# *Rotational Anisotropy Second Harmonic Generation for Broken Bulk Inversion Symmetry Detection*

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## Abstract

Second harmonic generation (SHG) is well known as a tool for probing the surface structure of nonlinear optical materials. When a coherent light source of frequency $\omega_1$ is incident upon certain materials, the light reflected from the material is twice the frequency, $\omega_2$, of the incident beam. Due to its selectivity for non-centrosymmetric materials, second harmonic generation was recently able to be used in identifying the breaking of inversion symmetry in the bulk of $Cd_2Re_2O_7$. Through the use of this technique a previously unknown electronic phase transition was discovered to be the cause of the broken parity in this material. This presents an interesting way in which the use of nonlinear optical techniques allows the inference of the material's functional properties from its structural symmetry. Here we present an optical scheme for second harmonic generation that was designed for the testing of novel materials to determine their electronic properties. We performed testing of the optical setup using a sample of GaAs, a well-known non-centrosymmetric semiconductor, and find an interesting angular dependence of the second harmonic signal. In addition to this, we will present data on measurements performed on single crystals of FeGe and $Cd_2Re_2O_7$.


## Introduction

In linear optical processes, electromagnetic radiation that is incident on a material interacts with the light wave in a directly proportional manner. A nonlinear optical process can be described as occurring "when the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the optical system." [1] For example, the polarization density of a linear interaction can be described as

$$\vec{\boldsymbol{P}} = \varepsilon_0 \chi \vec{\boldsymbol{E}} \qquad \text{(Eq. 1)}$$

where **P** is the induced electric dipole moment per unit volume, $\varepsilon_0$ is the permittivity of free space, $\chi$ is a constant of proportionality called the linear susceptibility, and **E** is the strength of an applied optical field. Optical linearity is typically observed because the intensity of normal light is quite low. In order for optical nonlinearity to be observed the incident light must be of extraordinary intensity, such as that from a laser. The description of the polarization of a nonlinear interaction would be a power series of the form

$$\vec{\boldsymbol{P}} = \varepsilon_0\left[\chi\vec{\boldsymbol{E}} + \chi^{(2)}\vec{\boldsymbol{E}}^2 + \chi^{(3)}\vec{\boldsymbol{E}}^3 + \cdots\right] = \vec{\boldsymbol{P}} + \vec{\boldsymbol{P}}^{(2)} + \vec{\boldsymbol{P}}^{(3)} + \cdots \qquad \text{(Eqn. 2)}$$

where $\chi^{(2)}$ and $\chi^{(3)}$ are the nonlinear susceptibilities. The nonlinear susceptibility is a tensor from whom information about the structural symmetry, and thus electronic and magnetic structure, of a material can be derived.

The nonlinear processes can be imagined as photons interacting with a material in such a way that its properties can be changed by this interaction. [2] One such response is SHG. According to this image, SHG can be considered as the simultaneous destruction of two photons of frequency $\omega_1$ incident on a material and the formation of a new photon of frequency $\omega_2 = 2\omega_1$. This occurs by a quantum-mechanical process in which there is a coherent virtual absorption-reemission event between the electrons in the crystal cell and the incident light wave.

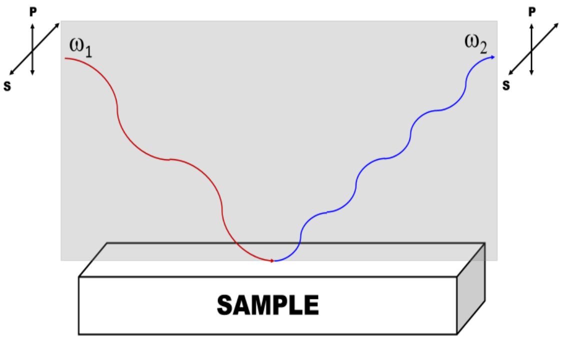


*Figure 1 Light, of frequency $w_1$, incident on the material is reflected at a new frequency $w_2$=$2w_1$. The input and output polarizations of the fundamental light and the second harmonic are selected dependent on the material.*

