ENHANCEMENT OF SHG IN FUSED SiO$_2$ BY CORONA POLING UNDER WATER, WATER VAPOR AND SALTY ENVIRONMENTS

Chun-An Tsai*, Jung Ning Wang*, Victor Chao-Wei-Kuo*, Tsung Yuan Cheng*, Wan-Rone Liou* and Adam Y. Wu*

Key words: SHG, poled fused silica glass.

ABSTRACT

We found that optical nonlinearity in SiO$_2$ glass sample can be greatly enhanced when sample is poled in wet and salty environments, and the nonlinearity in the sample can be reduced drastically when sample is washed in water. Possible causes for the observed enhancement and reduction of optical nonlinearity in SiO$_2$ glass are discussed.

I. INTRODUCTION

In 1961, the second harmonic generation (SHG) experiment of Franken et al. [27] marked the birth of the field of nonlinear optics. They directed a ruby laser beam at 6942 Å through a quartz crystal and observed ultraviolet radiation from the crystal at 3471 Å. Second harmonic generation of electromagnetic waves at low frequencies have been known for a long time. Harmonic generation of optical waves follows the same principle and should also be observable. The linear and nonlinear effects depend on the interaction between input and output electric fields of light in material. Power generated at the second harmonic frequency increases as the square of the intensity of the applied laser light. Although nonlinear effects are small perturbations of linear process, requiring high field strength to observe, there are ways to obtain substantial conversion efficiencies in many nonlinear optical materials.

In 1991, second-harmonic generation (SHG) in poled fused silica was reported by Myers et al. [18]. The effect draw much interests because of a multitude of potential device applications. Such applications include devices for electro-optic switching, frequency doubling crystals, linear electro-optic modulation and frequency conversion, which can be integrated monolithically into optical fibers and planer integrated circuit geometry. It has been shown that a large second-order nonlinearity $\chi^{(2)}$ in poled fused silicon of 1pm/V [18] can be induced in the near surface (~4 µm) region of commercial fused-silica optical flats by poling process using electric field of $E \approx 5 \times 10^4$V/cm and temperature at $250^\circ$C~$325^\circ$C [18].

In 1992, the values of second-order nonlinear coefficient $d_{33}$ of the corona poled glass films were estimated to be 0.5pm/V by Okada et al. [22]. The origin of the $\chi^{(2)}$ is considered to be related to the defects in the glass films. In 1993, the values of second-order nonlinear coefficient $d_{33}$ of about 0.5pm/V in corona poled corning 7059 glass films was reported by Okada et al. [23]. Nasu et al. in 1995 [20] reported that the intensity of SHG was the largest when the glasses were poled at 3kV and 200$^\circ$C for 4 hours, and $d_{33}$ was evaluated to be 0.37pm/V. The $d_{33}$ was evaluated to be 0.39 pm/V as reported by Henry et al. in 1995 [9]. In 1995, Lundquist et al. [14] reported SHG measurements on SiC films using pulsed laser ablation (PLA). $d_{33}$ was found to be as large as 10pm/V. In 1995, Henry et al. [10] observed optical nonlinearity in fused silica by proton implantation, averaged $\chi^{(2)}$ of the order of 1pm/V was induced in low-water fused silica, with isolated regions exhibiting $\chi^{(2)}$ as large as 1.6pm/V. In 1991, Harris et al. [8] reported the $\chi^{(2)}$ value of the effective second order nonlinear susceptibility for poled β-SiC to be 1.05x0.3pm/V.

In this paper, a corona poling process in fused silica samples under wet and salty environment at room temperature will be discussed. At a fixed poling field, we changed the temperature and water vapor conditions around the fused silica samples. We observed a large second harmonic generation from the samples. We observed that the nonlinearity in the poled sample can be reduced drastically by washing the samples in water. We found that the main cause of the nonlinearity resides not only inside the sample, but also resides mainly on the surface of the sample. We organize this paper in the following fashions: Section I is Introduction. In section II, we introduce the theoretical analysis. In section III, experimental procedure is discussed. The results and discussion of experiments are presented in section IV. The conclusion is given in section V.

---

Paper submitted 12/08/06; accepted 03/27/07. Author for correspondence:

Adam Y. Wu (e-mail: b6201@mail.sju.edu.tw).

* Department of Electrical Engineering, National Taiwan Ocean University,
Keelung, Taiwan, R.O.C.
II. THEORETICAL ANALYSIS

1. Effect of Second Harmonic Generation in Fused Silica Glass by Corona Poling

It is generally known that the intensity of the SHG of corona poled glass depends on the applied poling electric field, poling time, poling temperature, ion concentration in the air, defects and impurities on the glass surface, defects and impurities in the sample, we will discuss these factors in the following sections.

1) The Space-Charge Model

In the poled fused silica experiments, Myers et al. [18] proposed that the SHG originated from a space-charge region created by migrating impurity ions and electrons. Under the action of voltage applied to heated glass, impurity ions will drift to cathode where most of them are neutralised by incoming electrons, leaving behind a negatively charged depletion region near anode surface (assuming zero ionic conductivity at the anode). A high electrostatic field will then appear in a depletion region just below the anode, peaking at the interface. Assuming that all the ions reaching the cathode are neutralised, it can be shown that in steady-state the electric field $E_0$ at the anode interface, and the depletion region width $w$, are given by [12]

$$E_0 = \frac{w q N_v}{\epsilon}$$  \hspace{1cm} (1)

$$w = \sqrt{\frac{2 e V_{app}}{q N_v}}$$  \hspace{1cm} (2)

where $N_v$ is the number density of ions before poling, $q$ is the electronic charge, $\epsilon$ is the dielectric permittivity, $V_{app}$ is the applied voltage, and $E_0$ is the electric field inside sample.

2) Poling Time, Applied dc Field and Speed of Forming of Depletion Region

In 1975 Bethea [2] reported the nonlinear optical coefficient of the electric field induced second harmonic generation in glass. In 1996 Takebe et al. [26] reported the effective second-harmonic generation as a function of poling time and applied dc field. Two mechanisms have been proposed to explain the thermal poling phenomenon. One involves the orientation of bonds or dipoles and the other a frozen-in electric field, poling atmosphere. Their results demonstrated that the second harmonic generation is related to poling atmosphere [6,26].

and the spatial distribution of the induced $\chi^{(2)}$. The components of the second harmonic polarization in a glass subjected to a dc electric fields are given by

$$P_x = \varepsilon (d_{31}) E_z + \varepsilon (d_{31}) (E_x^2 + E_y^2)$$  \hspace{1cm} (3)

$$P_y = 2 \varepsilon (d_{31}) E_y E_z$$  \hspace{1cm} (4)

$$P_z = 2 \varepsilon (d_{31}) E_z E_z$$  \hspace{1cm} (5)

3) Corona Poling in Polymer Films and Other Materials

Corona poling is a powerful method for creating a large potential across many polymer films [6]. It can orient the nonlinear optical dopants noncentrosymmetrically in polymer matrix and thus large SHG intensities can be obtained [6,7]. Corona poling effect on surface space charge effects that occur at the film surface and in the bulk, and corona poling affecting the magnitude and the temporal stability of the SHG intensity, have been studied [6].

