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SIMULTANEOUS MEASUREMENT OF THERMAL PROPERTIES IN FERROELECTRIC CRYSTALS

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Simultaneous measurement of the influence of the electric field on specific heat, thermal conductivity and pyroelectric coefficient is described as a summary of previous papers. From these coefficients, which are determined by means of a flux calorimeter, the behaviour of other properties, such as thermal diffusivity and electrocaloric coefficient, is deduced.

The data are compared with the findings obtained by other authors with traditional methods.

For the optimum technological use of a ferroelectric material, it is necessary to know the behaviour of the coefficients which characterize that material. Some of these coefficients are easily measured, while others must be deduced from the measured data.

The behaviour of a crystal, especially when it is doped, depends on the way it has been grown, the thermal treatment, etc. Thus, it is difficult to compare published data in order to deduce the behaviour of other properties. This is due to the fact that the data have usually been obtained on different specimens and under different conditions.

In several recent papers [1–4] we have developed new methods of measurement with a flux calorimeter especially designed for the study of single-crystals under an applied electric field. This allows us to study one sample and to determine the influence of temperature and electric field on several coefficients, such as specific heat, pyroelectric coefficient, thermal conductivity and electrical susceptibility.

If these measurements are conveniently programmed and obtained under similar conditions on only one specimen, then we are able to obtain information about the behaviour of other parameters, such as pyroelectric figure of merit [5], electrocaloric coefficient [6], thermal diffusivity, etc.

In this paper we compile the most relevant points of these methods, compare some results with the findings of other authors, and discuss the advantages of our methods for the simultaneous measurement of thermophysical properties in ferroelectric materials.

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Flux calorimetry

Let us consider a sample placed between two identical fluxmeters (Fig. 1). Each fluxmeter has n thermocouples placed in series. (In our case [4] there are 48 cromel-constantan thermocouples, each 7 mm long and 0.25 mm in diameter.) The junctions of one side are attached to a silver plate serving as an electrode. A heater (an electric resistance whose thermal capacity is negligible with respect to that of the fluxmeter) is attached to the junctions and to the plate.

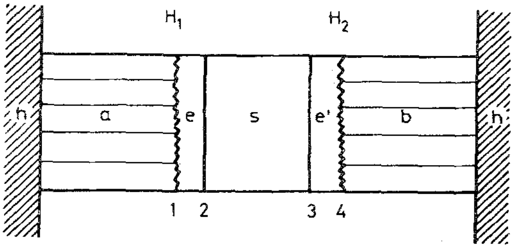

Fig. 1. Diagram of the thermopile: a,b) fluxmeters, e,e*) electrodes, s) sample, H_1, H_2) heaters and and h) heat sink

The junctions of the other side are attached to a heat sink (calorimetric block), which keeps the temperature of these junctions constant.

When heat is dissipated by the heaters or in the sample, a heat flux passes through the thermocouples, producing an e.m.f. proportional to this heat flux [7]. Heat is measured by integration of this e.m.f. The process of flux calorimetry measurement is generally started from a steady-state or equilibrium state and a final equilibrium or steady-state is obtained. Further, in the case of linear fluxmeters such as the one represented in Fig. 1, each medium forming the thermopile can be considered a solid bounded by two parallel planes.

Simultaneous measurement of thermophysical properties

To develop a new method of simultaneous measurement of thermophysical properties, we have studied [3] the linear heat conduction in a solid bounded by two parallel planes ($x=x_1$ and $x=x_2$) when unidimensional conduction is considered.

Through the use of the Laplace transform of the differential equation of heat conduction, the expressions for the heats Q_1 and Q_2 that have passed through each plane from one initial steady-state ($t=0$) to another steady-state ($t=t_1$) have been obtained:

$$\begin{aligned} Q_1 &= \int_0^{t_1} \frac{\theta_1(t)-\theta_2(t)}{R}\,\mathrm{d}t + C\left[\frac{\theta_1(t_1)-\theta_1(0)}{3} + \frac{\theta_2(t_1)-\theta_2(0)}{6}\right] - \frac{Q_0}{2} \\ Q_2 &= \int_0^{t_1} \frac{\theta_1(t)-\theta_2(t)}{R}\,\mathrm{d}t - C\left[\frac{\theta_1(t_1)-\theta_1(0)}{6} + \frac{\theta_2(t_1)-\theta_2(0)}{3}\right] + \frac{Q_0}{2} \end{aligned} \qquad (1)$$

where $\theta_1(t)$ and $\theta_2(t)$ are the temperatures at x_1 and x_2, respectively, C and R are the thermal capacity and thermal resistance of the solid, and Q_0 is the heat that has been uniformly dissipated in the solid between $t=0$ and $t=t_1$.

