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**Archives of Applied Science Research, 2015, 7 (7):75-82**
*(http://scholarsresearchlibrary.com/archive.html)*

**ISSN 0975-508X**
**CODEN (USA) AASRC9**

# Growth, characterization and measurement of third order non - linear optical properties of ammonium oxalate single crystals using Z-scan technique

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**ABSTRACT**

*Ammonium oxalate Single crystals were grown by the slow evaporation solution growth method using water as a solvent and subjected to optical characterization. Good optical quality of crystal was observed and the grown crystals were characterized by single crystal X-ray diffraction study which confirms that the grown crystal belongs to Pnma space group. The UV-Vis-NIR spectra reveal a low UV cut off value for Ammonium oxalate. Absence of SHG affirms the Centro-symmetric class of this crystal and hence the Z-scan technique is employed for THG. Through the Z-scan technique, the nonlinear refractive index* $n_2$ *and the absolute value of the third order non-linear optical susceptibility* $\chi^{(3)}$ *have been measured at the wavelength of 632.8nmand were found to be 2.3191 × 10-9cm2/W and 7.4278 × 10-6esurespectively. Also, at the same wavelength, the real* $\chi_R^{(3)}$ *and imaginary* $\chi_I^{(3)}$ *parts of susceptibility* $\chi^{(3)}$ *have been calculated as* $1.4228\times10^{-7}$ *esu and* $7.4264\times10^{-6}$ *esu respectively. Ammonium oxalate exhibits saturation absorption and self-defocusing performance and its non-linear absorption co-efficient* $\beta$ *is determined as7.4126 × 10-6 cm/W.*

**Keywords:** Ammonium Oxalate, Solution growth, single XRD,UV-Vis-NIR,Z-Scan, THG.

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## INTRODUCTION

Since the early days of nonlinear optics in the 1960s, the field has expanded dramatically and now it is a vast and vibrant field with limitless technological applications. Nonlinear optics is based on the phenomenon related to the interactions of coherent light radiation with matter under conditions in which the non-linear response of the atoms plays an important role. During the past three decades optics has secured a good place in application areas previously electronics made it. Due to the developments, non-linear optics hold guarantee for important applications in optical information processing, telecommunications and integrated optics.

One of the most intensively studied nonlinear optical phenomena is second harmonic generation (SHG) which is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The process occurs within a nonlinear medium, usually a crystal. Such frequency doubling processes are commonly used to produce green light (532 nm) from an Nd: YAG laser operating at 1064 nm. The light propagated

through a crystalline solid, which lacks a center of symmetry, generates light at higher harmonics of the applied frequency.

If SHG is found to be absent, Z-Scan technique[1-3] can be employed to investigate the third order NLO properties in Centrosymmetric class of crystals with high sensitivity and simplicity.To measure the magnitude of nonlinear absorption as well as the sign and magnitude of nonlinear refraction,Sheik Bahaedeveloped thissingle beam technique.

A laser beam propagating through a nonlinear medium will experience variations inboth amplitude and phase. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture Z-Scan. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction.On the other hand without an aperture, the mode of measurement is referred to as open aperture Z-Scan. These methods yield the real and imaginary parts of nonlinear susceptibility $\chi^{(3)}$ respectively.

## MATERIALS AND METHODS

### 1.1 EXPERIMENTAL SETUP

The experimental setup used to measure the nonlinear refractive index and absorption of our crystal sample in this work as depicted in the Figure 1.

