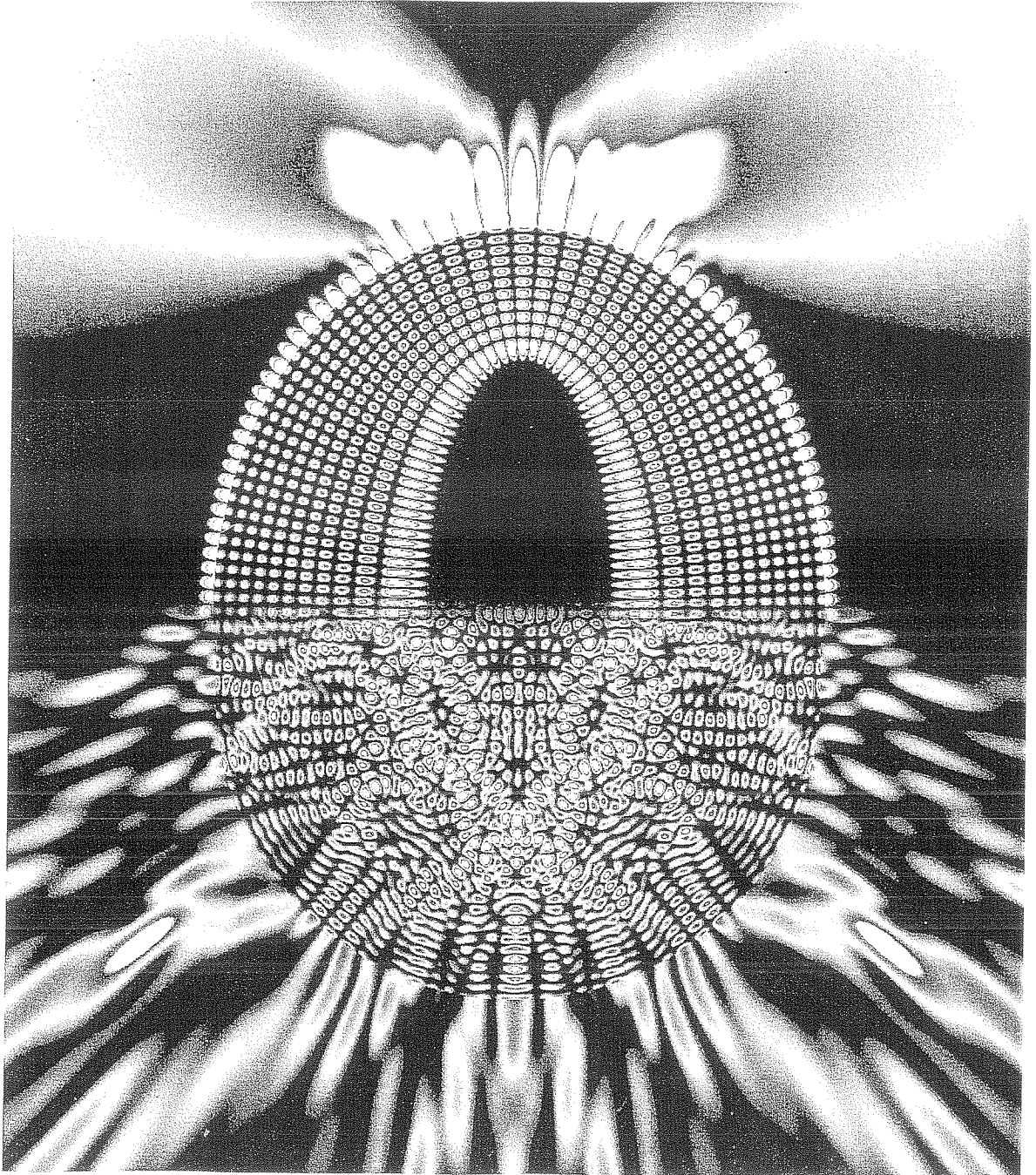




AUGUST
2005

PHYSICS TODAY



Einstein versus chaos

Pyroelectricity: From Ancient Curiosity to Modern Imaging Tool

Changes in the net dipole moment of certain materials form the basis for a broad range of IR detectors.

