High temperature photoacoustic cell

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Recibido el 11 de febrero de 1997; aceptado el 5 de agosto de 1997

We have designed and constructed a metallic container to enclose two kinds of photoacoustic cells: the open photoacoustic cell (OPC) and the closed photoacoustic cell (CPC). It is a modified and simplified version that highly differs from those described by M.A. Siqueira *et al.*, *J. Appl. Phys.* **51** (3) (1980); J. Fernández *et al.*, *J. Appl. Phys. D* **16** (1983). This device gives an easy and direct operability, does not use any refrigerating system, and does not carry a long resonator acoustic tube. Our cell permits to make thermal diffusivity measurements with variations of temperature, and to find first order phase transitions by changing the temperature in solid samples, in the range from 0 to 100°C, using the photoacoustic effect (PAE).

Keywords: Photoacoustic cell

Se ha diseñado y construído una cavidad metálica para alojar dos tipos de celdas fotoacústicas: la celda abierta y la celda cerrada. Esta es una versión modificada y simplificada, que difiere significativamente de la celda descrita por M.A. Siqueira *et al.*, *J. Appl. Phys.* **51** (3) (1980); J. Fernández *et al.*, *J. Appl. Phys. D* **16** (1983). Una de sus principales ventajas es la de ofrecer una operabilidad más directa y sencilla, ya que esta celda no utiliza ningún sistema de refrigeración y no lleva tubo largo de resonancia acústica. Permite realizar medidas de difusividad térmica con variación de temperatura y encontrar la temperatura de fusión de cuerpos sólidos, cuyo intervalo de cambio de fase (sólido → líquido) se encuentre entre los valores de 0 hasta 100°C, utilizando el efecto fotoacústico (EFA).

Descriptores: Celda fotoacústica

PACS: 43.38.Zp

1. Introduction

Photoacoustic (PA) signal generation: basic principles. In many of the works related to thermal and optical spectroscopic characterization of materials, the PAE has shown great adaptability and high resolution as an easy technique that produces satisfactory results applied in solids, liquids, gels, powders, and biological and vegetable materials. The versatility as well as the potentiality of photoacoustic spectroscopy PAS as a material characterization technique has been reviewed by several authors [1, 2]. Apart from providing direct optical absorption spectra, the PA technique can also be used to perform depth profile analysis, characterization of thermal properties [3] as well as investigation of nonradiative relaxation processes [4]. In a typical PA experimental arrangement a sample enclosed in an airtight cell is exposed to a chopped light beam. Fig. 1. The resulting periodic heating of the sample is strongly dependent upon the interplay of three factors, namely, optical absorption coefficient at the incident radiation wavelenght, light-into-heat conversion efficiency, as well as heat difussion through the sample. Dependence of the PA signal on the optical absorption coefficient allows us to perform spectroscopy, whereas the fact that the signal is also dependent upon the light-into-heat conversion efficiency means that the detected signal is sensitive to the nonradiative deexcitation processes within the sample.

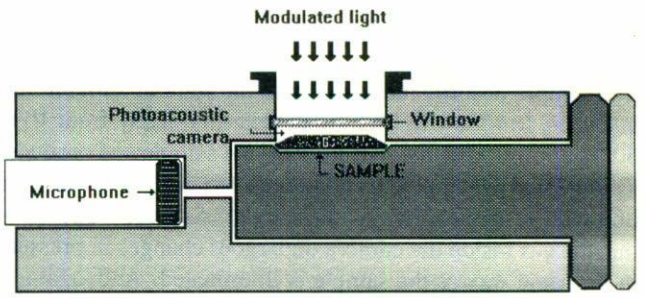

FIGURE 1. Cross section of the closed photoacoustic cell (CPA).

Finally, the fact that the PA signal depends on how the heat diffuses through the sample allows us to perform not only thermal characterization of the sample (*i.e.*, measurements of its thermal properties) but also to conduct thermal imaging. As a result of the periodic heating of the sample, the pressure in the cell oscillates at the chopping frequency and can be detected by a sensitive microphone coupled to the cell.

