CHAPTER-3

STUDIES ON GLYCINE COPPER SULPHATE (GCS) SINGLE CRYSTALS

3. 1 Introduction

Crystal growth is the basis for various technological advancements. Amino acids and their complexes find wide applications due to their dipolar nature. Creation of a new compound by mixing of two materials yields interesting properties which are not exhibited by the individual materials. In the last two decades, the blossoming of research on hybrid organic-inorganic crystals has been motivated in growing materials that combine the functional properties of organic and inorganic components [1-3]. Organic compounds are often formed by weak hydrogen and Van der Waals bonds and hence possess a high degree of charge delocalization leading to large NLO coefficients [4]. However, organic compounds frequently suffer from volatility, poor thermal stability, poor mechanical strength and undesirable growth habits making them unattractive for device fabrication. In order to overcome these difficulties, semiorganic crystals have been proposed in which the high optical nonlinearity of purely organic compound is combined with the favourable mechanical and thermal properties of inorganics [5]. Also they possess several attractive properties like high optical damage threshold, wide transparency range, adequate birefringence for phase matching which make them suitable for frequency doubling.

The zwitter ionic form of glycine molecule is capable of forming compounds easily [6]. Some complexes of glycine with HCl, LiSO₄, H₂SO₄,
H₃PO₃, CaNO₃, CoBr₂ form single crystals of different compounds [7-12]. Some of these are reported to have NLO properties and some are reported as not possessing NLO properties. Copper complexes have been largely investigated because of their pharmacological activities, antimicrobial, antiviral, antitumor and enzyme inhibiting properties. The copper complexes possess attractive magnetic properties, photoluminescence and novel structural properties and are used as potential drugs for therapeutic intervention in various diseases [13, 14]. Copper sulphate pentahydrate is a chemical which finds wide applications in various industries such as agriculture, metallurgy, mining etc. It possesses versatile roles like electrolyte, etching agent, anti-fouling paints etc. The atomic structure of copper sulphate pentahydrate reveals that copper atoms are coordinated by four oxygen atoms of water molecules and two oxygen atoms of sulphate groups [15]. In an attempt to discover new crystalline materials for industrial applications, a crystal was grown from a mixture of glycine and copper sulphate pentahydrate. In this chapter, a report on the growth and characterization of a new semiorganic single crystal, glycine copper sulphate is presented.

3.2 Synthesis and solubility

Glycine copper sulphate (GCS) salt was synthesized by dissolving analar grade glycine and copper sulphate pentahydrate salt in the stoichiometric ratio of 1:1 in de-ionized water. The solution was stirred for 3 hours using magnetic stirrer and then filtered. The synthesized salt was extracted according to the following reaction after evaporating the solvent.

\[ \text{CH}_2\text{NH}_2\text{COOH} + \text{CuSO}_4.5\text{H}_2\text{O} \rightarrow \text{Cu}[\text{CH}_2\text{NH}_2\text{COOH}]\text{SO}_4.5\text{H}_2\text{O} \]
Solubility is the amount of solute present in 100 ml of solvent. In solution growth technique, the size of a crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in that solvent. The solubility study of GCS sample was made at different temperatures by gravimetical method [16]. 50 ml of de-ionized water was taken in a beaker and synthesized salt of glycine copper sulphate was added step by step at room temperature and the solution was continuously stirred using magnetic stirrer. The addition of salt was done until the solution reaches the saturated state. The solute present in 25 ml of the solution was dried and weighed accurately. The same procedure was repeated for different temperatures. The variation of solubility with temperature is shown in Fig.3.1. The data could be fitted to the equation $S = a+bT$, where $S$ and $T$ are the solubility expressed in g/100 ml and temperature in degree Celsius respectively and the constants $a$ and $b$ are found to have values 46.70 g/100 ml, 1.33 g/100 ml/$^\circ$C respectively. GCS salt has positive temperature coefficient of solubility which enables that slow evaporation method is the suitable method for growing GCS crystals.
3.3 Crystal Growth