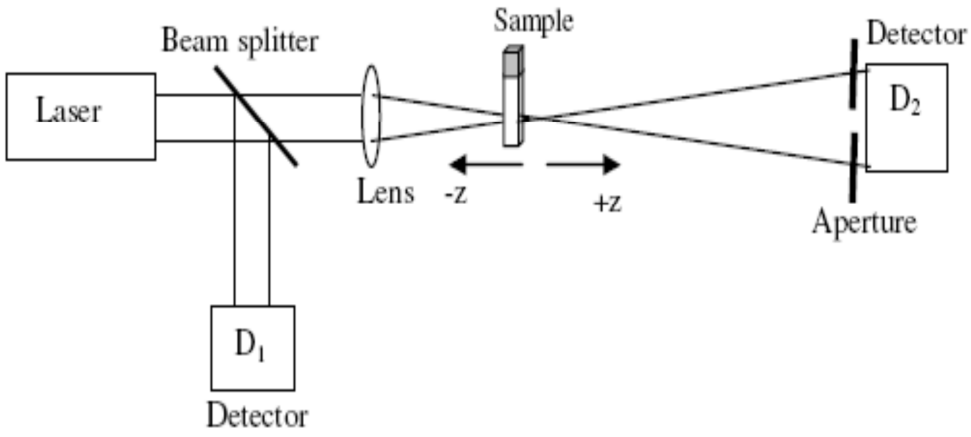



**Figure 1. Z-scan technique - Schematic diagram**

In the Z-scan technique, a tightly focused Gaussian beam is transmittedthrough a finite aperture in the far field is measured as a function of the sample position 'z' with respect to the focal plane. At each position, different light intensity is experienced bythe sample. A spatial beam broadening or narrowing in the far field is caused by the nonlinear refraction of the sample and thusthe fraction of light that passes through the aperture is modifiedas the sample position is changed. When the nonlinear refractive index of the medium is negative or positive, a typical peak-valley or valley-peak transmittance curve is obtained respectively. In the limit where the sample can be considered as thin, compared to the beam Rayleigh length $(L < z_0)$, it is possible to evaluate the maximum nonlinear phase-shift from the peak to valley variation of the measured transmittance curve and henceto obtain the nonlinear refractive index $n_2$,by knowing the incident laser power. It is possible to perform nonlinear absorption measurements by removing theaperture in the far field. Such Z-scan traces are expected to be symmetric with respect to the focal point $(z = 0)$ where they exhibit a minimum transmittance in the case of nonlinear absorption (multi-photon absorption) and a maximum transmittance for the saturation absorption.

Aclosed aperture Z-scan measurement is sensitive to both effectsfor media exhibiting both nonlinear refraction and absorption properties. Dividing the closed aperture data by the open aperture, one yields a Z-scan trace typical of a

purely refractive nonlinearity. The magnitude and sign of the non-linear refraction and non-linear absorption can also be simultaneously measuredwhich are associated with the real part $\chi_R^{(3)}$ and imaginary part $\chi_I^{(3)}$ of the third order non-linear susceptibilities. The Z-Scan technique has been used to measure the non-linear optical properties of semiconductors [4,5], dielectrics [6,7] organic or carbon-based molecules [8,9] and liquid crystals [10,11]. In this work, the growth of Ammonium Oxalatesingle crystals by the slow evaporationsolution growth method using de-ionized water as a solvent is presented. Single X-ray diffraction, optical absorption spectrum andZ-Scan measurements were carried out. Z-Scan results reveal that it is a potential candidate for the optical switching [12] and optical limiting [13].All-optical switching is based on either the spatial or temporal nonlinear responses of materials.

## MATERIALS AND CHARACTERIZATION METHODS

### 2.1CRYSTAL GROWTH

Using AR grade chemical and water as a solvent,Ammonium Oxalatecrystalwas grown by slow evaporation solution growth technique. Purification of the synthesized saltis made by successive re-crystallization process and thus clear crystals were obtainedwithin 18 days. Figure 2 shows the grown Ammonium Oxalatecrystal of dimensions $0.8 \times 1 \times 1.4\ cm^3$.

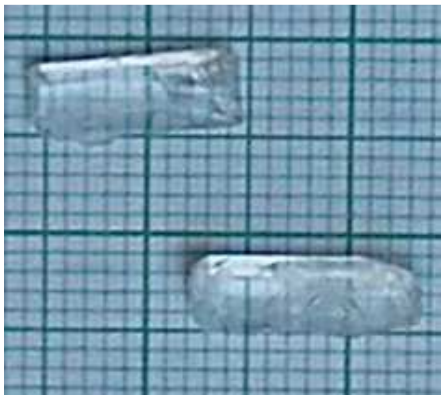


**Figure 2 Grown Crystals of Ammonium oxalate**

## RESULTS AND DISCUSSION

The study of optical transmission and absorption of the crystal by UV-Vis-NIR technique, Kurtz powder method for SHG conversion efficiency, Z-scan technique for NLO coefficients and Single crystal leads to the complete understanding of the linear and nonlinear optical behavior of the grown crystal.

Normally, the following characterization studies are carried out for understanding the physico-chemical nature of the grown crystals.

1)Crystal structure analysis by single crystal XRD
2)Optical transmittance property by using UV-Vis-NIR spectrometer
3)The nonlinear SHG optical property of the crystal by Kurtz-Perry powder technique
4)Third Order Non-Linear Optical Measurement using Z-scan technique

### 3.1 Single Crystal XRD

A non-destructive analytical technique which provides detailed information about the internal lattice ofthe grown crystalsincluding unit cell dimensions, Single crystal X-ray diffraction analysis has been carried out using Enraf - Nonius CAD-4 X-Ray diffractometer which confirms the lattice parameters of the grown crystal of Ammonium Oxalate and the following Table 1offers itssingle crystal data.

