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Photopyroelectric Microscopy of Porous Ceramics

J. J. A. Flores-Cuautle · A. Cruz-Orea · E. Suaste-Gomez

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Abstract Porous ceramics has capital importance in a wide variety of applications as in the case of gas and humidity sensors; in these applications an important fact is that the ceramic structure must insure intercommunication between one side and the other. Several techniques has been used in order to have information about the ceramic structure; among these, photopyroelectric (PPE) spectroscopy is an option to be used in porous ceramic structure characterization. In PPE microscopy, an image of the sample thermal response can be obtained by 2D scanning of a focused beam across a surface, which yields localized information on the possible presence of subsurface features which is an important property of porous ceramics. Recently porous ceramics based on barium titanate mixed with silicon dioxide have been developed to be used as gas and humidity sensors. By the use of PPE microscopy, porous ceramics were analyzed with two different resolutions as a result of the variation of the light modulation frequency. The light modulation frequency is related not only to scanning depth, but also to thermal scale length which gives us the minimum sample length that can be studied and is also related with its thermal diffusion length.

Keywords Photopyroelectric technique · Porous ceramic · Thermal scale length

1 Introduction

Photothermal (PT) methods have been developed to evaluate thermal and optical properties of materials. Various configurations can provide direct optical absorption spectra,

J. J. A. Flores-Cuautle (✉) · E. Suaste-Gomez
Department of Electrical Engineering, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Av. IPN No. 2508, San Pedro Zacatenco, DF, México
e-mail: jjflores@cinvestav.mx

A. Cruz-Orea
Department of Physics, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, A.P. 14-740, México, DF, México

characterization of thermal properties, and evaluation of nonradiative relaxation processes [1–3]. One PT technique is photopyroelectric (PPE) spectroscopy which uses a pyroelectric material as a sensor. Two main configurations are used for thermal characterizations of materials by the PPE technique, namely, the back and inverse configurations. In the back configuration detection, a laser beam, modulated in frequency and controlled power, is focused on the sample. The result is periodic temperature variations generated at the sample surface, which result in thermal waves that travel through the sample which can be reflected and scattered as a result of the features beneath the sample surface. Features that reflect and scatter thermal waves are related with those regions that present differences in any of its thermal parameters (density ρ, specific heat c, and thermal conductivity k [4]). By the use of the PPE technique, it is possible to obtain the amplitude and phase lag (related to heating light modulation) of the thermal waves in the sample. Pyroelectric signals contain information about thermal properties as well as the internal structure of a material. Consider a focused, modulated light beam impinging on a sample on one side, and a pyroelectric detector with good thermal contact on the other side. By x–y scanning of the modulated beam on the sample, it is possible to get images correlated with sample thermal properties, in a technique known as PPE microscopy.

There are different studies which deal with the use of thermal techniques to obtain thermal images of inhomogeneous structures like ion-implanted regions in semiconductors [5], electronic circuits [6,7], or plant leaves [8]; in these cases the inhomogeneous thermal properties give an idea of structure variations. In the case of ferroelectric ceramics, porosity represents a failing, even though there are cases where the porosity is the main concern among the applications for a given ceramic. Porous ceramics have important applications in gas and humidity sensors, and filtering for industrial, medical, and diagnostic devices [9–11]; thus, the ceramic structure must insure intercommunication between both sides.

In PPE microscopy an image of the sample thermal response can be obtained by 2D scanning of a focused beam across the sample surface, which yields localized information on the possible presence of subsurface features, which is an important property of porous ceramics. Recently porous ceramics based on barium titanate and quartz have been developed [12,13]; in this study those ceramics were analyzed by means of PPE microscopy. Different modulation frequencies were used for the same sample, with the same resolution in displacement. Results reveal a strong relationship between the light modulation frequency and thermal resolution in the image.

2 Experimental

2.1 Sample Preparation

Barium titanate-based porous ceramics were created from the mixed oxide method [14,15]. Barium titanate ($BaTiO_3$ 99.9 % + purity) and quartz (SiO_2 99 % + purity) were mixed at 95/5 ratio portions, with an initial grain size of 5 μm for $BaTiO_3$ and 25 μm for SiO_2, and membrane disks were formed. Afterward, these disks with 2 mm thickness were partially sintered in a programmable oven at 1100 °C. The relative density was calculated and the porosity p was found by the equation [16]: $p = 1 - \rho_p/\rho_t$ where ρ_p is the porous ceramic density and ρ_t is the theoretical ceramic density. In order to perform the thermal analysis of the sample, the thickness was reduced to 500 μm; finally thermal images were obtained by the PPE microscopy technique [17].