If we apply these expressions at the boundaries between the media forming the thermopile (Fig. 1) and start from different initial steady-states, we are able to determine the specific heat and thermal conductivity of the sample as follows:

a) To measure specific heat, we start from the steady-state obtained when the same power θ is dissipated by both heaters (Fig. 1). The temperature of the sample is then uniform. At the initial time the power is cut off, and the thermal equilibrium with the block is obtained at time t_1. The total e.m.f. given by both fluxmeters $(V(t) = V_a(t)+V_b(t))$ is measured as a function of time between 0 and t_1.

Using expressions (1) at the boundaries 1, 2, 3 and 4 in Fig. 1, we find [3] that the thermal capacity of the sample can be obtained from:

$$C = \frac{2n\varepsilon}{\alpha}(A - A^\circ) \qquad A = \int_0^{t_1} \frac{V(t)}{V^\circ}\,\mathrm{d}t$$

where ε is the thermoelectric power of the thermocouples, $V^\circ = V(t=0)$ is the initial e.m.f., $\alpha = V^\circ/W$ is the sensitivity of the fluxmeters and A° is the corresponding value of A when the experiment is carried out without sample and with both fluxmeters in thermal contact.

b) The measurement of thermal conductivity is begun from the initial steady-state obtained when a constant power is dissipated only by the heater, H_1, and thus there is a temperature gradient in the sample. The initial e.m.f. V_b^0 of the fluxmeter where heat is not dissipated is measured. At the initial time the power is cut off, and the e.m.f. $V(t)$ is measured up to time t_1, when the thermal equilibrium with the block is obtained.

The following expression is calculated:

$$S_1 = \int_0^{t_1} \frac{V(t)}{V_b^\circ}\,\mathrm{d}t$$

If both fluxmeters are completely identical. further experiments are not needed. Since there is always a slight difference between them. it is necessary to repeat this experiment with dissipation by only the other heater H_2. The following expression is calculated:

$$S_2 = \int_0^{t_1} \frac{V(t)}{V_a^\circ} dt$$

If expressions (1) are applied at the boundaries 1, 2, 3 and 4 in Fig. 1 in both cases, we find [3] that the thermal resistance of the sample can be calculated by:

$$R = \frac{\alpha}{2n\varepsilon}\left(\frac{S_1+S_2}{A} - \frac{S_1^0+S_2^0}{A^\circ}\right)$$

where S_1^0 and S_2^0 are the corresponding values of S_1 and S_2 when the experiments are carried out without sample.

Another possibility for the determination of the specific heat with the same device is the measurement of the time constant τ of the assembly. When a heat pulse is dissipated, the e.m.f. of the thermopile can be expressed [1] as a sum of exponentials. Because of the linearity for the fluxmeter and the materials used in its construction, in our case the largest time constant τ of these exponentials is approximately ten times as big as the following one. Thus, the return to experimental zero corresponds to a single exponential whose time constant τ depends on the thermal capacity of the sample, although a slight dependence on its thermal resistance is also found [1, 3].

This method is advantageous, because it is not necessary to obtain an initial steady-state. Thus, with respect to the above method, only half the time is needed to carry out the experiment. Nevertheless, this method needs a calibration with samples of known thermophysical properties, and can be used only when the thermal conductivity of the sample is constant.

The arrangement of the sample between electrodes allows us to apply a uniform electric field to the sample. Thus, we can measure the influence of electric field on specific heat and thermal conductivity. In addition, we can measure the adiabatic electrical susceptibility with a conventional capacitance bridge.

The measurement of the pyroelectric coefficient p is carried out by means of a calorimetric method as follows:

Let us consider the sample in thermal equilibrium with the block at temperature T and subjected to a uniform electric field E_1. When the electric field is suddenly increased up to a value E_2, an adiabatic change of temperature is produced in the sample (electrocaloric effect). This is because the electric relaxation time is much less than the thermal one. The sample then returns to thermal equilibrium with the block through the exchange of an amount of heat Q, which is measured.