**Table 1 The single crystal X-ray data for Ammonium Oxalate**

| | | | |
|---|---|---|---|
| System | Orthorhombic | | |
| Space group | Pnma | | |
| Lattice parameters | a = 3.823 Å | b = 8.102 Å | c = 10.375 Å |
| | α = 90° | β = 90° | γ = 90° |
| Volume (V) | 321.4 Å$^3$ | | |

### 3.2 UV –VIS-NIR SPECTRA OF AMMONIUM OXALATE

The UV-Vis-NIRabsorption spectra are very useful tool in the transmission range of the crystal for the study of NLO behaviour. Absorption spectra of the grown single crystals of Ammonium oxalate wererecordedusing VarianCary5EUVspectrophotometerintherange200-1100nm. The spectra reveal a low UV cut off value at 381 nm for Ammonium oxalate. The absorption is found to be low in range 380 to 1100 nm for Ammonium oxalate. Figure 2 shows the UV-Vis-NIR spectra of Ammonium oxalate.

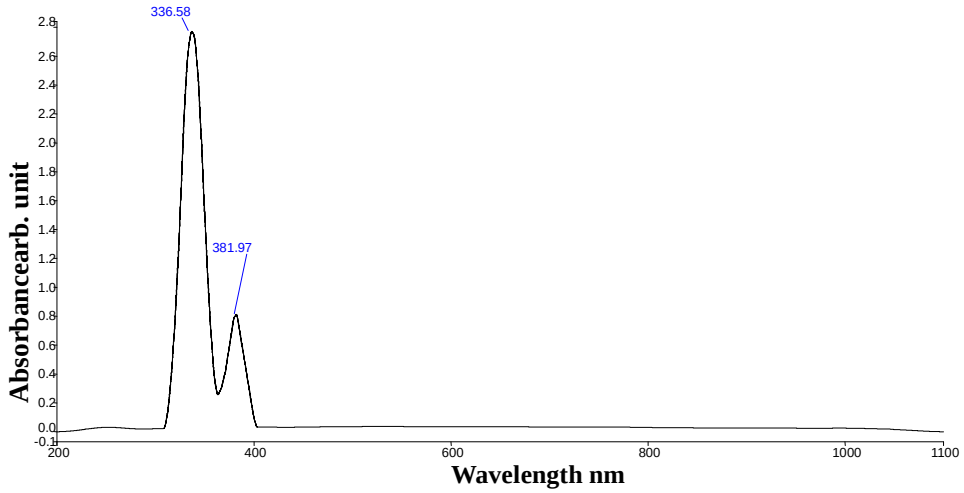



**Figure 2. UV-Vis-NIR Spectra of Ammonium Oxalate**

### 3.3NLO MEASUREMENTS

#### 3.3.1. SHG Measurement

Kurtz and Perry powder technique[14]experimental procedure for SHG measurement is detailed below. The SHG measurement of the grown crystals of Ammonium Oxalatehas been carried out in accordance with this classical powder method.

Powdered Ammonium Oxalatecrystalwith a particle size of around 150 µm is densely packed in a micro capillary tube. A Q-switched(a method for obtaining energetic pulses from lasers) Nd: YAG laser of wavelength 1064 nm (pulse width 8 ns, repetition rate 10 Hz) is made to fall normally on the pellet which holds the sample.The powdered Ammonium Oxalate through whichlight is propagated, did not generate a visible green light of 532 nm (second harmonic signal)and thus it lacks a center of symmetry. In view of the fact that SHG is found to be absent in the sample, Z-Scan techniquecan be employed to investigate the third order NLO properties in the Centrosymmetric class of grown crystals.Powdered KDP crystal is used as reference material.

#### 3.3.2. Refractive Index Measurement

By Brewster's angle method using He-Ne laserof wavelength 632.8 nm, the refractive index of the Ammonium Oxalate single crystal was determined. On a rotating mount a polished flattened single crystal is mounted at an angle varied from 0 to 90 degrees and when the crystal is perfectly perpendicular to the intra-cavity beam,the angular reading on the rotary stage was observed. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. For Ammonium Oxalatesingle crystal Brewster's angle $(\theta_P)$ is measured to be 57.48(degrees). The refractive index 'n' has been calculated using the equation $n = \tan\theta_P$ and is

found to be 1.5685, where $\theta_p$ is the polarizing angle.