2.2 PPE Experimental Setup

Figure 1 shows the PPE experimental setup. The excitation source is a fiber coupled laser diode, at 650 nm wavelength (BWTEK T55-369), modulated in intensity with the frequency controlled by the internal oscillator of a digital signal processing (DSP) lock-in amplifier. By the use of microscope objective lenses, the laser beam was focused on the ceramic surface.

The PPE cell is mounted on an x–y translation stage, driven by stepping motors. A PC was used in order to control the x–y translation and also to record the lock-in amplifier signal. The amplitude and phase of every point of the scanned sample were recorded. Two different resolutions in the thermal scale length (TSL) were obtained by varying the light modulation frequency.

The thermal diffusion length (μ) in the thermal wave theory is an important quantity: this parameter is defined as the distance that thermal waves travel inside the sample (in homogeneous materials) before the variation of temperature decays 63 %. The expression for this parameter is defined as [17]

$$\mu = \sqrt{\alpha/(\pi f)},$$

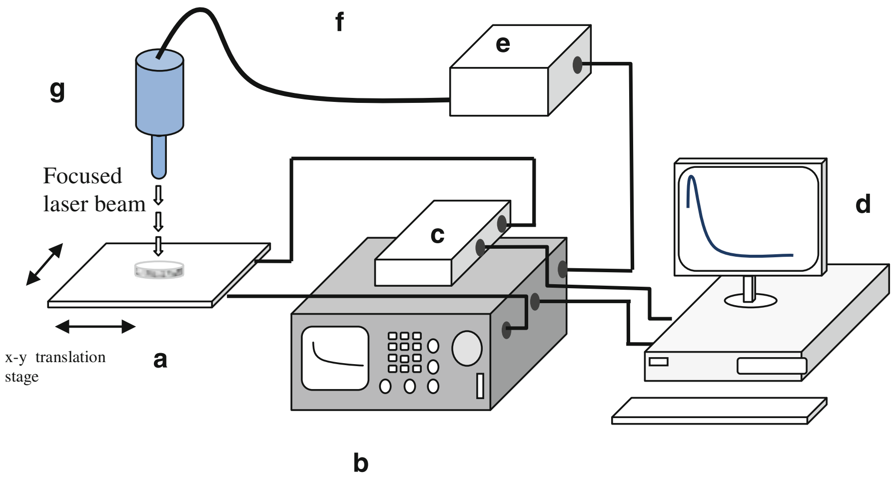

Fig. 1 Experimental setup used to obtain PT images of porous ceramic: (a) PPE cell, (b) lock-in amplifier, (c) x–y driver, (d) computer, (e) laser diode, (f) optical fiber, and (g) objective lenses

where α is the thermal diffusivity and f is the light modulation frequency. Based on this definition, it is possible to calculate how deep thermal images would be obtained; however, since α is a continuous function of material properties, it becomes a discontinuous function of localization for heterogeneous materials [18–20]. Even though it is possible to obtain useful information by using a modulation frequency that insures a thermally thick sample and μ far from the TSL of a typical size of the ceramic pore-grain (L_{pg}), by using frequency modulation between these limits, it is possible to obtain images related to material features.

3 Results and Discussion

Images at different modulation frequencies were obtained. Figure 2a shows an optical image of the ceramic. In Fig. 2b, it is possible to see the thermal image in the same region obtained from the signal amplitude at a light modulation frequency of 4 Hz. Since the reported thermal-diffusivity value for barium titanate ceramics is $\alpha = 0.014\ \text{cm}^2 \cdot \text{s}^{-1}$ [21], the thermal diffusion length calculated at 4 Hz is 337 μm which is less than the sample thickness; but, it is not possible to see ceramic features that can be observed with an optical microscope.

The PPE signal strongly depends on the thermal-diffusion length and ceramic pore-grain size as Fig. 2 shows. When $\mu > L_{pg}$ thermal waves respond neither to ceramic pore-grain boundaries nor to ceramic thermal features. This means that the sample can be treated as a homogeneous material. On the other hand when $\mu < L_{pg}$, then the pyroelectric signal is principally determined by the pore-grain boundary and the ceramic thermal properties, as can be seen in Fig. 3.

