

Perspective: Photopyroelectric effects and pyroelectric measurements: “Invited Review Article: Photopyroelectric calorimeter for the simultaneous thermal, optical, and structural characterization of samples over phase transitions” [Rev. Sci. Instrum. 82, 121101 (2011)]

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It is not an everyday occurrence that one is asked to provide perspective on two 21st century articles (one as titled above by U. Zammit *et al.* and an upcoming one by I. Lubomirsky and O. Stafsudd) that are based on physical phenomena discovered and recorded in classical antiquity, revisited and investigated repeatedly by scientists throughout the middle ages, and more recently from the 18th century to the present. This is the case with the phenomenon of pyroelectricity. The first description of the pyroelectric effect can be found in the book “*On Stones*” written by Theophrastus (approximately 372–287 BC) in 314 BC,¹ who noted that the mineral tourmaline attracted bits of ash and straw when heated. A book printed in 1497 titled *Hortus Sanitatis Major* contains several chapters describing minerals that very likely possess pyroelectric properties.¹ In 1707, Johann Georg Schmidt rediscovered tourmaline’s pyroelectric properties and Louis Lemery in 1717 published a paper describing pyroelectricity (but without using this term) in the journal of the time *Histoire de l’Academie Royale des Sciences*. In 1747, Linnaeus first related the phenomenon to electricity, although this was not proven until 1756 by Franz Ulrich Theodor Aepinus who presented his findings to the Royal Academy of Sciences in Berlin. Research in pyroelectricity became more sophisticated in the 19th century. In 1824, Sir David Brewster was the first author to use the term *pyroelectricity* in a paper entitled “*Observations of Pyro-Electricity of Minerals*”. Etymologically, the name is derived from the Greek word “ $\pi\nu\rho$ ” (fire). Later on, William Thomson (Lord Kelvin) in 1878 and Woldemar Voigt in 1897 associated an electric field with the pyroelectric effect and developed a theory for the physical processes behind pyroelectricity. Pierre Curie and his brother, Jacques Curie, studied pyroelectricity in the 1880s, leading to their discovery of some of the mechanisms behind piezoelectricity.

In modern pyroelectric physics the pyroelectric coefficient vector $\mathbf{p}(T)$ of a material exhibiting pyroelectricity is defined as the rate of change of the spontaneous polarization vector $\mathbf{P}(T, \mathbf{E}_{\text{ext}})$ with temperature,²

$$\vec{p}(T) \equiv \frac{\partial}{\partial T} \vec{P}(T, \vec{E}_{\text{ext}}) \Big|_{E_{\text{ext}}}. \quad (1)$$

In the absence of an applied external field, i.e., for $\mathbf{E}_{\text{ext}} = \mathbf{0}$, a thermal modulation of the material results in synchronous oscillation of the generally depth-dependent

polarization vector,

$$\Delta \vec{P}(z, t) = \vec{p}(T, z) \Delta T(z, t). \quad (2)$$

This amounts to a depth- and time-dependent internal electric field given by³

$$\Delta \vec{E}(z, t) = \frac{1}{\varepsilon_0} \vec{\chi}_e^{-1} : \vec{p}(T, z) \Delta T(z, t) \quad (3)$$

with ε_0 and χ_e being the dielectric constant and electric susceptibility tensor, respectively. Without loss of the general physics of the situation, the thermally excited pyroelectric element is almost always assumed to behave linearly and isotropically. Under these conditions both E and χ_e tensors are reduced to scalars, and the potential difference $\Delta V(t)$ developed across a pyroelectric capacitor of thickness L becomes⁴

$$\Delta V(t) \approx \frac{p_z}{\chi_e \varepsilon_0} \int_0^L \Delta T(z, t) dz, \quad (4)$$