2. Types of PA Cells

There are two types of cells to perform PA spectroscopy: one named "closed", Fig. 1 [1] because the sample to be analized

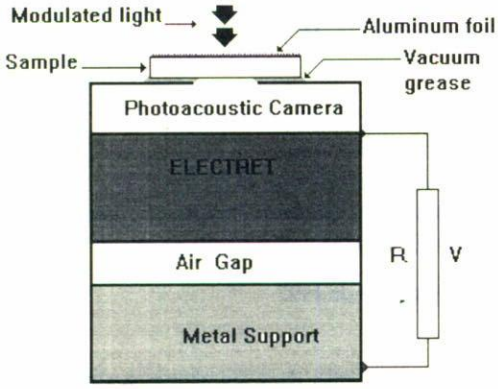

FIGURE 2. Cross section of the open photoacoustic cell (OPC).

is placed inside the so called camera, and the "open", Fig. 2, where the sample is outside of the cell, but is a main component of it [5]. Each cell has some specific intended uses:

2.1. Closed PA cell, CPA

The sample absorbs radiation from the light at different frequencies of the incident light, in the UV-visible-IR frequency regions, and at constant modulation frequency.

The sample could be optically opaque or transparent, and thermally thin or thick. Varying the temperature of the PA camera the sample inside it, undergoes changes in their optical and thermal properties, that can be detected by the PA effect.

2.2. Open PA cell, OPC

The sample absorbs radiation from the light at variable frequencies, from low to high frequencies, typically from 10 to 500Hz. This radiation goes through the sample and produces a modulated heat flux. The frequency variation limits the time of transit of the heat flux on the sample. As a consequence of this the gas inside the camera undergoes changes in pressure in the same way as the sample is illuminated. And, again, if the sample is heated by an external heat source the thermal and optical properties will change, and this can be detected by the OPC.

3. Theory

If a solid is placed in a gas filled cell and heated periodically in an intense light beam an acoustic signal is generated in the adjoining gas piston. The amplitude of the acoustic signal and its phase relation to the chopped light signal depend, among others, on the thermal diffusivity of the sample and should therefore be sensitive to any thermodynamic process occurring in the system. The measurements of the PAE were carried out with a non-dispersive arrangement something similar to that described in [6]. The sample support of

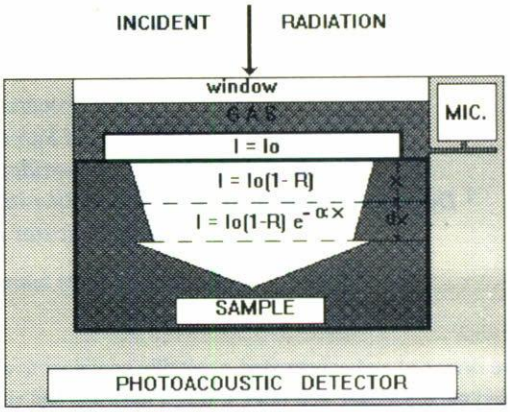

FIGURE 3. Scheme of the PA signal generation of the incident light beam deflections, after absorption and reflexion of light, by the sample.

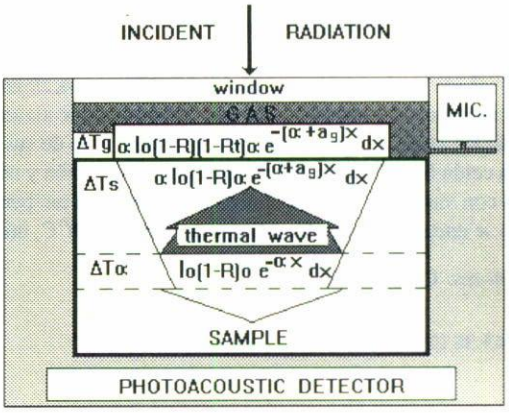

FIGURE 4. Unidimensional PA signal generation scheme that shows changes in temperature inside the sample and to the surrounding gas.

the PA cell was greatly modified in order to allow a variation of the sample temperature within the range 0 to 100°C where many of the solids are sensitive to processes such as a first order phase transition.

