Photothermal dielectric spectroscopy: A novel technique for the determination of the dielectric, pyroelectric and thermal properties of thin dielectric films.

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Abstract

A novel technique is described which combines dielectric measurements with a time- and frequency dependent photothermal excitation.

The sample, a thin metallized film, is placed in an aluminium ring which serves as a heat sink. At different temperatures both the dielectric and pyroelectric spectra are obtained by applying sequentially an ac-voltage and a modulated heat flux to the sample.

The thermal properties are assessed by the application of a local laser heating; the resulting increase in the mean sample temperature is recorded by high precision capacitance measurements at a fixed frequency. From the equilibrium increment $\Delta C(T)$ and the temperature dependence of the capacitance $C(T)$ we can find the temperature increment $\Delta T(T)$ and thus the thermal conductivity, while from the transient response $\Delta C(T,t)$ the thermal diffusivity can be obtained. Combination of all information further yields the pyroelectric coefficient and the specific heat.

Experiments on PVDF were performed at temperatures from -60 to 110° C to show the capabilities of the new method.

1. Introduction

The design and use of pyroelectric sensors as radiation detectors or for microcalorimetry requires reliable data of the pyroelectric, dielectric and thermal properties of the sensor material over a wide temperature and frequency range. Therefore, a measurement arrangement is desirable, that enables the assessment of the thermal and electrical properties of a material under the same experimental conditions.

For the determination of the thermal and pyroelectric properties of thin films several techniques have been introduced which apply thermal waves generated by pulsed or continuously modulated (laser) radiation, see e.g. [1-3].

The essential problem in thermal measurements is the accurate measurement of the small change in the sample temperature in response to a transient or sinusoidal heating. A technique using a thin-film bolometer evaporated onto the pyroelectric active sample is described in [1].

Here we present a method which yields all the required properties of a pyroelectric sample by performing two dielectric measurements and a LMM-measurement [2,3]. Its most prominent feature is that no temperature sensor is needed for the measurement of the sample temperature; the dielectric constant of the material is used as a temperature probe.

The procedure consists of a set of three measurements which are performed at each

temperature:

- 1° measurement of the dielectric response, preferably at several frequencies,
- 2° thermal pulse experiment with a time-dependent recording of the change in permittivity at a fixed frequency, and
- 3° measurement of the pyroelectric current at several frequencies.

2. Sample geometry and experimental set-up

A film of the pyroelectric material (here PVDF-electrets of 40 μ m) is fixed between aluminum rings with an inner diameter of 4mm (cf. Fig.1).

Fig.1 Sample arrangement. The parabolic radial temperature-profile is also shown.

The ring acts as a circular heat sink, the temperature T_0 of which is measured with a platinum resistor in a 4-wire configuration. A defocused laser beam, which provides a nearly homogeneous radiation across the exposed area, heats the sample either with a constant intensity Q_0 (thermal pulse experiment) or with a modulated intensity $Q_0 + Q_m \cos \omega t$ (LIMM).

Fig.2 Main components of the equipment. The electro-mechanically operated beam switch is used for the thermal pulse experiment.

A scheme of the experimental set-up is shown in Fig.2. The sample holder is placed in an evacuated, optical cryostat. The sample can be connected to a current-amplifier (Keithley model 428P), or to a precision RLC meter (HP 4284A, General Radio model 1689) by means of a programmable switch.

The combination current-amplifier + digital signal processing lock-in amplifier (Stanford Research model SR 850) allows pyroelectric measurements from 10^{-3} Hz to 10^5 Hz and is described elsewhere [3,4]. The dielectric response measurements we performed at frequencies from 20 Hz to 10^5 Hz.

3. Theory

3.1 Radial temperature distribution

Assuming a homogeneous heat flow Q_0 , an absorption coefficient η , and lateral heat

conduction as the only heat loss mechanism one can readily find the steady-state radial temperature increase $\Delta T(r)$ [2, 6]

$$\Delta T(r) = \frac{\eta Q_0}{4\pi r_0^2 k_s L_s} (r_0^2 - r^2) \quad (1)$$

Since the electrodes also take part in the heat conduction we have introduced in Eqn.1 a planar thermal conductivity k_s for the sample that accounts for the heat conduction of the film k_f and of the electrodes k_e by taking $k_s = k_f + 2k_e L_e / L_f$, in which L denotes the thickness. Since the 40 μm PVDF-film was metallized with 40nm aluminum, the heat conduction via the electrodes is of the same order as that of the PVDF, but this can now easily be accounted for in the data analysis.

Attention has been paid to the sample dimensions in order to minimize the radiation losses. Because these are proportional to the area and the emission coefficient of the sample, the heated area should be as small as possible while, in order to increase the heat conduction, the sample should be as thick as possible. On the other hand, the diameter/thickness ratio must be $L_s \ll r_0$ in order to fulfill the radial heat flow approximation.

3.2 Heat pulse experiment

After a time interval that exceeds the thermal time constant τ_{th} , the step in the heat flow Q_0 causes a rise in the mean temperature of the sample from T_0 to $T_0 + \Delta T$. ΔT can be derived by integrating eqn.(1) with respect to r :

$$\Delta \bar{T}(T_0) = \frac{\eta Q_0}{8\pi k_s L_s} \quad (2)$$

As a consequence of this stepwise increase, the permittivity of the sample will change from $\epsilon'(T_0)$ to $\epsilon'(T_0 + \Delta T) = \epsilon'(T_0) + \Delta\epsilon'$. After averaging the temperature coefficient of the permittivity $\partial\epsilon'/\partial T$ between T_0 and $T_0 + \Delta T$ one can calculate the temperature increment from

$$\Delta \bar{T}(T_0) = \left[\Delta\epsilon' \frac{\partial T}{\partial \epsilon'} \right]_{T_0} \quad (3)$$

The derivative $\partial\epsilon'/\partial T$ can be obtained from the dielectric response (experiment 1°) or from the step-experiment (2°) itself after completing the temperature scan.