Sidney B. Lang

One of the least-known properties of solid materials, pyroelectricity is rigorously defined as the temperature dependence of the spontaneous polarization in certain anisotropic solids.^{1–6} To appreciate the meaning of that definition and the nature of the pyroelectric effect, consider a simple example: a thin, parallel-sided sample of material, such as a tourmaline crystal or a ceramic disk of barium titanate, cut so that its crystallographic symmetry axis is perpendicular to the flat surfaces. The unit cells of pyroelectric materials have a dipole moment. The dipoles are packed so that the components of the dipole moment in each unit cell add up in the direction normal to the flat surfaces. The dipole moment per unit volume of the material is called the spontaneous polarization \mathbf{P}_s . Always nonzero in a pyroelectric material, \mathbf{P}_s exists in the absence of an applied electric field and is equivalent to a layer of bound charge on each flat surface of the sample.

Nearby free charges such as electrons or ions will be attracted to the sample (see figure 1). Imagine that conductive electrodes are then attached to the surfaces and connected through an ammeter having a low internal resistance. If the temperature of the sample is constant, then so is \mathbf{P}_s and no current flows through the circuit. But in most single crystals and ceramics, an increase in temperature causes the net dipole moment and, consequently, the spontaneous polarization to decrease. The quantity of bound charge then decreases, and the redistribution of free charges to compensate for the change in bound charge results in a current flow—the pyroelectric current—in the circuit.

If the sample had been cooled instead of heated, the current's sign would be reversed. Note that the pyroelectric effect is only observable during the period in which the temperature changes. In an open circuit, the free charges would simply remain on the electrodes and a voltage could be measured.

A large number of pyroelectric materials exist, including minerals such as tourmaline, single crystals such as triglycine sulfate, ceramics such as lead zirconate titanate, polymers such as polyvinylidene fluoride, and even biological materials, such as collagen. For a detailed treat-

ment of the relations between various properties of a material and how those properties contribute to the pyroelectric effect, see box 1.

Historical threads

This treatment of pyroelectricity in terms of a change in net dipole moment emerged in modern times. But as a phenomenon, the pyroelectric effect has been known for 24 centuries—the Greek philosopher Theophrastus probably wrote the earliest known account.⁷ He described a stone, called *lyngourion* in Greek or *lyncurium* in Latin, that had the property of attracting straws and bits of wood. Those attractions were no doubt the effects of electrostatic charges produced by temperature changes most probably in the mineral tourmaline.

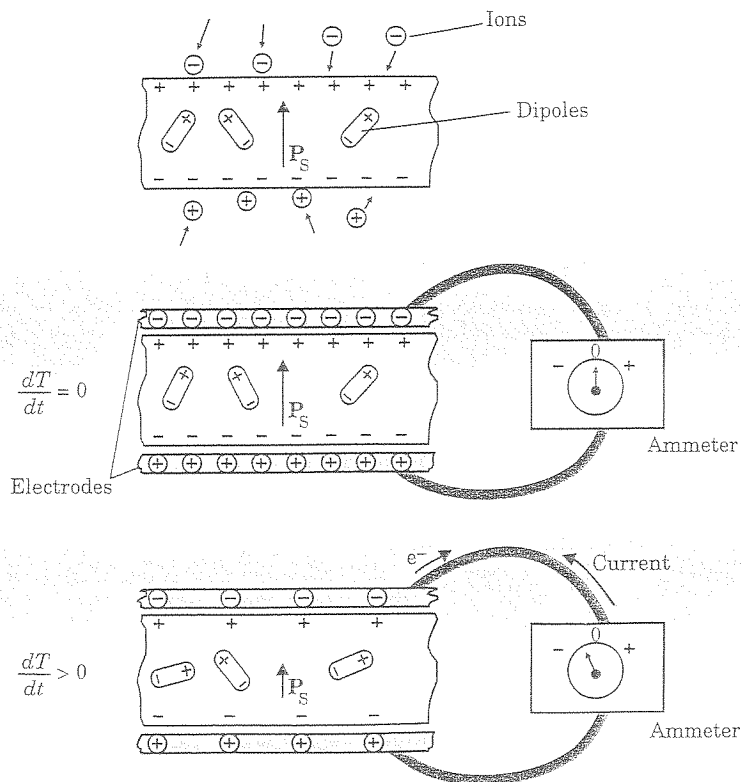


Figure 1. If a pyroelectric crystal with an intrinsic dipole moment (top) is fashioned into a circuit with electrodes attached on each surface (middle), an increase in temperature T prompts the spontaneous polarization \mathbf{P}_s to decrease as the dipole moments, on average, diminish in magnitude. The horizontal tilting of the dipoles, pictured at bottom, signifies the effect. A current flows to compensate for the change in bound charge that accumulates on the crystal edges. (Adapted from ref. 13.)

