Bulk characterization methods for non-centrosymmetric materials: second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity

Kang Min Ok, Eun Ok Chi and P. Shiv Halasyamani*

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Characterization methods for bulk non-centrosymmetric compounds are described. These methods include second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity. In this *tutorial review* with each phenomenon, details are given of the measurement techniques along with a brief history and background. Finally, data interpretation is discussed.

Introduction

Materials found in non-centrosymmetric (NCS), or acentric, crystal classes, *i.e.* crystal classes lacking a center of inversion, can exhibit a variety of technologically important physical properties. These include piezoelectricity, ferroelectricity, and pyroelectricity.[1] The relationships of these properties with respect to a particular crystal class have previously been discussed,[2] so only a brief outline will be given here. A diagram depicting the relationships between acentric crystal class and physical property appears in Fig. 1. Of the 21 NCS crystal classes, 11 are chiral, and therefore possess a 'handedness', whereas 10 are polar, *i.e.* they contain a dipole moment. Only five crystal classes—1, 2, 3, 4, and 6—exhibit chiral ***and*** polar symmetry. In addition to the aforementioned properties, two additional phenomena occur in acentric materials, second-harmonic generation (SHG) and piezoelectricity. Interestingly, the symmetry requirements for both phenomena are identical, as both are described mathematically by the same third rank tensor, d_{ijk}. A comprehensive description of the matrix

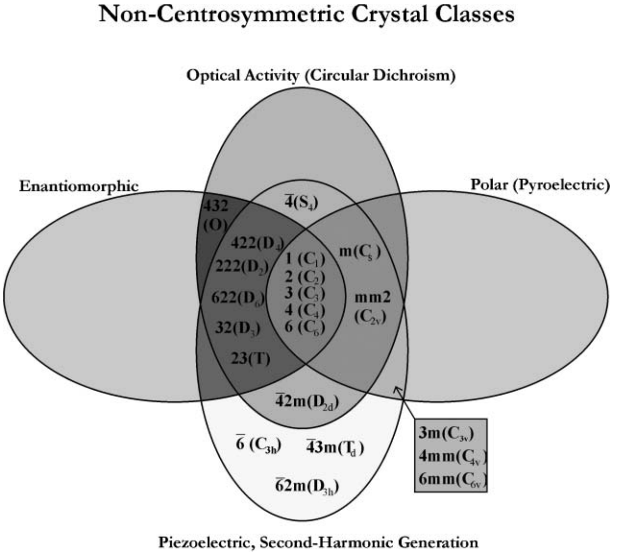
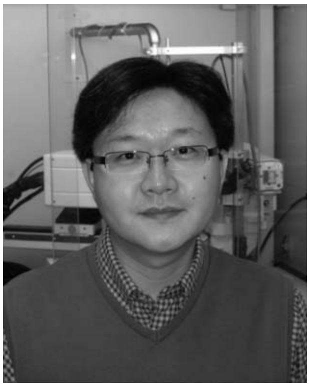


Fig. 1 Physical property inter-relationships in non-centrosymmetric crystal classes. (Reproduced with permission from *Chem. Mater.*, 1998, **10**, 2753–2769.[2] Copyright 1998 American Chemical Society.)

Department of Chemistry and Center for Materials Chemistry, University of Houston, Houston, TX 77204-5003, USA



Kang Min Ok

Kang Min Ok was born in Busan, Korea in 1970. He received his BS and MS in chemistry in 1996 and 1998, respectively, from Sogang University, where he worked for Professor Chong Shik Chin on the synthesis of Iridium-alkynyl organometallic compounds and catalytic oligomerization of terminal alkynes. In 2003, he received his PhD degree from the University of Houston under the direction of Professor P. Shiv Halasyamani. His thesis was focused on the new second-harmonic generating (SHG) mixed metal oxide materials. He has worked on the synthesis and characterization of new non-centrosymmetric materials with Professor P. Shiv Halasyamani as a postdoctoral research associate at the University of Houston. He is currently a postdoctoral associate at the University of Oxford, working for Prof. Dermot O'Hare.

Eun Ok Chi

Eun Ok Chi received her PhD in solid state chemistry from the Sung Kyun Kwan University in Korea in 1999 and she studied the synthesis of magnetoresistant materials and their electromagnetic properties at the Center for CMR (colossal magnetoresistance) Materials in KRISS (Korea Research Institute of Standards and Science). She joined Dr Halasyamani's group at the University of Houston as a post-doctoral associate in 2003. Her current research interest is to elucidate the relationship between crystal structure and physical properties of non-centrosymmetric materials.

mathematics and notation has been given by Nye.[1] As seen in Fig. 1, all acentric crystal classes except 432 (O) possess the correct symmetry for SHG and piezoelectric behavior. Additionally, although all polar materials exhibit the required symmetry for SHG and piezoelectricity, the converse is not true. With respect to polarity, two additional properties are possible, namely ferroelectricity and pyroelectricity. With the former, the material's dipole moment is reversible (switchable) in the presence of an applied voltage, whereas with the latter the dipole moment is not switchable. Thus all ferroelectric materials are pyroelectric, but the converse is not true.

