A Second Harmonic Analyzer for the Detection of Non-Centrosymmetry

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The existence of optical second harmonic generation has been shown to be a highly reliable and sensitive physical test for the detection of crystalline non-centrosymmetry. A second harmonic analyzer has been constructed which can resolve space group ambiguities arising from Friedel's Law with a confidence level greater than 99%. The system has been optimized for use with powdered crystalline samples so as to obviate the need for large single crystals and thus facilitates rapid determination of crystalline non-centrosymmetry. The present analyzer can routinely detect second harmonic generation at levels 1/1000 of that generated in a quartz standard, this is about an order of magnitude increase over previously reported systems. Data are reported on several materials including dibenzyldisulfide, and \((C_6H_5)_3 P\)\(_3\)CuBF\(_4\). The detection of structural phase transitions with the second harmonic analyzer is reported for BaTiO\(_3\), colemanite and phenanthrene. Second harmonic generation in the 'cubic' phase of BaTiO\(_3\) promises to be a powerful tool for determining the dynamics of the ferroelectric phase transition. It is the most direct method for establishing the existence or nonexistence of microscopic polar regions well above the Curie point in a nominally centrosymmetric phase.

I. Introduction

Crystal symmetry information is most often obtained by X-ray diffraction techniques. However, owing to Friedel's law, it is not possible to detect the absence of an inversion center by ordinary X-ray diffraction methods. Anomalous X-ray scattering, statistical tests (Wilson, 1949; Howells, Phillips & Rogers, 1950) or Patterson analysis (Buerger, 1950, 1960) can be used to resolve space group ambiguities arising from Friedel's law. Even with these widely used methods, many center of symmetry problems are still difficult to resolve, particularly in cases where centrosymmetrically located atoms of high atomic number exist in a non-centrosymmetric crystal. This paper describes an instrument of high sensitivity and reliability for resolving center of symmetry ambiguities through the use of optical second harmonic generation (SHG) in crystalline powders.

Physical tests can often provide useful ancillary data of crystallographic importance. The properties most commonly studied to supplement X-ray diffraction data are: (1) crystal morphology, (2) etch figures, (3) optical indicatrix/optical activity, (4) pyroelectricity, (5) piezoelectricity. From symmetry arguments (Nye, 1957) it can be shown that all the non-centrosymmetric point groups may have non-zero piezoelectric coefficients with the single exception of point group 432. The strength of the symmetry arguments coupled with the relative convenience of the Giebe-Scheibe (1925) technique makes the piezoelectric test an attractive physical test for non-centrosymmetry. Although second harmonic generation conversion efficiency can approach 90% in commercial phase-matched single-crystal devices, non-centrosymmetric crystalline powders typically have power conversion efficiencies of \(10^{-9}\) to \(10^{-14}\) (Kurtz & Dougherty, 1975). A 1.06 \(\mu\)m illumination source consisting of a single pulse, non-Q-switched laser can generate peak powers of about 2000 W, while standard laboratory photomultipliers can detect 5000 photons (\(\sim 10^{-12}\) W) of 0.53 \(\mu\)m second harmonic (SH) light, in a 300 \(\mu\)s pulse. These approximations, in agreement with those of Woolfson (1970), show that using SHG, highly

* A comparison of the Giebe Scheibe and SHG methods (Kurtz, 1972a), encompassing 86 non-centrosymmetric materials, found 31 cases where the SHG technique detected the lack of centrosymmetry while the piezoelectric test gave a null result. In no case was the converse true.
sensitive experimental devices can be constructed to
determine the absence of a center of symmetry.

While the SHG method is conceptually simple, there are significant problems in the practical applications of the technique. It will be shown that the strength of the SHG technique as a structural tool is that it provides an independent, sensitive and reliable means of rapidly determining crystallographic non-centrosymmetries, providing the proper design and operational methods are used.

The following sections will describe second harmonic generation, the design of a practical second harmonic analyzer, sample preparation, operational techniques, and typical applications of SHG to crystallographic problems.

II. Second harmonic generation

When a light wave of frequency \( \omega \) passes through a non-centrosymmetric crystal, the electric field \( E(\omega) \) associated with the wave induces a polarization \( P(2\omega) \) at twice the incident frequency, i.e. \( 2\omega \). This interaction is given by the tensor relation:

\[
P_i(2\omega) = \varepsilon_{0}d_{ijk}(2\omega)E_j(\omega)E_k(\omega).
\]

The absolute sign of the tensor element can be used to characterize the atomic arrangement (Abrahams, 1974), however for non-centrosymmetry determination, it is sufficient to consider the average SHG effect. The second harmonic power, \( P(2\omega) \) can be written:

\[
P(2\omega) = \frac{Kl_{c}^{2}P^{2}(\omega)}{A}
\]

where \( l_{c} \) is the coherence length, \( A \) the beam area, and \( K \) a material-dependent constant proportional to \( d(2\omega)^{2} \) with magnitude \( \sim 10^{-9} \text{ W}^{-1} \) for quartz (Kurtz & Dougherty, 1975).

III. Design of the second harmonic analyzer

An instrument to detect crystalline non-centrosymmetries reliably should meet the following criteria: (1) Have adequate sensitivity to provide a high confidence level in the results. (2) Be usable over the widest possible variety of single crystals and powders. (3) Provide a means of distinguishing the truly non-centrosymmetric case from spurious results. (4) Be easy to use, requiring no specialized knowledge of other disciplines, while being constructed at a reasonable cost in proportion to its task.