where the component of the pyroelectric coefficient vector along the line of integration (z axis) is given as $\mathbf{p} \cdot \mathbf{dr} = p_z dz$ and is assumed to be independent of the coordinate for linear, isotropic, and homogeneous pyroelectrics. Equation (4) shows the defining relation between the internal thermal field and the potential difference that appears between the two surfaces of a pyroelectric element. Pyroelectric heating can be implemented in many different ways, most prominently thermally, electrically, and/or optically. Thermal excitation can be effected through continuous ramping, heat pulse, and continuous oscillation as described in detail by Lubomirsky and Stafsudd. The optical excitation of pyroelectrics and other materials in contact with pyroelectric sensors to induce (photo)thermal responses is the realm of photopyroelectric (PPE) detection and constitutes the PPE effect. A historical bridge between pyroelectric measurements and PPE effects is exemplified by means of the Chynoweth method. In the periodic pulse technique, originally suggested in 1956 by Chynoweth,⁵ the sample to be measured is subjected to periodic, step-like heating. Practical implementation of the method requires a modulated light source (usually a modulated IR laser or a strong light source with a square-wave mechanical chopper), a current-to-voltage converter and an oscilloscope (preferably with an averaging option) (Fig. 4(a) in Lubomirsky and Stafsudd). The Chynoweth method,

in turn, is related to the laser flash method, proposed by Parker and co-workers of the U.S. Navy Radiological Defense Laboratory in 1961,⁶ the most popular method of measuring the thermal diffusivity of solids to-date. In this method the front face of a small, thermally insulated, and flat sample (usually disk-shaped) is subjected to a very short burst of radiant energy coming from a laser or a xenon flash lamp. The resulting temperature rise on the opposite (rear) face of the sample is measured and the thermal diffusivity is computed from the temperature rise vs. time data. The rear face temperature rise reaches usually from 1 °C to 3 °C. The classical way to calculate the thermal diffusivity from the experimental data is based on the knowledge of a characteristic point of temperature vs. time profiles – the half time ($t_{0.5}$), i.e., the time which corresponds to a rise in the temperature to half of its maximum value (T_{\max}).

In the Chynoweth configuration the pyroelectric element itself is the sample whose thermophysical and pyroelectric properties are measured; in the laser flash configuration, optical heating leads to thermal diffusivity determination, but does not involve pyroelectric detection. Photopyroelectric detection⁷ has bridged these configurations. The pyroelectric effect in pyroelectric films (polyvinylidene difluoride (PVDF) films or crystals of, e.g., LiTaO₃ slabs) depends on the piezoelectric properties of these materials. Piezoelectric polymers, such as PVDF, a long-chain semi-crystalline polymer with repeat of CH₂–CF₂ molecular units, also act as pyroelectric transducers. PVDF is coated on both sides with conductive metal to provide intimate electrical contact. The metal coatings eventually serve as the electrodes providing the output voltage. The first PPE applications for the measurement of the photothermal response of a sample placed in contact with the PVDF detector and excited by a laser beam of variable modulation frequency⁷ demonstrated the high potential of this technique for the optical and thermal evaluation of materials.⁸ Photopyroelectric evaluation of thermal properties consists in the measurement of temperature fluctuations in a sample on which a modulated beam of light impinges, resulting in non-radiative deexcitation processes that take place following the absorption of the intensity-modulated radiation. Due to the fact that thermal-wave propagation depends on the thermal diffusivity of a material, this thermophysical property can be evaluated from the frequency behavior of thermal-wave transport through the material and into the pyroelectric element across the sample-PVDF interface as described by Eq. (4).

Twenty seven years after the introduction of the PPE effect, the field has diversified in many directions that could have hardly been anticipated at its inception. A significant advancement appeared with the reverse photopyroelectric modification of the original configuration.⁹ In this configuration, light impinges directly on the surface of the pyroelectric sensor, which is in contact with the sample on its other side. A comprehensive discussion of PPE applications can be found in the literature.^{10–13} I will conclude this Perspective with a sampling of the most promising and popular directions, the PPE field has taken in the past quarter century.