Using several thermodynamic relations, we show [2] that the pyroelectric coefficient p is given by:

$$p = \frac{Q}{vT(E_2 - E_1)}$$

where v is the volume of the sample.

Experimental results

To examine the precision of these methods, we have measured the well-studied TGS ferroelectric crystal. Figure 2 depicts the specific heat c versus temperature. Our data for the non-singular part and specific heat jump (1.31 and 0.32 Jg^{-1} K^{-1}, respectively) [4] agree with those obtained by Taraskin [8].

Figure 3 shows the thermal conductivity k data; the value 0.55 $J(smK)^{-1}$ at 323 K agrees with the value obtained by Hellwig [9]. Figure 3 also presents the thermal diffusivity h obtained from the above data.

The influence of the electric field on the specific heat c_E in TGS was previously measured by Taraskin [8] using an adiabatic calorimeter with an applied field up to 150 V/cm.

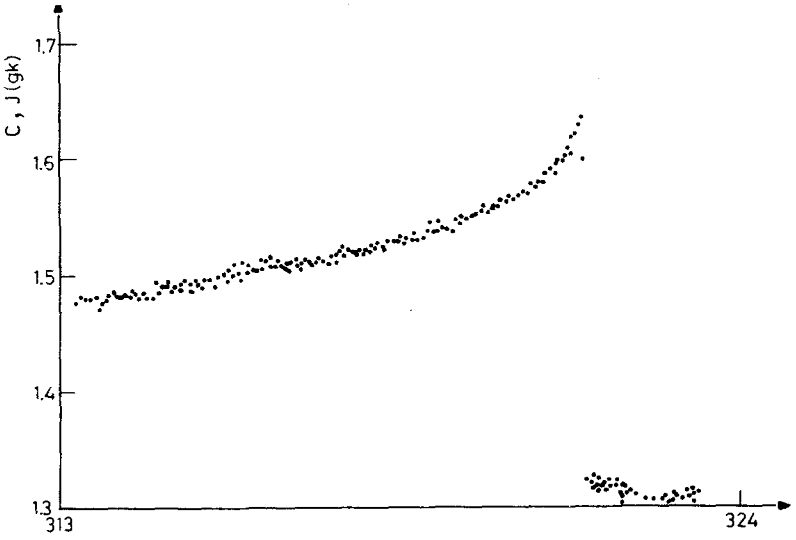

Fig. 2 Specific heat of TGS at nil applied electric field *vs.* temperature

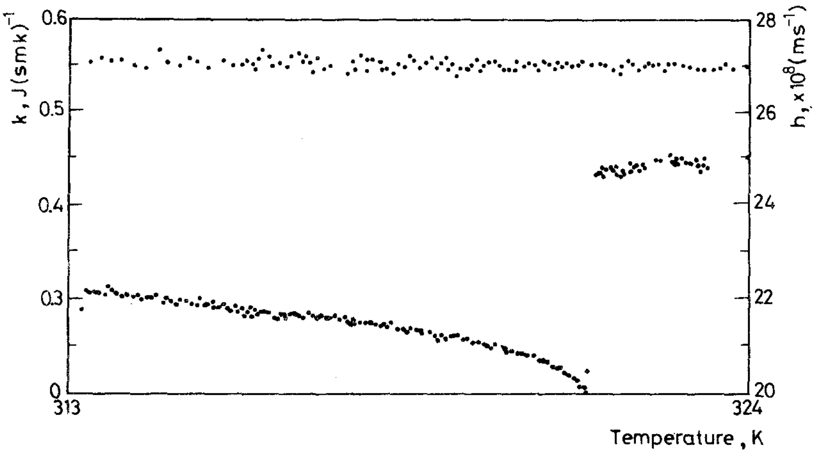

Fig. 3. Thermal conductivity k and thermal diffusivity h of TGS *vs.* temperature