This *tutorial review* focuses on methods that can be used to characterize NCS compounds, rather than strategies toward synthesizing new acentric materials. The latter has been discussed by us and others.[3–9] In addition, rigorous mathematical treatises on some of these phenomena have also been published.[1,10,11] We will focus on the characterization of bulk materials, as opposed to thin films or single crystals, since often with the latter large crystals (>5 mm) are necessary. The techniques described herein, however, can be used to measure single crystals; a requirement is that large untwinned single crystals are necessary. Often, these crystals must be cut and polished to expose specific crystallographic faces. Routinely growing, cutting, and polishing such crystals on new synthetic systems is exceptionally difficult.

We will discuss the characterization of second-harmonic generation, piezoelectric, pyroelectric, and ferroelectric properties in bulk NCS materials. Each of these phenomena has been discussed extensively in the literature,[10–15] so only a brief description of each phenomena will be given here.

Second-harmonic generation

Second-harmonic generation (SHG), or frequency doubling, can be defined as the conversion of a specific wavelength of light into half its original, *i.e.* $\lambda_1 \rightarrow \frac{1}{2}\lambda_1$, or with respect to frequency ω, $\omega_1 \rightarrow 2\omega_1$. The first report of second-harmonic generation (SHG) was described by Franken *et al.* in 1961,[16] who reported SHG on a quartz crystal using a ruby laser. Following this experimental result, Bloembergen and co-workers published their classic paper that provided a theoretical foundation for the origin of the non-linear optical susceptibility.[17] For several years following Franken's result, large single crystals were required to measure SHG. A seminal paper published in 1968 described a technique whereby SHG could be measured from polycrystalline samples.[12] It is this technique that we will describe in more detail.

P. Shiv Halasyamani

Professor P. Shiv Halasyamani received his PhD in Chemistry from Northwestern University in 1996 working for Professor Kenneth R. Poeppelmeier on the synthesis and characterization of new mixed metal oxy-fluoride materials. He did his post-doctoral research at Oxford University in the laboratory of Professor Dermot O'Hare investigating uranium hydrothermal chemistry as well as in situ diffraction. While at Oxford he was awarded a Junior Research Fellowship at Christ Church College. Professor Halasyamani joined the faculty of the Department of Chemistry at the University of Houston in 1999 and is currently an Associate Professor. His research focuses on the synthesis, characterization, and structure–property relationships in new non-centrosymmetric oxide materials. Professor Halasyamani's awards include NSF Career Grant, Beckman Young Investigator Award, the ExxonMobil Solid State Award, and the University of Houston Excellence in Research Award.

Piezoelectricity

Piezoelectricity, derived from the Greek *piezen*, meaning to press, was discovered in 1880 by Jacques and Pierre Curie.[18] They observed that some materials become electrically polarized when subjected to a mechanical force. Soon after, the converse effect was discovered wherein the application of a voltage resulted in a macroscopic strain. In 1910, Voigt published a standard reference detailing the electromechanical relationships in piezoelectric materials,[19] and a thorough review of the early history of piezoelectricity can be found in Cady's seminal book.[11] Thus with piezoelectricity, two effects are possible: direct and converse. Both direct and converse effects are used in a variety of applications. The direct effect results in generator action: the piezoelectric material converts mechanical energy to electrical energy. This generator action is used in solid-state batteries, sensing devices, and fuel lighting applications. The converse effect results in motor action: the piezoelectric material converts electrical energy to mechanical energy. This motor action is used in ultrasonic and acoustic applications, micromotor devices, and electromechanical transducers. We will describe measurements on bulk materials utilizing both direct and converse piezoelectric techniques.

Pyroelectricity

The pyroelectric effect may be defined as the change in spontaneous polarization, P_s, as a function of temperature.[20] The symmetry requirements for pyroelectricity are far more restrictive compared with SHG and piezoelectricity. To exhibit a spontaneous polarization, the material in question must crystallize in one of ten polar crystal classes (1, 2, 3, 4, 6, m, mm2, 3m, 4mm, or 6mm). Thus polarity is required for pyroelectric behavior. Determining the pyroelectric coefficient may be done two ways—either measuring the pyroelectric current or the pyroelectric charge.[21] We will describe both techniques.

