A dynamic method for determining the pyroelectric response of thin films

Marc Daglish

A DYNAMIC METHOD FOR DETERMINING THE PYROELECTRIC RESPONSE OF THIN FILMS

MARC DAGLISH
Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand

A dynamic method for quantitatively determining the pyroelectric coefficient of thin films is presented. The technique offers several advantages over competitive techniques. These advantages include,
- the ability to distinguish between reversible (pyroelectric) and irreversible thermally induced currents,
- a facility to study time-varying pyroelectric responses,
- more rapid determinations at room temperature, and
- higher measurement precision.

Details of the mechanical and electrical design of the instrument are given, together with examples of experimental data which illustrate the working operation of the equipment.

INTRODUCTION

Pyroelectricity is the term used to describe the temperature dependence of polarisation in certain insulating materials -including ferroelectrics- which possess a unique polar axis. Pyroelectrics develop an electric charge on heating or cooling, and it is this effect which has been commercially exploited since the 1960's[1] in devices such as fire alarms, movement sensors and thermal imagers.

Early investigations of pyroelectrics played a crucial role in the evolution of crystallography during the 19th century[2], in particular with regard to the discovery of 'piezoelectricity' by the Curies[3]. Among the first pyroelectrics to be studied were naturally-occurring minerals, such as tourmaline and wurtzite, however these were rapidly supplemented by a number of synthetic crystals, including lithium sulphate, and potassium tartrate. Further developments in materials technology have provided numerous highly active pyroelectrics[4,5] to meet current technological demands, these include single-crystals[6,7], polymers[8], glasses, ceramics[9,10], glass-ceramics[11], polymer-ceramic composites[12], Langmuir-Blodgett films[13], liquid crystals[14] and, most recently, oxide thin films[15-23].

Despite the scientific and technological importance of pyroelectricity, its material parameter -the pyroelectric coefficient- is often characterised with lower precision than corresponding material parameters such as relative permittivity and the piezoelectric coefficients. This is in large part due to a lack of commercial measurement equipment and an absence of measurement standards. A number of methods have been used to determine the pyroelectric coefficients of thin film dielectrics. The advantages and disadvantages of these methods are reviewed here. To permit meaningful comparisons between the measurements of different groups it would be advantageous if a 'standard' method could be adopted. In this paper a method is recommended for consideration as the standard.

DEFINITIONS AND CAVEATS

Theoretically a pyroelectric should exhibit a polarisation P which can be measured by determining the surface charge Q over an area A of the specimen: $P = \pm(Q/A)$. The electric displacement is given by the fundamental relation of dielectric theory:

$$D = \varepsilon_0 E + P \tag{1}$$

Under constant field E and stress σ, the pyroelectric coefficient is defined:

$$\lambda_i = \left(\frac{\partial D_i}{\partial T}\right)_{\sigma,E} \equiv \left(\frac{\partial P_i}{\partial T}\right)_{\sigma,E} \tag{2}$$

assuming i=3 (the polar axis), $\lambda = \left(\dfrac{\partial(Q/A)}{\partial T}\right)_{\sigma,E} \tag{3}$

$$\lambda = \frac{1}{A}\left(\frac{\partial Q}{\partial T}\right)_{\sigma,E} - \frac{Q}{A^2}\left(\frac{\partial A}{\partial T}\right)_{\sigma,E} \tag{4}$$

The change in area is usually ignored so that the accepted definition of the pyroelectric coefficient becomes,

$$\boxed{\lambda = \frac{1}{A}\left(\frac{\partial Q}{\partial T}\right)_{\sigma,E} \equiv \frac{i_p}{A\left(\dfrac{dT}{dt}\right)}} \tag{5}$$

where i_p is the pyroelectric current. This has been widely adopted[8], as the definition of the measured pyroelectric coefficient. (Convenient units are: $\mu C\ m^{-2}\ K^{-1}$.) λ is the *total* pyroelectric coefficient and comprises both a primary (constant strain X) and secondary (constant stress) components (see Nye[24] for derivations):

$$\lambda_{TOTAL} = \left(\frac{\partial D}{\partial T}\right)_{X,E} + \left(\frac{\partial D}{\partial X}\right)_{E,T}\left(\frac{\partial X}{\partial T}\right)_{\sigma,E} \tag{6}$$