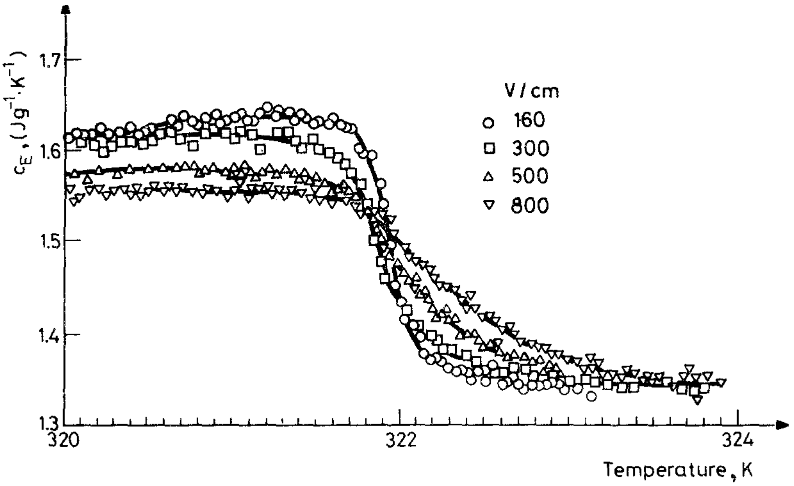

Fig. 4 Influence of electric field on specific heat of TGS. □ 160 V/cm, × 300 V/cm, ★ 500 V/cm, + 800 V/cm

Figure 4 gives our values of c_E for $E = 160, 300, 500$ and 800 V/cm. The behaviour at 160 V/cm agrees with that found by Taraskin, while for higher values of E the data confirm the predictions deduced from the mean field theory [10].

Our measurements of pyroelectric coefficient p agree qualitatively with those of Simony [11]. The data have been compared [6] with a scaled relation deduced from the static hypothesis [12]. Figure 5 shows this comparison, where $\hat{p} = pT_0/P_0$ and $\hat{E} = E/E_0$. T_0 is the transition temperature and $P_0 = 4.3 \cdot 10^{-6}$ C/cm^2 and

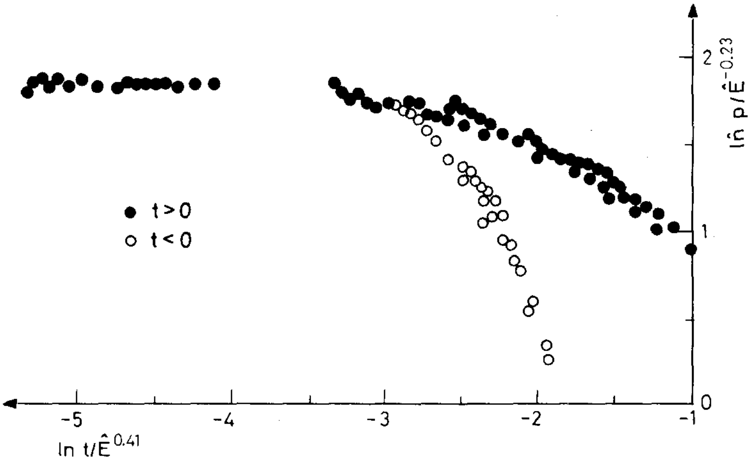

Fig. 5 Scaled relation of pyroelectric coefficient of TGS. × $t>0$, + $t<0$

$E_0=4.4\cdot 10^6$ V/cm are [13] the saturation polarization and the saturation internal field, respectively. It seems that p follows a scaling law.

The electrocaloric effect in TGS was studied by Strukov [14] by measuring the increase in temperature ΔT that the crystal undergoes when E is applied. The electrocaloric coefficient e is evaluated from the slopes of the plots ΔT versus E.

Figure 6 presents the values of e obtained from the above scaled relation and the c_E data, together with the theoretical values of e (deduced from the mean field theory) [10]. Our data closely approximate to the theoretical predictions.

Conclusions

The simultaneous measurement of specific heat c and thermal conductivity k is generally carried out by the transient method, in which the temperature increase of the sample in response to a heating pulse is measured. As AC modulations and AC amplification techniques are inapplicable, a large temperature gradient is generally required to give an adequate signal-to-noise ratio in the measured DC temperature difference.

The different procedures used in the measurement of the pyroelectric coefficient p demand the determination of several electric parameters and variation of the temperature of the sample. According to Lang [15], many important errors can be made in evaluating this coefficient, due to the lack of uniformity in the temperature of the sample and possible electric leaks.