Due to the fact that the thermal diffusivities of SiO_2 and $BaTiO_3$ are relatively close ($\alpha_{SiO_2} = 0.045\ \text{cm}^2 \cdot \text{s}^{-1}$ to $0.061\ \text{cm}^2 \cdot \text{s}^{-1}$ and $\alpha_{BaTiO_3} = 0.14\ \text{cm}^2 \cdot \text{s}^{-1}$) [21,22], it is hard to see differences in the recorded thermal images, only the pores, which contain air with a relatively high thermal diffusivity ($\alpha_{air} = 0.21\ \text{cm}^2 \cdot \text{s}^{-1}$) [23], are observed.

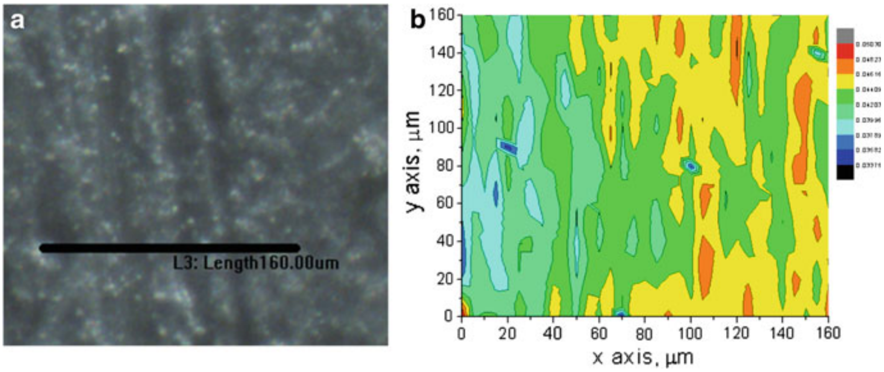

Fig. 2 (a) $BaTiO_3$–SiO_2 porous ceramic optical image with 160 μm *scale bar* and (b) thermal image obtained with the signal amplitude at 4 Hz for a scanned area of $160 \times 160\ \mu\text{m}^2$

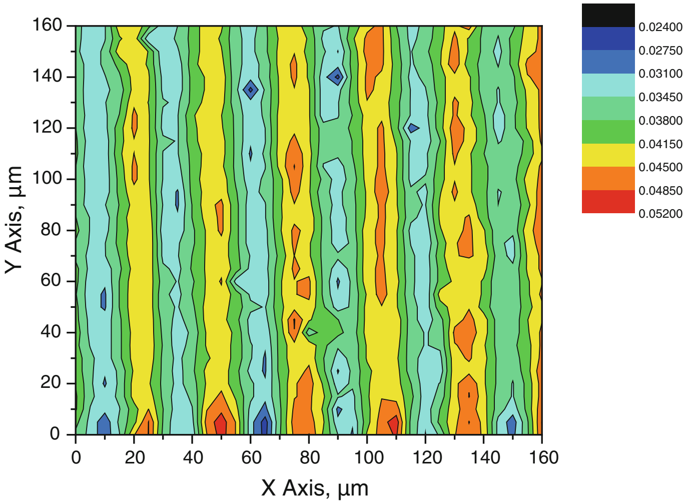

Fig. 3 $BaTiO_3$–SiO_2 porous ceramic thermal image obtained with the signal amplitude at 20 Hz laser modulation for a scanned area of 160 × 160 μm^2

4 Conclusions

There is an important relation in the modulation frequency, not only to the scanning depth, but also to the TSL which gives us the minimum sample length that can be studied and which is related to the thermal diffusion length. If the resultant images at low frequency reveal small variations in thermal properties due to the large TSL, then the material could be regarded as homogeneous and thermal images do not show detailed variation in ceramic structure. If images at high modulation frequencies show local variations in thermal properties and pores, then the ceramic structure near the sample surface can be seen; however, it is not possible to distinguish between silicon dioxide and barium titanate regions because the thermal diffusivity of both are relatively close when compared to the thermal diffusivity of air in the pores. The recorded thermal image thus highlights the pore regions with large PPE signal amplitudes.

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