the right corner of the theoretical surface in Fig.1 is closely reproduced experimentally, with an even greater anomalous hump. The cross sections along the two coordinates in the region with the steepest slope, are given in Fig.4. The relative phase sensitivities S_α and S_β are:

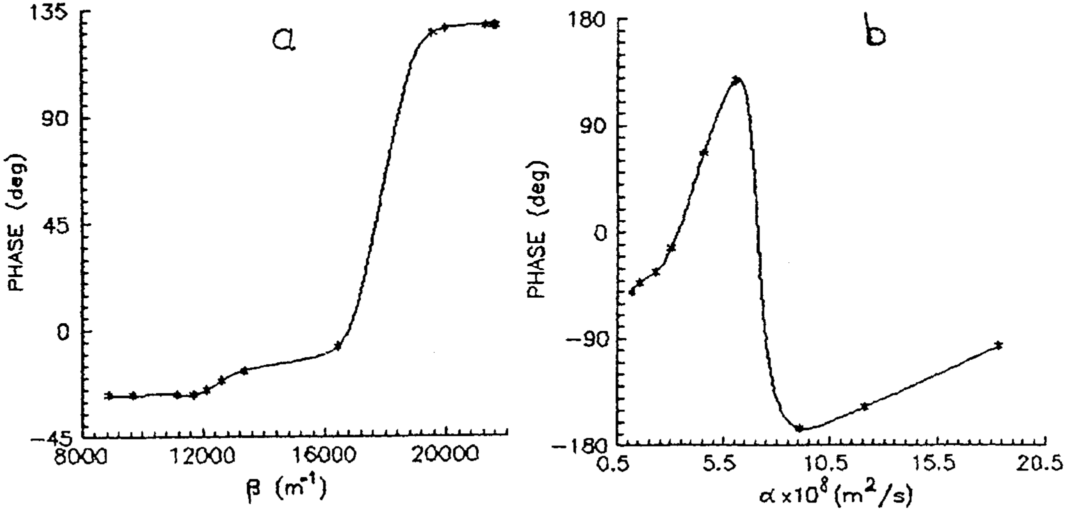

FIG.4. Experimental PPE signal phase vs. the sample optical absorption coefficient, for f=6Hz (a), and vs. the sample thermal diffusivity, for β=18000m^{-1} (b). The arrows mark the useful regions for the phase spectroscopy of the two parameters.

$$S_\alpha = (\Delta\alpha/\alpha)/\Delta\varphi = 0.16\%/\mathrm{deg}\ , \tag{4}$$

$$S_\beta = (\Delta\beta/\beta)/\Delta\varphi = 0.12\%/\mathrm{deg}\ . \tag{5}$$

In the absence of the phase anomaly, the two sensitivities would be only of the order of 1%/deg. Assuming the phase measurement is performed wit a resolution of 1deg, the figure for S_β is better than the capability of standard spectrophotometry, whereas S_α represents a far better performance than other thermal methods for the measurement of the thermal diffusivity. Additionally, the condition aL=6.27 offers an indirect estimation based only on optical measurements for the absolute value of the thermal diffusivity $\alpha=6.05\times10^{-8}m^2s^{-1}$.

CONCLUSION

A novel method is presented for the determination of small relative variations of a sample's optical absorption coefficient or thermal diffusivity, surpassing the resolution of conventional methods. The possible applications are: evincing the phase transitions with small specific heat discontinuity, temperature coefficient measurement of the thermal conductivity, of the absorption coefficient and of the refractive index, etc. The method has all the advantages of the photopyroelectric technique concerning the sample, i.e. small quantity, minimum preparation required, no need for optical quality, small cell with in situ measurement capability. However, the method is feasible only under restrictive experimental conditions, for optically and thermally thick samples with L=aL in the range 5-7. This condition can be met experimentally to some extent by choosing an appropriate value for the sample thickness L.

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