Ferroelectricity

A ferroelectric may be formally defined as a pyroelectric material that has a reversible, or 'switchable', polarization.[10] Thus the material must be polar, must possess a permanent dipole moment, and must be capable of having this moment reversed in the presence of an applied voltage. The former occurs if the material crystallizes in one of ten polar crystal classes (1, 2, 3, 4, 6, m, mm2, 3m, 4mm, or 6mm). Determining the latter is more involved. Polarization reversal, or ferroelectric hysteresis, may be measured through a Sawyer–Tower circuit.[22] Additionally, because of the relatively large voltages needed for polarization reversal, the material under investigation must be insulating. Another feature that is observed in some, but not all, ferroelectric materials is a dielectric anomaly at the Curie temperature. A maximum in the dielectric constant is often observed at the Curie temperature. This temperature indicates a phase-change to a centrosymmetric non-polar, *i.e.* non-ferroelectric, structure. We will describe measurement techniques that allow one to determine ferroelectric hysteresis curves.

This *tutorial review* is divided into four sections. Each section describes a specific NCS property, the history of the phenomena, and provides details on the measurement as well as an interpretation of the resulting data.

Second-harmonic generation

Second-harmonic generation (SHG), or frequency doubling, can be defined as the conversion of a specific wavelength of light into half its original, *i.e.* $\lambda_1 \rightarrow \frac{1}{2}\lambda_1$, or with respect to frequency ω, $\omega_1 \rightarrow 2\omega_1$. It was not until the invention of the laser in 1960 by Maiman[23] that sizeable non-linear optical effects, such as SHG, could be observed. The induced polarization, P, occurring in a material because of these large optical fields can be written as a power series: $P = \chi E + dE^2 + \ldots$ where χ is the linear electric susceptibility with the higher order terms leading to non-linear effects such as SHG. These non-linear effects are described by expanding the polarization:

$$P_i = \chi_{ij}E_j + \chi_{ijk}E_jE_k + \chi_{ijkl}E_jE_kE_l + \ldots$$

where χ_{ij} is the electric susceptibility, with the second-order non-linear coefficient described as χ_{ijk}. Third order terms, χ_{ijkl}, give rise to third harmonic generation. It is only in a non-centrosymmetric environment that $\chi_{ijk} \neq 0$. χ_{ijk} is a third-rank tensor, and in experimental SHG measurements is replaced by d_{ijk} coefficients, where $2d_{ijk} = \chi_{ijk}$.

After the discovery of SHG in 1961,[16] large crystals (several mm) were required to investigate the phenomenon. A technique, described in 1968, allowed one to determine the SHG efficiency of polycrystalline samples. It is this technique that we describe in more detail. At its most basic, the powder SHG technique requires very little instrumentation. Additionally, all of the instrumentation is commercially available. A typical set-up for powder SHG measurements is shown schematically in Fig. 2. A low energy laser, pulsed or continuous, is needed. Usually a commercially available Nd-YAG laser (1064 nm output) is used,[24] since any SHG will appear in the visible at 532 nm (green), and thus the experimentalist is literally able to see the SHG. The sample, a polycrystalline powder, is placed in a fused silica tube (a capillary tube can be used). For a 'quick and dirty measurement' that addresses the simple question of whether the material is SHG active or not, approximately 50 mg of sample is required. If more quantitative SHG information is desired, a larger amount of sample, around 1 g, is needed. A photomultiplier tube (PMT) connected to an oscilloscope is also required. Using the PMT and oscilloscope allows the user to collect SHG data on a standard and compare the results with newly synthesized materials. The entire system: laser, PMT, power supplies, optics, and oscilloscope must be placed on a flat surface. A laser table is ideal, since the various optical pieces can be attached to the table, but is not required. The total footprint of the system is 2′ × 6′; thus only a relatively small flat area is needed.

Measurement of SHG and data interpretation

Once the laser, PMT, and optics are aligned, collecting the SHG is reasonably straightforward. As previously stated, a small amount of the powder to be tested (~50 mg) is placed in a fused silica tube. The SHG of the new material may be compared with standard materials. SHG properties were first measured on α-SiO_2; thus the material is defined to have an efficiency of 1.0 (dimensionless). Most SHG efficiencies are

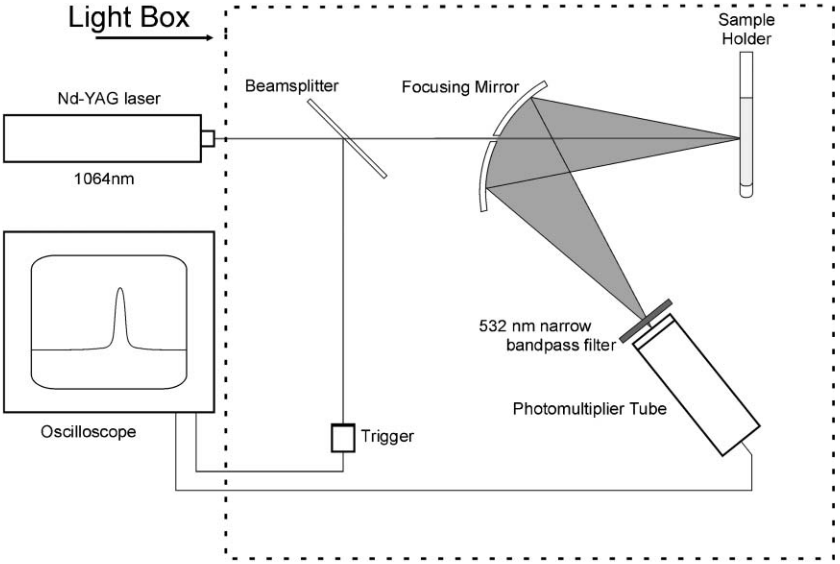


Fig. 2 Schematic diagram of a modified Kurtz–Powder Laser System.