The temperature of the sample was controlled by a Cu-constantan thermocouple placed in very close contact with the sample at the bottom (in the CPC), and at the side of the sample (in the OPC) where the acoustic signal was detected by an electrect microphone. The photoacoustic signal generation sequence is schematically described in Figs. 3 and 4 [7]. The light source is an Oriel high intensity Xe lamp of 1000 W, chopped at 200 Hz, and its intensity is given by I_o, at a distance $x = 0$ on the sample surface. The intensity of the absorbed light decays to a value $I_o(1-R)e^{-\beta x}$ in a depth x due to the radiation absorption of the sample, that has an optical absorption coefficient β.

Each layer dx that absorbs radiation has an oscillatory heating of frequency f, and its temperature change ΔT is

$$\Delta T = I_o(1-R)\beta e^{-\beta x}dx,$$

as indicated in Fig. 4.

Each sample layer is a source of thermal waves. In the schematic unidimensional flow of energy showed in Fig. 4., the thermal waves propagate from the sample bulk to the surface that is irradiated, and to the adjacent gas.

During propagation the thermal waves decay in $a_s = (\pi f/\alpha)^{\frac{1}{2}}$ where α is the sample thermal diffusivity. Accordingly, the temperature oscillatory amplitude in the surface is proportional to

$$\Delta T_s \ \alpha \ I_o(1-R)\beta e^{(-\beta+a_s)x} dx$$

for a thermal wave generated at a distance x.

A fraction R_t of the thermal wave is reflected again inside the sample by the surface, and generates a thermal oscillating amplitude ΔT_g, equals to:

$$\Delta T_s = I_o(1-R)(1-R_t)\beta e^{(-\beta+a_s)x} dx.$$

As we have seen before, the PA signal is generated by the gas thermal expansion and is produced by all the contributions, ΔT_g. Each of these contributions comes from layers in which the light beam energy is absorbed. These layers are very close to the surface in a way that the amplitude of the thermal wave contributes to the signal, when it crosses the sample-gas interface.

The light and thermal wave decay coefficients β, and a_s, respectively, play an important role in the PA signal generation. The term $\beta e^{(-\beta+a_s)x}$, in the temperature oscillation equation, leads to a linear dependence of the PA signal on the light absorption when $\beta \ll a_s$.

With this condition a sample thickness $L = (1/a_s)$, below the surface, contributes with 63% $(= e^{-a_s L})$ of the signal, and the rest 37% comes from the sample deeper layers. The decay length of the thermal wave refers to the sample depth of the PA measurement.

The possibility to vary the frequency of the incident light onto the sample, makes the PA measurements a useful tool research, because when the chopped frequency increases, the length of thermal decay diminishes, and so the depth of optical absorption detected. It happens because the thermal wave length, $L = (1/a_s) = (\alpha/\pi f)^{\frac{1}{2}}$, permits to do so. Furthermore, from the sample thermal diffusivity α, and the modulation frequency f we can adjust $L = (\alpha/\pi f)^{\frac{1}{2}}$ in the region of interest selecting f.

When the optical absorption coefficient $\beta \ll a_s$, the PA signal increases linearly with β. When β increases there is greater absorption inside a layer of thickness L, the one that efficiently transports heat to the gas.

What does it mean when the PA signal drops? The PA signal loose linearity (saturation condition) when the radiation absorption is continuously increasing and results in a high absorption inside the layer. It produces a rise of heat very close to the surface, and the PA signal does not increase any more (full saturation). After full saturation some kind of characteristic spectra can be seen due to changes in the spectrum, in the $(1-R)$ term of the PA signal equation.