* Additional symmetry constraints (Kleinman, 1962) can cause point groups 422 and 622 to have anomalously low SHG if there is little dispersion between \( \omega \) and \( 2\omega \). In practice, some dispersion always exists and known crystals in the classes 422 and 622 produce measurable SHG, e.g. TeO\(_{2}\) point group 422 (Chemla & Jerphagnon, 1972).
To meet these conditions we have built a laboratory tool, the second harmonic analyzer (SHA), to detect the absence of an inversion center. The SHA consists of three modules, a laser source, a sample chamber, and a detector assembly. A block diagram (Fig. 1) illustrates the basic operation of the system. The source consists of a pulsed Nd$^3^+$ ($\lambda=1.06 \mu m$) glass laser, followed by a collimating lens. Two Corning 7–56 filters are used to remove the visible flash lamp pump light. The intensity of the fundamental laser pulse is controlled by neutral density filters. The laser beam is then directed upwards by an adjustable mirror and focused into the sample chamber. If the crystal is non-centrosymmetric, visible light at 5300 Å (the second harmonic, SH, of the 1.06 μm fundamental beam) will be produced. The resultant light consisting of the SH and the fundamental is filtered by two Schott BG-18 filters to pass the SH but remove the 1.06 μm radiation. The filtered optical signal is then detected by a dual photomultiplier assembly, functioning as a highly efficient single wavelength (5300 Å) spectrometer. The photomultiplier signals are displayed on a standard oscilloscope.

The components of the SHA are shown partially disassembled in Fig. 2. The entire SHA, shown in Fig. 3, is enclosed and light tight so that the unit can be operated in a normal illuminated laboratory and the high-power pulsed-laser system presents no laser radiation hazard in normal operation.

3.1 Laser

Nd:glass lasers provide the most reasonable compromise between long life, high power, low cost and usable wavelengths, since most inorganic and organic crystalline solids are transparent at both the fundamental and the second harmonic wavelengths. In addition, high-gain, low-noise, photomultipliers are readily available to detect the visible second harmonic photons.

The laser rod and flashlamp are molded into a single replaceable unit* with mirrors evaporated directly on the rod. The laser requires no cooling or mirror alignment. It produces 300 μs long pulses† of 1 J, with a pulse height stability of better than 10% over a lifetime of >10$^5$ pulses. The laser is focused to a 3 mm diameter at the sample producing an average power density of ~50 kW/cm$^2$. This power density is many orders of magnitude lower than the single-crystal laser damage threshold (Fradin, Yablonovitch & Bass, 1972). The pump energy to the laser, provided by a bank of capacitors, is proportional to the square of the input voltage. Because of this nonlinearity, it was found convenient to keep the laser voltage supply fixed and to use neutral density filters to control the intensity of the fundamental laser pulse.

3.2 Sample stage

Sample powders are held on 15 mm diameter coverslips in a sliding sample holder. For the study of phase transitions, the sample temperature can be varied from −100°C to +300°C. Either limit can be reached from room temperature in approximately 30 min. Temperatures are controllable to ±1.0°C with gradients across the active sample area <2°C. The sample chamber is purged with a neutral gas to eliminate condensation in low-temperature operation.

3.3 SHG detection system

The second harmonic is measured by a dual detector assembly (Kurtz, 1972b) since, in addition to SHG, high-power lasers can produce other types of visible radiation from crystalline powders, which may overlap the second harmonic wavelength. For this reason, it is necessary to examine the spectral purity of the light from the sample. The SHG dual detector scheme acts as a simple spectrometer operating at a single wavelength, 5300 Å. Alternative schemes of detection have been reported using second harmonic generation as a means of resolving space group ambiguities. Kurtz & Perry (1968) measured both the fundamental (ω) and the SHG (2ω). Since $P_{2\omega} \ll P_\omega$, the waveshapes of the two signals could be compared as a verification that the measured SHG was in fact real. Shigorin & Shipulo (1973) have used a spectrometer to examine the dispersion of the scattered ‘SHG’ light.

In the present SHG detection system the transmitted visible light is spatially divided with a beam splitter. One third of the light is directed onto a 1P28A photomultiplier; the remaining two thirds of the beam is passed through a narrow band SHG filter (half width 50 Å) and detected with a second 1P28A photomultiplier. The electrical signals from both photomultipliers are simultaneously displayed on an oscilloscope.* The filtered signal channel is called the second harmonic channel; the unfiltered signal channel is denoted as the second harmonic reference channel. This dual system is optically and electrically balanced to produce nearly identical signals (Fig. 4) when the visible light generated by the sample is pure second harmonic. When visible light is generated by mechanisms other than SHG (we will generally call all such radiation ‘spurious’) unbalanced signals will be seen on the oscilloscope (Fig. 5). Since this spurious radiation is generally not as spectrally pure as the SHG, the reference channel signal will be more than an order

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* A dual-beam oscilloscope is preferable but operation with a dual-channel single-beam oscilloscope is possible. The photomultipliers are terminated with 100 kΩ load resistor. This output impedance adequately resolves the SHG pulse envelope while effectively integrating the laser structure to provide an adequate signal (10 mV to 10 V) for normal oscilloscope amplifiers.

† Within the 300 μs pulse envelope the laser contains a substructure of about 150 pulses of 0.4–0.7 μs duration. Examination of these individual pulses for noncentrosymmetry tests would only add unnecessary complexity to the electronics in the SHG detection stage.

of magnitude higher than the SHG channel. Without such a reference signal, the upper trace in Fig. 5 could be easily misinterpreted as second harmonic generation! This particular technique of signal detection has the further advantage that all of the SHG (or 'spurious signal') is produced by the same single laser pulse. Even though shot-to-shot uniformity of the laser of $\pm 10\%$ can easily be achieved, pulse reproducibility is not required to obtain a reliable SHG center-of-symmetry test. In addition, spurious radiation can be highly variable from shot to shot, which makes a comparison of sequential shots extremely difficult on the most sensitive ranges where even a true SHG signal will fluctuate in intensity because the number of photons is small.

