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XRD, SHG, OPTICAL AND MECHANICAL STUDIES OF GLYCINE DOPED MONO-UREA OXALIC ACID CRYSTALS

T. Manju[1] and P. Selvarajan[2]
[1]Research Scholar, Reg.No.7428, Department of Physics, Manonmaniam Sundaranar University, Abishekapatti , Tirunelveli, Tamilnadu, India.
[2]Associate Professor of Physics, Department of Physics, Aditanar College of Arts and Science, Tiruchendur, Tamilnadu, India.
(Affiliated to Manonmaniam Sundaranar University, Abishekapatti,Tirunelveli, Tamilnadu, India)

ABSTRACT

Single crystals of glycine doped mono-urea oxalic acid (GMUOA) were successfully grown by conventional solution growth method. Single crystal X-ray diffraction analysis reveals that the grown crystal belongs to monoclinic system. The transparency of the crystal was determined by UV-visible spectroscopy and optical band gap was determined. The mechanical parameters like hardness, work hardening coefficient and parameters of the sample were determined from the results of microhardness test. SHG efficiency of the GMUOA crystal was found by Kurtz-Perry powder method.

KEYWORDS : *Single Crystal, Solution Method, Doping, XRD, Microhardness, SHG, Transmittance, Energy Gap.*

INTRODUCTION

Second order nonlinear optical (NLO) and third order NLO crystals are interesting materials because they are capable of harmonic generating UV laser and visible laser light to be used in fields of optical communication, optical computing, optical data processing and photonics [1, 2]. Organic NLO materials may be second order or third order NLO materials and these crystals have low frequency dispersion, have low melting point, low mechanical strength and they have inherently high nonlinearity, high laser damage threshold values [3-5]. In this work, the organic NLO crystals like undoped and glycine doped urea oxalic acid crystals were grown and studied. Urea is hydrogen bonded, which leads to enough delocalization, yet it has strong localized features such as electrons in the carbonyl groups which contribute significantly to nonlinear response and it is reported that urea molecule forms an extensively hydrogen bonded host structure and combines with L-malic acid and L-tartaric acid to form interesting NLO materials [6, 7]. Krishnan *et al.* have reported about the growth and studies of urea succinic acid crystal [8]. It is reported that urea can be combined with oxalic acid in two ways forming two compounds viz., mono-urea oxalic acid and di-urea oxalic acid. The crystal structure of mono-urea oxalic acid and di-urea oxalic acid crystals have been solved and reported in the literature [9, 10]. It is revealed that organic and inorganic dopants can alter various properties of NLO crystals and hence it is decided to add glycine, a basic amino acid, into mono-urea oxalic acid crystals. Normally, organic NLO crystals could be grown by melt, by vapour or by solution [11-14]. Due to simplicity, glycine doped mono-urea oxalic acid crystals have been grown by solution method with slow evaporation technique. This paper reports the details of crystal growth and characterization of glycine doped mono-urea oxalic acid (GMUOA) crystals.

EXPERIMENTAL FOR CRYSTAL GROWTH

In this work, undoped mono-urea oxalic acid (MUOA) salt was synthesized using AR grade urea and oxalic acid in doubled distilled water by stiochiometric ratio 1:1. Urea was dissolved in water and oxalic acid was added to react with urea. Fully dissolved solution was stirred well for 3 hours to prepare a homogeneous solution. The prepared solution was filtered with Whatmann filter paper and kept for slow evaporation. In a similar manner, 2 mole% of glycine was added into the aqueous solution of mono-urea oxalic acid and the saturated solution was prepared. To control the temperature of the solution constant, a constant temperature bath (accuracy: ±0.01 ^{o}C) was used. After 3 to 4 days, the saturated solution was changed into supersaturated solution and then tiny crystals are formed in the solution. Bulk crystals of glycine doped mono-urea oxalic acid were harvested after a growth period of 30-35 days. The grown crystal of glycine doped MUOA crystal is shown in the diagram 1.