So far, many papers have used intense electric-field generated by a positive dc needle tip to change the ion orientation inside the sample [1,4,5,12,23,25,26]. This corona poling method provides not only large field on sample but also prevents any damage to sample surface due to physical contact. In such experiment a heater under the sample is commonly used to provide high temperature.

When heat is provided during corona poling, bond charges will be liberated and depletion region in the sample can be formed. In 1997 Aust et al. [1] performed an experiment by periodically poled a the Z-cut lithium niobate. The Makers Fringe scans taken before poling, it took about 30 minutes for temperature to cycle from 25°C to 200°C and back to 25°C. They spent 17 hours for the temperature cycle. After the experiment the sample was washed in water, they observed some thing interesting. There are some shifts in the Maker Fringes. It was first thought that these shifts are due to non-neutralized pyroelectric charge on the sample surface. Index changes due to a static electric field $E_{stat}$ are given by

$$\Delta n = - \frac{n_r}{2} r_{31} E_{stat}$$  \hspace{1cm} (6)

where $r_{31}$ is the linear electro-optic coefficient, $E_{stat}$ is the static electric field, and $n_r$ is the index of refraction. Calculation showed that magnitude of $E_{stat}$ is ~70 kV/mm . They therefore believed that some other phenomenon, such as surface effects or impurity migration, is causing the large fringe shifts in their annealed and unwashed samples. Their results showed that the Maker fringe analysis is very sensitive to the processing history of the material. It is unclear whether the observed effects arise from surface or bulk artifacts.

Takebe et al. [26] used different poling atmosphere in air and vacuum. Their result indicates that some species in the air, such as hydrogen or oxygen ions, may be involved in the poling process. Their results demonstrated that the second harmonic generation is related to poling atmosphere [6,26].
In our experiments, we found that SHG changes greatly when fused silica glass sample was first poled and then treated under various conditions. When we poled silica sample, with water vapor around the sample surface at room temperature, large nonlinearity in glass appeared. We believe that a detailed study of corona poling processes under rich water environment can provide useful information concerning the nonlinear optical properties in fused SiO₂.

2. Maker Fringes

The refractive index of optical materials at frequency 2ω may be different from that at frequency ω. Because of this dispersion, waves propagate in material associated with these two refractive indices may have two different velocities:

\[ C_i = \frac{C_{i,\omega}}{n_i(\omega)} = \frac{\omega}{k_i} \]  

(7)

\[ C_s = \frac{C_{s,2\omega}}{n_s(2\omega)} = \frac{\omega}{k_s} \]  

(8)

where \( C_i \) is the light velocity in vacuum, \( n_i(\omega) \) and \( n_s(2\omega) \) are the refractive indices for \( \omega \) and \( 2\omega \), \( c_i \) and \( c_s \) are the propagating phase velocities for \( \omega \) and \( 2\omega \), respectively. \( k_i \) and \( k_s \) are the wave vectors of ordinary and extraordinary ray, respectively.

From the above equations we note that: Wave propagates in material associated with the larger refractive index will move slower. Maker Fringes may result because of the phase difference \( \Delta k = |k_i - k_s| \) between the fundamental and the second harmonic wave [24]. Because the two waves travel at different velocities, the phase between the SH at one point in the sample is not in phase with that generated at a particular point in the sample. The destructive interference between two wave occurs and the SH signal starts to decrease. The phase mismatch will cause the second harmonic to go through periods of constructive and destructive interference as it propagates through the nonlinear material, producing oscillations at a period of twice the coherence length, \( \ell \). These are the Maker fringes [15].

Maker fringes utilize change of incident angle \( \theta \) so that traveling distance of wave in sample can cause the phase difference \( \Delta k \) between ordinary ray and extraordinary ray to interfere with each other so that oscillations in intensity are observed. This oscillation can be expressed as \( \sin^2 \phi \), and is related to the coherence length \( \ell \), through the following relations:

\[ \sin^2 \phi = \sin^2(\frac{\pi \ell}{\lambda \cos \theta}) \]  

(9)

\[ \ell(\theta) = \frac{\lambda}{4n_u \cos \theta_u - n_{u\alpha} \cos \theta_{u\alpha}} \]  

(10)

where \( \ell \) is the coherence length, \( \ell \) is the thickness of sample. \( n_u \) and \( n_{u\alpha} \) are the refractive indices of sample for waves at frequency \( \omega \) and \( 2\omega \), respectively. \( \theta_u \) and \( \theta_{u\alpha} \) are the refraction angles for waves with frequency \( \omega \) and \( 2\omega \), respectively.

Maker fringes also figure a period between oscillations corresponding to twice the coherence length, \( 2\ell \). If the optical path length of the nonlinearity is greater than one coherence length as the sample is rotated, the signal would exhibit Maker fringes. When the distance is an odd multiple number of the coherence length as the laser light is passing through the sample, the largest maximum intensity of SHG will be observed. In opposition, if the distance is an even multiple number of the coherence length, the intensity would be minimum.

3. Calculation for \( d_\alpha \) Values

Analyzing Maker fringes is a common method for researchers to obtain NLO coefficients of unknown samples. However, in order to obtain accurate value, a known reference value is usually used. For examples, reference values such as \( d_{11} \) in quartz, \( d_{33} \) in ADP, \( d_{36} \) in KDP, can be used [16].

According to reference [11], the formula for the intensity of the second harmonic can be written as:

\[ I_{2\omega} = \frac{512 \pi^3 A^2}{3} \times d^2 \times (\frac{\chi^{(2)}}{\chi^{(1)}})^2 \times \left( \frac{\sin^2 \phi}{(n_u^2 - n_{u\alpha}^2)^2} \right) \]  

(11)

\[ \phi = \frac{\pi \ell}{2} \left( \frac{4}{\lambda} \right) (n_u \cos \theta_u - n_{u\alpha} \cos \theta_{u\alpha}) \]  

(12)

where: \( I_{2\omega} \) is the intensity of SHG, \( A \) is the laser beam area. \( d \) is the nonlinear optical coefficient. \( I_\omega \) is the transmission factor at \( \omega \). \( T_{2\omega} \) is the transmission factor at \( 2\omega \). \( \theta \) is rotation angle. \( I_\omega \) is the intensity of fundamental beam, \( n_u \) is the refractive index at \( \omega \), \( n_{2\omega} \) is the refractive index at \( 2\omega \). \( \ell \) is sample thickness. \( \lambda \) is wavelength of the fundamental beam in air.