Next, the change in thermal conductivity k_s with temperature can be found by combining eqs.(2) and (3).

3.3 Pyroelectric response

For a homogeneously polarized free-standing film of thickness L_s illuminated with the periodical intensity Q_m the pyroelectric current is given by [1,2,5,6],

$$I_-(\omega) = \frac{\eta Q_m p}{c\rho L_s} \frac{i\omega\tau_{th}}{1 + i\omega\tau_{th}} \quad (4)$$

where p is the pyroelectric coefficient, c the specific heat, ρ the density and τ_{th} the thermal time constant. τ_{th} is determined by the radial heat loss to the heat sink. From the tangent of the phase shift of the pyroelectric current we can easily obtain the thermal time constant:

$$\tan \delta = \frac{Im(I_{-})}{Re(I_{-})} = \frac{1}{\omega \tau_{ph}} \quad (5)$$

Next the the (radial) thermal diffusivity $\alpha_s = k_s/cp$ can be calculated from τ_{ph} using

$$\alpha_s = \frac{r_0^2}{8\tau_{ph}} \quad (6)$$

which holds for this particular radial heat conduction model [5,6].

It is advisable to check the applicability of eqn.(4) at a frequency where the phase shift can be measured accurately to make sure that indeed the assumed thermal model is valid.

Further, the pyroelectric coefficient p can be calculated when the ratio Q_o/Q_m is known. Division of eqn.(4) by (2) yields for $\omega \tau_{ph} > 1$

$$p \approx \frac{I_{-}}{\Delta T} \frac{Q_o}{Q_m} \frac{1}{8\pi\alpha_s} \quad (7)$$

By inspection of eqn.(1) to (7) one sees, that one additional parameter is required in order to get the absolute values of k_s and cp . Therefore knowledge of one of the parameters k_s , cp , ηQ_s or ηQ_m at a certain temperature is necessary. This can e.g. easily be done by means of a DSC measurement at room temperature.

4. Results and discussion

The three sequential experiments executed at each temperature were mentioned in Sect.1. Although not strictly needed, knowledge about the dielectric spectrum $\epsilon^*(f,T)$ is useful for the assignment of the loss-peaks emerging in the other experimental results.

However, for a proper LIMM-analysis [4] of pyroelectric samples containing an inhomogeneous polarization knowledge of $\epsilon^*(f,T)$ is a necessity.

4.1 Thermal pulse experiment

Fig.3 shows the temporal dielectric response $\epsilon'(t)$ to a heat pulse (lasting about 1 min) for various temperatures between -54° and 104°C. All curves plotted are corrected by their linear baseline. The equilibrium value of $\Delta\epsilon'$, depicted by the solid line, is shown in Fig.4 together with the calculated derivative $\partial\epsilon'/\partial T$. Both curves show one pronounced peak corresponding to the glass transition of PVDF, a typical crystalline relaxation around 50°C and an upswing at about 90°C indicating the onset of the premelting of the crystallites.

Fig.3 Time-dependence of the change in permittivity during a thermal pulse experiment recorded at 1kHz at about 5°C intervals.

Fig.4 $\Delta\epsilon(T)$ from the pulse experiment and $\partial\epsilon'/\partial T$ calculated from ϵ' vs. T at 1kHz.

Fig.5 Calculated temperature increment and normalized thermal conductivity of the PVDF-sample.

Fig.5 shows the temperature increments $\Delta\bar{T}$ derived from the data given in Fig.4 using eqn.(3). Note, that the inverse temperature increment, which according to eqn.2 is proportional to the thermal conductivity k_s , still contains the electrode conduction.

The temperature dependence of the pyroelectric current at a frequency well above the thermal cut-off frequency ($f=12.8\text{Hz}$) is shown in Fig.6. The temperature dependence is characterized by the glass-transition (change in the slope at -30°C) and by a progressive increase from 60°C onwards.

From the low frequency part of the pyroelectric spectra the $\tan\delta$ was determined. We found at all temperatures a slope of 1 at 0.1Hz, within an error of 4% indicating that radiation losses are indeed negligible. The calculated thermal diffusivity α_s is given Fig.7. Finally, the (normalized) specific heat was calculated using $c_p=k_s/\alpha_s$, the result is also given in Fig.7. In contrast to k_s and α_s the specific heat does not contain a significant contribution from the metal electrodes.

Fig.6 Measured real component of the pyroelectric current at 12.8Hz and $\tan\delta = \text{Im}\{L_{-}\}/\text{Re}\{L_{-}\}$ obtained at 0.1Hz.

Fig.7 Lateral thermal diffusivity α_s calculated from $\tan\delta(T)$ using eqs.(5) and (6). Additionally, the normalized specific heat $c_p(T)/c_p(25^\circ\text{C})$ is plotted.

5. Conclusions and recommendations

A three-step procedure has been described for the combined measurement of the dielectric, pyroelectric and thermal properties of polymeric materials. The features of this technique have been demonstrated for an electret film of PVDF.

Although tested for a circular geometry, this method can also be applied for rectangular samples in order to determine the thermal properties in specific directions.

The capacitance-based temperature sensing technique might also be used for nonpyroelectric samples. In this case one can evaluate the thermal diffusivity from the decay-part of the thermal pulse experiment by fitting it with an exponential.

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