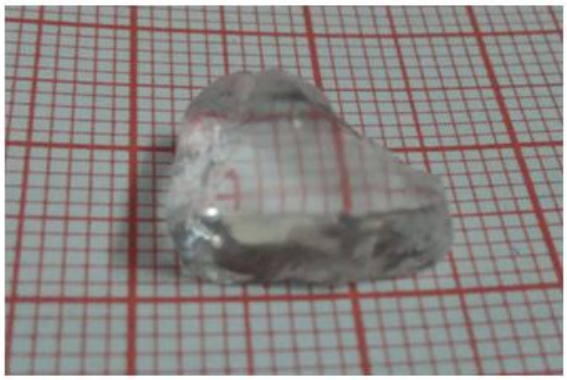

Fig.1. Photograph of glycine doped MUOA crystal

RESULTS AND DISCUSSION

MEASUREMENT OF SHG EFFICIENCY

The grown crystal of glycine doped MUOA was crushed into powder with the particle size of about 200-225 microns and was subjected to Kurtz-Perry powder technique [15] to find the second harmonic generation (SHG) efficiency. A Q-switched and Nd: YAG laser (1064 nm, Quanta ray series) was used as laser source. The second harmonic generation (SHG) behaviour of the sample was confirmed from the output of the laser beam having the green emission (λ=532 nm) and thus the sample is the potential materials for frequency conversion. The same procedure was used to test for the reference sample viz., potassium dihydrogen phosphate (KDP) crystal. Here it is to be mentioned that the size of KDP was kept almost the same as that of glycine doped MUOA sample. From the results, it is observed that the relative SHG efficiency of glycine doped MUOA crystal is 0.72 times that of KDP. The relevant SHG data for undoped MUOA, glycine doped MUOA and KDP are provided in the Table 1.

Table 1: SHG data for undoped mono-urea oxalic acid (MUOA), glycine doped MUOA and KDP samples

S.No.	Name of the Sample	Output Energy (milli joule)	Input Energy (joule)	Relative SHG efficiency
1	MUOA crystal	7.48	0.70	0.84
2	Glycine doped MUOA crystal	6.33	0.70	0.71
3	KDP (Reference)	8.91	0.70	1

FINDING THE LATTICE PARAMETERS BY XRD METHOD

X-ray diffraction (XRD) method is the best method to find the lattice parameters and hence the crystalline structure of the crystalline samples. XRD diffraction method can be classified into single crystal XRD and powder XRD methods. Since the sample in this work is in the form of single crystal, single crystal XRD method is used to find the crystal structure. A single crystal X-ray diffractometer with MoK_α radiation was adopted to find the lattice constants. A good quality and small- sized crystal of glycine doped MUOA was selected from the harvested crystals and it was subjected to single crystal XRD studies to obtain the required data. The obtained single crystal XRD data for the sample are a = 6.655 (3) Å, b = 13.104(2) Å, c = 6.865(5) Å, $\alpha = 90^o$, $\beta = 94.04\ (3)^o$, $\gamma = 90^o$ and V = 597.18(4) $Å^3$. From these data, it is confirmed that the grown glycine doped MUOA crystal has the monoclinic structure.

OPTICAL STUDIES

Linear optical stuides were carried out for the polished crystal of glycine doped mono-urea oxalic acid using a UV-visible spectrophotometer in the wavelength regiion 190-1100 nm. The recorded transmittance of the sample is shown in the figure 2. The absorption coefficient of the was determined using equation $\alpha = [2.303 \log_{10} (1/T)]/d$ where T is the transmittance and d is the thickness of the crystal. The plot of absorption coefficient versus wavelength for glycine doped mono-urea oxalic acid crystal is shown in inset of the figure 3. The optical transmittance is about75% in the visible region of the spectrum and it is very low at 244 nm and it is called as the UV cut-off wavelength of the sample. The absorption coefficient is observed to be low in the visible region of the spectrum. The optical band gap value of the sample was obtained using the Tauc's plot and this plot was drawn using the Tauc's relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ where E_g is the optical band gap of the crystal, h is the Planck's constant, ν is the frequency of light, α is the linear absorption coefficient and A is a constant [16,17]. The optical band gap of GMUOA crystal obtained from the Tauc's plot is 5.09 eV. The measurement of extinction coefficient is important for NLO crystals and it is calculated using the formula $K = \alpha\lambda / 4\pi$ where α is the absorption coefficient and λ is the wavelength of the light. The plot of extinction coefficient versus optical energy is shown in the figure 4. The result show that the extinction coefficient is very low in the visible region and it is high in the UV region especially at the fundamental absorption.