We can obtain the second order nonlinear optical susceptibility tensor matrix and fundamental wave in quartz as follows:

\[
\begin{bmatrix}
P_1 \\
P_2 \\
P_3
\end{bmatrix} =
\begin{bmatrix}
d_{11} & -d_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -d_{11} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -d_{11} & 0
\end{bmatrix} \times
\begin{bmatrix}
E_x^0 \\
E_y^0 \\
E_z^0 \\
E_x^2 \\
E_y^2 \\
2E_xE_y
\end{bmatrix}
\]

Expanding equation (13) we obtain:

\[
P_x = d_{11}E_x^2 - d_{11}E_y^2 + 2d_{11}E_xE_y
\]

\[
P_y = -2d_{11}E_xE_y - 2d_{11}E_xE_y
\]

(14)

\[
P_z = 0
\]

According to the Kleinmann symmetry, \( d_{11} = 0 \) in quartz crystal [11,13] and \( d_{11} \) is a positive value [4]. If we want to measure the \( d_{11} \) of a y-cut quartz, the rotation axis should be the
c-axis and the fundamental and extraordinary ray should both be P-waves. In such case, equation (14), becomes

\[ P_i = d_{i\alpha} E_i^2 \]  

(15)

From (11), we have: \[ t_\omega = \frac{2 \cos \theta}{n_\omega \cos \theta + \cos \theta} \]  

(16)

\[ T_\omega = \frac{2\cos \theta_{\omega}}{n_\omega \cos \theta + \cos \theta} \cdot \left( \cos \theta + n_\omega \cos \theta \right) \cdot \left( n_\omega \cos \theta + \cos \theta \right) \]  

(17)

where \( n_\omega = 1.53413 \) and \( n_{\omega a} = 1.54702 \) in quartz [11]. From experimental result we can choose the SHG intensity at a particular angle \( \theta \), and from the Snell’s law, we have:

\[ \sin \theta_\omega = \frac{\sin \theta}{n_\omega} \]  

(18)

\[ \theta_\omega = \sin^{-1}\left( \frac{\sin \theta}{n_\omega} \right) \]  

(19)

\[ \theta_{\omega a} = \sin^{-1}\left( \frac{\sin \theta}{n_{\omega a}} \right) \]  

(20)

From (11) to (20) we can obtain the relative \( d_{i\alpha} \) value of unknown samples with respect to that of quartz.

III. EXPERIMENTAL PROCEDURE

1. Samples

Quartz crystal is purchased from the Entrust SLEO Photonics Co., Ltd. The Y-cut (010) sample has dimensions 10mm×10mm×3mm. According to the SLEO Photonics Co., Ltd. the quartz crystal samples are produced by method of hydrothermal process. Hydrothermal process is a method imitates nature crystal growth. \( \text{SiO}_2 \) raw material was first melted at high temperature and then crystallized upon cooling on a seed plate of quartz single crystal. Proper-size crystals so grown are then collected. Because quartz concentration in melted solution is low in natural environment, it needs a long time for quartz to crystallize. Artificially, one can increase the concentration of \( \text{SiO}_2 \) in solution to reduce the crystalline time in laboratory.

Silica glass plates were purchased from the Heraeus Company of America. The specifications are Optosil I or Optosil II. The fabrication of glass is like this: First, crystal quartz is melted into molten form above 1750°C in a furnace and then is cooled down slowly to form glass at low temperature.

2. Instrument

We used a Model VC-50 diamond cutter purchased from the Leco Instrument Taiwan Ltd. to cut our samples. The diamond blade is 4” in diameter with a 0.5” arbor hole and 0.012” in thickness. The sample wafers were cut into proper sizes. We used mesh 1000 waterproof abrasive paper to polish the cut faces.

We used a Quanta-Ray GCR-200 Nd:YAG laser manufactured by the Spectral Physics Company. Its specifications are as follows:

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>1064nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetition Rate</td>
<td>10Hz</td>
</tr>
<tr>
<td>Energy</td>
<td>Q-Switch</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>8~9 ns</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>6mm</td>
</tr>
</tbody>
</table>

The PMT and the amplifier we used were both manufactured by the Hamamatsu Company. The model of PMT is R636 and the spectral response range is from 185 to 930nm. The model of amplifier is C5594. It has a wide frequency bandwidth from 50KHz~1.5GHz and a high gain of 36dB. It requires an applied bias voltage of \(+12~-+16\) V.

The oscilloscope we used was manufactured by the Tektronix Company manufactured, its model is TDS620A, and its triggering frequency can reach 500MHz. The Boxcar integrator was manufactured by the Stanford Research System Company, the model is System SR250. Its gate width can reach 1ns.

3. Methods for Conventional Corona Poling

In order to break the centrosymmetry in glass sample, we utilized the gas molecules surrounding the sample and the original molecules inside the sample ionized by heating and oriented by a high electric field. The experimental setup for corona poling is shown in Fig. 1. We used a thermocouple to monitor the temperature by a voltage meter. We controlled and kept the temperature of the sample at about 270°C [14,18,19,23]. A positive 4900V (with a small corona dc current of less than 0.1mA) was applied to a positive needle tip placed about 1cm above the sample. During the poling process, the temperature of the sample was kept at 270°C, and the voltage was kept at 4900V. The poling time was 270 minutes. Temperature was then reduced to room temperature with the electric field still applied.
As the sample was cooled down, the molecules in the sample remained in an oriented state as the material in the sample became thermally stable.

4. Experimental Setup

As shown in Fig. 2, a Q-switched Nd: YAG laser radiation of wavelength 1.064 μm was used. A high energy laser polarizer was used to differentiate polarization of the incoming beam. We define that wave is p-polarized when the polarization is parallel to the surface of our optical table, and s-polarized wave is the wave with the polarization perpendicular to the surface of the optical table. The angle between the normal of the polarizer and incident beam is 57°. The beam passing through the polarizer is p-polarized (96%) and the beam reflected from the polarizer s-polarized (99%). We chose the purer s-polarized wave as incident beam. Before the incident beam entering the system, it passed a 6mm-diameter hole made of steel to reduce the diameter of the beam and to make the beam cleaner and Gaussian like. The incident beam then passed through a λ/2 plate (multiple order of half wave retardation plate) for selecting s or p polarization.

After the λ/2 plate, we used a high energy laser harmonic separator for the 1064 nm radiation (Transmission > 99.5%) to make sure that the incident beam entering the sample was pure 1064 nm radiation. Because the sample thickness was only 1mm~2mm, we utilized a convex lens with a focal length of 150mm to focus the laser beam onto the sample surface. Sample was placed at the center of a rotational stage near the focal point of the beam. The diameter of the beam at sample was smaller than 1mm. The incremental step of the rotational stage was controlled to 0.01°.

