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On the use of photoacoustic technique for monitoring the thermal properties of lanthanum strontium cobalt ferrite–yttria stabilized zirconia two-layer systems

Leonardo Mota [a], Marcelo Gomes da Silva [a], Vanessa Pereira de Souza [a], Helion Vargas [a,*], Valtency Ferreira Guimarães [b], Herval Ramos Paes Júnior [b]

[a] Laboratório de Ciências Físicas, Centro de Ciência e Tecnologia, Universidade Estadual do Norte Fluminense Darcy Ribeiro, Avenida Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil
[b] Laboratório de Materiais Avançados, Centro de Ciência e Tecnologia, Universidade Estadual do Norte Fluminense Darcy Ribeiro, Avenida Alberto Lamego, 2000, 28013-602, Campos dos Goytacazes, RJ, Brazil

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ABSTRACT

In this work, lanthanum strontium cobalt ferrite ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) films deposited by spray-pyrolysis onto commercial yttria stabilized zirconia substrates were investigated by photothermal spectroscopy. It is shown that by using the thermal–electrical analogy model it is possible to obtain the thermal properties of two-layer composite systems simultaneously, without the need to spread them, and thus to evaluate the thermal mismatch between the substrate and the deposited film. The thermal diffusivity of the 8YSZ substrate was found to be 6.6×10^{-3} cm^2s^{-1}, whereas for the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ films it ranged between 0.47 and 9.26×10^{-4} cm^2s^{-1}. We have found that for film thickness beyond 3.06 μm the thermal expansion coefficient becomes relevant, indicating that the optimum film deposition time lies between 10 and 20 min.

1. Introduction

During the last 10 years, several efforts have been made worldwide toward the development of solid oxide fuel cells (SOFC). Usually, these materials are multilayered structures consisting of ceramics and metals, suitable to be operated at temperatures from 600 to 1000 °C [1–6]. Recent studies claim that lanthanum strontium cobalt ferrite (LSCF) perovskite is a good candidate to be used either as the cathode or as the anode of SOFC's [7,8]. However a drawback arises, i.e., the appearance of thermal mismatches between electrodes and electrolytes, that is due to their different thermal expansion coefficients [9].

Currently, two methods have been applied to evaluate the thermal expansion coefficients of perovskite-based ceramic materials, i.e., dilatometry and X-ray diffraction [10]. Other approaches to investigate their thermophysical properties (specific heat, c, thermal conductivity, k, thermal diffusivity, α, and thermal expansion coefficient, α_T) are based on the photoacoustic (PA) and related photothermal techniques [11–14].

Moreover, up to date, there is no information on the thermal properties of LSCF films on yttria stabilized zirconia ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$/8YSZ) two-layer system. In order to fill this lack of information, the open photoacoustic cell and a photothermal rise method under continuous light illumination [15] are used as a tool to investigate c, k, α and α_T of such materials.

2. Experimental details

2.1. Sample preparation

The LSCF films were deposited onto a commercial yttria stabilized zirconia using the spray-pyrolysis technique previously reported by several researchers [6]. The precursory solutions were prepared with $La(NO_3)_3.6H_2O$, $SrCl_2.6H_2O$, $Co(NO_3)_3.6H_2O$ and $Fe(NO)_3.9H_2O$ (Aldrich™) diluted in water and alcohol in the 1:3 ratios, resulting in a 0.03 mol L^{-1} solution concentration. The film depositions occurred at 400 °C, using a carrier gas pressure of 0.15 MPa, and 2.0 mL min^{-1} flow rate. The deposition time ranged from 10 to 40 min. Afterwards the samples were annealed in air at 800 °C during 60 min. Scanning electron microscopy (SEM) results indicated that the film thicknesses ranged between 3.06 μm and 14.7 μm.

