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Photothermal radiometry

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Abstract

This work describes the fundamentals and the technique's configuration of infrared photothermal radiometry, a non-invasive and non-destructive technique of outstanding importance in the group of techniques called photothermal techniques. It presents a revision of some thermal radiation concepts and the phenomenon of photothermal conversion as the basis of photothermal techniques, particularly the infrared photothermal radiometry technique. This work focuses on university professors and students interested in the development and applications of science and photothermal techniques.

Keywords: Photothermal radiometry; Photothermal conversion; Photothermal techniques; Thermal radiation.

Resumen

En este trabajo se describen los fundamentos y la configuración de la técnica de la radiometría fototérmica infrarroja, técnica no invasiva y no destructiva de destacada importancia dentro del grupo de las técnicas denominadas técnicas fototérmicas. Se presenta una revisión de algunos conceptos de radiación térmica y del fenómeno de conversión fototérmica como base de las técnicas fototérmicas, en particular de la técnica de radiometría fototérmica infrarroja. Este trabajo está dirigido a profesores y estudiantes universitarios interesados en el desarrollo y aplicaciones de la ciencia y las técnicas fototérmicas.

Palabras clave: Radiometría fototérmica; Conversión fototérmica; Técnicas fototérmicas; Radiación térmica.

I. INTRODUCTION

Photothermal radiometry (PTR) is part of the photothermal (PT) technique family, based on generating and detecting a medium's thermal response [1, 2]. Nordal and Kanstad first mentioned the photothermal radiometry technique in 1979 [3] when they presented it as a method for the spectroscopic analysis of semi-solid materials. The thermal response generation is based on the photothermal conversion phenomenon, which involves converting light energy into heat, raising the medium's internal energy, and consequently increasing its temperature.

Using a 1-D model for the heat flow and neglecting the heat lost through the lateral walls of the studied sample and convection heat lossest in 1981 Santos y Miranda [4] reported a quantitative derivation of an expression for the PTR signal modulated in both frequency and time domain. Salazar et al. in 2011 [5] reported the solution of the 1D heat diffusion equation with non-adiabatic boundary conditions. They concluded that heat losses at low frequencies affect the front and rear surface temperatures. In 2014, Suarez et al. [6] reported an analysis of the heat transfer through a homogeneous and isotropic solid excited by a square periodic light beam using PTR and numerical simulation by the finite element method. Considering convection and radiation heat losses to determine the thermal diffusivity of some low thermal conductivity materials, Martínez et al. in 2015 [7] obtained a theoretical model for the PT signal in the frequency domain on a 1D configuration, showing that convection and radiation heat losses must be considered for poor heat conductors at low frequencies. In 2019, Wong et al. [8] reported analytical and numerical models for the PTR technique, considering 2D heat diffusion for homogeneous finite solid samples, including radiation and convection heat losses through their surfaces. This paper is a divulgation work that aims to give an overview of the basics of the photothermal radiometry technique that can be useful for teachers and students taking their first contact with this subject. For this reason, the first part includes a review of some useful topics to better understanding the main topic of the paper.

II. PHOTOTHERMAL CONVERSION

PT conversion refers to the process of converting light energy into heat. When light energy hits the surface of a material, part of it is reflected, another is transmitted, and the material absorbs the rest (see Fig. 1). In non-luminescent materials, the absorbed energy is fully transformed into heat, propagating through the material and increasing its internal energy. Due to its temperature, the material's surface emits thermal radiation which –at room temperature-, mainly corresponds to the infrared region of the electromagnetic spectra, shifting to the visible region as the temperature increases. A surface's absorptance, commonly denoted by *a*, is the ratio between the absorbed and incident light energies. Absorptance depends upon the surface temperature and wavelength of incident radiation. The absorptance is dimensionless, and its value ranges from 0 to 1.

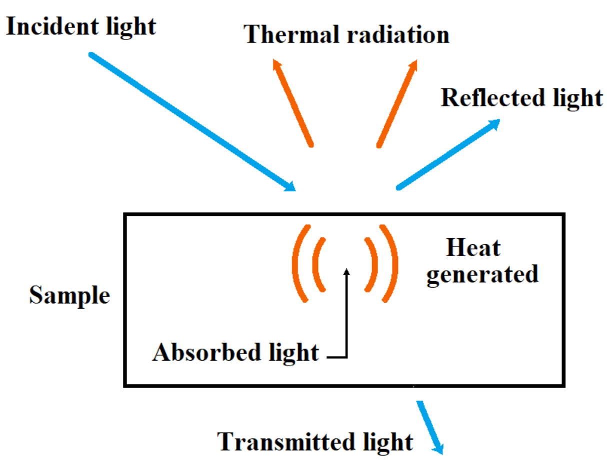

FIGURE 1. Photothermal conversion.