reported with respect to α-SiO_2: $BaTiO_3$ and urea both have SHG efficiencies of 400 × SiO_2, whereas $LiNbO_3$ has an efficiency of 600 × SiO_2.[12,25] Once the SHG of a polycrystalline sample of SiO_2 has been measured, it is very straightforward to roughly determine the SHG efficiency of any new material. If more accurate SHG information is required, additional experiments become necessary. Typically a larger amount of material is necessary, of the order of 1 g, and the powder needs to be sieved into particle sizes ranging between 20 μm and 120 μm. This may be done using commercially available sieves. Measuring the SHG as a function of particle size (20 μm–120 μm) has two advantages. First, the SHG efficiency is determined more accurately. Second, type 1 phase-matching information may be determined.[12] Type 1 phase-matching, or index matching, occurs when the phase velocity of the fundamental radiation (1064 nm) equals the second harmonic (532 nm). If type 1 phase-matching occurs, the SHG efficiency will increase with the particle size and plateau at a maximum value. If phase-matching does not occur, the SHG efficiency will reach a maximum value and then decrease, as the particle size increases. Phase-matching ($LiNbO_3$) and non-phase-matching (α-SiO_2) curves are shown in the diagrams below. Note that the curves are drawn to guide the eye, and are not a fit to the data.

These figures also clearly illustrate our earlier statement—accurate SHG efficiencies can *only* be determined by measuring similar particle size ranges. For example, if the SHG of α-SiO_2 is measured with particles >90 μm and the unknown material is measured at a smaller particle size, the SHG efficiency of the unknown material would be overestimated. Thus, it is critical that the SHG of SiO_2 and the unknown material be measured at the sample particle size range, *i.e.* 45–63 μm.

Once the phase-matching capabilities of the material are known, the bulk non-linear optical susceptibility, $\langle d_{\text{eff}} \rangle$, can be estimated. The values of $\langle d_{\text{eff}} \rangle$ for phase-matchable and non-phase matchable materials are:

$$\langle d_{\text{eff}} \rangle_{\text{PM}} = \left\{ \frac{I^{2\omega}(A)}{I^{2\omega}(LiNbO_3)} \times 7.98 \times 10^2 \right\}^{1/2}$$

$$\langle d_{\text{eff}} \rangle_{\text{NPM}} = \left\{ \frac{I^{2\omega}(A)}{I^{2\omega}(SiO_2)} \times 0.3048 \right\}^{1/2}$$

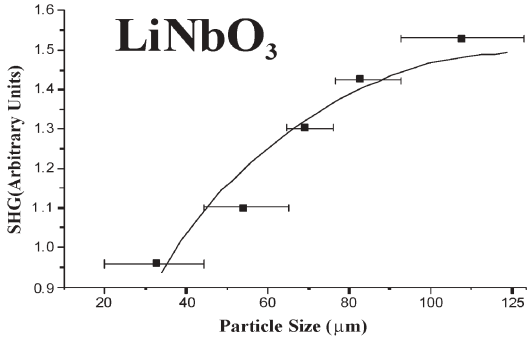
The SHG efficiency of the unknown compound (A) is either compared with $LiNbO_3$ (SHG efficiency of 600 × SiO_2) or SiO_2 depending on whether the material is phase-matchable (PM) or non-phase-matchable (NPM). The units for $\langle d_{eff} \rangle$ are picometers per volt (pm V^{-1}).