It is experimentally problematic to separately measure each component so that it is usually considered sufficient to measure the total coefficient. Of more importance is the necessity for uniform heating during both qualitative and quantitative pyroelectric measurements. If the temperature within any piezoelectric specimen is non-uniform, the resulting temperature gradient will create a unique polar axis which may generate a large additional pyroelectric effect. This is commonly termed "false" or "tertiary" pyroelectricity. It is observable in all piezoelectrics, even those which are not "true" pyroelectrics

(α-quartz is such an example). Special care must be taken to minimise the "false" contribution otherwise incorrect values or interpretations may result.

A REVIEW OF PREVIOUS MEASUREMENT TECHNIQUES

A convenient delineation between the available measurement techniques was proposed by Lang[4], who divided the methods into 3 groups: *static, indirect, and dynamic.* Static methods are those in which a specimen is subjected to an incremental change of temperature whilst measuring the charge displacement; measurements are taken at discrete temperatures only. These methods are time-consuming and are therefore rarely used. Indirect methods, as the name implies, derive values for the pyroelectric coefficient from measurements of a related parameter, such as polarisation. Dynamic methods involve the measurement of the pyroelectric current whilst continuously varying the specimen temperature; these are the most widely used methods. A summary of the most important techniques is given in Table I. Only the methods marked with an asterisk have been used in the measurement of thin films and it is these which are compared below.

Linear Temperature-Ramp (Byer-Roundy) Method[15-20]
The sample temperature is increased or decreased at a constant rate (dT/dt), whilst measuring the thermally stimulated current, I, flowing between the electrodes. The pyroelectric coefficient is then calculated (assuming I is solely due to a pyroelectric response) from equation (5).

The shortcomings of this method are, i) the difficulty of generating an accurate linear temperature rate, and evaluating this rate, ii) the inability of the technique to distinguish between the reversible pyroelectric current and irreversible thermally stimulated current - not necessarily entirely pyroelectric in origin - which can lead to gross errors on calculating the value of λ, and iii)

TABLE I A summary of the principal pyroelectric measurement techniques

STATIC	DYNAMIC	INDIRECT
1."Heat-burst" method[25]	1.*Linear temperature-ramp (Byer-Roundy) method[26]	1.*E-P measurements (Sawyer-Tower) with temperature[27]
	2.*Modulated radiant heating (Chynoweth) method[28]	2.Electrocaloric method[29]
	3.*Temperature oscillation, or 'a.c.' method[30]	
	4.Shunt-resistor method[31]	
	5.Charge-integration method[6]	
	6.Step-radiation method[32]	

from ii) it follows that valid measurements cannot be made whilst applying an external d.c. bias field, since the conduction current (also temperature-dependent) is not distinguishable from the pyroelectric current. It is an easy method to use, but unfortunately it is often employed without an appreciation of its limitations.

Field-Polarisation Measurements[22]

This method is rarely used since it requires extremely accurate measurements and does not allow for the stabilisation of the polarisation after poling.

Modulated Radiant Heating (Chynoweth) Method[17]

The sample is heated by a modulated radiant source such as a laser or a calibrated light source[33], and the resulting current between the electrodes measured. Quantitative determinations of the pyroelectric coefficient require a knowledge of the sample temperature variation: if the temperature modulation is periodic and regular it may be compared with the observed current, thereby allowing the pyroelectric coefficient to be calculated (equation (5)). To find the temperature variation it is necessary to have

accurate values for the heat capacity of the sample, emissivity of the illuminated surface, and information on the rate of heat transfer from and within the specimen. Since it can be difficult to find these values, this type of measurement often remains qualitative.