A parallel light passes through a convex lens will be focalized. When this focalized light passes through the focal point it will start to diverge, we added another convex lens with the incident beam enters a non-centrosymmetry same focal length as the previous one. When the c sample a new frequency which doubles the original one will be generated. In order to measure the pure intensity of frequency-doubled light, we used two different filters, one is a KG3 Schott Glass filter for passing wavelength at 532nm (the product number is 03FCG167) and another is a high energy laser harmonic separator for 532nm (Transmission > 99.5%). The bandpass specification is 532 ± 150nm for the Schott Glass filter and is 532 ± 50nm for the separator. These two filters can reduce all nongreen light to zero.

After the two filters, we used an analyzer to select the polarization of the second harmonic signal. The frequency-doubled 532nm radiation entered a SPEX monochromator for selecting the 532nm radiation. Signal was measured by a Hamamatsu R636 photomultiplier tube (PMT). Signal detected by the PMT and was further amplified by an amplifier of 56 dB. The signal was monitored by an oscilloscope and a boxcar integrator using 50Ω BNC cables. We utilized the oscilloscope to observe the waveform of the SHG and the boxcar integrator to filtrate out the noise and retain only the signal. The experimental setup is shown in Fig. 2.

5. Experimental Measurement

SiO2 glass samples were used in this experiment. Y-cut quartz sample of 3mm thick was used as reference. Before each experiment, we measured the background for the experiment. After the experiment was done, the reference sample was removed and the real sample was inserted for measurement. Each data point was the average of five or more data readings. The noise to signal ratio was kept below 3%.

We used an X-cut LiNbO3 crystal of 1mm thick to check if our experiment system was correct. In the test experiment of the
X-cut LiNbO₃ crystal, we applied the electric field along the Z-direction of the crystal. We measured the signals both in applied electric field and in zero field under the same conditions and obtained Fig. 3 and Fig. 4. These Figures indicate that our experiments can easily detect small oscillations of the Maker Fringes.

In this test experiment, the LiNbO₃ was cleaned with acetone (CH₃CO m.w.=58.08 g/mole) and methyl alcohol (CH₃OH). When the sample was dried, we painted Ag paste on the cut-faces of the sample uniformly and carefully. Then sample was baked in an oven so that moisture and organic material in the paint were driven away.

We utilized the corona poling to orient the surrounding molecules on the glass sample surface and the original molecules inside the glass sample. The corona poling process broke the centrosymmetry of the sample. In order to study the H₂O and salt effects in SHG, we have studied the SHG as a function of rotation angle (Maker fringes) in the samples prepared by the four poling methods under water and salt water environments as mentioned before. The conditions for these procedures are listed in Table 1.

IV. RESULTS AND DISCUSSION

In this section, we will use $d_{ij}$ instead of $\chi^{(2)}$ for detailed experimental interpretations of our results. The simple relation between $\chi^{(2)}$ and $d_{ij}$ is simply $\chi^{(2)} = 2d_{ij}$ [17,27]. We will discuss the enhancement of SHG in fused SiO₂ by corona poling under different environments. Since glass with a centrosymmetric structure can not be used to generate second-harmonic generation. Corona poling allows the localized hyperpolarizability to constructively interfere on the anode side of sample, forming a non-zero macroscopic susceptibility. The polarization of dipole moment is perpendicular to the sample surface, which is the preferred z-axis. If we ignore the components induced by the angle variation of the y-axis, the relation between second-order nonlinear susceptibility matrix and fundamental wave in poled glass can be expressed as follows:

$$
\begin{bmatrix}
  P_x \\
  P_y \\
  P_z \\
\end{bmatrix} =
\begin{bmatrix}
  0 & 0 & 0 & 0 & d_{15} & 0 \\
  0 & 0 & 0 & d_{ij} & 0 & 0 \\
  d_{31} & d_{31} & d_{31} & 0 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
  E_x^2 \\
  E_y^2 \\
  E_z^2 \\
  2E_xE_y \\
  2E_xE_z \\
  2E_yE_z \\
\end{bmatrix}
$$

When the Kleinmann symmetry holds, i.e. when the optical frequencies are within the transparency range of the medium, as is true with glass in visible region, we have $d_{15} = d_{31}$ [12]. For material with a single axis of symmetry and an effective $\chi^{(2)}$ created by corona poling, the additional symmetry condition of $d_{33} = 3d_{31}$ also exists [9,12,22]. From (21) we have:

$$
\begin{align*}
  P_x &= 2d_{31}E_x(\omega)E_z(\omega), \\
  P_y &= 2d_{31}E_y(\omega)E_z(\omega), \\
  P_z &= d_{31}(E_x^2(\omega) + E_y^2(\omega)) + d_{31}E_z^2(\omega). \\
\end{align*}
$$

The main purpose of this paper is to measure the electric field induced second harmonic generation in SiO₂ glass. Four methods for generating electric field in glass were used: 1) We used the standard corona poling at 270°C as reported by other researchers [18,19] and measured the intensity of SHG as a function of rotation angle. 2) We used the corona poling method with the assistance of water vapor around the sample. 3) We used the corona poling method with water drops placed on the sample surface at room temperature. 4) We used the corona poling method at the room temperature with some salty water drops placed on the sample surface at room temperature. The conditions for each experiment are shown in Table 1.

1. NLO Effect in SiO₂ Glass by Corona Poling at 270°C

In this section, we performed a similar corona poling experiment of SiO₂ at 270°C as reported by other researchers [18,19] and used the Maker Fringes equation to calculate $d_{eff}$ (See Appendix-B) and $d^{*eff}$ (See Table 3). After the poling experiment the sample was washed in water. We note here that Aust et al. had washed their lithium niobate sample in water after poling [1]. Since the sign of $d_{eff}$ and $d^{*eff}$ could not be determined directly in our experiment, the values of $d_{eff}$ and $d^{*eff}$ are absolute values.

The corona poling conditions are as follows: 1) The distance between the sample and the positive electrode needle tip is 1cm. 2) The poling voltage is 4900V. (3) The temperature is about 270°C. 4) The poling duration is about 270 minutes. These poling conditions are the same as those published before and are shown in Table 1. [3,8,9,10,12,14,19,20,21,22,23]

Fig. 5 shows the intensity of SHG as a function of rotation angle $\theta$ for a corona poled glass sample. Fig. 5 shows the results in the P-P mode. We chose the value of $I_{2\omega} = 80.8$ (relative arbitrary unit) at $\theta = 40^\circ$ as a reference point in this sample. In order to find the $d_{eff}$ value, we have to obtain all required parameters before substituting them into (11).
We chose the following known or measured values for further calculation:

For Fig. 5, case1: Parameters for glass sample, in the P-P mode:

\[ \theta = 40^\circ, \]
\[ I_{2\omega} = 80.8, \]
\[ n_{\omega} (1.064 \mu m) = 1.45, \]
\[ n_{2\omega} (0.532 \mu m) = 1.46 \] [19].