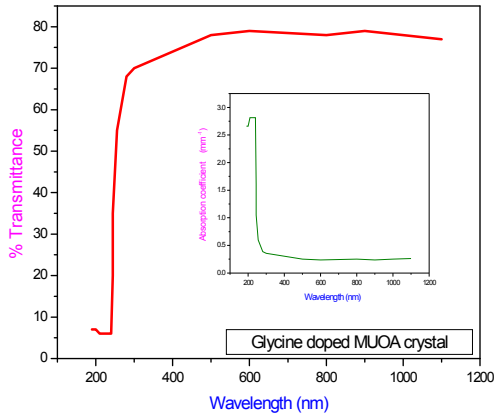

Fig.2.UV-visible transmittance spectrum of glycine doped MUOA crystal, Inset: Plot of absorpttion coefficient versuls wavelength for the same sample

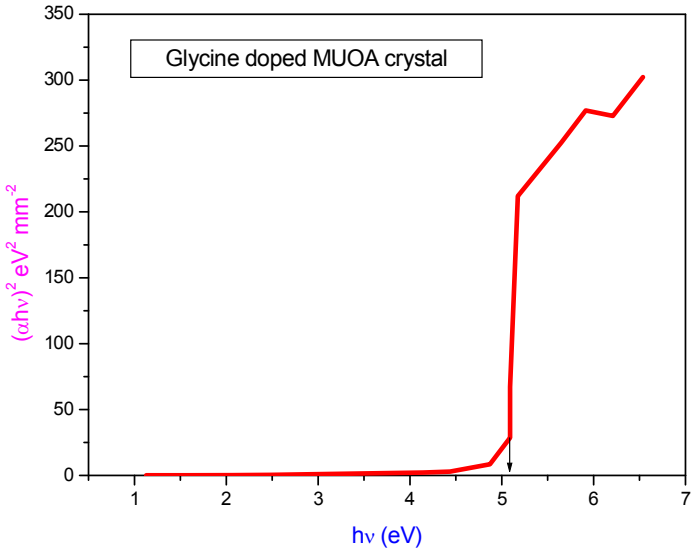

Fig.3. Tauc's plot for glycine doped mono-urea oxalic acid crystal

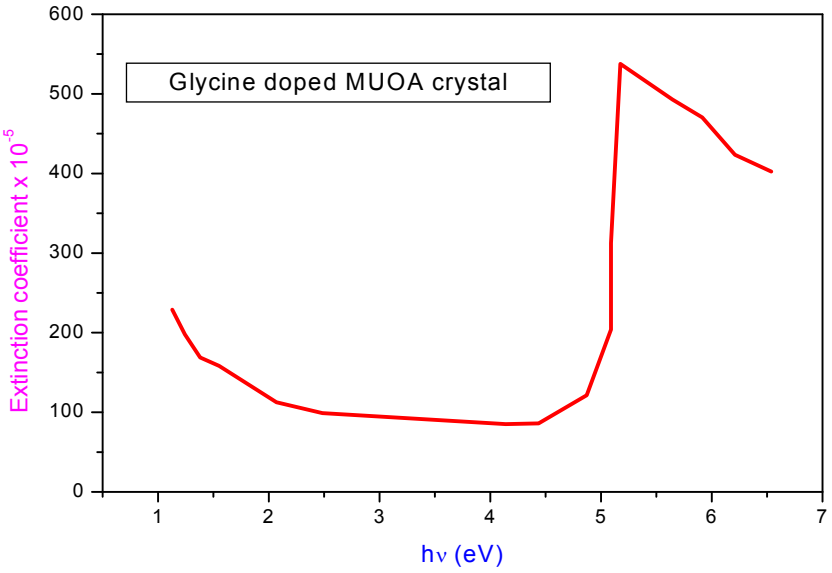

Fig.4.Plot of extinction coefficient versus optical energy for glycine doped MUOA crystal