Piezoelectricity

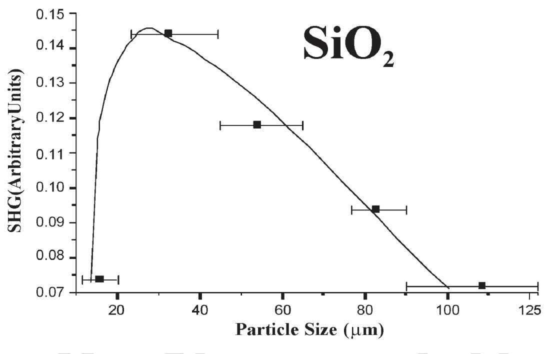
The piezoelectric phenomena occur as both the direct and converse effect.[11] With the direct effect, an external stress, σ_{jk}, results in a change in polarization, P_{i}, and is formulated as $P_{\text{i}} = d_{\text{ijk}}\sigma_{\text{jk}}$, where d_{ijk} (i, j, k = 1, 2, 3) is the piezoelectric charge coefficient, given in coulombs per newton (C N^{-1}). With the converse effect, an applied field, E_{i}, results in a strain, ε_{jk}, and is formulated as $\varepsilon_{\text{jk}} = d_{\text{ijk}}E_{\text{i}}$, where d_{ijk} is the piezoelectric strain coefficient, given in meters per volt (m V^{-1}). With both effects, d_{ijk} is a third rank tensor. It is important to note that the units for d_{ijk} when measuring direct or converse effects are equivalent, that is 1 C N^{-1} = 1 m V^{-1}. Often the piezoelectric equation is written as $P_{\text{i}} = d_{\text{ij}}\sigma_{\text{j}}$ (i = 1, 2, 3; j = 1, 2, … 6), where d_{ij} is the contracted notation for d_{ijk}.[1] It is important to note that d_{ij} does not transform as a second-rank tensor. The piezoelectric constants, both charge and strain, given as d_{ij}, are usually reported as one or more terms, d_{33}, d_{31}, and/or d_{15}. With d_{33} the induced polarization (strain) is parallel to the applied stress (electric field), whereas with d_{31} and d_{15} the induced polarizations (strains) are perpendicular to the applied stresses (electric fields). Another important variable with respect to piezoelectric devices is the electromechanical coupling factor, *k*. This factor describes the efficiency in the conversion of mechanical energy to electrical energy, the direct effect, or the conversion of electrical energy to mechanical energy, the converse effect. Generally large *k* values are desirable for efficient energy conversion, however the coupling term does not take into account dielectric or mechanical losses.

Sample preparation and measurements

Unlike the SHG measurement where a loose polycrystalline powder can be used, a well-sintered ceramic is necessary for bulk piezoelectric measurements. For our measurements, the dimensions of the sintered disk are a diameter of ½" and a thickness of approximately 1 mm. In addition, the ceramic must undergo electrical poling. With the poling technique, electrodes are applied to both sides of the sample–usually silver or gold has been sputtered or mechanically applied. The poling process takes place above room temperature (100–300 °C) and with an applied voltage (1000–2000 V) for 20–30 min. After



Phase-matchable



Non-Phase-matchable

poling the material has a response similar to a single crystal, where the entire ceramic acts as a single unit. Although poling will not align 100% of the crystallites, the extent of alignment is sufficient to measure the piezoelectric response. It is interesting to note that it was only in 1949 that poling was discovered to be critical in changing a seemingly inert ceramic into an electromechanically active material.[26] Before this time, the assumption was that the individual crystallites in a ceramic would effectively cancel, rendering the material useless for industrial applications.

Direct piezoelectric measurements

The direct piezoelectric effect occurs when a mechanical force on a material results in a change in polarization. The resultant piezoelectric charge constant, d, is a third rank tensor, d_{ijk}, and is measured in C N^{-1}. When this tensor notation is reduced to matrix notation,[1] the d_{ijk} terms become d_{ij}, with i = 1, 2, 3; j = 1, 2, … 6. As stated earlier, d_{ij} does not transform as a second-rank tensor. For both the direct as well as the converse effects, the d_{33} value of the material is usually reported. The subscripts specifically denote that what is being measured is a polarization parallel to the direction of the mechanical force. Lateral (d_{31}) and shear (d_{15}) polarizations may also be determined, but these measurements are usually done on specifically cut single crystals. To measure the direct piezoelectric effect, a static or quasi-static method is used. Although this method is less precise than the resonance method,[27] the ease of use and availability of instrumentation makes the static method preferable. The static method employs a Berlincourt d_{33} Meter, for which a number of commercial systems are available.[28] The instrument is very straightforward to use. A known force is applied to the poled ceramic, as well as to a standard piezoelectric. Comparing the resultant electric signals allows one to determine the d_{33} of the sample. The value of d_{33} is simply read off the meter. These meters can measure d_{33} charge constants within a few percent, with a range from 20–2000 pC N^{-1}.

Converse piezoelectric measurements

The d_{33} strain constant may be determined on bulk samples through converse piezoelectric measurements. As noted earlier, the strain constant is expressed in units of m V^{-1} that are equivalent to C N^{-1}. Converse piezoelectric measurements are more experimentally difficult compared with the direct measurements, but render greater accuracy. The converse measurements use an optical technique in order to measure the small strains in the sample caused by the application of a voltage. The experimental system is composed of a high voltage amplifier and interface as well as an optical sensor and probe. The optical probe remains stationary and is approximately 1 mm above the sample (see Fig. 3).

