Non-critically phase-matched second harmonic generation and third order nonlinearity in organic crystal glucuronic acid $\gamma_{\gamma}$ lactone
Ravi Kiran Saripalli, Naga Krishnakanth Katturi, Venugopal Rao Soma, H. L. Bhat, and Suja Elizabeth

Citation: Journal of Applied Physics 122, 223110 (2017);
View online: https://doi.org/10.1063/1.5008322
View Table of Contents: http://aip.scitation.org/toc/jap/122/22
Published by the American Institute of Physics

> Scilight
> Sharp, quick summaries illuminating the latest physics research

# Non-critically phase-matched second harmonic generation and third order nonlinearity in organic crystal glucuronic acid $\gamma$-lactone 

Ravi Kiran Saripalli, ${ }^{1, a)}$ Naga Krishnakanth Katturi, ${ }^{2}$ Venugopal Rao Soma, ${ }^{2}$ H. L. Bhat, ${ }^{1}$ and Suja Elizabeth ${ }^{1}$<br>${ }^{1}$ Department of Physics, Indian Institute of Science, Bangalore 560012, India<br>${ }^{2}$ Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, India

(Received 5 October 2017; accepted 27 November 2017; published online 14 December 2017)


#### Abstract

The linear, second order, and third order nonlinear optical properties of glucuronic acid $\gamma$-lactone single crystals were investigated. The optic axes and principal dielectric axes were identified through optical conoscopy and the principal refractive indices were obtained using the Brewster's angle method. Conic sections were observed which is perceived to be due to spontaneous non-collinear phase matching. The direction of collinear phase matching was determined and the $d_{\text {eff }}$ evaluated in this direction was $0.71 \mathrm{pm} / \mathrm{V}$. Open and closed aperture Z-scan measurements with femtosecond pulses revealed high third order nonlinearity in the form of self-defocusing, two-photon absorption, as well as saturable absorption. Published by AIP Publishing. https://doi.org/10.1063/1.5008322


## I. INTRODUCTION

The nonlinear optical (NLO) properties of organic materials are due to the presence of delocalized electrons in $\pi$ bonding orbitals and their magnitude depends on the extent of polarizability of these electrons. The search for new organic NLO materials is facilitated by ease in processing methods and prospects in novel applications. Organic NLO materials, in general, possess a high laser damage threshold, a low dielectric constant, and an enhanced speed of NLO response. ${ }^{1}$ Many organic crystals are known to have high non-linear coefficients. ${ }^{2-7}$ However, most of them exhibit a platy or needle type morphology and have a cutoff wavelength close to the second-harmonic wavelength ( 532 nm ) of the fundamental wavelength ( 1064 nm ) of the Nd:YAG laser. Saccharides, on the other hand, exhibit an extremely good UV transparency and offer a combination of attractive properties like chirality (ensuring that these materials crystallize in a non-centrosymmetric space group), large birefringence, low dispersion (permitting the possibility of phase-matched nonlinear optical applications), and can be synthesized in bulky morphologies. ${ }^{8-13}$

In our previous work, details of crystal growth, crystal structure, dielectric dispersion, and piezoelectricity of organic an NLO saccharide material, Glucuronic acid $\gamma$ Lactone (GAL) were reported. ${ }^{14}$ We had shown that GAL crystals possess a low UV cut-off, a large laser damage threshold, are phase-matchable, and display non-collinear phase matching. ${ }^{15}$ Thus, GAL is considered an excellent candidate for second-order NLO applications especially because it is highly transparent in the visible range and has a low UV-cutoff. GAL also has a high laser damage threshold when compared to other organic materials. ${ }^{14,15}$ Additionally, the existence of piezoelectric resonance along with high nonlinearity in GAL, makes it suitable for resonance enhanced electro-optic applications, where the requirement for a high
${ }^{\text {a) }}$ E-mail: saripark85@gmail.com
driving electric field for electro-optic modulation can be effectively overcome when operated at its piezoelectric resonance frequency. ${ }^{14,16}$ A complete understanding of optical properties is required for exploiting GAL crystals for various NLO and electro-optic applications. Here, we report a detailed study of the determination of principle refractive indices. A direction of phase matching was obtained by angle tuned non-critical phase matching and $d_{\text {eff }}$ along this direction was calculated.

Organic molecules with large third-order optical nonlinearities have many potential applications especially in optical switching due to their fast response times and in optical signal processing that show applied optical field intensity dependent refractive indices. ${ }^{17}$ This would facilitate the development of devices for all-optical signal processing. ${ }^{18-20}$ However, many organic crystals exhibiting high third order nonlinearity are usually either opaque in the visible wavelength range, or are difficult to grow into big sizes. ${ }^{21}$ Open and closed aperture z -scan measurements were made to analyze third order nonlinearity in GAL.

## II. EXPERIMENTAL DETAILS

Details of the single crystal growth of GAL have already been reported earlier. ${ }^{14}$ The grown crystals were sliced in the required orientation and polished before using them for further experiments.