Using the Snell’s law we obtain the refraction angles for \( \theta_{\omega} \) and \( \theta_{2\omega} \) as follows:

\[ \sin \theta = n_{\omega} \sin \theta_{\omega}, \]
\[ \theta_{\omega} = \sin^{-1} \left( \frac{\sin \theta}{n_{\omega}} \right) = 26.31^0, \]
\[ \sin \theta = n_{2\omega} \sin \theta_{2\omega}, \quad \theta_{2\omega} = \sin^{-1} \left( \frac{\sin \theta}{n_{2\omega}} \right) = 26.12^0. \]

The transmission factors for the fundamental beam and frequency-doubled beam are:

\[ t_{\omega} = \frac{2 \cos \theta}{n_{\omega} \cos \theta_{\omega} + \cos \theta} = 0.74, \]
\[ T_{2\omega} = 2 \cos \theta_{2\omega} \cdot n_{2\omega} \cdot \left( \cos \theta + n_{\omega} \cos \theta_{\omega} \right) \cdot \left( n_{\omega} \cos \theta_{\omega} + n_{2\omega} \cos \theta_{2\omega} \right) \div \left( n_{2\omega} \cos \theta_{2\omega} + \cos \theta \right)^2 = 1.58 \]

the coherence length is:

\[ l_{c} = \frac{\lambda}{4n_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega}} = 23.8 \mu m, \]
\[ \sin^2 \phi = \sin^2 \left( \frac{\pi d}{2l_{c}} \right) = 0.038. \]

By substituting the above parameters into (11) we obtain:

\[ \frac{I_{2\omega}}{I_{\omega}^2} = \frac{512 \pi^3}{A} \times d_{\text{eff}}^2 \times 34.03 \]  (23)

Using similar steps and methods, we chose \( I_{2\omega} = 68.1 \) (relative arbitrary unit) at \( \theta = 45^\circ \) in Fig. 5 as reference point for quartz reference crystal, and obtain the following parameters:

For Fig. 5, case 2: parameters for quartz reference sample, in the P-P mode:

\[ \theta = 45^\circ, \]
\[ I_{2\omega} = 68.1, \]
\[ d = 0.5 \] [3,4],
\[ n_{\omega} (1.064 \mu m) = 1.53413, \]
\[ n_{2\omega} (0.532 \mu m) = 1.54702 \] [11],
\[ \sin \theta = n_{\omega} \sin \theta_{\omega}, \]
\[ \theta_{\omega} = \sin^{-1} \left( \frac{\sin \theta}{n_{\omega}} \right) = 27.45^0, \]
\[ \sin \theta = n_{2\omega} \sin \theta_{2\omega}, \quad \theta_{2\omega} = \sin^{-1} \left( \frac{\sin \theta}{n_{2\omega}} \right) = 27.20^0, \]
\[ t_{\omega} = \frac{2 \cos \theta}{n_{\omega} \cos \theta_{\omega} + \cos \theta} = 0.68, \]
\[ T_{2\omega} = 2 \cos \theta_{2\omega} \cdot n_{2\omega} \cdot \left( \cos \theta + n_{\omega} \cos \theta_{\omega} \right) \cdot \left( n_{\omega} \cos \theta_{\omega} + n_{2\omega} \cos \theta_{2\omega} \right) \div \left( n_{2\omega} \cos \theta_{2\omega} + \cos \theta \right)^2 = 1.72 \]
\[ l_{c} = \frac{\lambda}{4n_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega}} = 18.33 \mu m, \]
\[ \sin^2 \phi = \sin^2 \left( \frac{\pi d}{2l_{c}} \right) = 0.25. \]

Substituting the above parameters into (11) and using (24) we obtain:

\[ \frac{I_{2\omega}}{I_{\omega}^2} = \frac{512 \pi^3}{A} \times 25.094 \times d_{\text{eff}}^2 \times 34.03 \]  (24)

Because we could not directly measure the thickness of the depletion layer on the anode side of poled sample, three possible thicknesses of the depletion layer of 3 \( \mu m \), 5 \( \mu m \) and 10 \( \mu m \) [14] were used. By dividing (24) with (23) to obtain \( d_{\text{eff}} \), we can express as follows:

when \( l = 3 \mu m \), \[ \frac{I_{2\omega}}{I_{\omega}^2} = \frac{512 \pi^3}{A} \times d_{\text{eff}}^2 \times 34.03 \]
\[ d_{\text{eff}} = 0.94 \text{ pm/V}, \]
when \( l = 5 \mu m \), \[ \frac{I_{2\omega}}{I_{\omega}^2} = \frac{512 \pi^3}{A} \times d_{\text{eff}}^2 \times 92.37 \]
\[ d_{\text{eff}} = 0.57 \text{ pm/V}, \]
when \( l = 10 \mu m \), \[ \frac{I_{2\omega}}{I_{\omega}^2} = \frac{512 \pi^3}{A} \times d_{\text{eff}}^2 \times 330.88 \]
\[ d_{\text{eff}} = 0.29 \text{ pm/V}. \]

There is only one peak in Fig. 5. This is because the nonlinear thickness \( l = 3 - 10 \mu m \) is smaller than the coherence length
In Fig. 6, after washing the poled sample for the P-P mode.

**Fig. 6.** After washing the poled sample for the P-P mode.

In Fig. 7, the NLO effect of glass under corona poling. The poling conditions are 4900V, 270°C, 270 minutes, water on the sample, P-P mode.

**Fig. 7.** The NLO effect of glass under corona poling. The poling conditions are 4900V, 270°C, 270 minutes, water on the sample, P-P mode.

\[ l = 23.8 \mu m \]  
Hence, we have to increase the optical path length in the sample by rotating the sample. When the sample rotation angle reached 40 degree, the intensity of SHG became maximum. At this angle, the optical path length of the laser beam passing through the sample is just one coherence length.

By comparing with Fig. 5, it is clear that if we assume that the thickness of the nonlinear region in glass is 5\( \mu m \), the calculated \( d_{eff} \) value of the poled glass of 0.56 pm/V is already larger than the \( d_{11} \) of quartz crystal, which is 0.5 pm/V.

We then used water to wash the poled sample, the results for the P-P mode are shown in Fig. 6. We can see from Fig. 6 the SHG intensity decreases dramatically. This leads us immediately to believe that the nonlinearity maybe due to some residual nonlinear region on the glass surface.