**3.3.3. Third Order Non-Linear Optical Measurement using Z-scan**

Z-scan technique is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient β and the nonlinear refractive index $n_2$. Due to the localized absorption of a tightly focused beam propagating through the absorbing sample, a spatial distribution of the temperature in the crystal surface is produced. Hence a spatial variation of the refractive index is also produced.This acts as a thermal lens which results in the phase distortion of the propagating beam. The difference between the peak and valley transmission $\left(\Delta T_{P-V}\right)$ is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{P-V} = 0.406\left(1-S\right)^{0.25}\left|\Delta\Phi_0\right| \quad \text{.....(1)}$$

where $\Delta\Phi_0$ is thenonlinear phase shift with the sample at focus (Z=0) specified as

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff} \quad \text{..... (2)}$$

The nonlinear refractive index $n_2$ is given by

$$n_2 = \frac{\Delta\Phi_0}{K\ I_0\ L_{eff}} \quad \text{..... (3)}$$

where, $K = \frac{2\pi}{\lambda}$ ( $\lambda$ is the laser wavelength), '$L_{eff}$' is the effective thickness of the sample andit can be determined using '$L_{eff}$'$= \frac{\left(1-e^{-\alpha L}\right)}{\alpha}$ '$L$' is the thickness of the sample. '$I_0$' is the intensity of the laser beam at the focus (Z=0) and α is linear absorption coefficient of the sample.

"S" is the transmittance of the aperture in the absence of a sample and can be calculated using the relation

$$S = 1-\exp\left(\frac{-2\ r_a^2}{\omega_a^2}\right) \quad \text{..... (4)}$$

where, $r_a$ is the aperture radius and $\omega_a$ is the beam radius at the aperture.

From open aperture Z-scan data, the non-linear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad \text{..... (5)}$$

where, ΔT is the one valley value at the open aperture Z-scan curve.

For saturable absorption the value of β will be positive and for two photon absorption it is negative. The real and imaginary parts of the third order Non-linear optical susceptibility $\chi^{(3)}$ are defined as

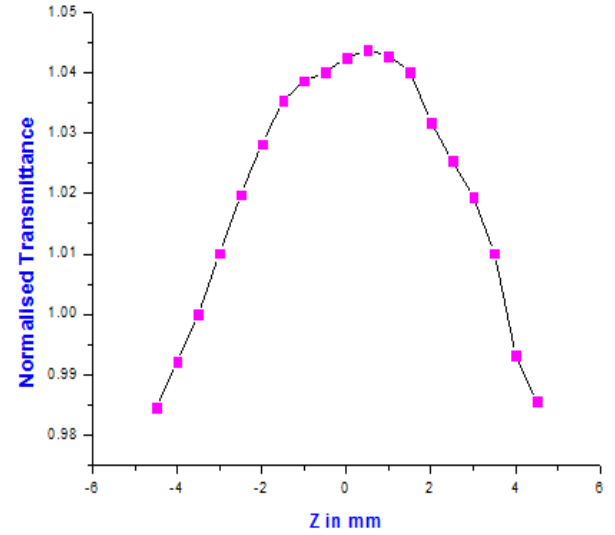
$$\text{Re}\ \chi^{(3)} = \frac{10^{-4}\times\left(\varepsilon_0 c^2 n_0^2 n_2\right)}{\pi} \quad \left(esu\right) \text{ and}$$

$$\text{Im}\ \chi^{(3)} = \frac{10^{-2}\times\left(\varepsilon_0 c^2 n_0^2 \lambda\ \beta\right)}{4\pi^2} \quad \left(esu\right) \text{ ..... (6)}$$

where, $\varepsilon_0$ is the vacuum permittivity, $n_0$ is the linear refractive index of the sample and $'c'$ is the velocity of light in vacuum. The formula to calculate the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is

$$\chi^{(3)} = \sqrt{\left(\text{Im}\ \chi^{(3)}\right)^2 + \left(\text{Re}\ \chi^{(3)}\right)^2} \quad (esu) \text{..... (7)}$$

The normalized transmittance for the Open Aperture (OA) curve of Ammonium Oxalate is shown in Figure 4. In this case, the transmission is symmetric with respect to the focus(Z=0),where it has a maximum transmission and it indicates that the sample exhibits Saturation Absorption (SA).



