

Growth and Characterization Studies of an Organic Nonlinear Optical Crystal - Oxalic Acid Dihydrate

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Abstract— An organic nonlinear optical (NLO) material, oxalic acid dihydrate (OAD) was grown by slow evaporation technique of solution growth method using the solvent tetrahydrofuran at constant temperature (35 °C). Single crystal X-ray diffraction (XRD) was utilized to determine the lattice parameters of the grown crystal and the crystalline nature was examined by powder XRD. The existence of various functional groups was observed by Fourier transform infrared (FT-IR) analysis. From Ultra violet-visible (UV-vis) study, the lower cut-off wavelength was indicated as 237 nm. The dielectric and photoconductivity analyses were also performed for the developed OAD crystal. The improved Kurtz and Perry powder technique was employed to find the second harmonic generation efficiency (SHG) of the crystal. The characterization results obtained throws light on the grown OAD crystal and conveys that is a good material to be utilized in the field of non-linear optics and applications.

Keywords-NLO organic crystal, OAD, XRD, SHG, Dielectric, Photoconductivity.

I. INTRODUCTION

Nonlinear optical materials proficiently reveal nonlinear optical phenomena, which are modification of light wavelength, amplification of light and conversion of the refractive index based on optical intensity. NLO crystals have high conversion efficiencies for second harmonic generation and that they are transparent in the visible and ultraviolet range which contributes them for fabricating various devices within the field of optoelectronics and photonics [1, 2]. Hence, Organic NLO materials are to be explored and extensively studied. The superiority of organic materials is that they will be modified and tuned with respect to their chemical structure and properties of materials based on our requirement i.e. they have large structural diversity [3]. Oxalic acid is a toxic organic compound belonging to the family of dicarboxylic acids and is also effective and viable compound for studies in the field of photonics in which two carboxyl clusters are combined instantly [4]. In 1953, Ahmed and Cruickshank first studied the crystal structure of oxalic acid dihydrate [5]. Further different authors have carried out research on the charge density of OAD [6-8]. L. Torgesen and J. Strassburger took up the work on the growth of oxalic acid and single crystals using various solvents and the solvent reactions on crystal nature have been reported [9]. Tetrahydrofuran (C_4H_8O) is an organic solvent; it can dissolve a wide variety of organic compounds and has a reasonable low boiling point. The low boiling point of a solvent is appropriate one as it could be removed easily by evaporation. From this incitement, this research work was undertaken to grow oxalic acid dihydrate ($C_2H_6O_6$) crystal using the solvent tetrahydrofuran from slow evaporation technique of solution growth method and the grown crystal has been placed to different experimental techniques like XRD studies, FTIR spectroscopy, UV-vis spectroscopy, dielectric study, photoconductivity analysis and powder SHG test.

Section I contain the introduction of the NLO materials, Oxalic acid dihydrate single crystal and the solvent tetrahydrofuran. Section II consist the related work of the OAD crystal, Section III involves the materials and methods, Section IV describes the result and discussion and section V explain the conclusion and future scopes.

II. RELATED WORK

The mechanism of thermal dehydration of monocrystalline oxalic acid dihydrate was studied under polarizing microscope in constant and linearly elevated temperatures by thermogravimetry [10]. Effects of water on crystallization in terahertz spectra: anhydrous oxalic acid and its dihydrate were presented [11]. X-ray analysis of hydrogen bonding within the structure of oxalic acid dihydrate [12] was explained and the gamma irradiation

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effects on the characteristics of potassium hydrogen oxalate oxalic acid dihydrate were studied optically [13]. Growth of oxalic acid single crystal and its different properties [14], pure and tryptophan doped oxalic acid crystal for antimicrobial activity [15] and Glycine oxalic acid for SHG efficiency [16] were also reported.