For calculation, we chose the value \( I_{2\omega} = 5 \) at \( \theta = 40^\circ \) as shown in the figure. In order to find the \( d_{11} \) value, we have to obtain all required parameters before substituting them into (11). The results are:

- when \( l = 3\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 22.80 \),
- \( d_{eff} = 0.076 \text{ pm/V} \),
- \( l = 5\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 61.87 \),
- \( d_{eff} = 0.046 \text{ pm/V} \),
- when \( l = 10\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 22.16 \),
- \( d_{eff} = 0.024 \text{ pm/V} \),
- when we assume \( l = 3\mu m \), we also found \( d_{eff} \) is 0.101 pm/V (See Table 3).

From these two experiments on unwashed and washed sample, we discovered that when the corona poled sample was washed by water; its SHG intensity decreases drastically. We believe that this phenomenon is related to some interaction between water and SiO\(_2\) under high electric field. It is possible that a thin new chemical compound such as SiOH or other material is formed on the glass surface. The following experiment was performed to clarify this situation.

In our next experiment, we change some conditions. We put several water drops on the surface of glass sample and performed the corona poling at 270°C. The results are shown in Fig. 7. Again, if we assume that the thickness of the depletion layer is 3\( \mu m \), 5\( \mu m \) or 10\( \mu m \), we obtain

- when \( l = 3\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 20.22 \),
- \( d_{eff} = 2.08 \text{ pm/V} \),
- when \( l = 5\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 54.75 \),
- \( d_{eff} = 1.27 \text{ pm/V} \),
- when \( l = 10\mu m \), \( \frac{I_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d^2_{eff} \times 193.62 \),
- \( d_{eff} = 0.67 \text{ pm/V} \).

When we assume \( l = 3\mu m \), we found that \( d_{eff} \) is 1.16 pm/V (See Table 3).

It is clear that \( d \) is more than two times as large as in the previous results, and that water can increase the nonlinear intensity. In Figs. 5, 6 and 7, we used (11) and calculated the intensity. The results are listed in Table 2. From Table 2 we can see that nonlinearity can be enhanced by water drop experiment and bleached by washing experiment. From Figs. 5 and 7 we can see that \( d_{eff} \) are 0.95pm/V and 2.08pm/V, respectively. From Figs. 5 and 7 we can also see that \( d_{eff} \) are 0.95pm/V and 1.16pm/V, respectively. This proves that glass indeed reacted with water in the corona poling process. Next, we want to know the relation between the poling time and SHG intensity.

2. **Time Duration for Corona Poling at 270°C**

In 1995 Myers et al. [19] reported effect of SHG in glass by changing the poling time and applied voltage. In 1996, Takebe et al. [26] also reported similar experiment. In this section, we want to know the relation between the SHG intensity and the poling time.

In this experiment the new conditions are that the time for poling was 180 minutes and we placed the water drops on the surface of the glass sample at 270°C. The result is shown in the Fig. 4.3a. The calculated coherence length is 23.2\( \mu m \), If we...
assume the nonlinear region is about $3\mu m$, $d_{eff}$ is calculated to be $0.71pm/V$ (See Table 2), and $d^{*}_{eff}$ is calculated to be $0.64pm/V$ (See Table 3).

From Figs. 7 and 8, we can see that the SHG intensity increases as the poling time increases. The results for the sample washed in water are shown in Fig. 9. We found that $d_{eff}$ decreases from $0.71 pm/V$ to $0.42 pm/V$ and $d^{*}_{eff}$ decreases from $0.64 pm/V$ to $0.42 pm/V$. As is clearly shown, after the sample was washed in water, the nonlinear optic coefficient decreased drastically.

3. NLO Effect in SiO$_2$ Glass by Corona Poling under Wet Environment at Room Temperature

In this section, our new conditions are the temperature was room temperature and water drops were placed on the sample surface. The results are shown in Fig. 10. The calculated $d_{eff}$ for the $3\mu m$ thick case is $1.33pm/V$ and $d^{*}_{eff}$ is $1.47pm/V$.

This result is interesting. From Figs. 7 and 10, we can see that $d_{eff}$ are $2.08 pm/V$ and $1.33 pm/V$, respectively. From Figs. 5 and 10, we can see that $d_{eff}$ are $0.95 pm/V$ and $1.33 pm/V$, respectively. It is clear that the SHG intensity is dependent more on water and less on temperature.

After the sample was washed by water the results are shown in Fig. 11. Again our calculations showed that $d_{eff}$ is $0.31pm/V$ and $d^{*}_{eff}$ is $0.26pm/V$. From Figs. 9 and 11, we can see that $d_{eff}$ are $0.42 pm/V$ and $0.31 pm/V$, respectively. It appears that SHG intensity was caused essentially by material formed on the glass surface when experiment was performed at room temperature. Since this material on the surface can be washed away or destroyed by water, it is clear that SHG intensity can be seen at high temperature because nonlinear region resides not only on the surface but also inside the sample.

4. NLO Effect in SiO$_2$ Glass by Corona Poling under Salty Environment at 270$^\circ$C

In this section, we want to find out the relationship between salt water and SiO$_2$. We prepared the salt-water solution by adding 1g of NaCl into 1000 c.c. of deionized water and put salty water solution drops on glass surface and then performed the corona poling process. Poling time was 270 minutes, temperature was about 270$^\circ$C, poling voltage was $4900V$, and distance between sample and the positive electrode needle tip was $1cm$.

The results are shown in Fig. 12. Again we assume that the thicknesses of the depletion layer is $3\mu m$, we obtain (by using the Maker Fringes method):

$$\frac{l_{2\omega}}{I_{\omega}} = \frac{512\pi^3}{A} \times d_{eff}^2 \times 16.25,$$

$$d_{eff} = 2.52 pm/V.$$

After this experiment, we observed that some residual stains or NaCl like particles seemed to appear on the glass surface. Since Fig. 12 does not show the Maker fringes, so if we used the Maker Fringe method to calculate the $d_{ij}$ value, the value obtained would be too small. This means that the value $d_{eff} = \ldots$
2.55 pm/V calculated using the Maker Fringe method may be too small for reality. We also calculated the $d_{*eff}$ used the total intensity method and obtain $d_{*eff}$ to be 3.99 pm/V. From Fig. 12, we believe that nonlinear region was thicker and more inhomogeneous than those formed under other conditions. After the sample was stored and washed in water for 1 week, We could not detect any SHG signal in this sample any more. We can see from Figs. 5 and 12 that the SHG intensity increases when there were salty water drops.