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Theophrastus and other writers of the two millennia that followed were far more interested in the origin of the stone and its possible therapeutic properties than they were in physical explanations. Theophrastus proposed that lyncourion was formed from the urine of a wild animal, later identified by Pliny the Elder as a lynx (see figure 2).^{1,2}

Two thousand years after Theophrastus, tourmaline's unusual physical properties were reintroduced to Europe through the publication in 1707 of a book entitled *Curiose Speculationes bey Schlaflosen Nächten* (Curious Speculations During Sleepless Nights). Its author, Johann Georg Schmidt, using the pen name Immer Gern Speculirt (Always Gladly Speculating), wrote a series of 48 dialogs, one of which contained a section describing hard and glassy bodies that were not magnetic. He described the experiences of Dutch gem cutters when they tested the durability of tourmaline in a fire:

The ingenious Dr. Daumius, chief physician to the Polish and Saxon troops on the Rhine, told me that, in the year 1703, the Dutch first brought from Ceylon in the East Indies a precious stone called tourmaline, turmale, or trip, which had the property of not only attracting the ashes from the warm or burning coals, as the magnet does iron, but also repelling them again.

Box 1. Crystal Properties and the Pyroelectric Effect

The triangular diagram below illustrates the thermodynamically reversible interactions that may occur among the thermal, mechanical, and electrical properties of a crystal; magnetic properties are ignored for simplicity. The lines joining pairs of circles signify that a small change in one of the variables produces a corresponding change in the other. The three short bold lines that connect pairs of thermal, elastic, and electric variables define the physical properties of heat capacity, elasticity, and electrical permittivity, respectively. As an example, a small increase in temperature θ produces an increase in entropy σ proportional to the heat capacity divided by temperature. The diagram also illustrates coupled effects, denoted by lines joining pairs of circles at different corners of the diagram.

Pyroelectricity is a coupled effect that relates a change in temperature to a change in electrical displacement \mathbf{D} (with units of C/m^2),

$$d\mathbf{D} = \mathbf{p}d\theta,$$

where \mathbf{p} is the pyroelectric coefficient (with units of $C/m^2 \cdot K$). Both displacement and the pyroelectric coefficient are vectors or first-rank tensors. The pyroelectric coefficient is defined by

$$\mathbf{p} = (\partial \mathbf{P}_s / \partial \theta)_{\mathbf{T}, \mathbf{E}},$$

where \mathbf{P}_s is the spontaneous polarization. The constraints are constant electric field \mathbf{E} , and constant elastic stress \mathbf{T} . Constant stress means that the crystal is not clamped, but completely free to expand or contract thermally.

The diagram's colored lines indicate that the two contributions make up pyroelectric effect. In the first, the crystal is rigidly clamped under constant strain S , to prevent expansion or contraction. A change in temperature causes a change in electric displacement as shown by the green line, which signifies the primary pyroelectric effect. The second contribution—the secondary pyroelectric effect—is a result of crystal

In 1717 the physician and chemist Louis Lemery wrote the first scientific description of pyroelectricity in a journal. The naturalist Carl von Linné (Linnaeus) was the first to relate the pyroelectric property of tourmaline to electricity; he called the mineral *lapis electricus*—electric stone. Experiments on tourmaline during the 18th century by Franz Ulrich Theodor Aepinus, Johann Karl Wilcke, Benjamin Wilson, Joseph Priestley, John Canton, and Torben Bergman made major contributions to the rapidly developing field of electrostatics.

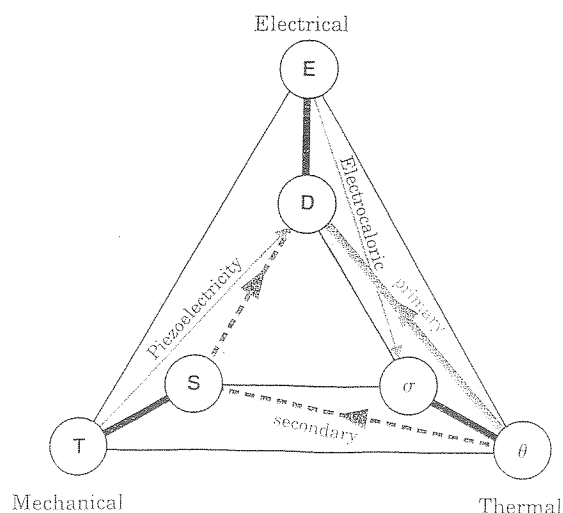
A more quantitative understanding of pyroelectricity emerged during the 19th century as more sophisticated research techniques were developed. In 1824 David Brewster, famous for his work in optics, was the first author to use the term "pyroelectricity." One of the materials he studied was a "tartrate of soda and potash"—Rochelle salt—the same material in which Joseph Valasek discovered ferroelectricity almost exactly a century later.