The most serious difficulty to overcome when using this method is that of ensuring that every part of the sample remains at the same temperature; the presence of temperature gradients within the sample cause tertiary pyroelectric effects which cannot be readily allowed for. Nonetheless, there are several advantages of the method which are: i) the measurement conditions closely resemble the operating conditions for device prototyping, ii) reversible and irreversible current response can be distinguished, iii) d.c. fields can be applied to the specimen during the measurement, iv) measurements can be made at discrete temperatures, or whilst continuously ramping temperature, and v) the frequency-dependence of the pyroelectric response can be analysed.

Temperature Oscillation, or 'a.c.' Method[21,23,34,35]

The temperature of the sample is modulated (by a Peltier device, or a heated gas) in a regular periodic fashion, whilst monitoring the current waveform. This method offers many of the advantages (ii) to iv)) listed above without being susceptible -provided precautions are taken- to non-uniform heating of the sample. It can be used to take quantitative measurements, at discrete temperatures, or whilst linearly ramping temperature. For these reasons this method is recommended for development as the standard method and is described in more detail in the following section.

EXPERIMENTAL REALISATION OF THE TEMPERATURE OSCILLATION METHOD

The instrument described below has been used to determine the pyroelectric coefficients of thin films by a temperature oscillation method. The equipment is used to apply a selected temperature waveform to a wafer of material whilst simultaneously measuring the specimen current. From a knowledge of the reversible sample current and a calculation of the differential of sample temperature, the pyroelectric coefficient is obtained though equation (5).

Thermal Module

The foremost requirement placed on a pyroelectric measurement technique is that it should be capable of distinguishing between reversible and irreversible TSC (thermally stimulated current) responses. By definition, a pyroelectric phenomenon must be *reversible* (i.e. the TSC response to a rate of change of temperature must be equal and opposite to that developed in response to an equal and opposite rate). The reversibility of the TSC was verified here by oscillating the temperature of the sample at a low frequency whilst simultaneously measuring the alternating and direct current responses.

In order that the rate of change of sample temperature might be accurately determined, two requirements needed to be satisfied: first, the temperature of the body which heated or cooled the sample had to be controlled in a regular periodic manner, amenable to simple analysis; second, that the heat-transfer between the temperature-controlled body and the sample was efficient. The design adopted here employed a Peltier effect device (Cambion Mfg Co., USA, 75 W thermoelectric module) to control the temperature of a *thermal module* containing the specimen (Figure 1). Heat-transfer between the module and the sample was achieved by flowing helium gas (Figure 1, item 6 & 10) through the module and over the specimen surfaces. The high thermal conductivity ($\kappa = 141.5$ mW m^{-1} K^{-1}) and diffusivity

($D=1.51 \text{ cm}^2 \text{ s}^{-1}$) of the helium, combined with the large surface-to-volume ratio of the sample, ensured efficient transfer.
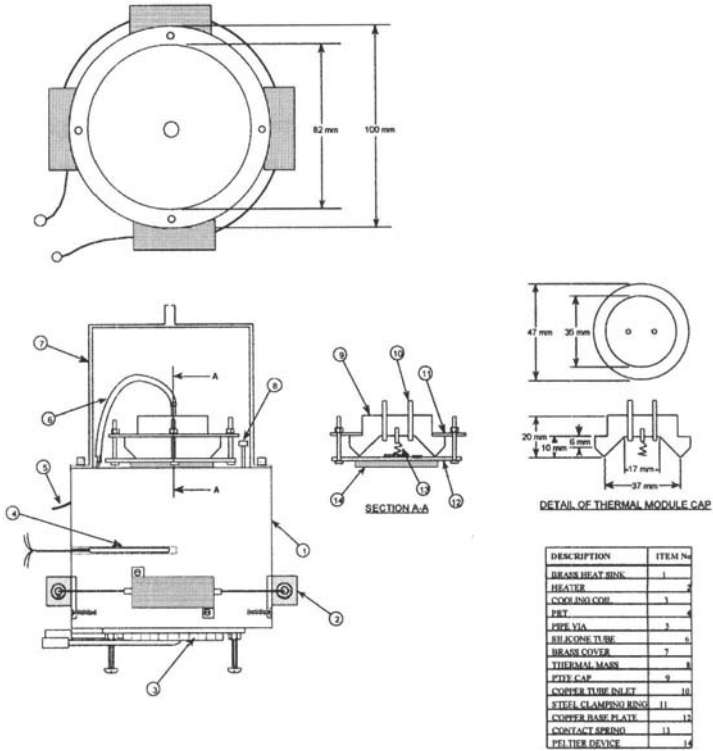

FIGURE 1   Drawing of the specimen holder assembly.