IV. Operation

The operation of the SHA for determining non-centrosymmetry can be divided into four steps: (1) sample preparation, (2) calibration of sensitivity with respect to an $\alpha$-SiO$_2$ standard, (3) measurement of unknown sample and comparison with standard, (4) check of precautions to insure validity of the result.

4.1 Sample preparation

Although single-crystal samples (less than 15 mm diameter and 4 mm thickness) can be examined by the SHA, the system has been designed to work with milligram amounts (typically 3–10 mg) of crystalline powder. Crystals for testing can be prepared with the same techniques used in the preparation of powder diffraction samples. Particles of 25 $\mu$m to 150 $\mu$m size are suitable for most SHG non-centrosymmetry tests.

Cleanliness is extremely important during sample preparation because of the high sensitivity of the technique. For the majority of SHG tests merely covering the samples with a Petri dish is adequate. However, small amounts of dust can enhance spurious signals and reduce the maximum achievable sensitivity. It is very important to maintain all glass surfaces in the 1.06 $\mu$m beam path, clean. Condensed matter from previous experiments can cause large spurious signals. Misleading results for weak SHG signals can occur if the sample is contaminated with trace amounts of truly non-centrosymmetric material such as crystalline quartz. The SHG system is capable of detecting less than five micrograms of quartz powder in an index matching liquid. Obviously, agate milling containers should be avoided. Alumina or lucite grinding containers are preferable. Methods for checking if an SHG signal is due to a contaminant are described under §5.4.

The effects of particle size and sample thickness have been described by Kurtz & Perry (1968), and Graja (1968). Fig. 6 shows that for multilayer samples, non-phase-matchable (NPM) powders peak in sensitivity near the coherence length ($\sim 20$ $\mu$m for $\alpha$-SiO$_2$) while samples of phase matchable (PM) powders level off in
sensitivity at a particle size $\geq 5$ times the coherence length. Graja (1968) has shown that monolayer samples have a uniform response for NPM materials while PM crystallites increase linearly up to eight times $l_c$. Typical coherence lengths fall in the range from 1 to 20 $\mu$m. We have found that in practice an ungraded powder sample containing particles from 20–150 $\mu$m is adequate for most non-centrosymmetry tests.

4.2 Index matching

Crystalline powders act as very efficient light scattering media. To minimize the scattering and achieve optimum test conditions, the sample powder should be mixed with a liquid of the same index of refraction as the crystal. Birefringent crystals can be matched at the average index. Index matching fluids are available from Cargille, Inc.* in the range 1.30 to 2.10. Additional lists of index matching liquids are given in International Tables for X-ray Crystallography (1965) (Vol. III, § 1.2).

Index matching prevents the scattering of generated second harmonic radiation and has empirically been found to reduce the occurrence of spurious radiation. In cases where it is impractical to index match the powder, because of a chemical reaction of the crystal with the oil, a relatively inert oil such as one of the silicone oils $\dagger$ ($n \approx 1.40–1.53$) can be used. The relative sensitivity of the SHA as a function of index mismatch is shown in Fig. 7. Index matching problems have not been found to be a serious practical limitation owing to the inherent high sensitivity of the technique, and the fact that non-centrosymmetric crystals with a refractive index above 1.8 exhibit strong SHG due to Miller’s rule (Miller, 1964) which states that the SHG coefficient is proportional to $(n^2 - 1)^3$.

SHG powder samples are most conveniently prepared by placing a drop of index oil on a 15 mm diameter coverslip which has been cleaned and is free of dust and scratches. Approximately 5–10 mg of powder are added to the appropriate index oil. The powder–oil mixture is then stirred to produce a uniform particle distribution over approximately an 8 mm diameter (the laser spot is 3 mm diameter). Small crystals can be crushed and prepared for SHG tests in less than five minutes.

4.3 Calibration

Before an unknown material is tested, a calibration check should be made with a standardized sample. Following Kurtz & Perry (1968), crystalline quartz (z-$\text{SiO}_2$) has been selected as a powder SHG standard. Quartz will produce an SHG signal about midway between the upper and lower experimental limits. High-purity z-$\text{SiO}_2$ is readily available at low cost and is chemically stable. A convenient standard consists of: (1) 10 mg z-$\text{SiO}_2$ of 37–44 $\mu$m particle size, (2) two drops of index matching fluid, $n = 1.552$. The standard should produce well balanced harmonic signals as shown in Fig. 8. Quartz standards varying by not more than 25% in SHG signal can be routinely prepared. Higher precision is possible but not necessary for non-centrosymmetry determinations.

Once a reference signal is established, a null check of the SHA should be performed at the highest sensitivity. An index-matched centrosymmetric com-

* Cargille, Inc., Cedar Grove, N.J.
$\dagger$ Dow-Corning Corporation, Midland, Michigan 48641.
pound such as KBr or NaCl or a clean blank slide can serve as a sample. This null check should yield only a few dark-current pulses. The null check will also verify that no contamination from previous experiments is present. If weak SHG is encountered, or expected, a reference point should be established for the 1/1000 quartz signal level. One may easily do this by monitoring the quartz standard with the beam attenuated by 15 db ($I = 0.03$ maximum), which will reduce the harmonic to 1/1000 of the maximum signal achievable from the quartz standard (Fig. 9).

4.4 Measurement and evaluation

Initial measurements should start with the sensitivity set at the quartz standard level, the ideal level can usually be determined in a few shots. A permanent record of the data can be made with an oscilloscope camera. At this stage, it is advisable to measure SHG at several values of the laser intensity in order to verify the SHG square law dependence with fundamental power (§ II).

