Alternative photopyroelectric detection method of phase transitions in ferroelectric materials

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An alternative photopyroelectric (PPE) configuration for phase transitions investigations in ferroelectric materials, used as pyroelectric sensors in a PPE detection cell, is proposed. The method is based on the temperature scan of the phase of the complex PPE signal. The technique uses the "front" PPE detection configuration, at two different chopping frequencies, in order to derive a dynamic thermal parameter, the thermal diffusivity. The suitability of the method was proved by measurements of the behaviour of the thermal diffusivity of tryglycine sulphate (TGS) close to the Curie point (49^0C) and for different external electric fields (ranging from 0 to 10 kV/m).

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1. Introduction

In principle, in the PPE method the temperature variation of a sample exposed to a modulated radiation is measured with a pyroelectric sensor, situated in intimate thermal contact with the sample [1, 2]. During last decades, two PPE detection configurations, "back" and "front", respectively, have been widely used for calorimetric purposes.

In the "back" configuration, a modulated light impinges on the front surface of a sample, and a pyroelectric sensor, situated in good thermal contact with the sample's rear side, measures the heat developed in the sample due to the absorption of radiation [3, 4]. In the "front" configuration, the radiation impinges on the front surface of the sensor, and the sample, in good thermal contact with its rear side, acts as a heat sink [5, 6].

The thermal parameters resulting directly from PPE measurements are usually the "fundamental" ones (present in the thermal diffusion equation and its solution): the thermal diffusivity and effusivity. By combining the information contained in the amplitude and phase of the complex PPE signal, one can obtain, not only the values of the thermal parameters, but their variation with temperature, composition, etc., as well. Thus, certain associated processes, as phase transitions, can be investigated by PPE method [3, 4, 6-12].

On the other hand, the thermal parameters in ferroelectric liquid crystals are anisotropic and it is important to measure them when the liquid crystals are in the ferroelectric phase. However, several types of liquid crystals become ferroelectric only shaped between two metalized glass surfaces chemically treated. For such geometry the classical calorimetric methods are difficult to be used for thermal characterization.

In this short communication we report on a new alternative approach for measurement of thermal diffusivity and phase transitions detection, suitable for such type of ferroelectric materials. The method is based on the information (contained in the phase of the PPE signal) collected from a ferroelectric material, used as pyroelectric sensor in a PPE detection cell. Based on a classical pyroelectric material, TGS, the paper wants to prove that the method is suitable for such an application.

2. Theory

A typical PPE detection cell, in a "front" configuration, consists of four layers: the incident layer, air (g), the pyroelectric sensor (p), the substrate (s) and again air (g) as backing. For such a PPE detection cell the normalised phase "Θ" of the PPE signal is given by [13-14]:

$$\Theta = \arctan\frac{(1+R_{sp})\sin(a_p L_p)e^{-a_p L_p}}{1-(1+R_{sp})\cos(a_p L_p)e^{-a_p L_p}} \tag{1}$$

where:

$$R_{sp} = (b_{sp}-1)/(b_{sp}+1);$$
$$b_{sp} = e_s / e_p;\ \ \sigma_s = (1+i)a_s; \tag{2}$$
$$\mu = \left(\frac{2\alpha}{\omega}\right)^{\frac{1}{2}}$$

In Eqs. (1-2) R_{sp} represents the reflection coefficient of the thermal wave at the 'sp' interface, ω is the angular chopping frequency of the incident radiation, L_p is the geometrical thickness of the pyroelectric sensor and σ and a are the complex thermal diffusion coefficient and the reciprocal of the thermal diffusion length ($a = 1/\mu$), α and e are the thermal diffusivity and effusivity, respectively.

We must emphasize that Eq. (1) is valid only for opaque pyroelectric sensor and for thermally thick substrate, as stated in [13]. The normalization signal was obtained with empty, directly irradiated sensor.

When performing measurements at two different chopping frequencies we obtain:

$$\frac{\tan(\Theta_1)}{\tan(\Theta_2)} = \frac{\exp(-L_p a_{p1})[\cos(L_P a_{p1})+\sin(L_P a_{p1})\tan(\Theta_1)]}{\exp(-L_p a_{p2})[\cos(L_P a_{p2})+\sin(L_P a_{p2})\tan(\Theta_2)]} \quad (3)$$

with $a_{p1,2} = (\pi f_{1,2}/\alpha_p)^{1/2}$. Eq. (3) indicates that one can obtain the thermal diffusivity of the pyroelectric material, used as sensor in the detection cell, by performing two measurements at two different chopping frequencies, providing the geometrical thickness of the sensor is known.

3. Experimental

The experimental set-up is a typical one for PPE calorimetry in the "front" configuration and it was presented in detail in [3] but some relevant details are presented further on. An Ar^+ laser (Spectra Physics) with stabilized power output at $\lambda = 514$ nm, modulated (at 3Hz and 12Hz, respectively) with an acousto-optical modulator (Intra Action), was used as radiation source. The lower face of a 500 μm thick TGS single crystalline pyroelectric sensor, provided with opaque Au electrodes on both faces, was directly irradiated. Silicon oil, with well known thermal properties, was selected as substrate; it filled the space inside a plastic ring (5 mm thick) situated on the rear electrical contact of the pyroelectric sensor. The sensor-substrate assembly was introduced in a thermostat [3]. A controlled temperature variation in the 42 – 51 ^{0}C range with a 50 mK/min step was performed. The PPE signal was processed with a digital lock-in amplifier (Stanford SR830). The temperature control and data acquisition were performed with adequate software. The typical signal to noise ratio was better than 10^3.