GCS crystals were grown by slow evaporation technique. Saturated solution was prepared from synthesized GCS salt using de-ionized water as solvent. The solution was continuously stirred for about 2 hours using magnetic stirrer at room temperature. The solution was filtered using Whatmann filter paper and then kept in a beaker covered with perforated sheet. Big-sized crystals were harvested from the solution after 60 days. The grown blue coloured crystal with the dimension of 22 mm x 9 mm x 6 mm is shown in Fig.3.2. The crystals remain stable under standard conditions.
3.4 EDAX analysis

Energy dispersive X-ray analysis (EDAX) is an analytical technique used for the elemental analysis of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. The EDAX detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium drifted silicon, solid state device. EDAX spectrum of the GCS sample was taken using JEOL model JED-2300 instrument and is shown in Fig.3.3. The observed peaks corresponding to various energies confirm the presence of the elements C, N, O, S and Cu in the sample.
3.5 XRD analysis

The grown GCS crystal was subjected to single crystal X-ray diffraction study using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_\alpha$ ($\lambda$=0.71069 Å) radiation to evaluate the lattice parameters. The crystal belongs to triclinic system with lattice parameters $a=6.134(3)$ Å, $b=6.425(2)$ Å, $c=10.964(1)$ Å, $\alpha=77.3(1)^\circ$, $\beta=82.33(2)^\circ$ and $\gamma=72.67(1)^\circ$. The observed lattice parameters of GCS crystal are compared with the reported lattice parameters of constituent elements like glycine [17] and copper sulphate [18, 19]. The lattice parameters of GCS crystal are quite different from that of constituent elements.

The powder XRD pattern of GCS crystal was taken in the range 10$^\circ$-70$^\circ$ at a rate of 10$^\circ$/min using X-ray diffractometer with CuK$_\alpha$ radiation. The various planes
of reflections observed in XRD pattern were indexed by using INDEXING software package and are shown in Fig.3.4. The lattice parameters of the GCS crystal were also obtained from the XRD peaks using the UNIT CELL software package. The lattice parameters obtained from powder XRD method are $a=5.968 \, \text{Å}$, $b=6.1447 \, \text{Å}$, $c=10.6466 \, \text{Å}$, $\alpha=76.8581^\circ$, $\beta=82.5092^\circ$ and $\gamma=72.8472^\circ$ and are found to agree well with those observed through single crystal XRD study. The crystallographic parameters such as $2\theta$, d-spacing, relative intensity and the $(h \, k \, l)$ values are given in table 3.1.

![Fig.3.4: Powder XRD pattern of GCS crystal](image)
Table 3.1
Powder XRD data for GCS sample

<table>
<thead>
<tr>
<th>S. No.</th>
<th>20 (degrees)</th>
<th>d-spacing (Å)</th>
<th>Relative intensity (%)</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.406</td>
<td>5.747</td>
<td>11.24</td>
<td>0 1 0</td>
</tr>
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<td>2</td>
<td>16.051</td>
<td>5.517</td>
<td>100</td>
<td>0 1 1</td>
</tr>
<tr>
<td>3</td>
<td>17.168</td>
<td>5.161</td>
<td>2.88</td>
<td>1 0 1</td>
</tr>
<tr>
<td>4</td>
<td>18.200</td>
<td>4.870</td>
<td>4.49</td>
<td>-1 0 1</td>
</tr>
<tr>
<td>5</td>
<td>18.687</td>
<td>4.744</td>
<td>9.07</td>
<td>1 1 0</td>
</tr>
<tr>
<td>6</td>
<td>20.643</td>
<td>4.299</td>
<td>2.75</td>
<td>0 1 2</td>
</tr>
<tr>
<td>7</td>
<td>22.203</td>
<td>4.000</td>
<td>12.70</td>
<td>-1 1 1</td>
</tr>
<tr>
<td>8</td>
<td>23.926</td>
<td>3.716</td>
<td>7.16</td>
<td>-1 0 2</td>
</tr>
<tr>
<td>9</td>
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<td>3.554</td>
<td>3.27</td>
<td>1 -1 0</td>
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<td>2.50</td>
<td>-1 -1 2</td>
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<td>2.754</td>
<td>13.85</td>
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<tr>
<td>12</td>
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<tr>
<td>13</td>
<td>48.807</td>
<td>1.864</td>
<td>2.77</td>
<td>3 2 1</td>
</tr>
</tbody>
</table>