For SHG to occur, not only is a coherent light source required, but the material upon which the light is incident must be non-centrosymmetric. As such, SHG can be used as a probe of surfaces, which lack a center of inversion, and the bulk of anisotropic materials. This caveat is specific to second order nonlinear phenomena, such as SHG. [3] This can be understood by considering the response of the material through the model of an anharmonic oscillator. In this way, one can consider the motion of an electron in a potential well for a material with inversion symmetry, in which the nonlinear polarizations must be equal and of opposite sign. This would result in the cancelation of the response. However, this is not the case for an anisotropic material as the response would be varied along the different components of the material's structure along which the field is interacting. The phenomenon is also dependent on the combination of the input/output combinations in the system (p-in/p-out, s-in/p-out. p-in/s-out, s-in/s-out).

This dependence on and sensitivity to the symmetry of the material for the generation of second harmonic makes this technique a valuable tool for the probing of materials that are non-centrosymmetric. This is evidence by a study done by Harter et al. who were recently able to characterize a previously unidentified phase transition in $Cd_2Re_2O_7$ using SHG. [4] At its critical temperature (~200 K) the material is known to take on a tetragonal structure from a cubic structure, breaking its three-fold rotational symmetry about the 111-axis. This was previously thought to be due to the freezing of a particular vibrational mode ($E_u$ symmetry soft phonon). The authors were able to determine that this phase transition occurs due to a different electronic transition (a $T_{2u}$ transition which results in the $E_u$ transition) by using SHG.

This presents a novel way to characterize the electronic, and magnetic, properties of a material through their inference from structural characterization. Using SHG to identify the symmetry elements, interesting magnetic and electronic properties in $Cd_2Re_2O_7$ and other materials were able to be explained. The use of this method creates the opportunity for the determination of great information about a material by using non-aggressive, relatively simple means.

## Materials/Methods

All optics were obtained from Thorlabs, Inc. unless otherwise specified. A motorized rotating stage used for sample mounting was also obtained from Thorlabs, Inc. A linear polarizer was used for the source beam before a half-wave plate to produce s-polarization. An EFL 90° Protected Silver 100Å Off-Axis Parabolic Mirror (from Edmund Optics) was used to focus the incident beam onto the sample. A long pass dichroic mirror with a 505nm