Weak SHG signals can often be resolved by superimposing oscilloscopic traces from four or five shots on the same camera record. An example of this technique is shown in Fig. 10 for the 1/10000 quartz level and in Fig. 11 for a centrosymmetric KBr sample. This multiple-shot technique is effectively a box-car integration method without the costly electronics.

The SHG data can be divided into four categories: (1) positive (+); true SHG detected, (2) weak SHG (weak): SHG level < 0.001 quartz, (3) negative (−): no detectable SHG at levels less than 0.001 of quartz, (4) null (0): no detectable SHG, but test sensitivities less than 0.001 of quartz. The failure to detect SHG is called a null result when the detection sensitivity is reduced because of absorption of the fundamental or the second harmonic by the crystal or because of index matching problems (see Fig. 7). The weak SHG results indicate experimental uncertainties, e.g., second phase impurities, possible sample decomposition or other phenomena unrelated to the SHG measurement itself.

V. Precautions and special techniques

5.1 Preferred orientation

The SHG powder technique relies on random orientation of particles. Occasionally a material will grind into platelets or highly acicular particles which lie on the sample slide with preferred orientation. As is the case in X-ray powder diffraction, the data from such a sample can be misinterpreted. An anomalously low (or high) SHG signal could be obtained from such preferential orientation. A reduced second harmonic generation in a material that already has intrinsically low SHG could fall below the detection level of the SHA. Random orientation can be restored by mixing the crystallites in a viscous or solidifying media such as: (1) Dow Corning 200 Silicone Fluid which is available in viscosities up to 2500000 centistokes,
(2) a clear varnish, (3) acrylic or epoxy resin, (4) KBr (standard infrared pellet technique).

Whenever unusual index matching techniques are used, it should be verified that the matching medium itself does not produce SHG under the operating conditions being used.

5.2 Absorbing materials

Crystals with moderate absorption coefficients ($\alpha < 10^3 \text{ cm}^{-1}$) at the second harmonic can be examined for non-centrosymmetry with approximately an order of magnitude decrease in sensitivity. For absorbing materials it is usually advantageous to have no more than a monolayer ($\sim 2-3$ mg) of crystalline powder on the sample slide.

5.3 Spurious signals

When it is necessary to use the highest sensitivity ranges of the SHA ($< 1/1000$ quartz levels), spurious signals, non-SHG in origin will occasionally occur. The spurious signals can be easily distinguished from SHG by any of the following tests: (1) spectral purity, (2) power dependence, (3) wave shape. The primary test is for spectral purity.

(1). Since the spurious signal is not as spectrally narrow as SHG, the reference (unfiltered) channel signal will be higher (approximately an order of magnitude) than the $2\omega$ channel (Fig. 5).

(2). SHG follows a square-law relationship as a function of input power ($P_{2\omega} \propto P_\omega^2$), whereas for the spurious radiation we have found spurious power $\propto (P_\omega)^x$, where $x$ varies from 6.5 to 8, depending on the sample. A plot of the spurious and SHG signals as a function of laser power is shown in Fig. 12. The crossover point indicates the condition for optimum SHG signal-to-noise ratio. The beam diameter and hence the maximum power density have been initially adjusted by the focusing lens to minimize spurious radiation. For the laser used in our SHA, this optimum beam diameter is approximately 3 mm. It must be emphasized that the laser power cannot be arbitrarily increased to bring the SHG signal to a detectable level because the spurious non-SHG signal has a different dependence on laser power density than SHG.

For sufficiently high powers, electric quadrupole, and magnetic dipole interactions can produce bulk SHG in centrosymmetric crystals (Terhune, Maker & Savage, 1962). It is far more prudent to incorporate higher gain in the detector rather than the source in order to assure that the sample itself is not altered by the measurement.

(3). With experience one can distinguish the difference in signal wave shape between the SHG and spurious signals. This technique, supplementary to tests (1) and (2), can permit SHG to be detected even in the presence of some spurious radiation.*

5.4 Weak signals and identification of non-centrosymmetric materials

Whereas the normal centro/non-centrosymmetric test normally requires 10 to 30 min to complete, extremely weak SHG signals occasionally arise which require that the sensitivity parameter be optimized. In that case: (1) the powdered sample should be properly index matched† and (2) the optimum particle size should be found.

For such very weak signals ($\lesssim 1/1000$ $\alpha$-SiO$_2$), it is clearly important to establish that the material is free of non-centrosymmetric contaminants, including second phases of the nominal material being tested. For example, if a non-centrosymmetric material with SHG coefficients 100 times those of quartz is mixed with a centrosymmetric crystalline powder, it would take 10 ppm to produce a signal level of 1/1000 quartz. The presence of a non-centrosymmetric contaminant can often be determined by mixing the sample powder in

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* Note added in proof: A gated pulse integrator with digital readout has been developed which can suppress the spurious background and resolve SHG in the presence of a spurious signal.

† A positive SHG test on a dry powder indicates non-centrosymmetry, but a negative test on a dry powder should be treated as a null result due to the effective reduction in sensitivity.
oils of different indices of refraction. The second harmonic light produced will be scattered by the powder–oil mixture, the amount of scattering will increase as the index of refraction mismatch of the powder and oil increases (Fig. 7). Knowing the index of refraction of the crystal in question, the index oil can be varied and a plot of SHG signal versus index oil will show a definite peak for the index-matched conditions (Fig. 13). The detected SHG produced by a possible contaminant can be reduced in intensity by about two orders of magnitude for a difference in indices of ~0.3. At this level, trace contaminants can easily be detected by microscopic examination or standard chemical techniques.