Shortly after Antoine Becquerel and others developed the electrometer, John Mothée Gaugain made the first precise measurements of pyroelectric charges in 1859. He reached some important conclusions: The total quantity of electricity produced by a crystal of tourmaline depends uniquely upon the limits within which its temperature is varied; within those limits, the amount of electricity produced during heating is the same as that produced during cooling, but with the signs of the charges reversed; and the

deformation: Thermal expansion causes a strain that alters the electric displacement via a piezoelectric process, as shown by the dashed red lines.

Measuring the primary effect directly is extremely difficult. But the secondary effect can be readily calculated from the values of the thermal expansion coefficient, the elastic stiffness, and the piezoelectric strain constant. So experimentally, the pyroelectric effect under the constraint of constant stress—the so-called total effect, the sum of red and green lines—is what is usually measured.

The table on page 33 lists the primary, secondary, and total pyroelectric coefficients of several materials for comparison.⁴ Moreover, it shows a division between ferroelectric and nonferroelectric materials. Ferroelectrics are pyroelectrics whose direction of polarization can be reversed by a sufficiently strong electric field. They are also characterized by



amount of charge produced is proportional to the cross-sectional area of the crystal and is independent of its length. William Thomson (Lord Kelvin) published the first major theoretical treatment of pyroelectricity in 1878; his paper included a prediction of the electrocaloric effect. Jacques and Pierre Curie proposed that the electrical effects due to nonuniform heating of quartz crystals might have been caused by pressure, a speculation that led to their 1880 discovery of piezoelectricity (related to pyroelectricity as discussed in box 1). During the latter part of the 19th century and the early decades of the 20th century, seven Nobel laureates—Wilhelm Röntgen, Pierre Curie, Gabriel Lippman, Heike Kammerlingh Onnes, Erwin Schrödinger, Archer J. P. Martin, and Max Born—published papers on pyroelectricity. These scientists are, of course, much better known for their research in other fields.

Joseph Valasek studied the properties of Rochelle salt and in 1920 discovered ferroelectricity. Then interest in pyroelectricity virtually vanished until 1938, when Yeou Ta published a paper that initiated the great growth that continues in the field today. Ta, a chemist at the Sorbonne in Paris, proposed that tourmaline crystals could be used as IR sensors in spectroscopy. Some research was conducted on pyroelectric IR detectors during and immediately after World War II in the UK, US, and Germany, but the results appeared only in classified documents. In 1962 J. Cooper made the first detailed analysis of the behavior of fast IR

detectors and conducted experiments using barium titanate. That year, I proposed the use of pyroelectric devices for measuring temperature changes as small as 0.2 μK . An explosive growth in theoretical studies, basic measurements, and applications had begun: More than 8500 papers on pyroelectricity have been published since 1960.⁸

Applications

The detection of long-wavelength IR radiation is of great interest in a wide range of applications.^{9–12} Two windows in the atmosphere exist—one from 3 to 5 μm and one from 8 to 14 μm —where the absorption due to water vapor and the scattering due to dust are minimal. The latter window is especially important because the peak in emission of the black-body curve for objects at 300 K occurs around 10 μm . Consequently, IR detectors with high sensitivity in this wavelength region can easily detect human beings and other warm-blooded animals.

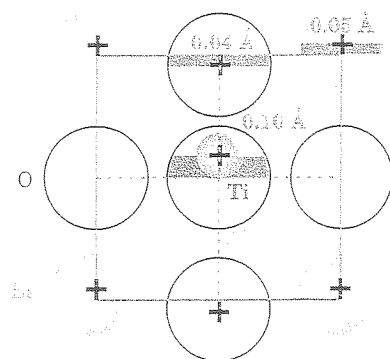
There are two general classes of IR detectors: quantum or photon, and thermal. Quantum detectors are based on the photoelectric effect and are produced from III–V or II–VI semiconductors such as gallium arsenide and mercury cadmium telluride. (The pyroelectric effect, based on different physics, does not depend on the size of the bandgap.) These materials are difficult to grow and fabricate into devices, and they require cooling, usually to 77 K, for operation in the long-wavelength IR spectrum. Astronomical quantum detectors are extremely sensitive in the far IR, but they do