## A. Conoscopy measurement

The GAL crystal plate is placed on a goniometer between two cross polarizers. A diverging beam of light is passed through the assembly and the interference pattern is imaged onto a screen. A continuous He:Ne laser (Melles Griot 05-LHR-171) of wavelength 633 nm and power 15 mW was used as the light source. The optical setup is illustrated in Fig. 1. The refractive indices along different directions between ordinary and extraordinary beams cause different interference


FIG. 1. Optical setup for conoscopy measurements.
patterns on the screen as the crystal is rotated. As the crystal is rotated in a way that the incident beam is along the optic axis of the crystal, a symmetric interference pattern with a definite minimum at the centre (or a melatope) is obtained. This is because the refractive indices of the two beams are the same along the optic axis. In biaxial crystals, two such orientations of the crystal exist which denote the directions of the two optic axes. Linear dark regions (Isogyres) are obtained in the interference patterns since zero transmission of light occurs perpendicular to either of the polarizers. Thus in uniaxial crystals, a perpendicular cross is obtained that matches the direction of the two polarizers. The position of isogyres is more complex in biaxial crystals.

## B. Refractive index measurement

Refractive indices were determined using the Brewster's angle method. ${ }^{22}$ At a particular angle of incidence, known as the Brewster's angle, the polarized light is perfectly transmitted through the crystal with no reflection. It has been demonstrated that refractive indices obtained by the Brewster's angle method are accurate to three decimals. ${ }^{23}$

Polarized light is incident on the surface of the crystal and the reflected light intensity is measured using a detector. The crystal is placed on a goniometer and rotated till the signal is minimum in the detector, which is the Brewster's angle. This method is accurate only when the refractive index is measured for visible wavelengths of light since the detector needs to be moved while the crystal plate is being rotated. The optical setup for refractive index measurement is shown in Fig. 2 and a schematic for a particular geometry of the experiment is illustrated in Fig. 3 for which the Brewster's angle, $\theta_{i}=\theta_{B} \Rightarrow\left|E_{r}\right|=0$ can be calculated using the following equation:

$$
\begin{equation*}
\tan ^{2} \theta_{B}=n_{z}^{2}\left(\frac{n_{x}^{2}-1}{n_{z}^{2}-1}\right), \tag{1}
\end{equation*}
$$



FIG. 2. Optical setup for refractive index measurements.


FIG. 3. Schematic showing a particular geometry for refractive index measurements.
where $n_{x}, n_{y}$, and $n_{z}$ are the refractive indices of the material along the $\mathrm{x}, \mathrm{y}$, and z axes of the crystal, respectively. Similarly, for x and y -cut crystals, the above equation is cyclic. By measuring the Brewster's angles along the three directions, the three equations can be solved to obtain the refractive indices along the three directions.

## C. Determination of $\boldsymbol{d}_{\text {eff }}$

The GAL crystal plate is mounted on a goniometer and the angle at which the laser beam is incident perpendicular to the plate is set to zero in the goniometer. A focused $\mathrm{TEM}_{00}$ laser beam of wavelength 1064 nm was incident perpendicular to the surface of the crystal plate after which a dichroic mirror is used to direct the second harmonic generated (SHG) 532 nm beam away from the fundamental beam. The intensities of both fundamental ( 1064 nm ) and generated ( 532 nm ) beams are monitored using a pyroelectric sensor (25BBDIF Ophir). The laser setup for angular phase matching is shown in Fig. 4.

## D. Z-scan measurements

The sign and magnitude of third-order nonlinearities can be determined using the Z-scan technique. This gives information about nonlinear absorption and nonlinear refraction coefficients. ${ }^{24,25}$ The sample is scanned through the focal plane of a tightly focused Gaussian beam. The method involves measurements with an aperture placed between the sample and the detector (closed aperture Z-scan) and those without the aperture (open aperture Z-scan). The optical setup used for closed aperture z -scan measurements is shown in Fig. 5.

Information on nonlinear contribution to the refractive index can be obtained by performing closed aperture Z-scan measurements. Here, the medium acts as an intensity dependent lens. As it is moved along the beam path, its effective focal length changes, since the incident intensity is varying. This is reflected in the intensity distribution at the aperture in the far field. The amount of energy transmitted through the aperture depends on the sample location on the z -axis and on the sign of the nonlinear refractive index coefficient $n_{2}$. Open aperture z-scan measurements were performed to obtain information about the non-linear absorption in the sample. A peak at the focus implies that there is saturable absorption in the


FIG. 4. Optical setup for angular phase matching.

FIG. 5. Optical setup for z -scan measurements.
sample. In order to estimate the dominant nonlinear absorption, whether it is a two-photon absorption (2PA) or a threephoton absorption (3PA), the experimental open aperture data are fitted using the theoretical formulation developed by Sheik Bahae et al. ${ }^{19}$ Here, the transmittance of the open aperture Z-scan curve for n-photon absorption is given by

$$
\begin{equation*}
T_{O A(n P A)}=1-\frac{\alpha_{n} I_{0}^{n-1} L_{e f f}^{(n)}}{n^{3 / 2}\left(1+\frac{z^{2}}{z_{0}^{2}}\right)^{n-1}} \tag{2}
\end{equation*}
$$

Transmittance for the two-photon $(\mathrm{n}=2)$ and threephoton $(\mathrm{n}=3)$ absorption was deduced as

$$
\begin{equation*}
T_{O A(2 P A)}=1-\frac{\alpha_{2} I_{0} l_{e f f}^{(2)}}{2^{3 / 2}\left(1+\frac{z^{2}}{z_{0}^{2}}\right)} ; \quad l_{e f f}^{(2)}=\frac{1-e^{-\alpha t}}{\alpha} \tag{3}
\end{equation*}
$$

and

$$
\begin{equation*}
T_{O A(3 P A)}=1-\frac{\alpha_{3} I_{o}^{2} l_{e f f}^{(3)}}{3^{3 / 2}\left(1+\frac{z^{2}}{z_{o}^{2}}\right)^{2}} ; \quad l_{e f f}^{(3)}=\frac{1-e^{-2 \alpha l}}{2 \alpha} \tag{4}
\end{equation*}
$$