Photopyroelectric calorimetry was introduced by the late Hans Coufal of IBM Almaden Laboratories.⁷ One of

the most widespread growth areas, *calorimetric* applications of PPE in simultaneous multiple thermophysical parameter measurements (typically thermal diffusivity, thermal effusivity, thermal conductivity, and heat capacity) have raised this measurement modality to an effective and unique tool for *in situ* measurements of thermophysical and thermodynamic parameters in situations of chemical reactions, evaporating species, solid-state decomposition, and other cases where there are few or no alternative analytical methodologies to perform these studies. This multiple parameter measurement capability of PPE detection was recognized early on¹⁴ and subsequently led to the rapidly growing use of the technique over more than a quarter century in studies of thermodynamic phase transitions. This topic is thoroughly covered in the accompanying article by Zammit *et al.*, as PPE measurements can provide extremely valuable and unique insights to the physics of phase transition through the simultaneous study of the behavior of several thermophysical properties at or around the transition temperature. Marinelli *et al.*¹⁵ first applied PPE calorimetry in the conventional laser-sample-detector configuration (defined as “back-detection” and discussed in the accompanying article by Zammit *et al.*). They used harmonic modulation of the laser beam power and obtained high-resolution simultaneous measurements of the thermal conductivity, thermal diffusivity, and specific heat over phase transitions in solids at low temperatures. An alternative methodology using cross correlation and spectral analysis, named “impulse-response photopyroelectric spectrometry” was subsequently introduced by Mandelis and co-workers¹⁶ for the simultaneous measurement of the same thermophysical properties of solids, with first application to the superconductor YBa₂Cu₃O_{7–x}. The field of simultaneous measurement of multiple thermophysical properties work falls within the growing branch of PPE detection directed to study the critical behavior of phase transitions which is reviewed in the accompanying article by Zammit *et al.* In exploring low-temperature calorimetry, Massot *et al.*¹⁷ measured thermal conductivity, thermal diffusivity, and specific heat simultaneously from the same heating or cooling run. They implemented a cryogenic system operating down to 10 K. Their setup was used to characterize the critical parameters of the antiferromagnetic SmMnO₃. Dadarlat and co-workers applied PPE calorimetry to liquid mixtures and composites.¹⁸ They used a PPE calorimetric method based on the effects of sample thickness on signal amplitude and phase¹⁹ and obtained accurate values of liquid sample thermophysical parameters. Room-temperature values of thermal parameters of some vegetable oils were measured. In addition, molecular associations in water-ethylene glycol mixtures and a sedimentation process in a SiO₂ colloidal solution were detected. The PPE method was found to be a potential alternative for thermal property investigations in nanofluids.

Latent heat evaluation by PPE calorimetry has been explored by Mercuri *et al.*²⁰ These authors implemented a frequency-dependent detection of the specific heat and of the latent heat exchanged over first order transitions. The method has been applied to the nematic-isotropic transition of 4-n-octyl-4'-cyanobiphenyl liquid crystal confined in a silica

nanoparticle network, where the specific heat shows a double peak structure.

Studies in food industry, agriculture, biology, and medicine using PPE detection have been reviewed by Chirtoc *et al.*²¹ Among those studies blood erythrocyte sedimentation research is a highlight with PPE detection generating sedimentation velocity profiles originating from different patients.

Measurements in gases, vapors, and liquids by photopyroelectric thermal-wave cavities (TWC) (Refs. 19 and 22) have been explored in the review by Matvienko and Mandelis.¹² Besides accurate and precise measurements of thermophysical properties of non-solid matter, PPE thermal-wave cavities have been used for studies of equations of state,²³ thermal infrared emissivity of fluids in simple instrumental configurations²⁴ and other thermophysical properties such as thermal effusivity.²⁵ PPE TWC detection holds a strong promise for measuring infrared emissivity values of liquids. These are experimentally difficult parameters to measure by other means. For example, only few reports on the emissivity of alcohols exist in the literature.^{26,27} Results for emissivity values reported in the literature are usually obtained using IR thermography; thus they are spectrally limited by the bandwidth of the IR camera. Up to now, measurements of infrared emissivity over the entire infrared spectrum have not been reported and no data appear to be available on the emissivity of water-alcohol mixtures.