PT conversion is commonly classified into three mechanisms: plasmonic localized heating, non-radiative relaxation, and thermal vibration [9,11]. This conversion is typically achieved using materials that can absorb light efficiently and transform it into thermal energy (heat). PT conversion efficiency depends on the material properties and the wavelength of the incident light. Materials with high absorption coefficients in the desired spectral range are often chosen for effective PT conversion, which is utilized for different purposes, including solar energy harvesting, PT therapy, water purification, and heat-assisted magnetic recording (HAMR), among others [12].

III. THERMAL RADIATION

Electromagnetic (EM) radiation is the EM energy emitted by matter due to changes in atoms and molecules' electronic, vibrational, and rotational states. Thermal radiation is that part of EM radiation whose wavelength ranges from ~ 200 nm to ~ 1 mm. It includes the near and middle UV (from 200 to 400 nm), the VIS (from 400 to 700 nm), and IR (from 700 nm to 1 mm) regions of the EM spectrum (Fig. 2). All surfaces emit it if their temperature is above absolute zero. It differs from other forms of EM radiation, such as gamma rays, X-rays, microwaves, and radio and TV waves, unrelated to temperature. The infrared region is divided into five regions: Near-infrared (wavelengths from 0.75 to 1.4 micrometers), short-wavelength infrared (wavelengths from 1.4 to 3 micrometers), medium infrared (wavelengths from 3 to 8 micrometers), long-wavelength infrared (wavelengths from 8 to 15 micrometers), and far infrared (wavelengths from 15 to 1000 micrometers).

Thermal radiation is a form of heat transfer different from conduction and convection. It can be transferred between two surfaces at different temperatures. It does not require a medium to propagate and can even spread through free space. It is how we perceive the heat coming from the Sun. Thermal radiation is a volumetric phenomenon. However, it is usually considered a surface phenomenon in opaque solids. The radiation emitted from the interior of these solids does not reach the surface, and the radiation incident from the outside is commonly absorbed within a few microns from its surface [13].

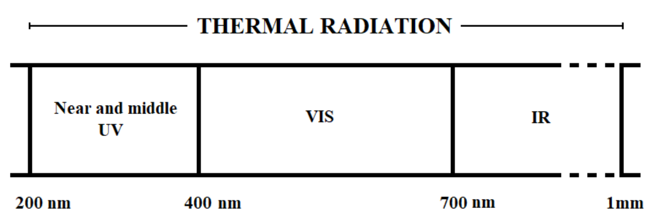

FIGURE 2. Thermal radiation region of the EM spectrum.

The flux of light energy, at a wavelength λ, per unit area leaving a surface is called spectral **exitance**, denoted by M_λ and its unit W/m^2. At room temperature (~300K), the maximum value of M_λ occurs around 10 μm (long-wavelength infrared region), and it moves to shorter wavelengths with increasing temperature. The total energy emitted per unit area by a surface is given by the Stefan-Boltzmann law [14, 15]:

$$M = \varepsilon \sigma T^4, \quad (1)$$

where $\sigma = 5.6697 \times 10^{-8}$ $Wm^{-2}K^{-4}$ is the Stefan-Boltzmann constant and ε is called either the **emittance** or the **emissivity** of the surface, whose value is in the range $0 \leq \varepsilon \leq 1$, where 0 indicates perfect reflectivity (no emission) and 1 indicates perfect blackbody (BB) behavior (complete emission). Emissivity measures of how closely a surface approximates a BB, for which $\varepsilon = 1$. A BB is an idealized concept in physics that refers to an object that completely absorbs all EM radiation incident upon it without reflecting or transmitting any of it. Furthermore, a BB is also a perfect radiation emitter, efficiently emitting radiation in all wavelengths according to its temperature [13].

Kirchhoff's law states that emissivity and the absorptivity of a surface at a given temperature and wavelength are equal. A surface with high absorbance for a given λ in the VIS region at room temperature will also have a high emittance to that λ; it will emit radiation almost like a BB at that temperature and that λ, which will be insignificant [14, 15].

IV. PHOTOTHERMAL RADIOMETRY

Fig. 3 shows a scheme of the PTR technique in a rear detection configuration. The monochromatic light beam emitted from a laser is intensity modulated. The light beam is then deflected by a flat mirror and directed perpendicularly on the underside of the sample. The light energy absorbed by the sample's surface is transformed in heat by PT conversion, which propagates toward the other side of the sample, which emit thermal radiation. A parabolic mirror reflects part of the radiation toward a second parabolic mirror, which reflects it and focuses perpendicularly toward the entrance of the IR detector. The sample and the first parabolic mirror can be placed inside a sealed cell with the air evacuated to rule out the effects of the thermal convection mechanism. This allows the evolution of the temperature of the sample's rear face to be measured as a function of time for the established modulation frequency. When the thermal radiation detected is that emitted by the incidence face, the technique is called the PTR technique in a front detection configuration. The experimental scheme changes but has a similar configuration.