The nonlinear refractive index $\left(n_{2}\right)$ is deduced from closed aperture measurements by fitting the data to

$$
\begin{equation*}
T_{C A}=1-\frac{4 \Delta \phi_{0}\left(z / z_{0}\right)}{\left[1+\left(z / z_{0}\right)^{2}\right]\left[9+\left(z / z_{0}\right)^{2}\right]} \tag{5}
\end{equation*}
$$

where $\Delta \varphi_{0}$ is the phase change of the laser beam due to the nonlinear refraction estimated using the theoretical fit to experimental (closed-aperture) data. The third order nonlinear refractive index $\left(n_{2}\right)$ is calculated from $\Delta \varphi_{0}$ as

$$
\begin{equation*}
n_{2}=\frac{\left|\Delta \phi_{0}\right| \lambda}{2 \pi I_{0} l_{e f f}} \tag{6}
\end{equation*}
$$

The nonlinear refractive index $n_{2}$ and the nonlinear absorption coefficient $\beta\left(\alpha_{2}\right)$ are related to the real and imaginary parts, respectively, of third order nonlinear optical susceptibility $\chi^{(3)}$ through the following relations: ${ }^{26-28}$

$$
\begin{gather*}
\chi^{(3)}=\chi_{R}^{(3)}+i \chi_{i}^{(3)}  \tag{7}\\
\chi_{R}^{(3)}=\frac{c n_{0}^{2}}{120 \pi^{2}} n_{2} \text { (Gaussian units), }  \tag{8}\\
\chi_{R}^{(3)}=\frac{4 n_{0}^{2} \varepsilon_{o} c}{3} n_{2} \text { (SI units) }  \tag{9}\\
\chi_{i}^{(3)}=\frac{c^{2} n_{0}^{2}}{240 \pi^{2} \omega} \beta \tag{10}
\end{gather*}
$$

Here, $n_{0}$ is the linear refractive index, $c$ is the velocity of light in vacuum, and $\omega$ is the angular frequency of the light field. Open and closed aperture measurements were performed for two wavelengths 800 nm and 700 nm . The parameters of the laser and sample used in the experiment are listed in Table I.

TABLE I. Summary of laser parameters and sample dimensions used in the Z-scan experiments.

| Parameters | 800 nm | 700 nm |
| :--- | :---: | :---: |
| Beam waist $\left(\omega_{0}\right)$ | $25.5 \mu \mathrm{~m}$ | $22.3 \mu \mathrm{~m}$ |
| Rayleigh range $\left(z_{0}\right)$ | 2.55 mm | 2.23 mm |
| Repetition rate $(r)$ | 86 MHz | 86 MHz |
| Pulse width $(t)$ | 150 fs | 150 fs |
| Pulse energy $\left(E_{p}\right)$ | 50 nJ | 50 nJ |
| Total avg. power $=E_{p}{ }^{*} r$ | 4.3 W | 4.3 W |
| Input power $(P)$ | 8 mW | 7.3 mW |
| Input energy $(E)=P / r$ | $9.302 \times 10^{-11} \mathrm{~J}$ | $8.488 \times 10^{-11} \mathrm{~J}$ |
| Input intensity $\left(I_{0}\right)=\frac{E}{t \times \pi\left(\frac{\omega_{0}}{2}\right)^{2}}$ | $0.121 \mathrm{GW} / \mathrm{cm}^{2}$ | $0.145 \mathrm{GW} / \mathrm{cm}^{2}$ |
|  |  |  |
| Sample thickness $(l)$ |  |  |
| Transmittance $(T)($ from UV-Vis data) | 0.7 | 2 mm |
| Linear absorption coefficient $\left(\alpha_{o}\right) \frac{-\ln T}{l}$ | $0.18 \mathrm{~mm}^{-1}$ | $0.18 \mathrm{~mm}{ }^{-1}$ |



FIG. 6. Conoscopic image corresponding to the optic axis at $8.5^{\circ}$ with respect to the a-axis.

## III. RESULTS AND DISCUSSION

## A. Optical conoscopy

The (101) plate of the GAL crystal was mounted on a goniometer with a 633 nm laser beam incident perpendicular to the plate. This geometry was set at zero angle of the goniometer. The crystal is rotated about the b-axis which coincides with the rotation axis of the goniometer. The first optic axis was obtained by rotating the plate by $35.6^{\circ}$ in the anticlockwise direction. Thus, one of the optic axis is at $8.5^{\circ}$ with respect to the a-axis. When the (101) plate was rotated in the clockwise direction (from $0^{\circ}$ ) by $85.6^{\circ}$, the second optic axis was found at $42.25^{\circ}$ with respect to the c-axis. GAL crystallizes in the monoclinic symmetry with the $\mathrm{P} 2_{1}$ space group, and the dielectric $y$-axis matches with the crystallographic baxis. The two angular bisectors to the optic axis yield the directions of the x and z dielectric axes. The conoscopic images corresponding to the two optic axes of the crystal are shown in Figs. 6 and 7. Figure 8 shows the orientation of the


FIG. 7. Conoscopic image corresponding to the optic axis at $42.25^{\circ}$ with respect to the c -axis.