TABLE 1. Pyroelectric Coefficients of Various Materials (Units: $\mu\text{C}/\text{m}^2\text{K}$)

Material	Primary coefficient	Secondary coefficient	Total coefficient
Ferroelectrics			
Poled ceramic			
BaTiO ₃	-260	+60	-200
PbZr _{0.95} Ti _{0.05} O ₃	-305.7	+37.7	-268
Crystal			
LiNbO ₃	-95.8	+12.8	-83
LiTaO ₃	-175	-1	-176
Pb ₅ Ge ₃ O ₁₁	-110.5	+15.5	-95
Ba ₂ NaNb ₅ O ₁₅	-141.7	+41.7	-100
Sr _{0.5} Ba _{0.5} Nb ₂ O ₆	-502	-48	-550
(CH ₂ CF ₂) _n	-14	-13	-27
Triglycine sulfate	+60	-330	-270
Nonferroelectrics			
Crystal			
CdSe	-2.94	-0.56	-3.5
CdS	-3.0	-1.0	-4.0
ZnO	-6.9	-2.5	-9.4
Tourmaline	-0.48	-3.52	-4.0
Li ₂ SO ₄ • 2H ₂ O	+60.2	+26.1	+86.3

the Curie temperature T_C , above which the material is paraelectric (nonpolar). Below T_C , ferroelectrics are polar and can exhibit pyroelectricity. These materials generally have larger pyroelectric coefficients than nonferroelectrics and are of greater interest for applications.

An effect called tertiary pyroelectricity is produced by nonuniform heating causing nonuniform stresses that can re-



sult in polarization through a piezoelectric effect. Tertiary pyroelectricity is of little interest now, although it was probably responsible for many of the unusual effects observed by early workers. The electrocaloric effect is an inverse pyroelectric effect, in which a change in an applied electric field produces a change in entropy and, consequently, a change in temperature.

The existence of the pyroelectric effect in any solid material requires that three conditions be satisfied: The molecular structure must have a nonzero dipole moment; the material must have no center of symmetry; and the material must have either no axis of rotational symmetry or a single axis of rotational symmetry that is not included in an inversion axis. Of the 32 crystal point-group symmetries, only 10 permit the existence of pyroelectricity.

The lattice model above shows a projection of the unit cell of barium titanate (BaTiO₃) on the (100) plane at a temperature of 291 K. The displacement of the atoms from their equilibrium positions on a cubic lattice gives rise to the spontaneous polarization; its variation with temperature is the pyroelectric effect.



Figure 2. The mythological origin of pyroelectric crystals dates back to about 315 BC, when the Greek philosopher Theophrastus wrote his treatise "On stones," about *lyncurium* (tourmaline, most likely) and other minerals. Just 14 pages long, that text was a valuable work on mineralogy for 18 centuries. The hand-colored woodcuts shown here illustrate *Hortus Sanitatis Major* (The Garden of Health), a book published in 1497 that describes medicinal and therapeutic values of plants, animals, and minerals in terms of superstitious views held in the late Middle Ages. The hardness of lyncurium contrasts with the softness of amber, whose formation is pictured in the top left. The sketch on the right depicts Theophrastus's bizarre belief that pyroelectric lyncurium comes from the urine of a lynx.

require very low-temperature cooling (see the article by Paul Richards and Craig McCreight in *PHYSICS TODAY*, February 2005, page 41). Thermal detectors convert the energy of IR photons into heat and are usually operated at ambient temperatures. They are not restricted to use in limited wavebands as are quantum detectors. Thermal devices are much cheaper but less sensitive.

Pyroelectric thermal detectors have five main advantages:

- ▶ Sensitivity over a very large spectral bandwidth—in principle, over the entire electromagnetic spectrum, depending on the absorption characteristics of the pyroelectric material and its electrodes.
- ▶ Sensitivity over a very wide temperature range—from a few degrees kelvin to hundreds, depending on pyroelectric material.
- ▶ Low power requirements—just enough to drive the field effect transistor that amplifies the signal.
- ▶ Fast response, over periods as short as picoseconds.
- ▶ Low-cost manufacture from inexpensive materials.

Because pyroelectric devices only respond to changes in temperature, they are used to observe moving objects in a scene or stationary objects through a light chopper; run at video frequencies (usually 25 to 60 Hz), the light chopper provides a continuous source of temperature variation that allows the material to generate charge while a scene is monitored.