2.2. Simultaneous measurements of thermal diffusivity and thermal expansion coefficient

The OPC experimental setup consisted of an argon laser (Omnichrome), operating at 488 nm wavelength and a mechanical chopper (EG&G Instruments, model 651). The sample was mounted directly on the top of a cylindrical electret microphone (the front air chamber

* Corresponding author. Tel.: +55 22 2739 7044; fax: +55 22 2739 7177.
E-mail address: vargas@uenf.br (H. Vargas).

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adjacent to the metallized electret diaphragm plays the role of the usual gas chamber of conventional PA spectroscopy). A detailed discussion of the OPC detection is given elsewhere [15], and the experimental configuration used in this work is depicted in Fig. 1. The signal was detected using a lock-in amplifier (Perkin Elmer Instruments, model 5210), which was interfaced with a computer through a GPIB (General Purpose Interface Bus) port to record the PA amplitude and phase as a function of the chopper modulation frequency.

The theoretical model used to fit the data was developed by assuming that the LSCF sample is optically opaque ($l_\beta \ll l_s$) and thermally thick ($\mu_s \ll l_s$), where l_β is the optical penetration depth, μ_s the thermal diffusion length and l_s the sample thickness. By solving the thermal diffusion and the thermoelastic equations, the microphone output voltage can be written as [16]:

$$V = \left[V_0 \frac{j\omega RC}{1+j\omega RC}\frac{\beta I_0}{T_0 l_g \sigma_g k_s \sigma_s}\right] \times \left[\frac{1-\exp\left(-l_g\sigma_g\right)}{\sinh(l_s\sigma_s)} - \frac{3\Re^4\alpha_T T_0\sqrt{\alpha_s}}{2\Re_c^2 l_s^2\sqrt{\alpha_g}} \times \frac{\frac{l_s\sigma_s}{2}\sinh(l_s\sigma_s)-\cosh(l_s\sigma_s)+1}{l_s\sigma_s\sinh(l_s\sigma_s)}\right]\exp(j\omega t), \quad (1)$$

where I_0 is the intensity of the incident radiation, V_0 is a constant dependent on the microphone characteristics, RC is the microphone response time; l_i, k_i and α_i are, respectively, length, thermal conductivity and thermal diffusivity of the material i. T_0 is the room temperature, β is the surface absorption coefficient and $\sigma_i = (1+j)a_i$ is the thermal diffusion coefficient with $a_i = \sqrt{\frac{\pi f}{\alpha_i}}$. The subscript i denotes the sample (s) and the gas (g) media. $\Re$ represents the support radius of the sample and $\Re_c$ is the radius of the PA chamber in front of the microphone diaphragm.

The first term in Eq. (1) is due to the thermal diffusion from the periodically heated sample to the air inside the photoacoustic chamber, whereas the second one represents the sample thermal expansion contribution. By fitting the experimental PA amplitude or phase as a function of the modulation frequency, we can readily obtain α and α_T of any two-layer system, by leaving them as adjustable parameters.