In this paper, some methods for simultaneous measurement of these properties

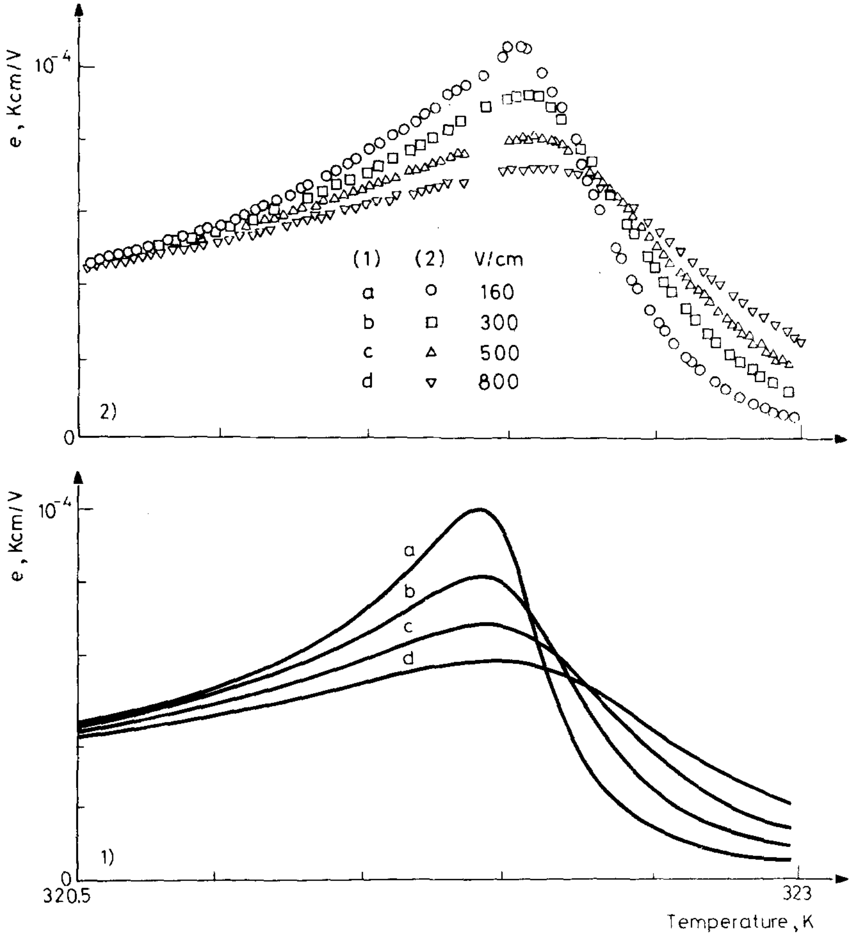

Fig. 6 Experimental and theoretical values of the electrocaloric coefficient of TGS *vs.* temperature.

using a flux calorimetry technique have been described. The determinations are carried out by measuring quantities of heat, and neither measurement of a temperature gradient nor comparison with a sample of known thermophysical properties is needed.

Since the measurement of temperature variations is unnecessary, and fluxmeters with a high number of thermocouples can be used, the sensitivity of these methods is high. Thus, it is possible to perform the experiments with a small temperature variation ($\simeq$0.01 deg), which is very convenient in the high-resolution study of second-order phase transitions, where a pronounced peak of these magnitudes can occur. In addition, the influence of an applied electric field on these parameters can be obtained.

As stated above, it is difficult to compare published data to deduce the behaviour of other magnitudes. If our methods are used, the measurement of c, k, p and susceptibility χ of only one specimen can be carried out using the same device at similar temperatures and applied electric fields, so that we are able to compare these data and to deduce the behaviour of other properties, thereby allowing a systematic study of the sample.

The agreement of our results with both theory and the findings obtained by other authors guarantees the validity of these methods for a systematic study of the thermal properties of ferroelectric crystals under an applied electric field.

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Zusammenfassung – In Zusammenfassung vorhergehender Arbeiten wurde die simultane Messung des Einflusses von elektrischen Feldern auf spezifische Wärme, Wärmeleitfähigkeit und pyroelektrischen Koeffizienten beschrieben. Auf Grundlage dieser Konstanten, die mittels eines Fluxkalorimeters bestimmt wurden, konnte das Verhalten anderer Eigenschaften wie z. B. thermische Diffusionskonstante und elektrokalorischer Koeffizient abgeleitet werden. Die Daten wurden mit durch herkömmliche Methoden erhaltenen Ergebnissen anderer Autoren verglichen.

Резюме — Описано одновременное измерения влияния электрического поля на теплоемкость, удельную теплопроводность и пироэлектрический коэффициент ферроэлектриков. На основе полученных величин, определенных с помощью калориметра в потоке, были установлены и такие параметры, как термопроводимость и электротепловой коэффициент. Данные были сопоставлены с данными других авторов, полученными обычными методами.