FIG. 8. Crystallographic orientation in the a-c plane of the crystal showing the orientation of the crystallographic, optic, and dielectric axes.
crystallographic axes, optic axes, and the dielectric axes in the a-c plane. The plates (of approximately 2 mm thickness) were cut perpendicular to the $\mathrm{x}, \mathrm{y}$, and z directions.

## B. Refractive index determination

The refractive indices obtained along the $x, y$, and $z$ directions at different wavelengths are tabulated in Table II. The results reveal that GAL has a large birefringence of about 0.04 . The dispersion in the refractive index was fitted to the Sellmeier equation ${ }^{29}$ of the form (ignoring higherorder terms; $\lambda$ is in nm )

$$
\begin{equation*}
n^{2}=A+\frac{B \lambda^{2}}{\lambda^{2}-C} \tag{11}
\end{equation*}
$$

The fitting is shown in Fig. 9. The equations obtained from the fit are

$$
\begin{equation*}
n_{x}^{2}=2.827-\frac{0.795 \lambda^{2}}{\lambda^{2}+330946.565} \tag{12}
\end{equation*}
$$

TABLE II. Refractive indices measured along the $\mathrm{x}, \mathrm{y}$, and z directions for different wavelengths.

| Wavelength (nm) | $n_{x}$ | $n_{y}$ | $n_{z}$ |
| :--- | :---: | :---: | :---: |
| 405 | 1.601 | 1.632 | 1.644 |
| 532 | 1.570 | 1.603 | 1.610 |
| 543.5 | 1.566 | 1.596 | 1.606 |
| 594.1 | 1.552 | 1.584 | 1.595 |
| 632.8 | 1.548 | 1.578 | 1.588 |
| 700 | (not measured) | 1.560 | (not measured) |
| 800 | (not measured) | 1.540 | (not measured) |



FIG. 9. Dispersion in refractive indices fitted well to Sellmeir equations.

$$
\begin{align*}
& n_{y}^{2}=2.874-\frac{0.954 \lambda^{2}}{\lambda^{2}+676186.023}  \tag{13}\\
& n_{z}^{2}=3.062-\frac{0.834 \lambda^{2}}{\lambda^{2}+217631.596} \tag{14}
\end{align*}
$$

The angle $\left(V_{z}\right)$ between the z -axis and the optic axis calculated for 633 nm wavelength was $V_{z}=\sin ^{-1}\left(\frac{n_{z}}{n_{y}} \sqrt{\frac{n_{y}^{2}-n_{x}^{2}}{n_{z}^{2}-n_{x}^{2}}}\right)$ $=60.47^{\circ}$ which matches the angle obtained from the conoscopy measurement $\left(60.50^{\circ}\right)$.

## C. Phase matching and determination of the second-order nonlinear co-efficient

In addition to the well known collinear phase matching directions in nonlinear optical crystals, there can be in general, a wide range of phase-matched noncollinear second-harmonic-generation (SHG) processes for arbitrary propagation directions in them. ${ }^{30,31}$ When a focused TEM $_{00}$ beam of wavelength 1064 nm is incident perpendicular to the surface of the (101) plate, two green rings are observed around the intense spot of the fundamental wavelength on a laser beam visualizer (wavelength range: 190 nm to 1600 nm ). Figure 10 shows the two green rings observed on a black screen. The crystals exhibit conic sections formed due to spontaneous non-collinear second harmonic generation. Such non-


FIG. 10. Two rings clearly observed on a screen indicating that GAL is a type II phase-matching crystal.
collinear phase matching occurs only in materials with high birefringence. The observation of two rings in GAL indicates that it is a type II SHG crystal. ${ }^{32}$ When the (101) plate of the crystal is rotated about the b-axis in the clockwise direction, the diameter of the rings decreases. After about a $10^{\circ}$ rotation, the rings converge to a spot of high intensity, which is the direction of collinear phase matching. Thus, we see energy transfer from the non-collinear to collinear phase matching. As the crystal is further rotated away, the spot diverges into two rings. This is clearly seen in Fig. 11.

Thus, one direction of phase matching through critical angle tuning was obtained by carefully rotating different plates of the crystal and by observing the output on a screen. The direction of collinear phase matching was observed to be the closest to the z -axis of the crystal at $14.85^{\circ}$ in the anticlockwise direction from the z-direction (Fig. 12). For further calculations along the phase matched direction, the refractive index of GAL along this phase-matched direction was approximated as $n_{z}$. An accurate determination of the $d_{\text {eff }}$ in GAL crystals is possible if we cut the crystal perpendicular to the phase matched direction. This would allow us to calculate the refractive indices along this direction. However, cutting the crystal perpendicular to the phase matched direction was impractical, as this direction was very close to the cleavage planes of the crystal and cracks were developed within the crystal while attempting to cut along this direction.


FIG. 11. Energy transfer from the non-collinear to collinear direction in the angular phase matching experiment.


FIG. 12. The phase matched direction is obtained by rotating the (101) plate by $10^{\circ}$ in the anti-clockwise direction. It is $14.85^{\circ}$ from the z-axis of the crystal.