To avoid the spurious influence of tertiary pyroelectric effects, it was necessary to ensure that all parts of the sample remained at the same temperature. This situation was approached here by using by mounting the specimen on a series of concentric knife-edges, cut from the copper base plate of the thermal module.

A brass cylinder supported, the thermal module, and acted as a large heat-sink and a thermal reference: the temperature of the cylinder remained

effectively independent of short-term ambient temperature fluctuations. Resting on the upper surface of the sink, a removable brass cover formed an electrical and environmental shield around the thermal module. Electrical and gas connections to the module were made via channels through the brass cylinder.

The author is aware a of variant on this system (Dept. Physics, Univ. of Leeds, UK, 1988) which relied entirely on a heated gas-flow to modulate the sample temperature. However this approach was susceptible to problems with, i) piezoelectric noise due to 'eddies' in the flow at the high flow-rates which were necessary for efficient heat-transfer, ii) non-uniform heat-transfer, and iii) inaccurate determination of true sample temperature.

Control and Measurement

Temperature control and measurement

The temperature-control circuit for the thermal module employed two copper-constantan thermocouples connected in series. One junction was provided by a foil thermocouple cemented onto the top surface of the copper base plate at the periphery of the knife-edges; the second junction was formed between the opposite end of the constantan foil and a reference thermal mass (Figure 1, item 8). The thermal mass was necessary to minimise the effect of local changes of heat-sink temperature during the operation of the Peltier device. Insulated copper wires were attached to the thermal mass and the copper junction of the foil thermocouple, thus completing the thermocouple assembly.

The copper wires from the thermocouple passed out of the heat sink and through a copper braid sheath to a thermocouple amplifier (Figure 2, item 1). The amplified thermocouple signal was compared with a reference waveform produced by a voltage waveform generator. The result of this comparison was

proportional to the difference between the reference and the thermocouple signals, and was used to control the power amplifier (Figure 2, item 3) which in turn supplied the current to the Peltier device. A feedback loop (Figure 3) was thus established, so that the amplitude, frequency, and character of the module temperature waveform could be controlled from the function generator. Typically a modulation frequency of 10 to 100 mHz was chosen, at an amplitude of 150 mV, equivalent to a 1 K peak-peak temperature oscillation.

Specimen temperature was monitored using a four-lead, thin film platinum resistance thermometer (Nulectrohms Ltd, UK: PS 1.1328) which was cemented with a thermally conductive adhesive onto the copper plate at a point close to the specimen. The resistance of the thermometer was monitored by a digital multimeter. The multimeter was interfaced onto the IEEE-488 network, thereby permitting the temperature measurement to be automated.

The temperature of the heat-sink was controlled by a combination of electrical heaters -positioned concentrically around the axis of the cylinder- and a cooling coil, attached to its base. Flowing liquid nitrogen was used as the coolant in the coil, and the heaters were powered from a temperature controller. A platinum resistance thermometer (Nulelectrohms Ltd, UK: PS 1.21006) embedded in the centre of the brass block, served as the temperature sensor for the temperature control circuit. The reference temperature could be set in the range 120 K to 400 K.