III. MATERIAL AND METHODS

Commercially available oxalic acid dihydrate was dissolved by tetrahydrofuran and the mixture was stirred well for about one hour by a magnetic stirrer. The saturated solution of OAD was filtered through a Whatmann (No 42 grade) filter paper into a clean dry beaker, to get rid of the suspended impurities. The filtrate was kept at a constant temperature water bath for crystal growth and the temperature of the bath was kept at 35 °C. Owing to slow evaporation of the solution, high quality optical single crystals of oxalic acid dihydrate were harvested within 15-20 days time. The snapshot of grown OAD crystal is displayed in figure 1.

IV. RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis

A Bruker AXS X-ray diffractometer was used for single crystal XRD analysis to describe the unit cell parameters of the as grown OAD crystal. The identified cell parameters are a=6.108 Å, b=3.610 Å, c=11.849 Å, V=254.3 Å³ and β =103.29°. This determines that the OAD single crystal befits to monoclinic system along with a space group of P2₁/n.

Powder X-ray diffraction analysis

The powder XRD pattern of OAD crystal was performed by JEOL-JDX 8030 X-ray diffractometer along Nickel filtered CuK α (λ =1.5405 Å) radiation. The sample was scanned for 2 θ values from the range 10-90° at a scan rate of 2° per minute. The diffraction pattern recorded for the grown crystal is shown below in figure 2. The sharp and well-defined Bragg's peaks affirm the crystallinity of the grown sample. The prominent peak has been obtained at 2 θ values of 12.127° and the XRD record consists of several low intensity lines also.



Figure 1. The snapshot of OAD crystal



UV- visible spectroscopy

Optical absorption spectrum conveys inexorable detail regarding the structure of the molecules by reason of the absorption in the UV and visible light includes stimulation of electrons in an orbit from the ground state to the excited energy state [17]. During UV spectral analysis the optical transmittance window, the transparency and the lower cutoff wavelength is pre-eminent for the realization of SHG output within the range using diode laser. The electronic absorption spectrum of the OAD crystal was recorded by employing a Perkin-Elmer Lambda 35 spectrometer in the wavelength region from 200 to 1100 nm. The Electronic absorption spectrum indicates the change in that the percentage of absorption in the defined wavelength range and this spectrum obtained for the sample under study is shown in figure 3 and it displays the fact that OAD crystal is optically transparent (around 90%) in the entire visible region. These kinds of high transparent materials are suitable for optoelectronic applications [18, 19]. The lower cut-off wavelength of grown OAD single crystal was found to be 237 nm.



Figure 3. Electronic absorption spectrum of OAD crystal

FT-IR spectral analysis

The FTIR spectrum brings particulars about the molecular structure of the compound, modes of vibration and the presence of functional groups. The analysis has employed Thermo Nicolet V-200 FT-IR spectrometer by KBr pellet

method within the wave number range of 450 to 4500 cm⁻¹. The recorded FT-IR spectrum of OAD sample is presented in figure 4. From the observations the presence of following specific groups were corroborated. The strong OH band is 3476 cm⁻¹ attributed to fundamental stretching vibrations of –OH groups. The C=O stretching mode vibration is obtained at 1690 cm⁻¹. The absorptions at 1255 cm⁻¹ is assigned for C-OH vibration and also the peak at 720 cm⁻¹ is assigned for O-H out of plane bending. These values are strongly suited with the previous reported values [20].

Dielectric study

The dielectric properties are related to the electro-optic property of materials. The dielectric study was preformed for the grown crystal with 3532-50 Hioki LCR meter in the frequency range from 50 Hz to 5 MHz at various temperatures (273 K, 283 K, 293 K, 303 K, 313 K, 323 K and 333K). The opposite faces of the crystal were coated with an electronic grade silver paste for good electrical contact betwixt the crystal and the electrodes. A silver pasted crystal was kept in between copper plates and the measurement was taken. Dielectric constant of the material has been calculated using the formula given below.

$$\varepsilon_{\rm r} = \frac{{\rm C}a}{\varepsilon_{\rm o}A}$$

Where, 'C' is the capacitance of the crystal, 'd' denotes the thickness of the crystal, 'A' indicates the area of the crystal and ' ε_{o} ' denotes the permittivity of free space (8.85x 10⁻¹² Farad/m). Figure 5 depicts the variation of the dielectric constant with applied frequency for the sample at different temperatures. At a particular applied frequency, it is found that the dielectric constant increases with temperature. Further the dielectric constant is very high at low frequencies and have become stable at high frequencies as it leads to the space charge polarization. Figure 6 indicates the dielectric loss increases in low frequencies and decreases at high frequencies. When the temperature increases, dielectric loss also rises. Low value of dielectric loss retains the sample in enhanced optical quality with low defects [21, 22].