Infrared detectors, such as the two types sketched in figure 3, can consist of single pyroelectric elements or one- or two-dimensional arrays of elements. Densely spaced 2D arrays generate a thermal image, similar to the visible-light image of a television. Some of the applications of IR pyroelectric detectors include intrusion detectors and burglar alarms, flame and fire detectors, IR spectrometers, laser de-

tectors, and pollution monitors. Other major areas of pyroelectric research and applications unrelated to IR detection include electron-emission devices and the measurement of thermal and optical properties of materials.

Device configurations

The most important component of any pyroelectric device is the detector material. Triglycine sulfate (TGS) and its isomorphs have very favorable properties, including high pyroelectric coefficients and relatively low permittivity. Despite their hygroscopic nature, these materials are a favorite for high-sensitivity applications. Lithium tantalate is very stable because of its high Curie temperature and insensitivity to humidity and vacuum, and is often used for space applications. Polyvinylidene fluoride polymer (PVDF) and its copolymers have low pyroelectric coefficients but their low thermal conductivity and dielectric constant make them useful for large-area detectors and arrays. Ceramics based on the lead zirconate titanate system are probably the most widely used materials; relatively cheap to manufacture, they are both mechanically and chemically robust. Variation of the Zr/Ti ratio and the addition of dopants permit great variation in the physical properties of these ceramics.

Thermally isolated from its surroundings, the detector element is usually coated with a blackened thin film to increase the light absorption. Low-noise and high-impedance amplifiers are necessary to detect the small amount of charge produced by heating, and typical circuits incorporate a field effect transistor with an appropriate load resistor or an operational amplifier with a feedback resistor to boost the signal. Doping the detector with various elements can control the detector's resistance and thereby eliminate the load resistor.¹²

Pyroelectric elements can also be configured to attenuate noise from ambient temperature changes and from vibrations. In the configuration shown in figure 3a, for instance, two elements are connected in electrical opposition and one is shielded from the radiation source. A germanium window is often chosen for devices because it is opaque to visible light but transparent at wavelengths near 10 μm . For details on the response and noise levels of pyroelectric detectors, see box 2.

Some of the more unusual applications of single-element detectors have been in space missions. The earliest space-related application was the vertical temperature-profile radiometer, launched into Earth's orbit in 1972. The *Pioneer Venus Orbiter* launched in 1978 was used to map cloud temperatures on Venus. The sounder probe of that mission was dropped into the planet's atmosphere to measure the net thermal flux. The *Galileo* mission launched in 1989 included a photopolarimeter-radiometer to determine thermal radiation on Jupiter and its moons. The