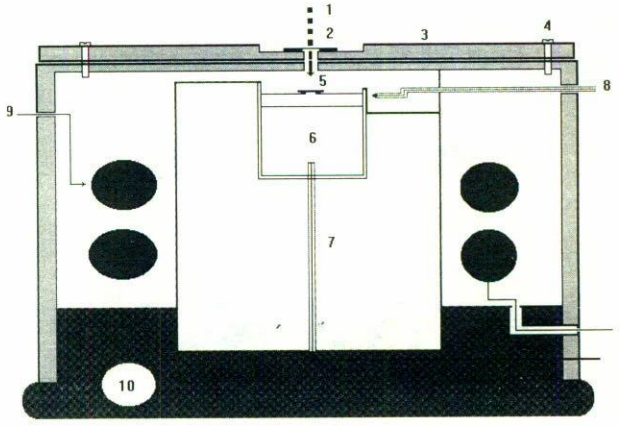

FIGURE 5. High temperature cavity for the OPC.

The air inside the camera reacts adiabatically [8] and the value of the sound wave speed does not vary. Absorption and diffusion of light by the sample creates the thermal pulse.

The acoustic pressure, in the Open PA Cell configuration is

$$\delta P = \left(\frac{\gamma P_o}{T_o}\right)\langle T_g\rangle;$$

γ, is the specific heats ratio (C_v/C_p). In the last equation $T_g > T_o$, we suppose some increment in pressure, and $\langle T_g\rangle$ is the temperature fluctuation spatially averaged.

4. Experiment

In order to detect first order phase transitions, all measurements were performed by changing continuously the temperature; the amplitude and phase angle of the PA signal were recorded both as function of time and temperature. During the melting of the solid, all the available heat is absorbed by this process, *i.e.*, the sample acts as a heat sink for those heat pulses that result from the dissipation of the radiation energy absorbed by Gallium, for instance. No thermal energy will be periodically transmitted from the sample to the surrounding gas during the melting process and as a consequence a collapse of the amplitude and a change of the phase angle is expected to occur. A number of PA tests are made at ambient temperature ($\approx 26°$C). Using the so called High Temperature PA Cell we can rise the temperature up to 100°C. The temperature rises caused by the incident radiation on the sample is a fraction of degree, so they are ignored.

Heating of the cavity is a slow process to insure thermodynamic stable conditions for each measurement. See Fig. 5 and Fig. 6 for the OPC and CPA Cell, respectively. It is possible to find suspected changes in the thermal and optical parameters of the sample, at these temperatures.

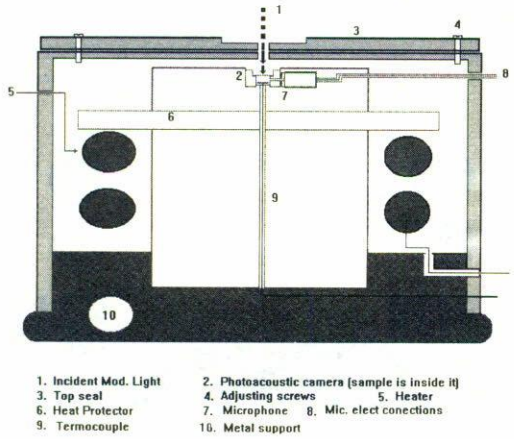

FIGURE 6. High temperature cavity for the CPA Cell.

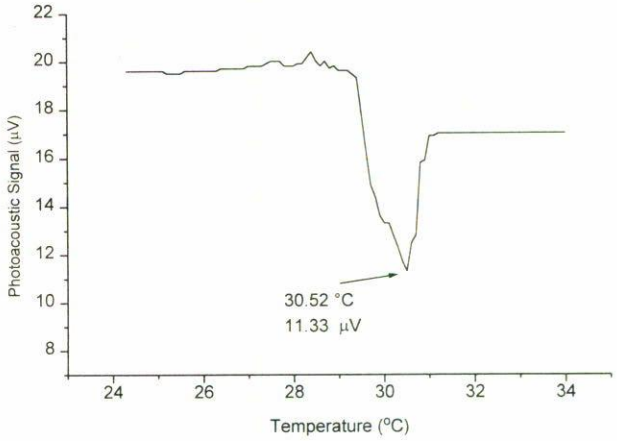

FIGURE 7. Plot of the first order phase transition temperature for gallium, in the CPA cell.