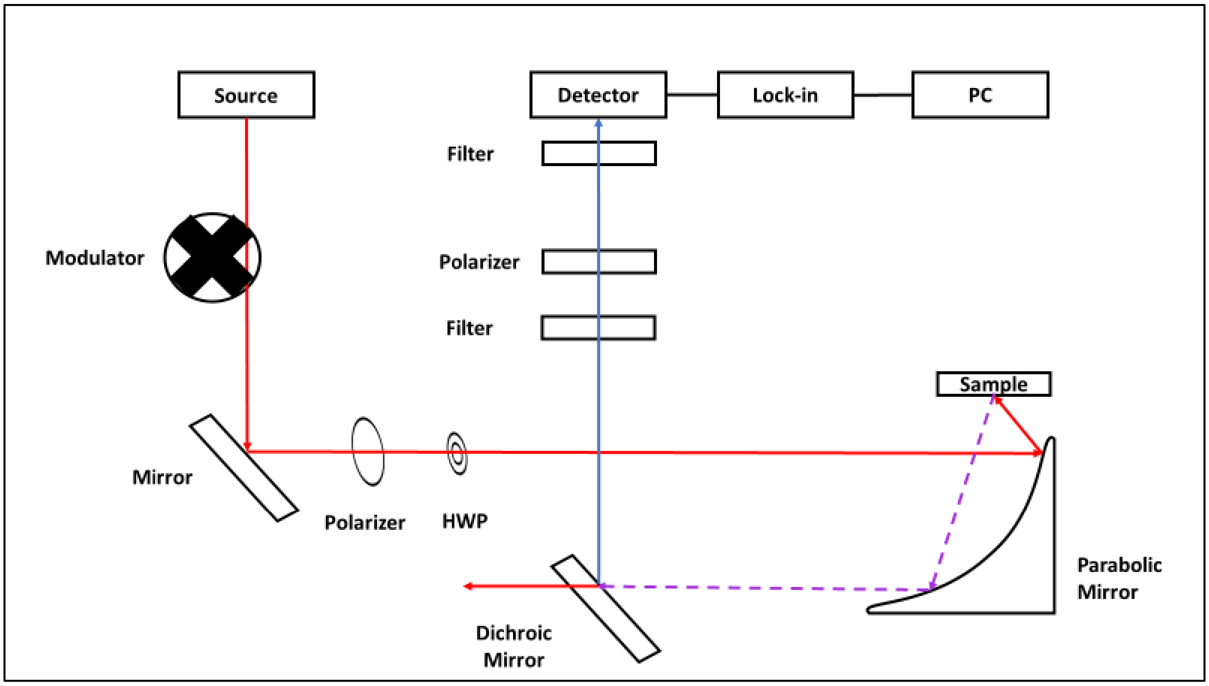


*Figure 2 Second harmonic generation optical scheme. The signal was modulated immediately after the source. The linear polarizer and half-wave plate immediately after first mirror are to select the polarization of the incident beam on the sample. An off axis parabolic mirror is used to focus the beam onto the sample and reflect the second harmonic onto the dichroic mirror which filters any reflected fundamental and directs the second harmonic onto the detector. The filter after the dichroic mirror is to further filter any reflected fundamental from reaching the detector. The final polarizer serves to select the polarization of the second harmonic onto the detector. The detector signal is then fed into a lock-in to extract the SHG signal from any noise detected.*

cutoff was used to filter any transmitted fundamental frequency light, $\omega_1$, and reflect the second harmonic to the detector. Additionally, a BG39 Colored Glass Bandpass Filter (for 360 - 580 nm) was used to further prevent the transmission of any fundamental to the detector. A Glan-Laser alpha-BBO Polarizer (V-coated for 405 nm) was used for p-polarization immediately before the detector. A 200-1100 nm Si photodetector from Thorlabs, Inc. served as a receiver for the second harmonic signal. This was used with an EG&G DSP SR7260 Lock-in Amplifier.

An ELL8K Elliptec piezoelectric resonant motor rotating stage was used to for mounting the sample material. A program was written using LabVIEW to control the position of the rotating stage and to coordinate the stage's movements with the recording of data from the lock-in amplifier. The algorithm used for the movement/data collection cycle is outlined in Fig. 3. Options for homing the stage, movement to an "absolute" position (relative to the home position), movement to a position relative to the current position, setting the jog step size, and the collection of data using absolute or relative steps.

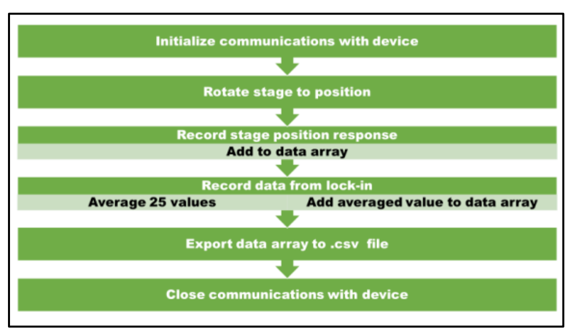


*Figure 3 Algorithm showing the data collection cycle in which the rotating stage moves a set step size, records the stage's position, records an averaging of collected output values from the lock-in amplifier, and outputs the data to a file for analysis.*

Data was collected by rotating the sample through a full revolution using the absolute data collection mode by 10-degree steps, averaging 25 data points at each step. Values were recorded at room temperature under various lighting conditions. Data was collected under normal room lighting, with the lights turned off, and with the system covered by a box, with the room lights on. Multiple trials were run under the various conditions to see their reproducibility. Various combinations of input/output polarizations were tried to find the optimal combination for the sample being examined.

## Results/Discussion

Data was collected for samples of FeGe (111) and GaAs (111). Plots of the measured signal as a function of angle of incidence were consistent under varied light conditions (room lighting, lights off, and boxed system). For FeGe plots of P-in/P-out and S-in/S-out gave similar curves (Fig 4 A). For GaAs, only S-in/S-out polarization gave a distinct curve (Fig 4 B). The data collected for FeGe using P-in/P-out polarization was consistent and reproducible under the varied light conditions. The data collected for GaAs using P-in/P-out polarization was consistent and reproducible under the varied light conditions. The data collected for both samples showed polarization and angular dependence.