In the native state, or zero voltage, a finite amount of light is collected in reflection from the sample. When the voltage is applied the sample undergoes a macroscopic strain and the amount of light collected by the optical sensor changes. The change in collected light is converted to a displacement change, in m V^{-1}. Mathematically, d_{33} may then be calculated through: $d_{33} = S/E = \Delta t/V$, where S is the strain, E is the field strength (in V m^{-1}), Δt is the change in thickness, and V is the applied voltage. A plot of strain *vs.* electric field produces the commonly observed butterfly curves, similar to the one shown in Fig. 4. The equation also indicates that d_{33} depends on the *change* in thickness of the sample, not the initial sample thickness. The magnitude of the piezoelectric response can vary greatly among oxide materials. For example, ZnO, $LiNbO_3$, and $LiTaO_3$ have d_{33} values of around 10 pC N^{-1}, whereas $BaTiO_3$ and PZT (lead zirconate titanate) have corresponding d_{33} coefficients of approximately 190 and between 100–600 pC N^{-1} for PZT compositions.[21]

Pyroelectricity

The pyroelectric effect may be defined as the change in spontaneous polarization, P_s, as a function of temperature. The pyroelectric coefficient, $\boldsymbol{p}$, a vector, in units of μC m^{-2} K, can be defined as:

$$\boldsymbol{p} = \frac{\mathrm{d}P_s}{\mathrm{d}T}$$

with the spontaneous polarization, P_s, temperature, T, given in units of μC m^{-2} and K respectively. Surprisingly, the effect has been known for over 2400 years, with the first account attributed to the Greek philosopher Theophrastus. He described a stone,

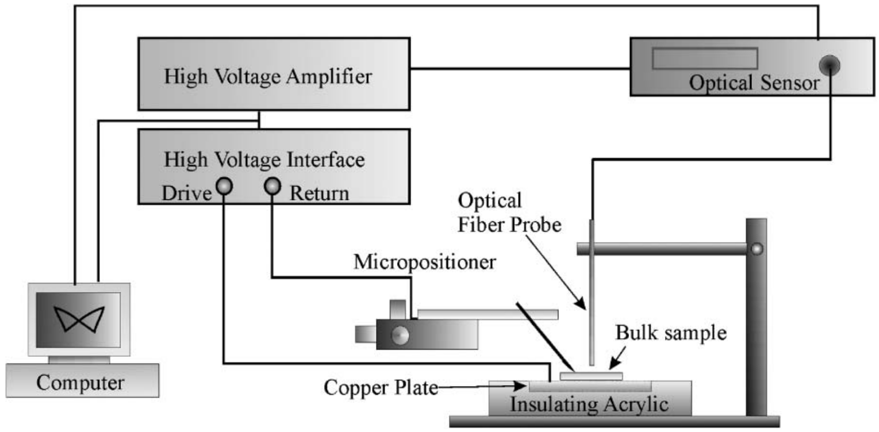


Fig. 3 Experimental system to measure converse piezoelectric effects.

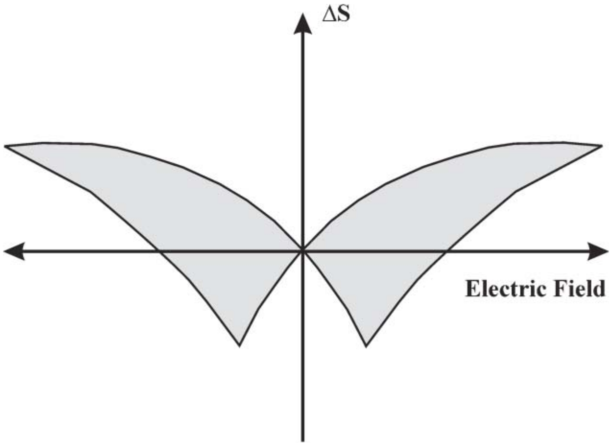


Fig. 4 Butterfly loop observed in converse piezoelectric measurements.

lyngourion—probably tourmaline—that was capable of attracting straw and pieces of wood. A thorough and comprehensive description and history of the phenomenon may be found in Lang's seminal text and recent paper.[15,20] The first researcher to use the term pyroelectricity was Brewster in 1824.[29] Interestingly, the material Brewster investigated, Rochelle salt, was studied nearly a century later by Valasek in his discovery of ferroelectricity.[30,31] The pyroelectric effect was mainly an academic curiosity until 1938, when Y. Ta suggested that tourmaline crystals could be used as an infrared sensor.[32] After this publication, and with the onset of the Second World War, investigation into pyroelectricity grew rapidly and remains an active area of current research among chemists, material scientists and engineers. Currently, pyroelectrics are mainly used for thermal detectors. Pyroelectric devices respond to changes in temperature and therefore can be used to detect and observe stationary or moving objects. A few of the applications for pyroelectric detectors include burglar alarms, pollution monitors, and the measurement of thermal properties of materials.