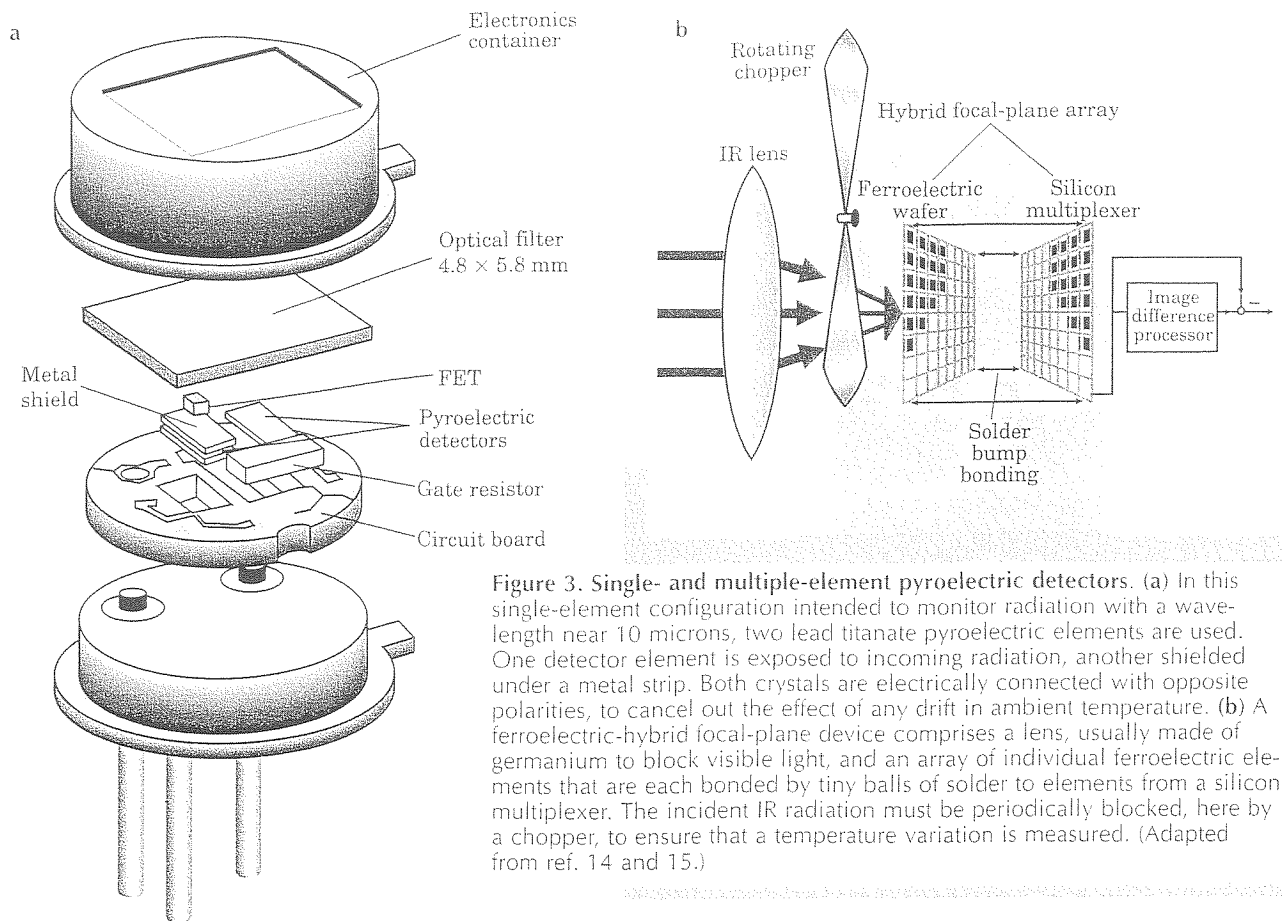


Figure 3. Single- and multiple-element pyroelectric detectors. (a) In this single-element configuration intended to monitor radiation with a wavelength near 10 microns, two lead titanate pyroelectric elements are used. One detector element is exposed to incoming radiation, another shielded under a metal strip. Both crystals are electrically connected with opposite polarities, to cancel out the effect of any drift in ambient temperature. (b) A ferroelectric-hybrid focal-plane device comprises a lens, usually made of germanium to block visible light, and an array of individual ferroelectric elements that are each bonded by tiny balls of solder to elements from a silicon multiplexer. The incident IR radiation must be periodically blocked, here by a chopper, to ensure that a temperature variation is measured. (Adapted from ref. 14 and 15.)

Box 2. Characterization of Pyroelectric Elements

A well-understood theory describes the response and noise sources of pyroelectric IR detectors.^{9-12,14} The pyroelectric current I generated per watt of input power, W_0 , is called the current responsivity,

$$R_I = \frac{I}{W_0} = \frac{\eta p A \omega}{G (1 + \omega^2 \tau_T^2)^{1/2}}$$

where p is the pyroelectric coefficient amplitude, η is the detector electrode absorptivity, A is the cross-sectional area of detector, ω is the radiation modulation frequency, G is the thermal conductance to surroundings, and τ_T is the thermal time constant (to account for heat losses to surroundings). Multiplying the current responsivity by the impedance of the circuit produces the voltage responsivity,

$$R_V = \frac{V_p}{W_0} = \frac{R_T \eta p A \omega}{G (1 + \omega^2 \tau_T^2)^{1/2} (1 + \omega^2 \tau_E^2)^{1/2}}$$

where τ_E is the electrical time constant (to account for RC losses in the circuit) and R_T is the total resistance of the detector element and circuitry. R_V has a maximum at a frequency between the reciprocals of the thermal and electrical time constants.

There are three major noise sources in a simple pyroelectric detector: thermal noise, dielectric (Johnson) noise, and amplifier noise (input-voltage, input-current, and shunt-resistor noise). Johnson noise is usually dominant above frequencies of 20 Hz. And environmental noise can arise due to ambient temperature fluctuations, mechanical vibration, and electromagnetic fluctuations. A signal-to-noise ratio is given by the noise-equivalent power,

$$NEP = \frac{V_N}{(\Delta f)^{1/2} R_V}$$

where V_N is the root mean square noise voltage and the NEP is normalized by the square root of the device bandwidth Δf . Both thermal and Johnson noise are proportional to the square root of the area of the detector. This gives rise to one of the most frequently used parameters, the area-normalized (or specific) detectivity,