A plot of signal intensity vs. angle of incidence which shows the expected symmetry was calculated for a cubic crystal structure with P-in/P-out polarizations for the expected SHG signal. As both crystals have a cubic crystal structure, it was expected that they would display the same (three-fold) symmetry. A polar plot of FeGe demonstrated what appeared to be

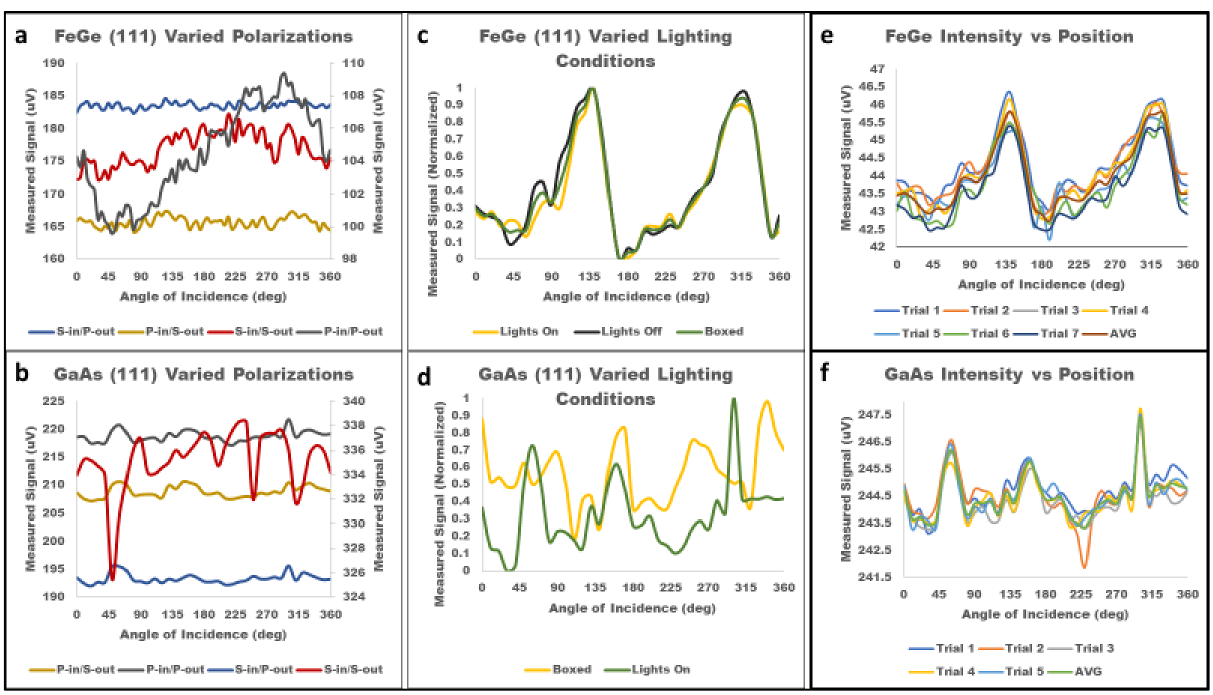


*Figure 4 Plots of the measured signal vs. the angle of incidence under various conditions. The various polarization combinations for a) FeGe and b) GaAs. Using P-in/P-out polarization; c) FeGe was examined under normal room lighting, in darkness, and with the optical setup covered, and d) GaAs was examined under normal room lighting and with the optical setup covered. Multiple trials were run using P-in/P-out polarization for e) FeGe and f) GaAs, which yielded reproducible results.*

two-fold symmetry, which was not expected. A polar plot of GaAs appeared to show three-fold symmetry.

Although GaAs demonstrated what appeared to be the correct symmetry, it is difficult to conclusively identify the nature of the signal being detected as in both results there is significant noise in the data recorded. Further work to be performed would to be done would be the optimization of the setup for the reduction of noise interference and identification of the actual nature of the signal being detected.