The particle size dependence of powder SHG (Fig. 6) can be used to provide additional information for the weakly non-centrosymmetric case. If a trace contaminant is highly non-centrosymmetric, it will often be phase matchable. Measuring samples of various particle sizes (<25 μm to >150 μm) at the optimum index match should provide enough data to determine if a re-examination of the compound itself is warranted.

VI. Applications

In the course of this study, several distinct types of crystallographic problems have been investigated with the second harmonic powder technique on our SHA: (1) space group ambiguities, (2) order–disorder problems, and (3) phase transformations.

Problems during refinement frequently arise because of small deviations of a few light atoms in the cell from centrosymmetric positions. Since SHG is produced from the interaction of the electric field of the laser pulse with the outer electrons of the most polarizable atoms in the structure, this optical technique is particularly suitable for sensing non-centrosymmetric oxygen or hydrogen positions (Shigorin & Shipulo, 1974).

6.1 Materials survey

Nearly a hundred* compounds, some of which are listed in Table 1, have been investigated for crystallographers on the SHA. Several selected examples are described in the following sections.

6.2 Space group determination

6.2.1 Thyroxine derivatives. The crystal structures of a series of important thyroid hormones, hormone precursors, and hormone analogs are being studied (Cody, 1974; Cody & Duax, 1973) in order to establish the structural requirements for maximum thyroid activity. Crystalline samples of several thyroid active compounds were provided by the Medical Foundation of Buffalo and tested in the SHA (see Table 1).

* Perhaps an order of magnitude more have been examined by the powder method on different experimental setups at the Naval Res. Lab., DuPont Res. Labs., Bell Telephone Labs., National Phys. Lab., Centre Nat. de Telecommunications, Raytheon, and several Japanese, Russian and Italian laboratories. Most of this work was done for nonlinear optical materials survey purposes, rather than structure determinations.

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![Fig. 13. SHG intensity versus refractive index of matching oil. Samples were 0.7 to 1.0 mg of 44-77 μm α-SiO₂ and had varying thicknesses.](image-url)
One of these, 3,5-dinitro-L-tyrosine provides a particularly illustrative case of the application of SHG as an aid in structure refinement. This crystal was assigned to space group P1 with two asymmetric units (Cody, Greiner & DeJarnette, 1972). However, the intensity statistics appeared to be centric (i.e. normally distributed) since the heavy atoms were situated in centrosymmetric positions. Although the compound was a deep yellow color and the exact index of refraction unknown, powder tests gave a clearly positive