Sample preparation and measurement

The sample preparation for a bulk pyroelectric measurement is very similar to what is required for a bulk piezoelectric measurement. A well-sintered ceramic disk that has been electrically poled is required. Determining the pyroelectric coefficient may be divided into two groups—the measurement of the pyroelectric current and the measurement of the charge.[21] We will describe measurement techniques for both groups. In addition, the pyroelectric effect can be subdivided into primary and secondary effects. The primary effect is observed when the material is rigidly clamped under a constant strain to prevent any thermal expansion or contraction. Secondary effects occur when the material is permitted to deform, *i.e.* the material is under constant stress. Thermal expansion results in a strain that changes the spontaneous polarization attributable to the piezoelectric effect. Thus the secondary pyroelectric effect includes contributions caused by piezoelectricity. Exclusively measuring the pyroelectric coefficient under constant strain is experimentally very difficult. What is experimentally measured is the total pyroelectric effect exhibited by the material—the sum of the primary and secondary effects.

Pyroelectric current

The most straightforward technique to measure the pyroelectric current is the direct method.[33] With the direct method, the pyroelectric material is heated uniformly at a constant rate, *i.e.* $\frac{\Delta T}{\Delta t} = 1-2\,^{\circ}\mathrm{C\ min^{-1}}$. The pyroelectric coefficient is determined by measuring the pyroelectric current, given by $i(T) = A\left(\frac{\Delta T}{\Delta t}\right)\boldsymbol{p}$, where A is the sample area. Thus a plot of $\boldsymbol{p}(T)$ over a wide range of temperature can be easily obtained. More experimentally complicated methods may also be used to determine the pyroelectric current. These include radiation heating[34] and capacitive charging.[35] These methods are more accurate compared with the direct method, but experimentally more complicated.

Pyroelectric charge

The original method for measuring the pyroelectric charge was developed in 1915.[36] This technique, known as the static method, determines the charge, *i.e.* polarization, of the material as a function of temperature. The technique works very well at discrete temperatures. The static method was improved upon by Glass, with an integration technique that allowed for larger changes in temperature.[37] The pyroelectric coefficient may be obtained by graphical differentiation. A schematic of the static method is shown in Fig. 5. If the material under investigation is ferroelectric, *i.e.* the polarization is reversible, the pyroelectric coefficient may be

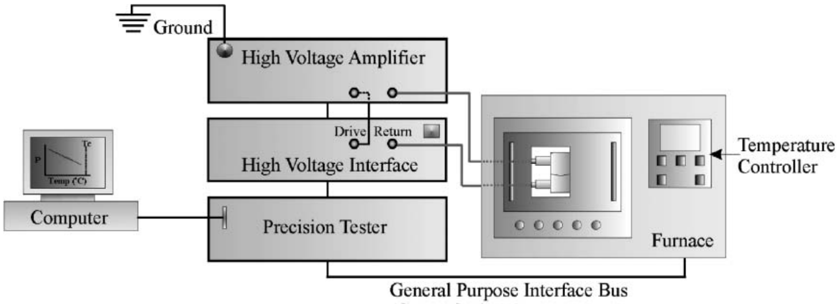


Fig. 5 Schematic of the static method for determining the pyroelectric coefficient

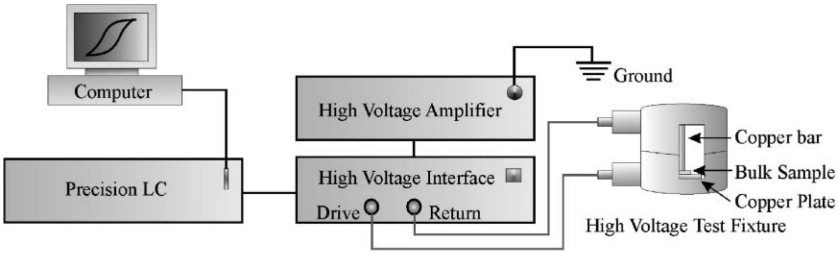


Fig. 6 Experimental Sawyer–Tower Circuit.

determined by measuring the temperature dependence of the remanent polarization. The remanent polarization is determined through a Sawyer–Tower loop (see the Ferroelectricity section).[22] As with the piezoelectric technique discussed earlier, graphical differentiation is used.

Clearly, ferroelectric and non-ferroelectric pyroelectrics are possible, and the pyroelectric coefficient varies widely between the two groups. The pyroelectric coefficients for ferroelectrics such as $BaTiO_3$, $LiNbO_3$, and $LiTaO_3$ are -200, -83, and -176 μC m^{-2} K respectively, whereas for non-ferroelectrics such as ZnO, tourmaline, and CdS the corresponding values are -9.4, -4.0, and -4.0 μC m^{-2} K respectively.[15]