To determine the conversion efficiency in the phase matched direction, a dichroic mirror was used to separate the generated 532 nm beam from the incident 1064 nm beam. The energy of input and generated beams was measured. The optical setup used is illustrated in Fig. 4. When a 1064 nm beam of 23 mJ energy was incident in the phase matched direction of the crystal ( 2 mm thickness), an output of 1.6 mJ energy was observed for the generated 532 nm beam in the power meter. This corresponds to a conversion efficiency of 0.07 .

To calculate the effective NLO coefficient $\left(d_{e f f}\right)$, the conversion efficiency $(\eta)$ was substituted in the equation

$$
\begin{equation*}
\eta=\frac{I_{2 \omega}}{I_{\omega}}=\frac{2 \omega^{2} d_{e f f}^{2} l^{2}}{n_{2 \omega} n_{\omega}^{2} c^{3} \varepsilon_{o}}\left(\frac{\sin (\Delta k l / 2)}{\Delta k l / 2}\right)^{2} I_{\omega} \tag{15}
\end{equation*}
$$

In the phase matched direction, $l$ is the length of the crystal in the phase matched direction $\left(l=2 / \cos 10^{\circ} \mathrm{mm}\right)$, $\Delta k=0$, and the refractive index is approximately $n_{z}, n_{\omega}$ $=n_{z}(1064 \mathrm{~nm})=1.537$, and $n_{2 \omega}=n_{z}(532 \mathrm{~nm})=1.610$. On substituting these, we get $d_{\text {eff }}$ as $0.71 \mathrm{pm} / \mathrm{V}$. This is about 1.8 times the effective NLO coefficient $d_{36}$ of KDP
$\left(d_{36}=0.39 \mathrm{pm} / \mathrm{V}\right) .^{33,34}$ The same experimental setup was used to determine the $d_{e f f}$ of KDP along its phase matched direction (Type II). The obtained $d_{e f f}$ value of 0.31 was close to the reported value of $0.33 .{ }^{34}$ The $d_{\text {eff }}$ value of GAL is comparable to several organic NLO materials, few of which are listed in Table III. For GAL, $\chi^{(2)}$ is of the order of $10^{-12} \mathrm{~m} / \mathrm{V}$.

No polarization dependent absorption was observed in GAL and hence under the Kleinmann symmetry, four independent tensor elements $\left(d_{i l}\right)$ are required to be determined for GAL. The SHG tensor for GAL (monoclinic crystal with $\mathrm{y} \| \mathrm{b})$ is given as: $d_{i l}=\left[\begin{array}{cccccc}0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{14} & 0 \\ d_{15} & d_{24} & d_{33} & 0 & 0 & d_{14}\end{array}\right]$.
In the current study, we have determined only one direction of phase-matching by rotating the angle $\theta$ of the crystal for a specific angle $\varphi$. To determine the components of the SHG tensor, we need to rotate the crystal along both these angles to determine the $\theta$ versus $\varphi$ phase matching map and also the walk-off parameters. The determination of $d_{i l}$ for GAL is currently under progress and will be communicated in the near future.

## D. Third order nonlinearity

The open aperture data for 800 nm wavelength fitted only to the 2 PA process and fitting for the 3PA did not converge as shown in Fig. 13. The fitting of the open aperture and closed aperture experimental data is shown in Figs. 13-16. The open aperture curves for both wavelengths show maximum transmittance at the focus ( $\mathrm{z}=0$ ) which indicates saturable absorption in GAL. Here, the absorption coefficient decreases when measured using a high laser intensity and is given by the expression ${ }^{26}$

$$
\begin{equation*}
\alpha=\frac{\alpha_{o}}{1+I / I_{s}} \tag{16}
\end{equation*}
$$

where, $\alpha_{o}$ is the low-intensity absorption co-efficient (obtained from UV-Vis data) and $I_{s}$ is a parameter known as the saturation intensity. The 800 nm open aperture experimental data was fitted using Eq. (3) and by treating the linear absorption coefficient $\alpha$ and nonlinear absorption coefficient $\beta$ $\left(\alpha_{2}\right)$ as parameters. From the fitting, we obtained the parameters as $\beta=-3.51 \times 10^{-9} \mathrm{~cm} / \mathrm{W}$ and $\alpha=0.142 \mathrm{~mm}^{-1}$, and

TABLE III. $d_{e f f}$ values of few organic crystals.

| Material | Symmetry | Wavelength (nm) | $d_{\text {eff }}(\mathrm{pm} / \mathrm{V})$ |
| :--- | :---: | :---: | :---: |
| GAL | $\mathrm{P} 2_{1}$ | 1064 | 0.71 |
| Urea | $\overline{4} 2 \mathrm{~m}$ | 1064 | 1.418 |
| Saccharose | $\mathrm{P} 2_{1}$ | $\ldots$ | 0.078 |
| L-Arginine Phosphate Monohydrate (LAP) | $\mathrm{P} 2_{1}$ | 1064 |  |
| Deuterated L-Arginine Phosphate (DLAP) | $\mathrm{P} 2_{1}$ | 1064 | 0.37 |
| L-Pyrrolidone-2-carboxylic Acid (L-PCA) | $\mathrm{P} 2_{1} 2_{1} 2_{1}$ | 532 | 0.32 |
| L-Arginine maleate dihydrate (LAMD) | P 1 | 1064 | 0.61 |
| m-Dinitrobenzene (MDNB) | $\mathrm{Pna} 2_{1}$ | 1064 | 0.63 |
| m-Bis(aminomethyl)benzene (BAMB) | mm 2 | 1064 | 0.96 |
| L-N-(5-Nitro-2-pyridyl)leucinol (NPLO) | 2 | 1064 | 2.7 |



FIG. 13. Open aperture data for 800 nm fitted to the open aperture equation for two-photon absorption and the fitting did not converge for three-photon absorption.
thus, a saturation intensity of $I_{s}=0.45 \mathrm{GW} / \mathrm{cm}^{2}$ was estimated from Eq. (16).