$$D^* = \frac{A^{1/2}}{NEP}$$

To appreciate typical magnitudes of the responsivity and detectivity of a pyroelectric, consider a 0.01 mm² lanthanum-modified lead titanate (PLT) element supported on a thin ceramic membrane.¹¹ The maximum voltage responsivity was calculated to be about 40 000 V/W at a modulation frequency of 1 Hz. The maximum current responsivity was 50 μ A/W and the maximum D^* was 6.4×10^9 cm Hz^{1/2}/W at 5 Hz. The theoretical maximum value of D^* in any pyroelectric detector occurs if all noise sources other than thermal noise are eliminated; the effect of thermal noise cannot be eliminated.¹ The detectivity corresponding to thermal noise alone at 300 K is 1.8×10^{10} , one to two orders of magnitude higher than the best contemporary values. That disparity leaves room for improvement as new types of materials and improved circuitry are developed in coming years.

In practice, a detector element should be thin to maximize the temperature rise and mounted so as to minimize heat loss to the substrate. Low thermal-conductivity insulators or bridge-like constructions are often used in devices. A large pyroelectric coefficient and small values of dielectric permittivity are also required.

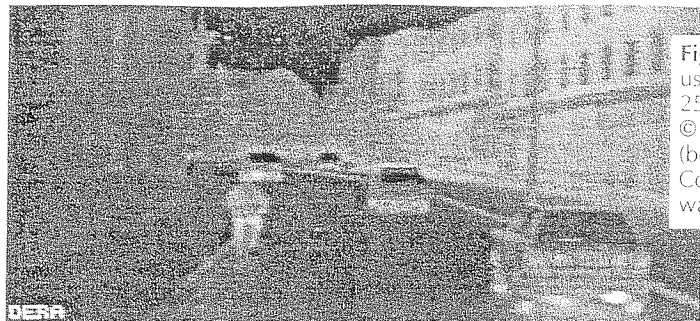
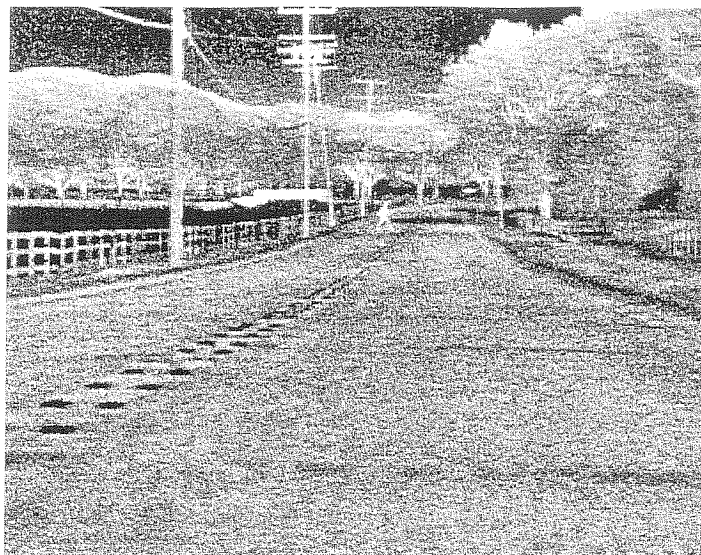


Figure 4. Pyroelectric imaging. These images were taken using a ferroelectric-hybrid focal-plane array (top) having 256×128 pixels (courtesy of DERA Malvern, Crown © 1989 and 1998) and a micromachined thin-film array (bottom) with 320×240 pixels (courtesy of Raytheon Commercial Electronics). Lighter colors correspond to warmer temperatures.



temporary versions have as many as 384×288 pixels and an NETD as low as 75 mK. Micromachined thin-film elements with even lower NETDs are under development.

Applications exist in areas as diverse as fire fighting, law enforcement and border patrol, land mine detection, building surveillance, process control, vision testing, facial recognition, and traffic control. Figure 4 shows two examples of the image resolution pyroelectric devices can reach.

Toward future technology

Physicists and engineers are likely to develop increasingly sensitive pyroelectric devices. Current research has probably reached the sensitivity limit of pure materials, but devices composed of multiple layers having different compositions and materials offer new possibilities. Incorporating thin-film pyroelectrics directly on semiconductor substrates is emerging as an important research area and IR detection and imaging using pyroelectrics is likely to become much more widespread as costs go down. Important areas to watch for might include nighttime visual aids for automobile drivers, devices that

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