Ferroelectricity

A ferroelectric may be formally defined as a pyroelectric material that has a reversible, or 'switchable', polarization. Ferroelectricity was discovered in *ca.* 1920 by Valasek[30,31] in Rochelle salt ($NaKC_4H_4O_6{\cdot}4H_2O$)—a material that was known at the time for its piezoelectric and pyroelectric properties. For years after this discovery, ferroelectricity was viewed simply as a scientific curiosity, and was thought to occur only rarely in materials. Then in 1935, the first family of ferroelectrics was discovered in KH_2PO_4 and related materials.[38,39] The first non-hydrogen bonded ferroelectric, $BaTiO_3$, was subsequently discovered in *ca.* 1945 by Wul and Goldman in the Soviet Union and von Hippel's group in the United States.[40,41] Until this discovery it was assumed that hydrogen bonding was necessary for ferroelectricity to occur. The fact that oxides could exhibit ferroelectric behavior ushered in a new era, and soon thereafter a number of ferroelectric oxides were discovered. A thorough and rigorous discussion that encompasses all aspects of ferroelectricity may be found in the comprehensive text by Lines and Glass.[10]

Sample preparation and hysteresis loop

Similar to piezoelectric measurements, for ferroelectric measurements a well-sintered and dense (>95%) ceramic disk that has been electrically poled is necessary. The circuit design for measuring ferroelectric hysteresis curves was published in 1930.[22] Since that time there have been a few reports modifying the original design,[42,43] but the overall concept has not changed in over 70 years. At its most basic, a linear capacitor is placed in series with the sample. An AC or DC voltage is then applied. The voltage measured across the capacitor is equivalent to the polarization of the sample (see Fig. 6). The measurement of spontaneous polarization on the order of 5–50 μC cm^{-2} in bulk samples requires voltages in excess of 1000 V. The circuit is used to measure a ferroelectric hysteresis loop, *i.e.* the material's switchability in the presence of an applied voltage (see Fig. 7). The hysteresis loop is determined by measuring the polarization of the material, in μC cm^{-2}, as a function of applied voltage, V. The full details of a ferroelectric hystersis loop have been extensively discussed,[44] so only a brief description will be given here. Several points of the loop are of interest, the spontaneous (P_s) and remanent (P_r) polarizations, the coercive field (E_c), and the general shape of the loop. In a ferroelectric material, when all of the dipole moments are aligned, the material is considered saturated since an increase in applied voltage will not increase the polarization. The linear extrapolation of the curve back to the polarization axis represents the spontaneous polarization ($+P_s$). As the applied voltage is reduced from its maximum positive value to zero, some dipole moments will remain aligned, and a remanent polarization ($+P_r$) is observed. As the applied voltage spans the range from its maximum positive to negative values, $-P_s$ and $-P_r$, will be observed. Structurally all of the dipole moments have switched from the positive to the negative—the up and down arrows in Fig. 7. This is the 'switchability' alluded to earlier. Additional information that

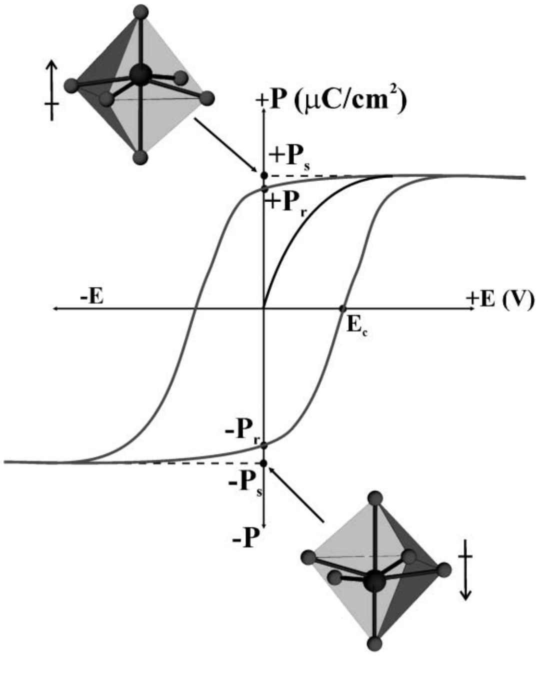


Fig. 7 Ferroelectric hysteresis loop (polarization *vs.* applied voltage).

can be obtained from a ferroelectric hysteresis loop includes the coercive field (E_c) and the shape of the loop. The coercive field is the magnitude of the external applied voltage necessary to remove all the polarization in the material. The E_c as well as the shape of the loop, *i.e.* the 'squareness' or sharpness, are sample preparation dependent and are influenced by grain size and homogeneity.[44]

As previously stated, ferroelectrics may be divided into two groups, hydrogen bonding and non-hydrogen bonding. The spontaneous polarization, P_s, values vary greatly between the two groups. With KH_2PO_4 and related materials, P_s values range from 4.0–6.0 $\mu C\ cm^{-2}$, whereas with oxides such as $BaTiO_3$ and $LiNbO_3$ the corresponding values are 26 and 71 $\mu C\ cm^{-2}$ respectively.[10]

Summary

We have described characterization techniques on bulk materials for measuring four 'acentric' properties—second-harmonic generation, piezoelectricity, pyroelectricity, and ferroelectricity. These techniques may also be used for investigating single crystals, however, large (~5 mm) untwinned crystals are required. All of the techniques described utilize commercially available instrumentation that are relatively straightforward to assemble in any laboratory.

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