Table 1. Results of investigation of some compounds on the SHA

<table>
<thead>
<tr>
<th>Compound</th>
<th>+/−/0</th>
<th>Space group</th>
<th>Structure references or comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzyl disulfide</td>
<td>−</td>
<td>C2/c</td>
<td>Srinivasan &amp; Vijayalakshmi (1972). Classical space group ambiguity</td>
</tr>
<tr>
<td>Colemanite</td>
<td>+</td>
<td>P21/a</td>
<td>Phase transition at −5°C to P2. (see text) Christ, Clark &amp; Evans (1958)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>+</td>
<td>P2</td>
<td>Phase transition T~72°C (see text) Trotter (1963)</td>
</tr>
<tr>
<td>1:10 Phenanthroline hydrate</td>
<td>+</td>
<td>P31m</td>
<td>Donnay, Donnay &amp; Harding (1965)</td>
</tr>
<tr>
<td>Thalidomide</td>
<td>0</td>
<td>Pmca</td>
<td>Order-disorder (see text). Kirfel (1975)</td>
</tr>
<tr>
<td>Thiamine pyrophosphate</td>
<td>+</td>
<td>P1 or P1̅</td>
<td>Vitamin B1 (see text). Blank, Wood, Pletcher &amp; Sax (1975)</td>
</tr>
<tr>
<td>[(C6H5)3P]3CuBF4</td>
<td>(weak)</td>
<td>P4 or P4/m</td>
<td></td>
</tr>
<tr>
<td>Pb5GeO5</td>
<td>0</td>
<td>C2/m</td>
<td></td>
</tr>
<tr>
<td>β-Ga2O3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(C6H5)3N]3[InCl3]</td>
<td>(weak)</td>
<td>P4/m</td>
<td></td>
</tr>
<tr>
<td>3,5,3'-Triiodothyroacetic acid</td>
<td>+</td>
<td>C2/c</td>
<td>Cody &amp; Duax (1973)</td>
</tr>
<tr>
<td>3,5-Dinitro-L-tyrosine</td>
<td>+</td>
<td>P1</td>
<td>Light brown powder. Cody (1975)</td>
</tr>
<tr>
<td>1-Acetyl-4'-methoxy-3,5-diododiphenylamine</td>
<td>−</td>
<td>P1 or P1̅</td>
<td>Yellow powder (see text). Cody (1975) (centric statistics)</td>
</tr>
<tr>
<td>P2NiNOC1</td>
<td>0</td>
<td>P21</td>
<td>(see text) Cody (1975)</td>
</tr>
<tr>
<td>Ba3Pt/O7</td>
<td>0</td>
<td>P21/b</td>
<td>Robertson &amp; White (1956)</td>
</tr>
<tr>
<td>1,2-Benzanthracene</td>
<td>+</td>
<td>P22,21</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>−</td>
<td>Fm3m</td>
<td>Centrosymmetric standard</td>
</tr>
<tr>
<td>NaCl</td>
<td>−</td>
<td>Fm3m</td>
<td>Centrosymmetric standard</td>
</tr>
<tr>
<td>Indium acetylacetonate</td>
<td>−</td>
<td>mm</td>
<td>Previous space group ambiguity</td>
</tr>
<tr>
<td>KBr</td>
<td>−</td>
<td>Fm3m</td>
<td>Centrosymmetric standard</td>
</tr>
<tr>
<td>SrTeO3</td>
<td>+</td>
<td>Cc</td>
<td>Originally reported as C2/c. Piezoelectricity measured in one of 100 single crystal specimens. Yamada &amp; Iwasaki (1973)</td>
</tr>
<tr>
<td>Nd(IO3).H2O</td>
<td>+</td>
<td>P21</td>
<td>Liminga, Abrahams &amp; Bernstein (1974). Samples run by above authors on the SHA described in this article</td>
</tr>
<tr>
<td>Spodumene</td>
<td>−</td>
<td>I2/c</td>
<td>Weak SHG in one of 10 samples, second phase suspected</td>
</tr>
<tr>
<td>l(+)-Glutamic acid HCl</td>
<td>+</td>
<td>(C2/c, I2</td>
<td></td>
</tr>
<tr>
<td>(NH4)2C2O4.H2O</td>
<td>+</td>
<td>P22,21</td>
<td></td>
</tr>
<tr>
<td>CaF2</td>
<td>−</td>
<td>Fm3m</td>
<td>Poor index match, second phase suspected</td>
</tr>
<tr>
<td>Ca3(PO4)2Cl</td>
<td>0</td>
<td>P21/b</td>
<td>Samples from two sources. Poor index match. Second phase suspected</td>
</tr>
<tr>
<td>Ca3(P04)2F</td>
<td>−, 0</td>
<td>P63/m</td>
<td></td>
</tr>
<tr>
<td>Tetraethylammonium tetra-chloroinden Et4N(InCl4)</td>
<td>+</td>
<td>P6/m</td>
<td>Trotter, Einstein &amp; Tuck (1969)</td>
</tr>
<tr>
<td>Pb3GeO5</td>
<td>+</td>
<td>P3</td>
<td>Newnham, Wolfe &amp; Darlington (1973)</td>
</tr>
<tr>
<td>α-TiO2 (rutile)</td>
<td>0</td>
<td>P4/m</td>
<td>High refractive index test specimen</td>
</tr>
<tr>
<td>Al2O3</td>
<td>+</td>
<td>P21</td>
<td>High refractive index test specimen</td>
</tr>
<tr>
<td>Triglycine sulfate</td>
<td>+</td>
<td>P4/m</td>
<td>No SHG above 49°C; phase transition to P21/m</td>
</tr>
<tr>
<td>BaTiO3</td>
<td>+</td>
<td>Phase transition detected, see text</td>
<td></td>
</tr>
<tr>
<td>(Et4N)4[PbF2]</td>
<td>0</td>
<td>R3c</td>
<td>Red powder</td>
</tr>
<tr>
<td>(PMePh3)3[CNIPr]PF6</td>
<td>−</td>
<td>P21</td>
<td>Brown powder</td>
</tr>
<tr>
<td>Pt(H2N)2[NH4]2H2FICBF4</td>
<td>0</td>
<td>P4/m</td>
<td>Gray powder</td>
</tr>
<tr>
<td>Tetraethylammonium chloride Et4NCl</td>
<td>0</td>
<td>P21/a</td>
<td></td>
</tr>
<tr>
<td>Ovalene</td>
<td>0</td>
<td>Pca21</td>
<td>Et4Ni given as 4, Wait &amp; Powell (1958)</td>
</tr>
<tr>
<td>KI03F2</td>
<td>+</td>
<td>F43m</td>
<td>Tan powder. Showed two-photon fluorescence</td>
</tr>
<tr>
<td>GaAs</td>
<td>+</td>
<td></td>
<td>Abrahams, Bernstein &amp; Nassau (1974). Samples run by these authors on this SHA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Heavily absorbing. High d coefficients</td>
</tr>
</tbody>
</table>
SHG response on three different samples, indicating that the original assignment to P1 was correct. The time required to verify the non-centrosymmetric nature of this crystal was about 30 min.

6.2.2 [Fe(das)2NO(NCS)] [PF6]2. The space group of the title compound, an iron diarsine complex, was reported to be either C2/c or Cc (Johnson, 1974). Because of the large number of atoms in the cell and the uncertainty in the space group, the structure refinement was using copious amounts of computer time. The crystals were red in color, heavily absorbing the green second harmonic light. Despite these limitations, a positive SHG signal was obtained with only 1 mg of sample demonstrating the correct space group to be Cc. The structure refinement is now in progress.

6.2.3 [(C2HshN)2InCI5. The tetraethylammonium salts of InCl3- and TICl3- are isomorphous and isostructural, crystallizing in space group P4/n (Brown, Einstein & Tuck, 1969). Infrared and Raman studies indicate that the InCl3- site symmetry could be C2 rather than C4. The C2 site symmetry would require the crystal to be in space group P4 rather than P4/n (Joy, Gaughan, Wharf, Shrider & Dougherty, 1975). SHG powder tests on the SHA found a very faint positive SHG signal (less than 0.001 of quartz). The SHG signals were observed with the multiple-shot, superimposition method described in § 4.4. The crystals were index matched to achieve high sensitivity for the powder method, but chemical integrity of the compound was a problem. [(C2HshN)2InCI5 can decompose, producing (C2HshN)2InCI4, space group P63mc, (Trotter, Einstein & Tuck, 1969) which is non-centrosymmetric (SHG intensity ~-SiO2). It was found that a concentration of about 1 part in 1000 of the Et4NInCI4 mixed in with (Et4N)2InCI5 would be sufficient to produce the SHG signal found in the InCl3 salt. Chemical and infrared analyses of the samples were required after the SHG tests. Preliminary evidence indicates that the weak positive SHG test was found in the true [(C2HshN)2InCI5 salts. It is clear that, taken alone, the SHG data in this case are inconclusive. The SHG powder test was only one technique of many necessary to investigate the crystal structures of [(C2HshN)2In]2(TICl3).