3.6 FTIR analysis

The Fourier Transform Infrared (FTIR) spectrum of GCS sample was recorded in the range of 400-4500 cm\(^{-1}\) with Perkin Elmer Fourier transform infrared spectrometer using KBr pellet technique. The functional groups present in GCS crystal were identified with the help of reported data [20-23, 19]. The FTIR
spectrum is depicted in Fig.3.5 and the corresponding vibrational group assignments are presented in table 3.2.

Fig.3.5: FTIR spectrum of GCS crystal

The stretching vibrations of the water molecule are observed in the region 3300 - 3600 cm\(^{-1}\). In general, free SO\(_4^{2-}\) ion has 4 fundamental vibrations namely, a non-degenerate mode (\(v_1\)) at 981 cm\(^{-1}\) and a doubly degenerated mode (\(v_2\)) at 449 cm\(^{-1}\) and a triply degenerated vibrations (\(v_3\) and \(v_4\)) at 1143 cm\(^{-1}\) and 617 cm\(^{-1}\) respectively. All these four vibrations are observed in the FTIR spectrum. The absorbance peaks due to carboxylic group is observed at 1411 cm\(^{-1}\) and the absorption peaks due to NH\(_3^+\) group are observed at 1620 cm\(^{-1}\) and 3150 cm\(^{-1}\).
Table 3.2

Vibrational group assignments for GCS crystal

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>449.38</td>
<td>$\nu_2$SO$_4$</td>
</tr>
<tr>
<td>617.18</td>
<td>$\nu_4$SO$_4$</td>
</tr>
<tr>
<td>777.26</td>
<td>Liberation mode of water molecule</td>
</tr>
<tr>
<td>871.76</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>981.70</td>
<td>$\nu_1$SO$_4$</td>
</tr>
<tr>
<td>1093.56</td>
<td>$\nu_3$SO$_4$</td>
</tr>
<tr>
<td>1143.71</td>
<td>$\nu_3$SO$_4$</td>
</tr>
<tr>
<td>1315.36</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>1411.80</td>
<td>COO$^-$ stretching</td>
</tr>
<tr>
<td>1620.09</td>
<td>NH$_3^+$ bending</td>
</tr>
<tr>
<td>3150.28</td>
<td>NH$_3^+$ stretching</td>
</tr>
<tr>
<td>3357.89</td>
<td>O-H stretching</td>
</tr>
</tbody>
</table>

3.7 Optical spectral studies

The optical spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in the $\sigma$ and $\pi$ orbitals from the ground state to higher states [24]. The UV transmission spectrum was recorded using Lamda 35 spectrometer in the range of 190 nm to 1100 nm with a crystal of thickness 2 mm. The UV-Vis-NIR absorbance
and transmittance spectra of GCS crystal are shown in Figs.3.6 and 3.7 respectively.

**Fig.3.6:** Optical absorbance spectrum of GCS crystal

**Fig.3.7:** Optical transmittance spectrum of GCS crystal
From the results, it is evident that GCS crystal has UV cut off wavelength at 200 nm and it is the intrinsic property of amino acids. The cut off wavelength and the transmission levels are in good agreement with the reported values [18, 25, 26]. The GCS crystals show an absorption peak in the NIR region which is the characteristic property of copper sulphate. This may be due to electronic transitions associated within the sample [27]. NIR absorbing materials find applications in photonics, telecommunications and in the devices that operate in the NIR region [28]. Growing better optical quality crystals from more rigorously purified solution may reduce the optical losses in the higher wavelength range.