The closed aperture Z-scan data revealed a peak followed by a valley in the normalized transmittance of GAL. This indicates that GAL has a negative nonlinear refraction or self-defocusing. The closed aperture experimental data was fitted using Eq. (5), with $\Delta \phi$ as the fitting parameter. For both wavelengths, the value of $\Delta \phi$ estimated was found to be less than $\pi$. The values of the nonlinear optical parameters obtained for both wavelengths are tabulated in Table IV. It must be noted that the estimated values are with a degree of uncertainty arising from errors in beam waist measurements and calibration of neutral density filters. Since the experiments were performed with high repetition rate $(86 \mathrm{MHz})$ pulses, a significant thermal contribution is expected in the observed large NLO coefficients. A shoulder appears in the open aperture data corresponding to 700 nm (Fig. 15) as we approach the focus (at $z=-1$ ) which is likely to be due to the thermal contributions arising from high repetition rate of the input laser beam. However, the value of $\beta$ obtained from the fitting seemed fairly reasonable and has the same order


FIG. 14. Closed aperture data for 800 nm fitted to the closed aperture equation.


FIG. 15. Open aperture data for 700 nm fitted to the open aperture equation for two-photon absorption.
of magnitude. These measurements help us relate the types of third-order nonlinearities present in GAL and to obtain a good estimate of the corresponding parameters.

In general, there are two types of organic crystals that are studied for third-order NLO properties, which are polymeric crystals and charge-transfer (CT) salts. ${ }^{42}$ Polymeric crystals are crystallized from $\pi$-conjugated polymers. The third-order NLO parameters of these crystals are slightly different from the polymers, but are of the same magnitude. Poly-(2,4-hexadiyn-1,6-diol-bis( $p$-toluenesulfonate) (PTS) is a popular example of a polydiacetylene polymeric crystal having a large $\chi^{(3)} .{ }^{43}$ However, it is difficult to process and has long tails in its transient optical response at high laser intensities. ${ }^{42}$ Polymeric crystals of polyacetylenes are known to possess extremely an large $\chi^{(3)}$ but are not stable in air and need protection to prevent oxidative degradation. ${ }^{42}$ Organic charge-transfer salts are mixed stacked structures and exhibit high third-order nonlinearity. However, they are difficult to grow into big sizes and generally have large absorption in the visible range. ${ }^{21}$ Perylene/tetracyanoethylene (TCNE), Pyrene/TCNE, and Naphthanthracene/TCNE are examples of CT complexes showing very large $\chi^{(3)}$, but have large


FIG. 16. Closed aperture data for 700 nm fitted to the closed aperture equation.

TABLE IV. Third-order NLO parameters of GAL obtained by Z-scan measurements.

| Wavelength <br> $(\mathrm{nm})$ | $\beta(\mathrm{cm} / \mathrm{W})$ [obtained from <br> fitting with Eq. (3)] $\left(\times 10^{-9}\right)$ | $\Delta \phi_{0}$ [obtained from fitting <br> with Eq. (5)] | $n_{2}\left(\mathrm{~cm}^{2} / \mathrm{W}\right)\left(\times 10^{-13}\right)$ | $\chi_{i}^{(3)}($ esu $)\left(\times 10^{-12}\right)$ | $\chi_{R}^{(3)}($ esu $)\left(\times 10^{-11}\right)$ |
| :--- | :---: | :---: | :---: | :---: | :---: |$\chi^{(3)(\text { esu })\left(\times 10^{-11}\right)}$|  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
| 800 | -3.51 | 0.78 | -4.87 | -1.34 |
| 700 | -4.86 | 1.58 | -7.23 | -1.67 |

TABLE V. $\chi^{(3)}$ values of few organic crystals.

| Material | Input Wavelength (nm) | $\|\beta\|(\mathrm{cm} / \mathrm{W})\left(\times 10^{-9}\right)$ | $\chi^{(3)}(\mathrm{esu})\left(\times 10^{-12}\right)$ | Reference |
| :---: | :---: | :---: | :---: | :---: |
| $\underline{\text { Molecular crystals }}$ |  |  |  |  |
| GAL | 800 | 3.51 | 29.3 | This work |
| 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one | 900 | 2 | 9 | 44 |
| 3,4-Dimethoxy-4-methoxychalcone | 800 | 1.7 | 6.68 | 45 |
| 1-(4-aminophenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-en-1-one | 780 | 18.2 | 1.89 | 27 |
| (2E)-1-(1,3-Benzodioxol-5-yl)-3-[4-(dimethyl amino)phenyl] prop-2-en-1-one | 532 | $\ldots$ | 0.19 | 28 |
| Polymeric crystals |  |  |  |  |
| Polyacetylene | 1064 | $\ldots$ | 9000 | 46 |
| Poly-(2,4-hexadiyn-1,6-diol-bis-(p-toluenesulfonate)) (PTS) | 2620 | $\ldots$ | 160 | 43,47 |
| Poly-(5,7-dodecadiyne-1,2-diol-bis-(phenylurethane)) (TCDU) | 2620 | $\ldots$ | 37 | 47 |
| Charge transfer complex salts |  |  |  |  |
| Perylene/tetracyanoethylene (TCNE) | 530 | $\ldots$ | 1000 | 17,21 |
| Pyrene/TCNE | 530 | $\ldots$ | 230 | 21 |
| Naphthanthracene/TCNE | 530 | $\ldots$ | 130 | 21 |

absorption in the 300 nm to 500 nm wavelength range which is a disadvantage for applications. ${ }^{21}$