Sample current measurement

The top electrode of the sample (typically a sputtered gold disc) was contacted by a copper spring attached to the underside of the cap and thence to a copper wire passing out of the module. This arrangement eliminated the transfer of mechanical disturbances to the specimen and, since the contact strip was

within the thermal module, it did not appreciably increase the effective
thermal mass of the specimen. Contact to the bottom sample electrode was
achieved by etching a corner of the film and providing a connection to the
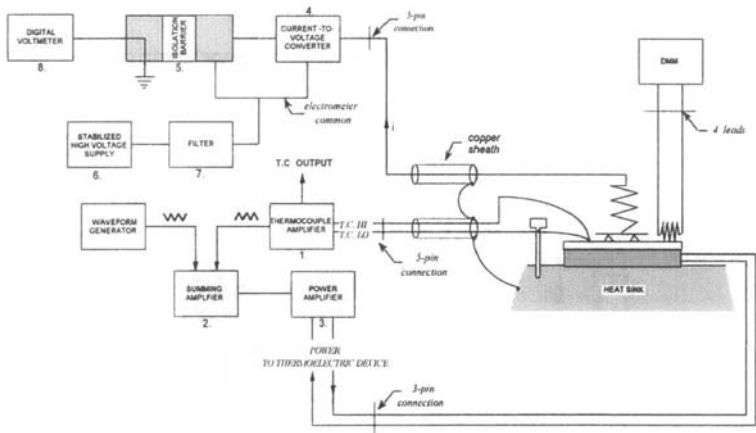copper plate with a droplet of silver conductive paint.

FIGURE 2   Schematic of system components.

A PTFE insulated wire carried the signal from the top sample electrode,
via a copper sheath, to a current-to-voltage converter/electrometer (Figure 2,
item 4). The high-level voltage output from the converter became the input
signal to an isolation amplifier Burr Brown ISO102 (Figure 2, item 5; and
Figure 4) which transmitted the voltage signal to a voltmeter (Figure 2, item
8), whilst protecting the electrometer chip from any large voltages which may
be applied across the specimen. This arrangement permitted high voltages (up
to 350 V) to be applied to the sample by connecting a stabilized high voltage
supply, via a low-pass filter, to the current-to-voltage converter common line.
The use of a programmable multimeter to measure the output voltage from
the circuit allowed the measurement of sample current to be completely
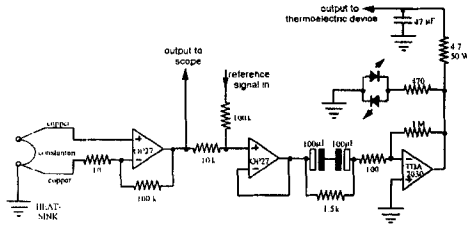automated.

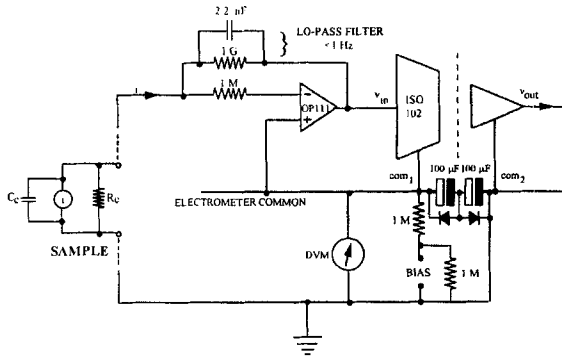FIGURE 3   Temperature control circuit for thermoelectric device.

FIGURE 4   Electrometer amplifier circuit.

DATA TREATMENT AND OPERATIONAL EXAMPLES

An automated analysis was established to find the values of the temperature differential and current over each sampling period. To facilitate this calculation, a triangular temperature waveform was usually chosen so as to generate a square-wave pyroelectric current. A fast Fourier transform was mathematically applied to the current data to find the amplitude of the (fundamental) square wave response, and the method-of-least-squares (applied to the linear portions of the waveform) was used to find the corresponding value of the temperature differential. From a knowledge of the temperature differential and the current amplitude, the pyroelectric coefficient

was calculated, by substituting these values into equation (5). An example of a typical set of current and temperature waveforms is given in Figure 5(a).