An external electric field having an intensity of 0 kV/m, 1 kV/m, 6 kV/m and 10 kV/m, provided by the internal generator of the lock-in amplifier, was applied on the electrodes of the TGS sensor.

4. Results

Typical results, obtained for the phase of the PPE signal for a 500 μm thick TGS single crystal, with silicon oil as substrate (together with the normalization signal - directly irradiated empty sensor) are displayed in Fig. 1. The external electric field was 6 kV/m.

The critical behaviour of the thermal diffusivity for three values of the external electric field, as obtained from Eq.(3), is displayed in Fig. 3.

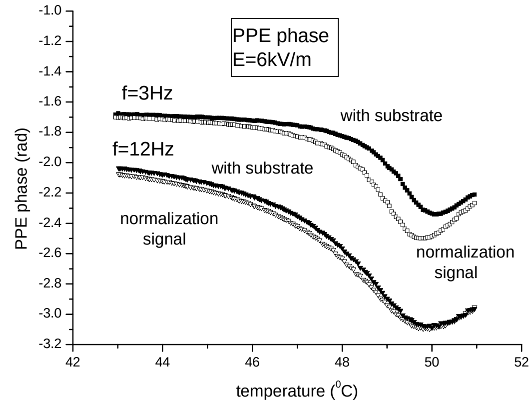

Fig.1. Temperature scans of the phase of the PPE signal, for a 500μm thick TGS single crystal, around the ferroelectric Curie temperature, for 3Hz and 12Hz chopping frequencies, and an external electric field of 6kV/m.

Fig. 2 presents the normalized phases of the PPE signal for the two frequencies.

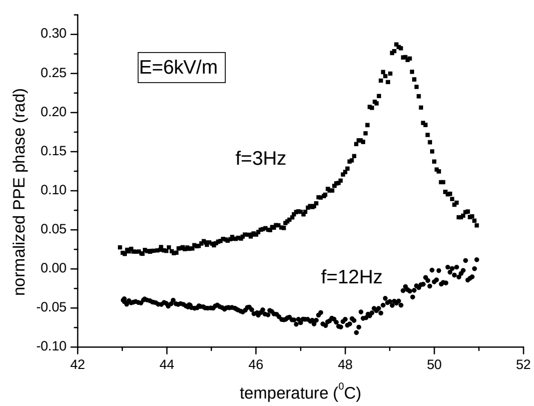

Fig. 2. Same as Fig.1, but for the normalized phase.

Examining Fig. 3 we notice the typical behavior (critical slowing down) of thermal diffusivity for a second order phase transition. The external electric field has the well known influence on the phase transition: it increases the Curie temperature and enlarges the critical region. The values of the Curie points are in good agreement with those obtained from the direct measurement of the PPE amplitude (Fig.4).

5. Conclusions

The PPE calorimetry, in the “front” detection configuration, was used to measure the critical behaviour of the thermal diffusivity of a ferroelectric (TGS single crystal) material.

In a traditional PPE experiment the information on the sample properties is collected and processed. In our approach we collect the information on the thermal properties of the pyroelectric sensor, and this is the main novel aspect of the detection scheme described in this short note.

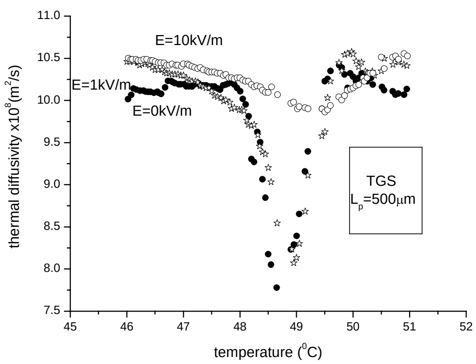

Fig.3. Critical behaviour of the thermal diffusivity of TGS for 0 kV/m (empty rhombs); 1 kV/m (stars) and 10 kV/m (filled rhombs).

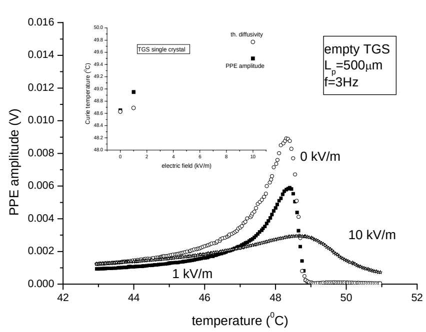

Fig.4. Typical behaviour of the amplitude of the PPE signal for empty TGS sensor and for three values of the external electric field. Insertion: The Curie temperature vs. electric field, as obtained from thermal diffusivity and PPE amplitude (inflection point).

We selected the phase of the PPE signal (and not the amplitude) as source of information due to the well known advantages: the phase is independent on the fluctuations of the incident radiation and the signal to noise ratio is higher. Measurements at two different chopping frequencies and calibration procedures were necessary in order to eliminate the instrumental factors and to obtain a mathematical equation depending on solely one thermal parameter, which is the thermal diffusivity.

The applied external electric field has a typical influence on the critical region of the para-ferroelectric phase transition of TGS: both the Curie temperature and the thickness of the critical region slightly increase with increasing value of the electric field.

The results obtained for the value of the thermal diffusivity of TGS and for the value of the Curie temperatures are in good agreement with data reported in the literature and obtained by other techniques [15, 16]

Finally, we must emphasize that the method speculates the fact that the investigated ferroelectric material is pyroelectric as well. The method was used on a classical TGS crystal, but, as mentioned in the Introduction, it appears to be a suitable alternative in studying the thermal properties of the ferroelectric liquid crystals, when the ferroelectric state is imposed by a given layered geometry.

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