GAL crystals on the other hand, have high transmission in the visible wavelength range with a low UV-cutoff at 250 nm , can grow to big sizes, and are stable in air up to their melting point at $171^{\circ} \mathrm{C} .{ }^{14,15}$ Our measurements show that the magnitude of $\chi^{(3)}$ for GAL is reasonably large and has a much larger value among the recently reported molecular crystals. Some selected popular organic crystals and their third-order nonlinear optical properties are listed in Table V for comparison. The second-order absorption $(\beta)$ in GAL is comparable to the typical values for molecular crystals. This makes GAL an attractive material for various NLO, electrooptics, and switching applications.

## IV. CONCLUSIONS

Detailed results of the linear and nonlinear optical properties in an organic NLO single crystal, Glucuronic acid $\gamma$ Lactone (GAL) are reported. The dielectric axes of GAL were determined through conoscopy measurements. Once the $\mathrm{x}, \mathrm{y}$, and z directions were determined, the refractive indices of GAL along these directions were determined for several wavelengths. The dispersion in the refractive index was fitted to Sellmeir equations by which the refractive index at any wavelength could be calculated. Conic sections, formed due to spontaneous non-collinear second harmonic generation, were observed as two rings when projected onto a screen. This is a consequence of the GAL crystal being highly birefringent, and can be classified as a type II second harmonic crystal. By rotating the crystal and observing the rings on the screen, the direction of collinear phase matching was determined when these rings collapsed into an intense
spot. This direction is the closest to the z-axis of the crystal by $14.85^{\circ}$ in the anti-clockwise direction. The $d_{\text {eff }}$ along this direction was calculated as $0.71 \mathrm{pm} / \mathrm{V}$ for input pulses of 1064 nm wavelength. This value is in comparison to that reported in many organic NLO materials and almost twice that of inorganic crystal KDP. From the closed aperture Zscan measurements, we observed that GAL possesses a negative nonlinear refraction and the value of $n_{2}$ was obtained as $\sim 10^{-13} \mathrm{~cm}^{2} / \mathrm{W}$. The open aperture measurement reveals saturable absorption in GAL with a saturation intensity $\left(I_{s}\right)$ of $0.45 \mathrm{GW} / \mathrm{cm}^{2}$. The data converged only to two photon absorption and the 2PA coefficient ( $\beta$ ) was obtained as $\sim 10^{-9} \mathrm{~cm} / \mathrm{W}$. The magnitude of the nonlinear optical susceptibility $\chi^{(3)}$ was $\sim 10^{-19} \mathrm{~m}^{2} / \mathrm{V}^{2}$. The large second and third-order nonlinear optical susceptibilities make GAL a potential candidate for various NLO applications.