The optical absorption coefficient ($\alpha$) was calculated using the following equation

$$\alpha = (1/d) \ln (1/T)$$

where $T$ is the transmittance and $d$ is the thickness of the crystal, neglecting the inflection coefficient. Assuming parabolic trends, the relation between $\alpha$ and $h\nu$ [29] is given by

$$\alpha = A(h\nu-E_g)^n / h\nu$$

where $E_g$ is optical band gap of the crystal, $n$ and $A$ are constants. In a crystalline material, either direct or indirect optical transitions are possible depending on the band structure of the material. There will be a single linear region in direct transition and two linear portions in indirect transition. For a direct transition, $n=1/2$ or $3/2$ depending on whether the transition is allowed or forbidden in quantum mechanical sense. Similarly, $n=2$ or 3 for indirect allowed and forbidden transition respectively [30]. The relation between $\alpha$ and $h\nu$ is plotted in Fig.3.8. The plot has single linear region, hence it corresponds to direct optical transition.
The optical band gap is determined using Tauc’s procedure by plotting \((\alpha h\nu)^2\) versus \(h\nu\) [31] as shown in Fig.3.9 and is found to be 4.2 eV.

**Fig.3.8: Plot of \(\alpha\) versus \(h\nu\) for GCS crystal**

**Fig.3.9: Plot of \((\alpha h\nu)^2\) versus \(h\nu\) for GCS crystal**
3.8 Microhardness study

Hardness is a measure of material resistance to localized plastic deformation. The microhardness characterization is extremely important as far as the device fabrication is concerned. The smooth surface of GCS crystal was subjected to microhardness study at room temperature using a Vickers microhardness tester fitted with a diamond indenter. Loads of 25, 50 and 100 grams were applied on the crystal for a fixed time interval of 10 seconds. The external work applied by the indenter is converted into a strain energy component proportional to the volume of the resultant impression and a surface energy component proportional to the area of resultant impression [32]. The hardness of the crystal is calculated using the relation

$$H_V = 1.8544 \frac{P}{d^2} \text{ (kg/mm}^2\text{)}$$  \hspace{1cm} (3.3)

where $P$ is the applied load in kg and $d$ is the length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid [33]. The phenomenon of testing the dependence of microhardness of a solid on the applied load (low level) is known as Indentation Size Effect [34]. According to the normal Indentation Size Effect (ISE), microhardness of crystal decreases with increasing load and in Reverse Indentation Size Effect (RISE), hardness number increases with increase in load [35]. A plot of the hardness number and the load is depicted in Fig.3.10. From the figure, it is observed that the hardness value of GCS crystal increases with increase in applied load and hence shows reverse indentation size effect.
The relation connecting the applied load and diagonal length of the indenter is given by Meyer’s law $P = ad^n$, where $n$ is the Meyer’s index (work hardening coefficient) [36]. The Meyer’s index is calculated from the slope of straight line drawn between log $P$ and log $d$ as shown in Fig.3.11 and the obtained value is 3.486 for GCS crystal. From careful observations on various materials, Onitsch [37] and Hanneman [38] pointed out that an ‘$n$’ lies between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials. Hence, GCS crystal belongs to soft materials. According to Kick’s law, $n$ is less than 2 for normal ISE behavior, $n$ is greater than 2 for RISE and the hardness is independent of applied load when $n$ is equal to 2 [39].
The relationship between load and size of the indentation is given by well known Meyer’s law as

$$P = k_1 d^n$$  \hspace{1cm} (3.4)

where $k_1$ is the material constant which can be obtained from the slope of the plot of $P$ versus $d^n$. Since the material takes some time to revert to the elastic mode after every indentation, a correction factor $x$, a measure of dislocation density of the material is applied to the $d$ value. According to Kick’s law [40],

$$P = k_2 (d+x)^2$$  \hspace{1cm} (3.5)

On combining Meyer’s law and Kick’s law, the relation becomes

$$d^{n/2} = \left(\frac{k_2}{k_1}\right)^{1/2} d + \left(\frac{k_2}{k_1}\right)^{1/2} x$$  \hspace{1cm} (3.6)
The slope of the plot $d^{n/2}$ versus $d$ yields $(k_2/k_1)^{1/2}$ and $x$ is measured from the intercept on Y-axis. According to Kick’s law, $x$ is positive when $n < 2$ and negative for $n > 2$ [41]. The hardness parameters $k_1$, $k_2$ and $x$ were calculated for GCS crystal and are depicted in table 3.3.