6.3 Order-disorder problems related to non-centrosymmetry

SHG can often provide rapid information on disorder within the unit cell. Examples discussed below are 9-methyl-10-chloromethylanthracene, thalidomide, and thiamine pyrophosphate tetrahydrate (Vitamin B1). Detection of dynamic disorder will be discussed in reference to the study of phase transitions.

6.3.1 9-Methyl-10-chloromethylanthracene (MS-23). MS-23 has been shown to crystallize in space group P212121 by Carrell & Glusker (1973). During the course of the structure refinement (R=14%) the possibility occurred that there was a disorder in the percentage of methyl groups attached to the '9' position of the anthracene.

A 50% disorder would require the space group to be Pmca whereas unequal distributions would occur in space group P212121. SHG powder tests on the brown colored crystals of this substance gave a strong SHG response. The refinement was continued in P212121, accounting for the disorder, and the structure was successfully completed (R=4°0) (Carrell, 1975).

6.3.2 Thalidomide. Refinement of the structure of thalidomide by Kirfel (1975) allowed the possibilities of a partially disordered centrosymmetric cell (Pmca) or a non-centrosymmetric cell (P21ca) displaying pseudo-centrosymmetry. Structure refinements with both models led to slightly better R values for the former case. Second harmonic generation tests showed no detectable signal and thus provided independent data, consistent with the choice of structure.

6.3.3 Thiamine pyrophosphate tetrahydrate (TPP.4H2O). Crystals of Vitamin B1 (TPP.4H2O) are triclinic, Z=4. Structure refinement (Blank, Wood, Pletcher & Sax, 1975) in space group P1 to an R of 4.5°0 indicated the
existence of a single hydrogen bridge connecting the $B$ molecules of the tetramolecular cell, whereas the $A$ molecules were connected by a double hydrogen bridge making the correct space group $P1$.

Powdered crystallites of TPP showed a weak (less than 0.001 of quartz) but reproducible SHG signal providing ancillary evidence of a disordered $P1$ structure, i.e. $P1$. Due to the weak signal, the TPP samples were prepared in several index-matching oils following the precautions detailed earlier in §§ 4.4 and 5.4. The presence of a second phase TPP, $41\text{H}_2\text{O}$, space group $P1$ (Wood, 1975) was found to make an exact index match impossible.

6.4 Phase transformations

The disappearance of SHG or change in its intensity can be used to study structural phase transformations. The SHA was used to investigate phase transitions in BaTiO$_3$, the mineral colemanite, and in the aromatic hydrocarbon, phenanthrene. In addition, a weak clearly distinguishable SHG signal was seen in the cubic phase of BaTiO$_3$, $Pm3m$, suggesting the possibility of dynamic disorder (Yamada, Shirane & Linz, 1969; Demjanov & Solov’ev, 1970; Ortmann, Schwalbe & Vogt, 1975).

6.4.1 BaTiO$_3$. Phase transitions can be observed in crystalline powders for both centro–non-centrosymmetric and non-centro–non-centrosymmetric cases. The latter can be distinguished in powder because the spatial average of the non-linear optical coefficients is generally different above and below the transition temperature.

The phase transitions in BaTiO$_3$ are clearly distinguished through changes in the SHG signal (Fig. 14). Second harmonic generation was observed in the high-temperature cubic phase in both powders and single-crystal specimens. Pyroelectricity above the ferroelectric Curie point in BaTiO$_3$ was reported by Chynoweth (1956), Disorder in NaNO$_2$ above $T_c$ was studied by means of SHG (Vogt, 1973). Since the equilibrium structure above $T_c$ is cubic, $Pm3m$ (Megaw, 1952), a plausible hypothesis for the high-temperature anomalous SHG is dynamic disorder, possibly coupled with local polarization fluctuations.

A recent study of second harmonic generation in the cubic phase of BaTiO$_3$ by Ortmann et al. (1975) is consistent with the results shown in Fig. 14. Since quadrupole effects are forbidden by symmetry in the $m3m$ point group of the ideal perovskite, these authors concluded that the 'observed SHG is due to a disturbance of the cubic symmetry by residual ferroelectric domains'. A recent study of Raman scattering in KNbO$_3$ by Bell & Raccah (1975) suggests the presence of a disordered structure similar to that proposed by Lambert & Comes (1969). Lambert’s results are based on their observations of thermal diffuse X-ray scattering in both BaTiO$_3$ and KNbO$_3$. We feel that second harmonic generation can be an important tool for studying order–disorder as well as displace phase transitions in nominally centrosymmetric structures. A more detailed study of the SHG in the range $120-230\text{C}$ is in progress and will be reported at a later date.

6.4.2 Colemanite. The mineral colemanite, CaB$_3$O$_4$(OH)$_3$, H$_2$O, is of interest because it is the only known naturally occurring ferroelectric. The room-temperature structure, solved by Christ, Clark & Evans (1958), was of great importance since it involved one of the first applications of the direct methods of Hauptman & Karle (1953). The reported phase transition occurring at $\sim 5\text{C}$ (Goldsmith, 1956; Chynoweth, 1957) has been interpreted from the room temperature structure by Christ et al. (1958). At room temperature, colemanite is in space group $P2_1/a$; the cell contains two water molecules joined by a disordered hydrogen bond. Below the transition temperature, the hydrogen bond is permanently polarized, destroying the center of symmetry and converting the crystal to space group $P2$ (Holuj & Petch, 1958).