[^0]${ }^{11}$ K. Raghavendra Rao, R. Sanathkumar, H. L. Bhat, and S. Elizabeth, Appl. Phys. B 122, 270 (2016).
${ }^{12}$ K. Raghavendra Rao, C. Aneesh, H. L. Bhat, S. Elizabeth, M. S. Pavan, and T. N. Guru Row, Cryst. Growth Des. 13, 97 (2013).
${ }^{13}$ K. Raghavendra Rao, H. L. Bhat, and S. Elizabeth, CrystEngComm 15, 6594 (2013).
${ }^{14}$ R. K. Saripalli, T. Chakraborthy, H. L. Bhat, and S. Elizabeth, Appl. Phys. A 122(4), 438 (2016).
${ }^{15}$ R. K. Saripalli, H. L. Bhat, and S. Elizabeth, Opt. Eng. 56(1), 011025 (2016).
${ }^{16}$ M. V. Shankar, K. B. R. Varma, R. T. Bailey, F. R. Cruickshank, D. Pugh, and J. N. Sherwood, J. Appl. Phys. 81, 2370 (1997).
${ }^{17}$ T. Gotoh, T. Kondoh, K. Egawa, and K-I. Kubodera, J. Opt. Soc. Am. B 6, 703 (1989).
${ }^{18}$ F. Kazjar, J. Messier, and C. Rosilio, J. Appl. Phys. 60, 3040 (1986).
${ }^{19}$ Nonlinear Optical Properties of Organic Molecules and Crystals, edited by D. S. Chemla and J. Zyss (Academic Press, New York, 1987), Vol. 1.
${ }^{20}$ G. I. Stegeman and A. Miller, Background and Components, Vol. 1 of Photonics in switching, edited by E. Midwinter (Academic, Boston, Massachusetts, 1993).
${ }^{21}$ Q. Gong, Z. Xia, Y. H. Zou, X. Meng, L. Wei, and F. Li, Appl. Phys. Lett. 59, 381 (1991).
${ }^{22}$ D. J. De Smet, Am. J. Phys. 62, 246 (1994).
${ }^{23}$ C. H. Grossman and A. F. Garito, Mol. Cryst. Liq. Cryst. 168, 225 (1989).
${ }^{24}$ M. S. Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. VanStryland, IEEE Quantum Electron. 26, 760 (1990).
${ }^{25}$ D. Swain, P. T. Anusha, T. S. Prashant, S. P. Tewari, T. Sarma, P. K. Panda, and S. Venugopal Rao, Appl. Phys. Lett. 100, 141109 (2012).
${ }^{26}$ R. W. Boyd, Nonlinear Optics, 3rd ed. (Academic Press, 2009).
${ }^{27}$ G. Bing, J. Wei, P. S. Patil, and S. M. Dharma Prakash, J. Appl. Phys. 103, 103511 (2008).
${ }^{28}$ S. Shettigar, P. Poornesh, G. Umesh, B. K. Sarojini, B. Narayana, and K. Prakash Kamath, Opt. Laser Technol. 42, 1162 (2010).
${ }^{29}$ W. Sellmeier, Ann. Phys. Chem. 219(6), 272 (1871).
${ }^{30}$ P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Lett. 8, 21 (1962).
${ }^{31}$ D. A. Kleinman, A. Ashkin, and G. D. Boyd, Phys. Rev. 145, 338 (1966).
${ }^{32}$ R. Trebino, Appl. Opt. 20(12), 2090-2096 (1981).
${ }^{33}$ J. H. McFee, G. D. Boyd, and P. H. Schmidt, Appl. Phys. Lett. 17, 57 (1970).
${ }^{34}$ R. C. Eckardt, H. Masuda, Y. X. Fan, and R. L. Bycr, IEEE J. Quantum Electron. 26, 922 (1990).
${ }^{35}$ J. M. Halbout and C. L. Tang, IEEE J. Quantum Electron. 18, 410-415 (1982).
${ }^{36}$ B. V. Bokut, J. Appl. Spectrosc. 7, 425 (1967).
${ }^{37}$ G. Wójcik, I. Mossakowska, J. Holband, and W. Bartkowiak, Acta Cryst. B58, 998 (2002).
${ }^{38}$ V. G. Dmitriev and D. N. Nikogosyan, Opt. Commun. 95, 173 (1993).
${ }^{39}$ D. A. Roberts, IEEE J. Quantum Electron. 28, 2057 (1992).
${ }^{40}$ V. G. Dmitriev and D. N. Nikogosyan, Opt. Commun. 95, 173-182 (1993).
${ }^{41}$ T. Ukachi, T. Shigemoto, H. Komatsu, and T. Sugiyama, J. Opt. Soc. Am. B 10, 1372-1378 (1993).
${ }^{42}$ W. Nie, Adv. Mater. 5, 520 (1993).
${ }^{43}$ G. M. Carter, M. K. Thakur, Y. J. Chen, and J. V. Hryniewicz, Appl. Phys. Lett. 47, 457 (1985).
${ }^{44}$ P. S. Patil, P. Ajay Kumar, S. Venugopal Rao, and G. Bhagavannarayana, Opt. Laser Technol. 71, 108 (2015).
${ }^{45}$ P. S. Patil, S. R. Maidur, S. Venugopal Rao, and S. M. Dharma Prakash, Opt. Laser Technol. 81, 70 (2016).
${ }^{46}$ F. Krausz, E. Wintner, and G. Leising, Phys. Rev. B 39, 3701 (1989).
${ }^{47}$ C. Sauteret, J. P. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, and R. R. Chance, Phys. Rev. Lett. 36, 956 (1976).


[^0]:    ${ }^{1}$ J. L. Bredas, C. Adant, P. Tackx, A. Persoons, and B. M. Pierce, Chem. Rev. 94(1), 243 (1994).
    ${ }^{2}$ T. Mallik, T. Kar, G. Bocelli, and A. Musattib, Sci. Technol. Adv. Mater. 6, 508 (2005).
    ${ }^{3}$ V. G. Dmitriev, G. G. Gurzadyan, and D. N. Nikogosyan, Handbook of Nonlinear Optical Crystals (Springer, 1997).
    ${ }^{4}$ H. J. Scheel and T. Fukuda, Crystal Growth Technology (Wiley, 2003).
    ${ }^{5}$ M. Kitazawa, R. Higuchi, and M. Takahashi, Appl. Phys. Lett. 64, 2477 (1994).
    ${ }^{6}$ D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono, and G. Kennedy, IEEE J. Quantum Electron. 25(2), 179-193 (1989).
    ${ }^{7}$ Z. H. Sun, W. T. Yu, X. F. Cheng, X. Q. Wang, G. H. Zhang, G. Yu, H. L. Fan, and D. Xu, Opt. Mater. 30, 1001 (2008).
    ${ }^{8}$ G. Bourhill, K. Mansour, K. J. Perry, L. Khundkar, E. T. Sleva, R. Kern, J. W. Perry, I. D. Williams, and S. K. Kurtz, Proc. SPIE 1853, 110 (1993).
    ${ }^{9}$ G. Bourhill, K. Mansour, K. J. Perry, L. Khundkar, E. T. Sleva, R. Kern, J. W. Perry, I. D. Williams, and S. K. Kurtz, Chem. Mater. 5, 802 (1993).
    ${ }^{10}$ K. Raghavendra Rao, H. L. Bhat, and S. Elizabeth, Mater. Chem. Phys. 137, 756 (2013).