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Photoconductivity analysis

Photoconductivity is an optical occurrence in which a material becomes more conductive because of the absorption of electromagnetic radiation like visible light, UV light or gamma radiation. Photoconductivity study was carried out utilizing a Keithley electrometer (Model 6517B) at different temperature along with applied input voltage from 1 V to 10 V. Polished crystals were selected and thin copper wire was connected on both the sides of the sample with the assistance of silver paste. 100 W halogen lamp consisting iodine vapour and tungston filament has been used as a radiation source for the photoconductivity analysis. The variations in conductivity of sample in the presence of light as well as in the absence of light (dark current) were recorded. Photocurrent and dark current measurements were performed as a function of applied electric field. The figure 7 conveys the variation of the photocurrent and dark current with the applied input voltage. Current is directly proportional to the applied input voltage; it is obvious that the dark current is greater than photocurrent. It is concluded that OAD single crystal reveals that the negative photoconductivity nature on the basis of the reduction of charge carriers in the presence of radiation [23].



Figure 5. Dielectric constant Vs log frequency at various temperatures for OAD crystal



Figure 6. Dielectric loss Vs log frequency at various temperatures for OAD crystal



applied field

Powder SHG measurement

The basic and broadly adopted technique to affirm the SHG from second order NLO materials is that the Kurtz and Perry powder technique. The powder SHG test for the grown OAD single crystal was performed by using modified Kurtz and Perry powder SHG method [24]. The SHG efficiency of the crystal was calculated by Q-switched Nd: YAG laser with the input wavelength of 1064 nm. The laser input pulse of 3.2 mJ was directed towards the sample and the SHG nature is affirmed by the green light emission. The output signal of 19 mV was obtained for OAD single crystal under study. The KDP was used as the reference material and the SHG efficiency of OAD single crystal is found to be 1.8 times higher than that of KDP.

The SHG efficiencies of certain reported oxalic acid mixed crystals along with UV cutoff wavelength are compared with OAD and specified in table 1. It is noticed that OAD crystal exhibits high SHG efficiency when compared to the other mixed organic crystals and OAD crystal in the

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present study is relatively a promising NLO material for nonlinear optical applications.

Crystal	UV cut off wavelength (nm)	SHG efficiency
L – Arginine semi – oxalate [25]	-	0.32
L – Citrulline oxalate [26]	311	0.40
Glycinium oxalate [27]	305	0.87
Lithium hydrogen oxalate monohydrate [28]	-	0.91
L – Alaninium oxalate [29]	250	1.20
γ – Glycine ammonium oxalate [30]	-	1.48
Oxalic acid dihydrate [Present work]	237	1.80

Table 1. Optical property of oxalate crystals

V. CONCLUSION AND FUTURE SCOPE

Optically good characteristic oxalic acid dihydrate single crystals were effectively grown by slow evaporation solution growth technique using the solvent tetrahydrofuran at a constant temperature (35 °C). The cell parameter values are determined by single crystal XRD and the powder XRD analysis authenticates the crystalline nature of the grown crystal. The high transparency of the crystal is leads itself as an apt material for optoelectronic applications. FT-IR analysis substantiates the modes of vibration of the molecular groups present in the crystal. From the dielectric study, dielectric constant is very high at low frequency and increases with rise in temperature. The grown crystal reveals the negative photoconductivity nature and the second harmonic generation efficiency is 1.8 times greater than that of KDP. The good transparency, low dielectric constant and low dielectric loss with high nonlinearity have corroborated the OAD crystal as a promising material for the fabrication of SHG and optoelectronic devices.

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