5. NLO Effect in SiO$_2$ Glass by Corona Poling under Water Vapor Environment at 270°C

In 1992, Okada et al. [22] reported that it is charge separation in glass films which caused the observed $\chi^{(2)}$ in Ge-doped optical fibers. Glasses are generally good insulators. Thermally grown amorphous SiO$_2$ films, for example, have an energy band gap of approximately 8–9 eV, are good insulator. However, defects exist in glass films prepared by rf sputtering. These defects form energy states in between conduction band and valence band, which are associated with trapped electrons. When a strong electric field is applied to a glass film by corona poling, the trapped electrons at defects jump over energy barriers and move to other trap sites. This electron migration occurs in the direction of the electric field and the charges accumulate on one side of the film to set up an internal static electric field $E_{si}$ in the film. This static electric field acts on the third-order optical nonlinearity $\chi^{(3)}$ of the glass film and, as a result, the $\chi^{(2)}$ ($\chi^{(2)} \approx \chi^{(3)} E_{si}$) appears in the film [22].

In 1995, Henry et al. [10] reported the optical nonlinearity induced in fused silica through proton implantation. The average $\chi^{(2)}$ is of the order 1 pm/V. In 1996, Takebe et al. [16] reported SHG signal from fused silica by corona poling both in air and in vacuum at 280°C. The SHG intensity decreases as the poling time increases in vacuum [16]. These two papers proposed that SHG intensity is related to some defects in fused silica and some ion species in air, such as hydrogen or oxygen ions, during the poling process.

In this experiment we placed the sample in water steam during corona poling at 270°C. We generated the water steam around the sample by heating water in a pot. The result is shown in Fig. 13. If we assume that the nonlinear region thickness is 3 μm thick, then the calculated $d_{eff}$ is almost 1.02 pm/V and $d_{*eff}$ is 1.64 pm/V. We can see from Figs. 5 and 13 that the SHG intensity increases when there was water vapor. Since Fig. 13 looks very different from Figs. 5, 7, 8, and 10, we speculate that water vapor caused inhomogeneous nonlinear region to form in the sample.

In all the water washing experiment SHG intensity decreases very drastically. When we compared Fig. 5 with Fig. 6, we found that $d_{eff}$ decreases from 0.95 pm/V to 0.076 pm/V. In Figs. 8 and 9, $d_{eff}$ decreases from 0.75 pm/V to 0.42 pm/V. In Figs. 10 and 11, $d_{eff}$ decreases from 1.32 pm/V to 0.305 pm/V. In salt water experiment as shown in Fig. 12, $d_{eff}$ decreases from 2.52 pm/V to 0 pm/V after washing.

We believe that the cations impinged on the sample under high dc field. This phenomenon generates four effects: First, cations impinged on the sample produce defects on sample surface. Second, cations can be implanted into the sample. Third, cations can reacted with SiO$_2$ or other ions to form new chemical compounds on sample surface. Fourth, cations may form dipole moment not only on the sample surface but also...
inside the sample. In general, proton implantation requires high energy. It seemed that our experiment did not employ energy high enough for substantial implantation to occur. The third and fourth effects influenced more than first and second effects. The dipole moments on the sample surface may be due to H₂O (See Fig. 14(a)), and inside the sample may be due to SiOH (See Fig. 14(b)(c)(d).) or SiO₂ [9].

We found that nonlinearity really increases in our samples after poling processes as discussed in this paper, they are somewhat inhomogeneous on the surface or inside the samples. This should be examined in more details by researches in the future.

V. CONCLUSION

We had performed a series of experiments on fused SiO₂ glass samples in this paper. We treated the samples with water, water vapor and salt water during corona poling, SHG intensity from samples were detected. We used the Maker Fringes method to calculate the nonlinear optical coefficients in the SiO₂ samples using a corona poled glass sample as reference. (See Fig. 15.) In our calculation χ(2) of a corona poled glass sample reference is about 1pm/V. This is close to the values reported by several other researchers [5,10,19].

We believe that some dipole moments form both on the glass sample surface and near the top surface inside the sample. The impurities cause some dipole moments to form near the surface region inside the sample. In particular, oxygen or hydrogen or other ions obtain energy from corona poling process can form some new chemical compounds both on the glass surface and near the top surface inside the sample. (See Fig. 16.)

We found that when water drop is placed on fused SiO₂ surface during the corona poling, large nonlinearity will be formed in the sample. After the sample is washed in water, SHG intensity decreases drastically. We propose that water, H₂ and some other ions can form hydrogen bonds on the glass surface under the corona poling. These species can be washed away or destroyed by water. We also propose that SiOH is formed inside the fused SiO₂, it can not be washed away by water easily.

It appears that SHG signal comes more from sample surface than from inside the sample, as is shown clearly in washing experiments in Figs. 6, 9 and 11. The nonlinear materials formed on the surface or inside the sample can lose their nonlinearities by water washing and can even be washed away by water. The SHG intensity in samples decreases very drastically after washing, as shown in all our corona poling experiments under water, water vapor and salty environments. In order for water to reach the nonlinear regions, nanocracks or nano-channels may be formed in the sample so that water can enter the nanocracks and the nanochannels and wash the nonlinear regions.

The thickness of the nonlinear region is about 3 ~ 10μm, formed by corona poling. This small region can contribute large nonlinearity. We tried effectively to increase the strength or the thickness of the nonlinear region by using different corona poling processes under water, water vapour and salty environment, enhancement effects on nonlinearity in SiO₂ glass were observed. How to further increase the nonlinearity in SiO₂ glass will be an important task in the future.

APPENDIX

Table 1. Sample condition.

| Figure 5 | (1) The distance between the sample and the positive electrode needle tip is 1cm. (2) The poling voltage is 4900V. (3) The temperature was about 270°C. (4) The poling time is about 270 minutes. P-P mode. dₜ=0.95pm/V. |
| Figure 6 | Experimental results for sample in Figure 5 washed by water. P-P mode. dₜ=0.08pm/V. d*=0.10pm/V |
| Figure 7 | (1) Distance between sample and the positive electrode needle tip is 1cm. (2) The poling voltage is 4900V. (3) Experiment temperature was about 270°C. (4) Poling time was 270 minutes. (5) Water |
drops were placed on the surface of glass. P-P mode.
\[ d_{\text{eff}} = 2.08 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 1.16 \text{pm/V}. \]

**Figure 8**
(1) Distance between sample and the positive electrode needle tip is 1 cm. (2) The poling voltage is 4900 V. (3) Experiment temperature was about 270°C. (4) The poling time was 180 minutes. (5) Water drops were placed on glass sample. P-P mode.
\[ d_{\text{eff}} = 0.70 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 0.64 \text{pm/V}. \]

**Figure 9**
Experimental results for sample in Figure 8 washed by water. P-P mode.
\[ d_{\text{eff}} = 0.42 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 0.42 \text{pm/V}. \]