The equipment could be operated in two modes: fixed reference temperature (as described above), or ramped reference temperature. In the second mode, the sample experienced a constant linear rate of temperature change, superimposed on the temperature oscillation. In this case measurements of the pyroelectric coefficient were calculated continuously over the desired range of temperatures.
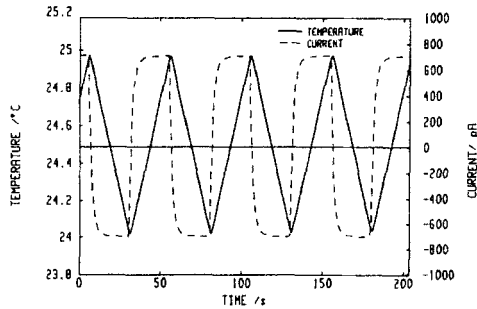

FIGURE 5(a)   Current and temperature waveforms (fixed T)
(λ=223 μC m^2 K^{-1} at a temperature of 24.5°C; where A=0.785 cm^2).

The calculations described above remained unaffected by the superposition of the temperature ramp provided its value was chosen to be less than 4x(amplitude of T oscillation)x(measurement frequency). The difference here was that the symmetry line ('baseline') for the current trace was offset from zero, by a d.c. current component (Figure 5(b)), which originated from i) the pyroelectric current in response to the linear change of T, and ii) irreversible TSC. The variation of the pyroelectric coefficient and irreversible current could be readily displayed as a function of temperature. An example of the temperature dependence of the pyroelectric coefficient of a thin film sample is shown in Figure 6.

When the sample was subjected to an applied d.c. field, the analysis remained unaffected except that the d.c. offset current now contained an additional current component which was due to conduction through the sample. An example of the pyroelectric current as a function of electric field is given in Figure 7.
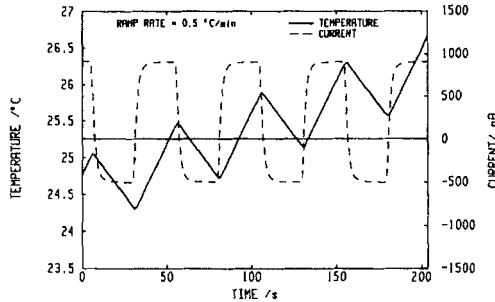

FIGURE 5(b)   Current and temperature waveforms (ramped T).

DISCUSSION AND CONCLUSIONS

The temperature oscillation method, described here, is a precise (better than 1%, typically 0.1 $\mu C \, m^2 \, K^{-1}$) and reliable method for determining the pyroelectric coefficient of thin films. The method avoids ambiguities which can result from the presence of irreversible current responses and is experimentally both fast and convenient for use at discrete temperatures, including room temperature. Because the reference temperature can be fixed, it is also straightforward to study the time dependence of the pyroelectric coefficient. This is extremely useful for monitoring the stabilisation of the pyroelectric response, in particular after poling. In cases where distortions in the current trace are present, they are immediately apparent, and can provide useful information about the thin film, for example, 'saw-toothed' current traces often indicate the presence of space-charged layers.
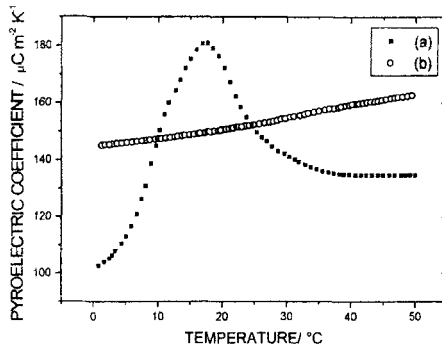
FIGURE 6   Pyroelectric coefficient as a function of temperature for a lead titanate thin film (a) low temperature, and (b) high temperature pyrolysis.
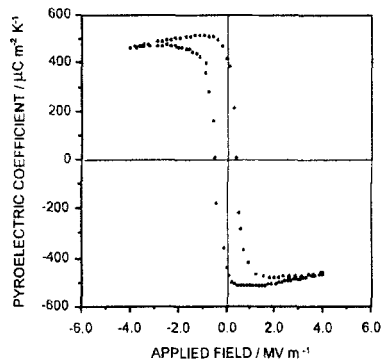

FIGURE 7   Pyroelectric coefficient as a function of applied field for a disordered lead scandium tantalate at -60°C.

Further improvements to the system have recently been made to allow higher temperature measurements (>400°C) and the use of a multiple electrode contacts. Details of these improvements will be published shortly.