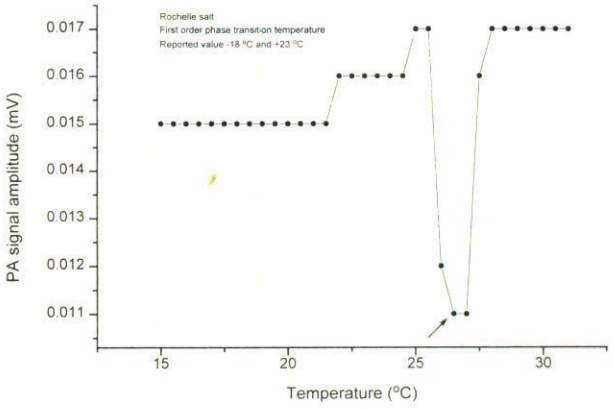

FIGURE 8. Plot of the first order phase transition temperature for Rochelle-salt, in the CPA cell, reported values $-18°C$ and $+23°C$.

The temperature of the sample was controlled by a termocouple placed in contact with the sample at the bottom of the cell. We use a Systron (VA) regulator to properly adjust voltages. The CPA cell, inmersed in the high temperature cavity, has a thermodynamic behaviour similar to the OPC. Just we know that the OPC is highly recommended to evaluate the thermal diffusivity of many materials, and performs a kind of "depth profile" of the sample, accordingly with the frequency variations of the incident radiation.

In a general way the CPA cell can achieve an absorption process in the whole lamp radiation spectrum. The sample absorbs more or less radiation accordingly with the incident frequency, from the Ultraviolet to the Infrared, and we can perform investigations related with changes in thermal properties, and perform first order phase transitions research in solids. Figure 7 shows the temperature variation of the PA signal of gallium, in the region around the melting point (reported value, 29.8°C), and Fig. 8, shows that of the Rochelle salt.

Conclusions

In this study we have described two types of photoacoustic cells which can be used to find first order phase transitions, and thermal diffusivities measurements in solids with variations of temperature, by changing the temperature of the samples, in the range from 0 to 100°C.

Both, the OPC and CPA cell were designed, made and tested in our laboratory using non expensive materials. The metallic container of these two cells greatly differs from those reported in [4], and [5] in that it does not use any refrigerating system and any long resonator acoustic tube to connect the microphone to the cell. By improving the data adquisition, we are actually attempt to use this model to detect glasslike phase transition in tortilla corn flour.

1. H. Vargas and L.C.M. Miranda, *Phys. Rep.* **161** (1988) 43.
2. A.C. Tam, *Rev. Mod. Phys.* **58** No.2 (1986).
3. M.J. Adams and G.F. Kirkbright, *Analyst* **102** (1977) 678.
4. G.A.R. Lima, M.L. Baesso, Z.P. Arguello, E.C. da Silva, H. Vargas, and L.C.M. Miranda, *Phys. Rev. B.* **36** (1987) 9812.
5. M.V. Marquezini, N. Cella, A.M. Mansanares, H. Vargas, and L.C.M. Miranda, *Meas. Sci. Tech* **2** (1991).
6. M.A. Siqueira, C.C. Ghizoni, J.I. Vargas, E.A. Menezes, H. Vargas, and L.C.M. Miranda, *J. Appl. Phys.* **51** (1980) 3.
7. J.F. McClelland, R.W. Jones, S. Luo, and L.M. Seaverson, *A Practical Guide to FTIR PA Spectroscopy Proper Sample Handle with Today's IR Instruments*, (CRC Press, 1980).
8. A. Rosencwaig and A. Gersho, *J. Appl. Phys* **47** (1976) 1.
9. J. Fernandez, J. Etxeberría, M.J. Tello, and A. López Echarri, *J. Phys. D: Appl. Phys.* **16** (1983) 269.
10. A. Torres-Filho, N.F. Leite, L.C.M. Miranda, N. Cella, and H. Vargas, *J. Appl. Phys.* **66** (1989) 1.