Powder crystallites of colemanite were mixed in 1:590 index oil; no attempt was made to grade particle size or to optimize refractive index matching. No SHG was detected at room temperature; upon cooling, SHG was detected at $-5 \pm 1\text{C}$ and persisted to $-25\text{C}$. The same temperature dependence was observed in the heating cycle with no measurable hysteresis in the transition temperature. Thus, a second-order-like transition consistent with the interpretations of Christ et al. (1958) is suggested.

6.4.3 Phenanthrene. The aromatic hydrocarbon, phenanthrene, C$_{14}$H$_{10}$, was investigated by Trotter (1963) and found to be monoclinic, space group $P2_1$, at room temperature. Arndt & Damask (1966) measured a heat capacity anomaly near 70°C indicating the presence of a phase transition. Matsumoto & Fukuda (1967) reported a phase change at about 70°C where X-ray data show the symmetry and the space group appear to be unaltered but the cell dimension and angle change on going through the transition. Spielberg, Arndt, Damask & Lefkowitz (1971) investigated the phenanthrene phase transition with neutron inelastic scattering and dielectric methods. They speculated that an observed dielectric anomaly in the $a$ direction could be due to a field-induced permanent dipole moment.

With the SHA, the phase transition in phenanthrene powder was measured (Fig. 15). The transition at $72 \pm 1\text{C}$, detected by SHG, appears second-order-like in character. There is no trace of second harmonic generation above $72\text{C}$, which fact provides the first definitive evidence that the high-temperature phase of transition was not distinguishable under polarized light (Spielberg et al., 1971) the transition most likely occurring is that between the crystal classes 2 and 2/$m$. Optical observation of any mimetic twinning occur-
A SECOND HARMONIC ANALYZER TO DETECT NON-CENTROSYMMETRY

PHENANTHRENE, C_{14}H_{10} IMMERSED IN SILICONE OIL (DC-200)

SOURCE: ALDRICH CHEMICAL CO.
UNGRADED COMMERCIAL POWDER - 98% PURITY

Fig. 15. SHG versus temperature in phenanthrene demonstrating a phase transition to a centrosymmetric space group. Starting from 22°C, the powder was heated above T_c (80°C), the temperature was then reduced to show the reproducibility of the phase change and finally taken above the melting point (102°C). After cooling the phenanthrene to below T_c, an SHG signal was observed indicating that the material had recrystallized.

VII. Discussion

The second harmonic powder technique is seen to be a sensitive and rapid means for detection of non-centrosymmetry. This technique can provide independent ancillary data to aid the crystallographer in several ways.

1) An SHA can aid in the decision on whether or not to refine a structure. SHG data can also help one decide whether or not to re-examine an earlier structure.

2) Center-of-symmetry data can reduce the number of false starts in structure refinements.

3) For X-ray service groups, SHG can provide rapid centrosymmetry data which might be useful in itself. For example, some order–disorder and molecular configuration questions could be answered without the need of a complete structure refinement.

The number of center-of-symmetry problems which a crystallographer encounters depends on the types of compounds studied. The extent of this problem can be reasonably estimated from the diffraction symbols in International Tables for X-ray Crystallography (1965). Of the 230 space groups, 50 (22%) are uniquely defined by diffraction. A reliable center-of-symmetry test would allow 115 (50%) space groups to be uniquely determined.*

Perhaps a more useful interpretation can be seen if the statistical data of Nowacki (Donnay & Nowacki, 1954) are combined with the diffraction symbols. With these data, it was found that the 50 space groups unique by diffraction encompass 33% of the compounds surveyed.† A center-of-symmetry determination in combination with diffraction would allow 67% of the materials to have their space group uniquely defined. Fig. 16 enumerates the percentages of resolvable compounds within each Laue class.

The reliability of center-of-symmetry data provided by the SHG method has been studied by Kurtz (1972a, 1975). Based upon the statistical distribution of the nonlinear optical coefficients responsible for SHG, Kurtz has determined that a system with a detection sensitivity for a signal approximately 1/250 of a quartz standard has a 99% probability of detecting non-centrosymmetry. This estimate was the primary basis for the classification of SHG data in the measurement and evaluation section. The 1/250 limit was extended to 1/1000 as a safety factor. No errors in centro/non-

ring in the low-temperature phase would be impossible, as the twin walls would be constrained to lie along the twofold axis (Fousek & Janovek, 1969), and thus would produce identical cross sections of the optical indicatrix.

The exact mechanisms of the phenanthrene phase transition are still not understood and the high-temperature structure appears to be a problem worthy of study.

* A space group is only denoted as uniquely definable in the strictest sense. Enantiomorphic pairs or choices between space groups, easily resolvable through the chemistry of the compound, are termed unresolvable. For example, an SHG test indicating P2 or Pm over P2/m is treated as not resolvable.
† Metals were excluded.
centrosymmetric space group assignments have occurred in the course of this study. This is certainly due in part to our rather prudent safeguards.

As with any other new method, the true test of this technique can only be time. A definition of the practical limits of the SHG powder test for determining noncentrosymmetry will only be firmly established when a very large number of problem compounds have been investigated by crystallographers using SHG in conjunction with standard X-ray methods.

We are grateful to Fred Y. Masson, William Slade, Richard Sweet, and Robert Seymour for their assistance in the design and construction of the second harmonic analyzer. We thank the many crystallographers who have provided samples and given unpublished information on their structural problems. The patience and encouragement of Dr. D. D. King throughout this project is sincerely acknowledged.

References