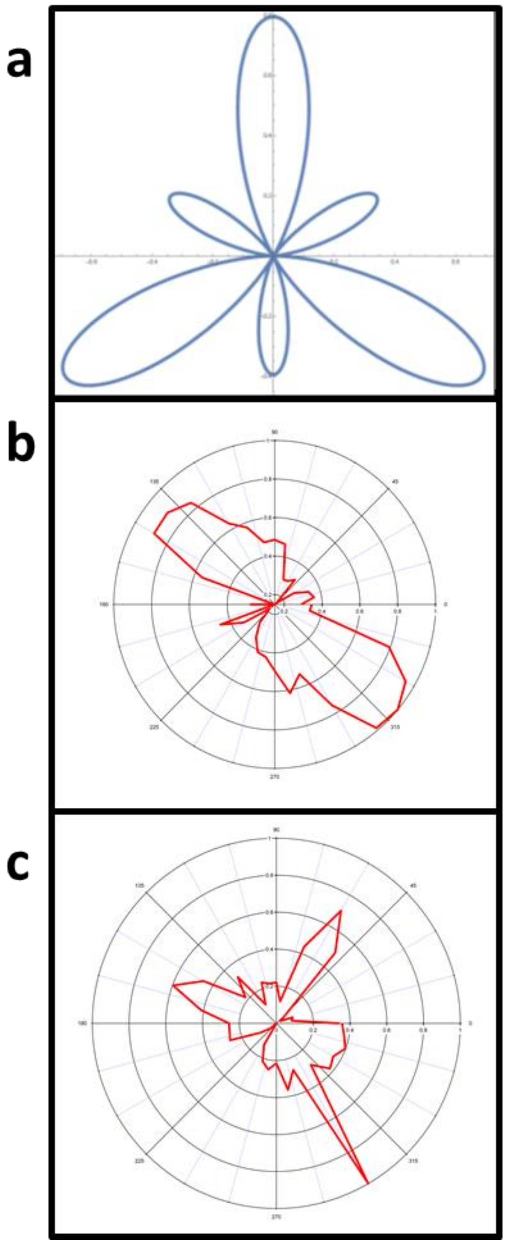


*Figure 5 Polar plots of signal intensity vs. angle of incidence for a) a generic cubic structure using P-in/P-out polarizations, b) FeGe (111) normalized measured signal, with Pi-in/P-out polarization and c) GaAs (111) normalized measured signal, with Pi-in/P-out polarization.*

## Summary

An optical setup was designed and developed for second harmonic generation. The setup is used as a highly sensitive probe of a material's symmetry. A program was written in LabVIEW to control the experimental setup and record data. Single crystal samples of FeGe (111) and GaAs (111) were studied with the setup. GaAs was chosen as a sample because it is well documented for its second order nonlinear response. FeGe was chosen as it is an interesting material that has not been studied extensively using this method.

The data collected for FeGe and GaAs was reproducible under varied lighting conditions, that demonstrated a polarization and angle dependence. The expected result for a generic cubic (111) crystal was calculated, which gave three-fold symmetry. As both samples studied have this crystal structure, it was expected that they would both demonstrate the same three-fold symmetry.

The data collected for FeGe showed what appeared to be a two-fold symmetry that was not expected. The GaAs showed what appeared to be three-fold symmetry, but showed significant noise. With these results, the nature of the signal detected is still inconclusive.

**REFERENCES**

1. R.W. Boyd, *Nonlinear Optics* (Elsevier Academic Press, New York, 2008).
2. R.W. Munn And C.N. Ironside, *Principles and Applications of Nonlinear* Optical Materials (Blackie Academic & Professional, London, 1993).
3. G.C. Baldwin, *An Introduction to Nonlinear Optics* (Plenum Press, New York, 1969).
4. J.W. Harter, Z.Y. Zhao, J.-Q. Yan, D.G. Mandrus, And D. Hsieh, Science 356, 295 (2017).
5. D.H. Torchinsky And D. Hsieh, Magnetic Characterization Techniques for Nanomaterials 1 (2016).
6. M. Fiebig, V.V. Pavlov, And R.V. Pisarev, Journal of The Optical Society of America B 22, 96 (2005).