Acknowledgements

References

[1.] J. Cooper, *Rev. Sci. Instrum.*, **33**[1], 92 (1962).

[2.] D. Brewster, *Edinburg. J. of Science*, 1[II], 208 (1824).

[3.] J.P. Curie, and P. Curie, *Compt. Rend. Acad. Sci. Paris*, **91**, 294 (1880).

[4.] S.B. Lang, *Sourcebook of pyroelectricity* (Gordon and Breach, London,1974).

[5.] R.W. Whatmore, *Rep. Prog. Phys.*, **49**, 1335 (1986).

[6.] A.M. Glass, *J .Appl. Phys.*, **40**[12], 4699 (1969).

[7.] J.P. Remeika, and A.M. Glass, *Mat. Res Bull.*, **5**, 37 (1970).

[8.] G.R. Davies, *Int. Phys. Conf. Ser.*, **No.58**, 50 (1980).

[9.] D. Luff, et al., *Trans. and Journal Brit. Ceram. Soc.*, **73**[7], 251 (1974).

[10.] R.W. Whatmore, *New ferroelectrics for infrared detectors*, Allen Clark Research Centre (Annual Review), 1979), p.79.

[11.] W. Xie, Z. Ding, and P. Zhang, *J. Am. Cer. Soc.*, **79**[12], 3336 (1996).

[12.] R.E. Newnham, et al., *Ferroelectrics*, **27**, 49 (1980).

[13.] G.G. Roberts, *Ferroelectrics*, **91**, 21 (1989).

[14.] S. Bini and R. Capoletti, *Electrets* (Electrochem. Soc., New York 1973), p.66.

[15.] R. Takayama, and Y. Tomita, *Ferroelectrics*, **118**, 325 (1991).

[16.] M. Adachi, T. Matsuzaki, T. Yamada, T. Shiosaki and A. Kawabata, *Jpn. J. Appl. Phys.*, **26**[4], 550 (1987).

[17.] D.L. Polla, C. Ye, and T. Tamagawa, *Appl. Phys. Lett.*, **59**, 3539 (1991).

[18.] R. Watton, *Integrated Ferroelectrics*, **4**, 175 (1994).

[19.] M. Kobune, S. Fujii, R. Takayama and A. Tomozawa, Jpn. J. Appl. Phys., **35**[1/9B], 4980 (1996).

[20.] W. Peiying, et al., *Sensors and Actuators*, **A49**, 187 (1995).

[21.] A. Patel, et al. *Brit. Ceram. Proc.*, **52**, 77 (1994).

[22.] E. Yamaka, et al. *J. Vac. Sci. Technol.*, **A6**[5], 2921 (1988).

[23.] Y. Huang, M. Daglish, I. Reaney and A. Bell, *Third Euro-Ceramics*, **2**, 699 (1993).

[24.] J.F. Nye, *Physical properties of crystals* (OUP, London 1957).

[25.] W. Ackermann, *Am. Phys. (Leipzig)*, **46**, 197 (1915).

[26.] R.L. Byer, and C.B. Roundy, *Ferroelectrics*, **3**, 333 (1972).

[27.] C.B. Sawyer, and C.H. Tower, *Phys. Rev.*, **35**, 269 (1930).

[28.] A.G. Chynoweth, *J. Appl. Phys.*, **27**, 78 (1956).

[29.] G.G. Wiseman, *NASA report*, **CR-1080** (1967).

[30.] N.P. Hartley, P.T. Squire, and E.H., Putley, *J. Phys. E*, **5**, 787 (1972).

[31.] S.B. Lang and F. Steckel, *Rev. Sci. Instrum.*, **36**, 929 (1965).

[32.] M. Simhony, and A. Shaulov, *Appl. Phys. Lett.*, **21**, 375 (1972).

[33.] S.T. Liu, J.D. Heaps, and O.N.Tufte, *Ferroelectrics*, **3**, 281 (1972).

[34.] M. Daglish, Ph.D. thesis dissertation, Univ. Leeds, UK (1990).

[35.] R. Watton and A. Todd., *Brit. Ceram. Proc.*, **41**, 205 (1989).