### Table 3.3  
**Hardness parameters of GCS crystal**

<table>
<thead>
<tr>
<th>Meyer’s index</th>
<th>$k_1$ $(10^3 \text{ kg/mm}^2)$</th>
<th>$k_2$ $(10^2 \text{ kg/mm}^2)$</th>
<th>$x$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.486</td>
<td>5.778</td>
<td>1.258</td>
<td>-14.98</td>
</tr>
</tbody>
</table>

#### 3.9 Thermal analysis

The TG/DTA curves were recorded for GCS crystal in the temperature range from 25 °C to 1000 °C at the heating rate of 10 °C/min in the nitrogen atmosphere using the instrument NETZSCHSTA 409C/CD. The GCS sample weighing 26.270 mg was taken for the measurement. The TG/DTA curves of GCS crystal are shown in Fig.3.12. In the TG trace, a mass change of 28 % occurs in the temperature region 80 °C-135 °C due to elimination of three water molecules and thus the material gets reduced to dihydrous glycine copper sulphate. The next melting transition starts at 226.8 °C and ends at 260 °C with a sharp melting band of 33.3 °C. A mass change of 7.3% occurs in this region due to elimination of remaining two water molecules [42, 43, 19]. Also, there is no appearance of major weight loss until the next transition starts at 675 °C. In the temperature range between 675 °C and 800 °C, a mass change of 31% takes place and 29% of the sample remains stable beyond 1000 °C [44, 45]. The high thermal stability ensures
the suitability of the material for applications in lasers where the crystals are required to withstand high temperature [46].

![TG/DTA curves of GCS crystal](image)

**Fig.3.12: TG/DTA curves of GCS crystal**

### 3.10 Second order and third order NLO studies

Second order NLO study was carried out by measuring second harmonic generation (SHG) efficiency using Kurtz-Perry powder technique [47]. The fundamental beam of wavelength 1064 nm from a Q-switched Nd:YAG laser with input energy 1.6 joule was used in this study. The grown crystal of GCS was ground into fine microcrystalline powder and densely packed between transparent glass slides. Microcrystalline sample of KDP was used for comparison of conversion efficiency of the grown sample. The second harmonic generation from
a crystal can be confirmed by the emission of green radiation. But, it is observed that there is no emission of green radiation from GCS crystal and it gives the evidence that the GCS crystal is centrosymmetric material and it has no second order NLO activity.

Z-scan technique [48] was used to study the third order NLO behaviour of crystals. This is a simple and sensitive single beam technique for measuring the change in phase induced on a laser beam upon propagation through a nonlinear material. Additionally, it helps to determine nonlinear absorption coefficient and nonlinear optical refraction for optical materials. The beam was focused using a convex lens and the focal point has been taken at $Z=0$. The sample is placed at the focus point of the lens and then moved along the $Z$-axis through a distance of $\pm Z_o$, which is called Rayleigh length. The normalized transmission of the crystal is measured at positions with respect to the focus of the beam [49].

There are two modes in the Z-scan analysis namely, open and closed aperture modes. In the closed aperture method, an aperture is placed in front of the detector to prevent some of the light from reaching the detector. Hence, only the central region of the cone of light reaches the detector. The detector is now sensitive to any focusing or defocusing that a sample may induce. In the open aperture method, the aperture is removed to allow all the light to reach the detector and hence sets the normalized transmittance. This method is used in order to measure the nonlinear absorption which arises due to absorption of two photons. The optically transparent GCS crystal of about 1 mm thickness and He-Ne laser of wavelength 632.8 nm were used in this experiment. The obtained open and closed
aperture Z-scan curves are presented in Figs. 3.13 and 3.14 respectively. The Z-scan curves are characterized by a prefocal transmittance maximum (peak) followed by a postfocal transmittance minimum (valley) intensity. The transmittance difference between peak and valley ($\Delta T_{p,v}$), linear transmittance aperture (S), the third-order nonlinear refractive index ($n_2$) of the crystal, the nonlinear absorption coefficient ($\beta$) and the third order nonlinear optical susceptibility ($\chi^3$) were determined as the procedure given in the literature [50, 51].