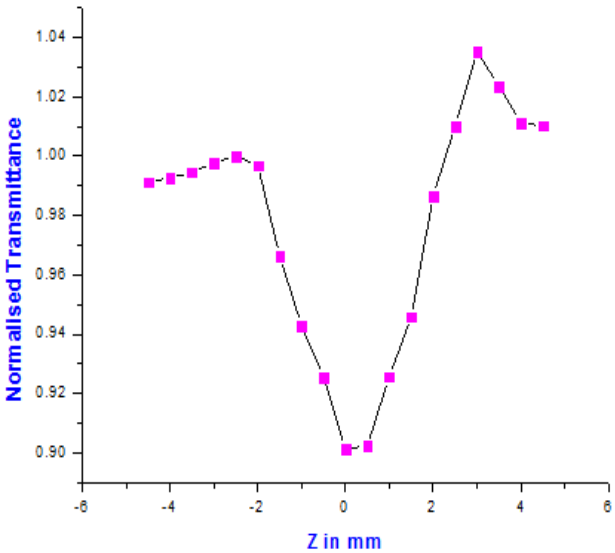




**Figure4OpenAperturecurveofAmmonium OxalateFigure5 ClosedAperture CurveofAmmonium Oxalate**

In addition, thenormalized transmittance for closed aperture curve of (CA) of Ammonium Oxalate is showninFigure5. The peak to valley configuration of the curve implies that it exhibits a self de-focusing effect as the refractive index change is negative. This possibly will be an advantage for the application in protection of optical sensors. From the closed aperture Z –scan curve, it is seen that the prefocal transmittance peak is followed by the post focal valley which is the mark of negative nonlinearity [15].

Figure 6 shows the division curve of the grown sample by combining Open Aperture (OA) and Closed Aperture (CA) curves. To calculate third order susceptibility of the grown material, the division curve is used.

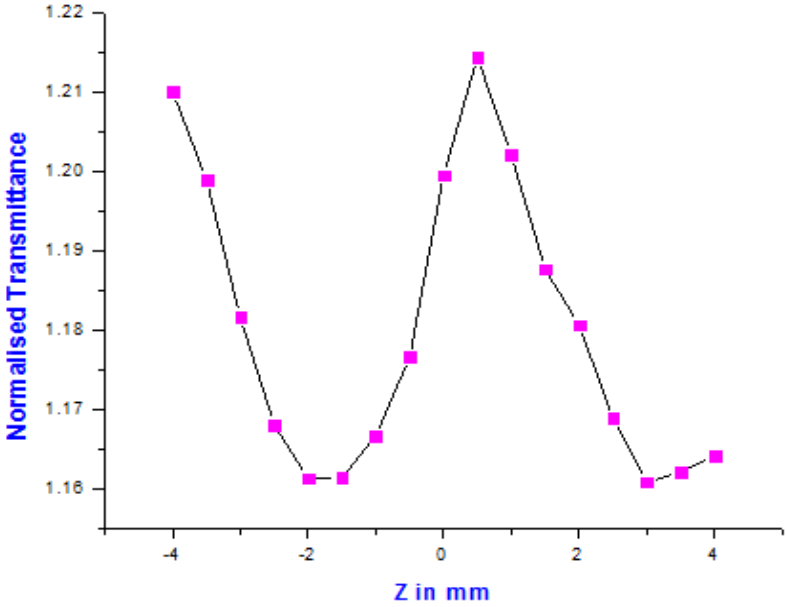



**Figure 6 Division Curve of Ammonium Oxalate**

The calculated value of the nonlinear refractive index $n_2$ is found to be 2.3191 × $10^{-9}$cm$^2$/W. As the material has a negative refractive index, it results in self – defocusing nature. It can be concluded from the open aperture Z-scan curve that the nonlinear absorption is regarded as saturation absorption. The nonlinear absorption coefficient $(\beta)$ is found to be7.4126 × $10^{-6}$ cm/W. The real and imaginary parts of third order non-linear optical susceptibility $\chi^{(3)}$ have been measured at 632.8 nm and were found to be 1.4228 × $10^{-7}$ esu and 7.4264 × $10^{-6}$ esu respectively. Also, the absolute value of the third order non-linear optical susceptibility $\chi^{(3)}$ is 7.4278 × $10^{-6}$ esu.

## CONCLUSION

In summary, third-order nonlinear optical parameters of Ammonium Oxalate single crystal were studied using Z-scan technique with 632.8 nm laser pulses. The absence of SHG efficiency confirms the centro-symmetry nature of the crystal. The Z-scan results indicate the molecules exhibits negative nonlinear refractive index and its magnitude is of the order of 2.3191 × $10^{-9}$cm$^2$/W. Hence, the sample investigated seems to be a promising candidate for future photonic and optoelectronic applications such as optical limiting and switching.

**Acknowledgements**
The authors are grateful to Professor Dr. D.Sastikumar, National Institute of Technology, Tiruchirappalli for providing the Z-Scan facility. Also the authors acknowledge Professor P.K.Palanichamy, Department of Physics, Anna University, Chennai and Dr.V. Natarajan, A.P, Rajalakshmi Institute of Technology, Chennai for their valuable suggestions.

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