Combinations of PPE with other photothermal techniques are still rare, but very promising and versatile. An important example of photothermal confluence is the combined photoacoustic and photopyroelectric use by Thoen and Glorieux²⁸ for the study of thermal properties of condensed matter and for thermal-wave probing of all kinds of materials and structures. These authors gave a brief account of the basic aspects of the standard photoacoustic model with acoustic microphone detection and of a setup with an alternative detection technique with a pyroelectric transducer. The possibilities of these combined schemes for the simultaneous measurement of the specific heat capacity and thermal conductivity were illustrated with results from a study of the Curie point of gadolinium and for liquid crystals.

Applications of PPE to ferroelectrics and pyroelectrics are new areas which tend to integrate the two domains of pyroelectricity and photopyroelectric effects into studies for the improvement of pyroelectric sensors. The work by Dadarlat *et al.*⁹ on PPE studies of ferroelectric materials is seminal as it addresses the relevance of the measurement of their thermal parameters for evaluating the figure of merit of IR sensors²⁹ or pyroelectric accelerators.³⁰ When the pyroelectric element is used as a sensor in a PPE experiment, knowledge of these parameters is crucial, because other measured properties depend of these values and, conversely, characterization of pyroelectric detectors using the photopyroelectric technique³¹ adds much desired consistency and a wealth of sensor information to the PPE measurement. This is important as it has been shown³² that pyroelectric parameters have slightly different values as a function of the composition/purity of ferroelectric materials.

Last, but not least on this informal list of keynote applications, is the realm of *photopyroelectric spectroscopy* (PPES).

The interested reader can consult the review articles.^{11,13} Spectroscopic applications were paramount at the introduction of the photopyroelectric effect,^{7,8} at a time when photothermal techniques, notably photoacoustic spectroscopy, were at their peak popularity as high-dynamic-range, simple spectroscopic methods requiring little or no sample preparation. PPES flourished in the areas of non-radiative quantum yield spectroscopy in solids,³³ including photopyroelectric deconvolution of bulk and surface optical absorption solid-state spectra (e.g., in $\text{Ti}^{3+}:\text{Al}_2\text{O}_3$ crystals³⁴). Contemporaneous studies of the spectroscopic capabilities (reflection, absorption, and transmission) of PPES appeared³⁵ and the use of pyroelectric sensors to monitor surface plasmon amplification for the development of chemical sensors extended the boundaries of PPES to nanoparticle spectroscopy.³⁶ More recently, these boundaries were further extended to the spectroscopy of ceramics, such as $\text{Sb}_2\text{O}_3\text{-ZnO}$,³⁷ and of polymers, such as polyaniline films.³⁸

Owing to its ability to measure thermal energy released from non-radiative electron-hole (or carrier-defect state) recombinations, PPES has been making a strong impact in the field of semiconductor science and technology. Mandelis *et al.*³⁹ have presented PPE spectra of a Si:H thin semiconducting films on quartz. Kumar⁴⁰ has given an excellent review of the effects on the thermal-wave signal produced in PPE experiments using harmonically modulated photocarrier densities (“photo-carrier waves”) optically excited in semiconductor electronic devices.

In this issue, the article by U. Zammit and his co-workers on phase transition studies using thermal, optical, and structural characterization represents the state-of-the-art in the evolution of photopyroelectric detection as an analytical calorimetric methodology. A second article by I. Lubomirsky and O. Stafsudd is in queue for publication. It describes classical and modern, most popular and important pyroelectric characterization methodologies. The confluence of these two domains has been, as I briefly mentioned above, relatively scarce, yet it is extremely important in the evolution of pyroelectric/photopyroelectric technologies as sensitive calorimetric and photothermal solutions in the race to meet the demand for non-destructive characterization techniques of materials and devices of ever increasing sophistication and shrinking size.

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