**Figure 10**
(1) Distance between the sample and the positive electrode needle tip was 1 cm. (2) The poling voltage is 4900 V. (3) Temperature was room temperature. (4) Poling time was 270 minutes. (5) Water drops were placed on the glass sample surface. P-P mode.
\[ d_{\text{eff}} = 1.33 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 1.47 \text{pm/V}. \]

**Figure 11**
Experimental results for sample in Figure 10 washed by water. P-P mode.
\[ d_{\text{eff}} = 0.30 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 0.26 \text{pm/V}. \]

**Figure 12**
(1) Distance between sample and the positive electrode needle tip is 1 cm. (2) The poling voltage is 4900 V. (3) Experiment temperature was about 270°C. (4) Poling time was 270 minutes. (5) Salty water on glass surface. P-P mode.
\[ d_{\text{eff}} = 2.52 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 3.99 \text{pm/V}. \]

**Figure 13**
(1) Distance between sample and the positive electrode needle tip is 1 cm. (2) The poling voltage is 4900 V. (3) Experiment temperature was about 270°C. (4) Poling time was 270 minutes. (5) Water vapor around the glass sample. P-P mode.
\[ d_{\text{eff}} = 1.07 \text{pm/V}, \]
\[ d_{\text{eff}}^* = 1.64 \text{pm/V}. \]

**Table 2. Experimental results.**
Assume that nonlinear region is about 3 µm thick:

**Figure 5**
(1) \( \theta_{\omega} = \sin^{-1}(\sin \theta / n_{\omega}) \)
(2) \( \theta_{2\omega} = \sin^{-1}(\sin \theta / n_{2\omega}) \)
(3) \( \theta_{\omega} = 26.31^\circ \)
(4) \( \theta_{2\omega} = 26.12^\circ \)
(5) \( t_{\omega} = \frac{2 \cos \theta}{n_{\omega} \cos \theta_{\omega} + \cos \theta} = 0.74 \)
(6) \( T_{2\omega} = \frac{2 \cos \theta_{2\omega} \times n_{2\omega} \times (\cos \theta + n_{\omega} \cos \theta_{\omega})}{(n_{\omega} \cos \theta_{\omega} + n_{2\omega} \cos \theta_{2\omega}) \div (n_{2\omega} \cos \theta_{2\omega} + \cos \theta)} = 1.58 \)
(7) \( l_{\omega} = 4 \nu_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega} \)
(8) \( \sin^2 \phi = \sin^2 \left( \frac{\pi l}{2l_c} \right) = 0.04 \)
(9) \( d_{\text{eff}} = 0.95 \text{ pm/V}. \)

**Figure 6**
(1) \( G_{\text{quartz}} = 40^\circ; I_{2\omega} = 7.36 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 40^\circ; I_{2\omega} = 5.00 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 0.08 \text{ pm/V} \)
(4) \( l_c = 23.8 \mu m \)

**Figure 7**
(1) \( G_{\text{quartz}} = 50^\circ; I_{2\omega} = 27.1 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 50^\circ; I_{2\omega} = 113 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 2.08 \text{ pm/V} \)
(4) \( l_c = 22.6 \mu m \)

**Figure 8**
(1) \( G_{\text{quartz}} = 50^\circ; I_{2\omega} = 68.0 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 45^\circ; I_{2\omega} = 41.5 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 0.70 \text{ pm/V} \)
(4) \( l_c = 23.2 \mu m \)

**Figure 9**
(1) \( G_{\text{quartz}} = 50^\circ; I_{2\omega} = 68.0 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 45^\circ; I_{2\omega} = 13.0 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 0.42 \text{ pm/V} \)
(4) \( l_c = 22.2 \mu m \)

**Figure 10**
(1) \( G_{\text{quartz}} = 45^\circ; I_{2\omega} = 15.2 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 50^\circ; I_{2\omega} = 28.8 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 1.33 \text{ pm/V} \)
(4) \( l_c = 22.0 \mu m \)

**Figure 11**
(1) \( G_{\text{quartz}} = 50^\circ; I_{2\omega} = 68.0 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 50^\circ; I_{2\omega} = 6.08 \text{ (relative arbitrary unit)} \)
(3) \( d_{\text{eff}} = 0.30 \text{ pm/V} \)
(4) \( l_c = 22.6 \mu m \)

**Figure 12**
(1) \( G_{\text{quartz}} = 45^\circ; I_{2\omega} = 23.1 \text{ (relative arbitrary unit)} \)
(2) \( G_{\text{sample}} = 55^\circ; I_{2\omega} = 133 \text{ (relative arbitrary unit)} \)
(3) \(d_{eff}=2.52 \text{pm/V}\),
(4) \(l_c = 21.98 \mu \text{m}\).

Figure 13

(1) \(\theta_{\text{quartz}} = 50^\circ\); \(I_{2\omega} = 56.9\) (relative arbitrary unit),
(2) \(\theta_{\text{sample}} = 50^\circ\); \(I_{2\omega} = 56.9\) (relative arbitrary unit),
(3) \(d_{eff} = 1.07 \text{pm/V}\),
(4) \(l_c = 23.2 \mu \text{m}\).

Table 3. The \(d_{eff}^*\) approximate calculation.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Total intensity from (0^\circ) to (60^\circ) by (\frac{512 \pi^3}{A} I_\omega)</th>
<th>Approximate (d_{eff}^*) value:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 5</td>
<td>123.0 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 6</td>
<td>1.407 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 7</td>
<td>185.2 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 8</td>
<td>56.98 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 9</td>
<td>23.03 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 10</td>
<td>297.3 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 11</td>
<td>9.492 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 12</td>
<td>2183.9 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 13</td>
<td>368.3 (relative arbitrary unit).</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 5</td>
<td>0.94 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 6</td>
<td>0.10 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 7</td>
<td>1.16 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 8</td>
<td>0.64 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 9</td>
<td>0.42 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 10</td>
<td>1.47 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 11</td>
<td>0.26 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 12</td>
<td>3.99 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
<tr>
<td>Figure 13</td>
<td>1.64 pm/V.</td>
<td>(\sqrt{\text{(total area of SHG)}}) (relative arbitrary unit).</td>
</tr>
</tbody>
</table>

We used the data for both quartz and sample and calculated \(\frac{512 \pi^3}{A} I_\omega\) for every Figure, then divide the total intensity from \(0^\circ\) to \(60^\circ\) by \(\frac{512 \pi^3}{A} I_\omega\). From equation (11) we used the \(d_{eff}\) (Fig. 5) as reference and obtained the approximation effect \(d_{eff}^*\) value:

\[
d_{eff}^* = \frac{d_{eff}}{\sqrt{\text{(total area of SHG)}}}
\]

Assuming nonlinear region is \(3 \mu \text{m}\), we used (11) and obtained \(d_{eff}^*\) for each figures as listed in Table 3.

REFERENCES