![Fig. 3.13: Plot of transmittance versus position of GCS crystal in open aperture mode](image)
Fig.3.14: Plot of transmittance versus position of GCS crystal in closed aperture mode

The transmittance change from peak to valley is a characteristic of self focusing. The difference in transmission between peak and valley ($\Delta T_{p-v}$) is

$$\Delta T_{p-v} = 0.406 \left(1-S\right)^{0.25} |\Delta \Phi|$$  \hspace{1cm} (3.7)

where $S$ is the linear aperture transmittance and $|\Delta \Phi|$ is the axis phase shift.

$$S = 1 - \exp\left(-\frac{2r_s^2}{\omega_a^2}\right)$$  \hspace{1cm} (3.8)

where $r_s$ and $\omega_a$ are the aperture radius and beam radius respectively. The effective thickness $L_{\text{eff}}$ of the sample is

$$L_{\text{eff}} = \frac{[1-\exp(-\alpha t)]}{\alpha}$$  \hspace{1cm} (3.9)
where L and κ are the thickness of the sample and linear absorption coefficient respectively. The third order nonlinear refractive index \( n_2 \) is calculated using the following relation

\[
 n_2 = \frac{\Delta \Phi \lambda}{2 \pi I_0 L_{eff}} 
\]  
(3.10)

The nonlinear absorption coefficient \( \beta \) is given by

\[
 \beta = \frac{2 \sqrt{2} \Delta \Phi}{I_0 L_{eff}} 
\]  
(3.11)

The nonlinear refractive index is independent of nonlinear absorption coefficient. Thus, the third order responses, the real and imaginary parts of the third order nonlinear optical susceptibility can be determined using the following relations

\[
 Re \chi^{(3)} = \frac{10^{-4} z_o c^2 \kappa^5 n_2 n_z}{\pi} 
\]  
(3.12)

\[
 Im \chi^{(3)} = \frac{10^{-3} z_o c^2 \kappa^5 \lambda \beta}{4\pi} 
\]  
(3.13)

The absolute value of third order nonlinear optical susceptibility was calculated using the relations

\[
 |\chi| = \sqrt{(Re \chi^{(3)})^2 + (Im \chi^{(3)})^2} 
\]  
(3.14)

In closed aperture Z-scan curve, the prefocal transmittance peak is followed by the post focal valley which is the characteristics of negative nonlinearity. The nonlinear refractive index \( n_2 \) was calculated to be \(-1.25 \times 10^{-11}\) m\(^2\)/W. As the
material has a negative nonlinear refractive index, it results in self-defocusing of the material. The value of nonlinear absorption coefficient (β) estimated from the open aperture Z-scan curve is $2.97 \times 10^{-4}$ m/W. Using the equations 3.12, 3.13 and 3.14, the third order nonlinear susceptibility of GCS crystal was found to be $1.2557 \times 10^{-7}$ esu.

### 3.11 Laser damage threshold measurement

The optical tolerance ability of a material is an important factor for NLO applications. The grown GCS crystal was subjected to laser damage threshold measurement. For this, the output from the Q-switched Nd:YAG laser was rendered to fall on the crystal placed at the focus of the converging lens. During laser irradiation, the power meter records the energy density of the input laser beam for which the crystal gets damaged. The LDT value was determined using the formula $P = \frac{E}{\pi \tau r^2}$ where $E$ is the energy in mJ, $\tau$ is the pulse width in ns and $r$ is radius of the spot in mm [52, 53]. Laser damage threshold value is found to be 0.58 GW/cm$^2$ for GCS crystal.
References