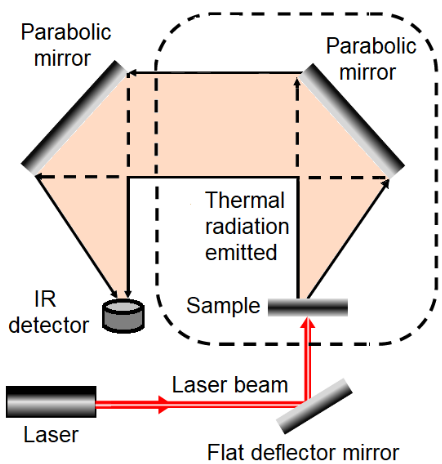

FIGURE 3. Photothermal radiometry technique scheme.

The generated heat flux density at any point at depth x from the sample incidence surface due to the absorption of light energy of wavelength λ and intensity I_0 [W/m^2] modulated at a frequency $\omega = 2\pi f$ can be expressed as:

$$\phi_g = \frac{\eta(1-R_\lambda)\beta I_0}{2}(1+e^{i\omega t})e^{-\beta x}, \qquad (2)$$

were β and R_λ are the sample absorption and reflection coefficients at a wavelength λ, respectively, and η is the light energy into heat conversion efficiency [1, 2]. If the sample is homogenous and isotropic, the heat diffusion equation models the heat transport as follows:

$$\nabla^2 \Delta T - \alpha^{-1}\frac{\partial}{\partial t}\Delta T = 0, \qquad (3)$$

where α is the thermal diffusivity, t is the time, and $\Delta T = T - T_0$ is the sample temperature variation from room temperature T_0. The solution of Eq. (3) is constrained by the following initial and boundary conditions:

$$\lim_{t\to 0}\Delta T = 0, \qquad \phi_{cond} + \phi_{conv} + \phi_{rad}|_{S_i} = \phi_i, \qquad (4)$$

were ϕ_i denotes the heat flux through the *ith* sample surface S_i, ϕ_{cond} is the conductive heat flux, given by the Fourier heat conduction, ϕ_{conv} represents the convective heat flux, provided by Newton's law of cooling, and ϕ_{rad} is the thermal radiation flux, described by Stefan Boltzmann law, Eq. (1).

Solving the problem given by Eqs. 3 and 4 allows for determining the optical and thermal properties involved. However, obtaining the complete solution is not easy. In references [4, 5, 6, 7, 8], particular solutions are reported under certain approximations. Among the most important are reducing the problem to one dimension, disregarding the edges effect, and omitting the thermal convection mechanism. As an alternative to the complexity of the problem, numerical analysis using the finite element method has been used to obtain particular solutions closer to physical reality. References [6] and [8] report the results.

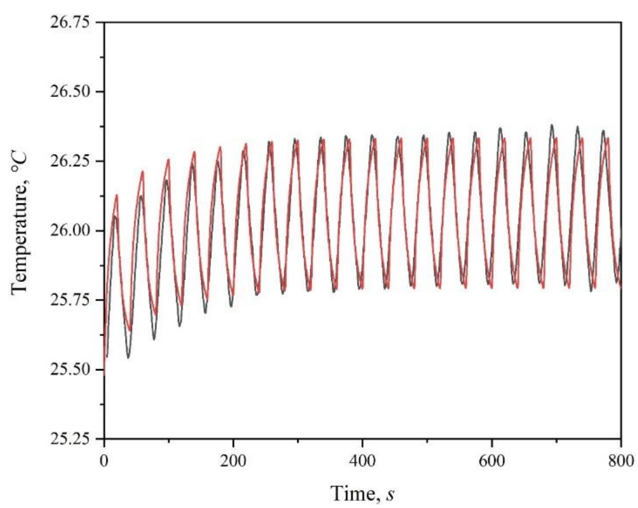

FIGURE 4. The experimental (black line) and numerical simulation (red line) of temperature evolution over time for a Teflon sample measured by PTR technique.

Fig. 4 shows a graph of temperature vs. time measured with a PTR technique in a rear detection configuration for a Teflon sample. It used a 25 mHz modulation frequency, 3 mW laser beam power, and 1.00×10^{-5} torr vacuum. The black line represents the experimental result, and the red one is the numerical simulation using the finite element method. The rem arkable agreement between both results demonstrates the potential of numerical analysis for the analysis of experimental results obtained using the PTR technique in determining materials' optical and thermal properties.

V. CONCLUSIONS

We presented the fundamentals of the infrared photothermal radiometry technique, a non-invasive and non-destructive technique of great value in the photothermal characterization of materials, in a descriptive and accessible way to university professors and students. However, a bibliography is provided that can be consulted by those who wish to know more about a specific topic. We consider that the topics covered in this work may be helpful to non-specialists who are interested in photothermal conversion and its applications, a topic that has grown significantly in recent years.

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