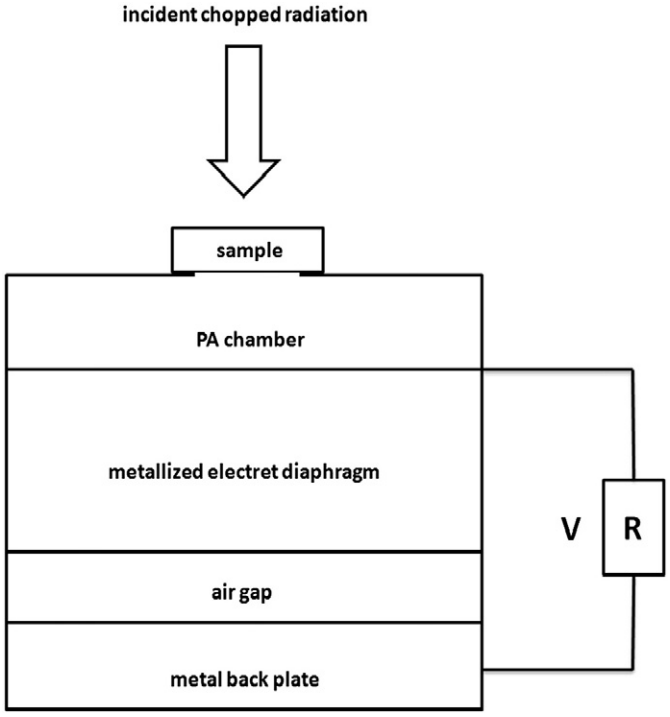

Fig. 1. Schematic cross-section of the open photoacoustic cell.

2.3. Measurements of specific heat capacity

The specific heat capacity (ρc) was measured using the photothermal technique of temperature evolution induced by continuous illumination of the specimen in vacuum (ρ is the sample density). In order to get the sample emissivity equals to unit, i.e., $\varepsilon = 1$ its surface was painted black. A T-type thermocouple thin-wire was connected on the sample backside, whose output was measured as a function of time by using a multimeter (Hewlett Packard 34401A) attached to a computer through a GPIB port. Then it was placed inside a vacuum-sealed Dewar. The sample front surface was illuminated by a focused argon laser beam through an optical glass window in the Dewar. The temperature evolution was monitored from the room temperature up to the sample temperature saturation, obeying Eq. (2). Then excitation laser beam was turned off, and the temperature variation was recorded till it turned back to room temperature, following Eq. (3) [15,17,18].

$$\Delta T\uparrow = \frac{I_0}{H}\left[1-\exp\left(\frac{-t}{\tau}\right)\right] \quad (2)$$

$$\Delta T\downarrow = \frac{I_0}{H}\left[\exp\left(\frac{-t}{\tau}\right)\right] \quad (3)$$

Here, I_0 is the incident light intensity, $\tau = \frac{l_s\rho c}{2H}$ is the thermal relaxation time, $H = 4\sigma T_0^3$ is the heat transfer coefficient, where σ is the Stefan–Boltzmann constant, T_0 is the room temperature and t is the time variable.

3. Results and discussion

The OPC configuration is very sensitive to the sample surface radiation absorption. Once yttria stabilized zirconia seemed to be transparent to the laser beam (what does not happen to the films), it was necessary to take care to prevent that heating light to reach the

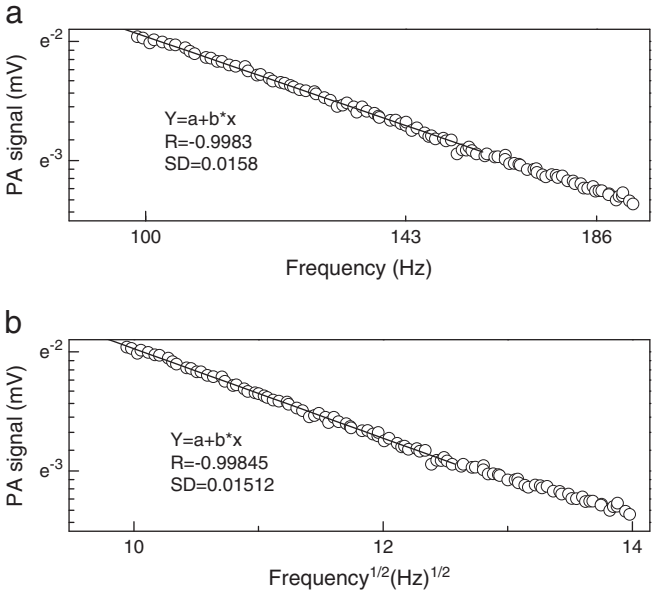

Fig. 2. (a) Photoacoustic amplitude as a function of the modulation frequency. The fit indicates a thermal diffusion as the main contribution for the PA signal generation, characterized by a typical exponential behavior. (b) Photoacoustic amplitude as a function of the frequency square root. The solid line represents the best fit according to Eq. (4).