MICROHARDNESS STUDIES

Hardness is one of the mechanical parameters and it depends on the parameters like lattice energy, Debye temperature, heat of formation and interatomic spacing. Measurement of hardness is a non-destructive testing method and this measurement is useful for device fabrication. Since low loads are applied on the soft crystalline sample for checking the mechanical strength, the corresponding hardness is called as the microhardness. The measurement of microhardness of glycine doped mono-urea oxalic acid crystal was done using a Vickers microhardness tester at room temperature. A good quality crystal without a crack or fault was selected from the heap of the harvested crystals and it was used for this study. The crystal was mounted properly on the base of the microscope. Now, the selected crystal was indented gently by loads varying from 20 to100 g for a period of 10 s using Vickers diamond indenter attached to an incident ray research microscope. The average value of the diagonals of indentation (d) on the sample was measured using the eyepiece of the microscope. The Vickers hardness (H_v) number at different loads was determined using the formula $H_v = 1.8544\ P/d^2$ where P is the applied load. The plot of microharohardness versus the applied load is presented in the figure 5. The hardness number increases with increase of the applied load and this is due to the reverse indentation size effect. Due to crack formation at the applied load of 75 g, there is slight decrease of hardness at the applied load of 100 g. Due to formation of crack on the crystal at 75 g, the hardness test was not carried out beyond 100 g.

To find the work hardening coefficient, the Meyer's law $P = k_1 d^n$ is used. Here, k_1 is the material constant; n is the Meyer's index or work hardening coefficient [18]. If logarithm is taken on both sides, the equation is changed to $\log P = \log k_1 + n \log d$. Hence, a plot is drawn between log P versus log d (Fig.6) and the work hardening coefficient (n) is found out. The obtained value of work hardening coefficient for glycine doped MUOA crystal is 2.594. Since this value is more than 1.6, the grown doped crystal belongs to the soft material category. After every indentation, the sample will revert to the elastic process, a correction factor 'x' must be introduced in the Meyer's law and it is given by $P = k_2 (d+ x)^2$. This law is known as the Kick's law [19]. According to Kick's law, n is less than 2 for normal indentation size effect (NSE) behavior and n is greater than 2 for reverse indentation size effect (RISE). If n is equal to 2, the hardness is independent of applied load. When Meyer's law and Kick's law are combined, the relation obtained is given below.

$$d^{n/2} = (k_2/k_1)^{1/2} d + (k_2/k_1)^{1/2} x$$

The above equation is an equation of straight line with the slope of $(k_2/k_1)^{1/2}$ and with the intercept of $(k_2/k_1)^{1/2}$ x. A plot is drawn between $d^{n/2}$ and d and it is presented in the figure 7 and the values x, k1 and k_2 are obtained using this graph and these values are given in the Table-2.

The nonlinear hardness behaviour of the crystals can be explained by Hays-Kendall's relation P= W + Ad2 where P is the applied load, d is the average diagonal indentation length, W is the minimum load to initiate plastic deformation in gram or resistance pressure, A is the load-independent constant [20]. The values of W and A are obtained from the plot drawn between P versus d^2 as shown in the figure 8. The obtained values of W and A are – 14.382 g and 0.0626 respectively. Since these values are negative, the samples exhibit behaviour of reverse indentation size effect. The corrected size independent hardness (H_o) is determined using the relation H_o=1.8544 A. The evaluated value of H_o for glycine doped MUOA crystal is 0.1161 g/μm^2.

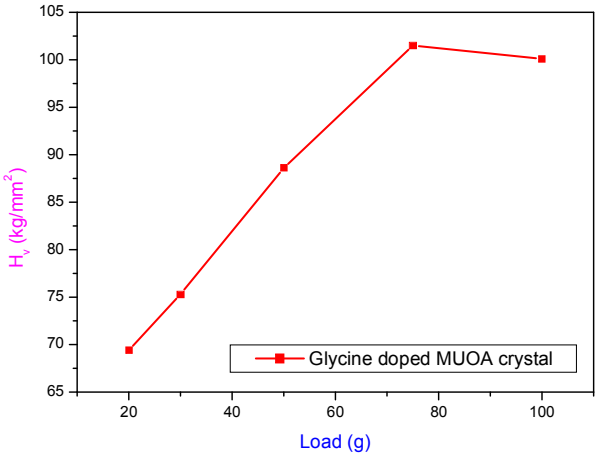

Fig. 5. Plot of H_v versus applied load for glycine doped MUOA crystal

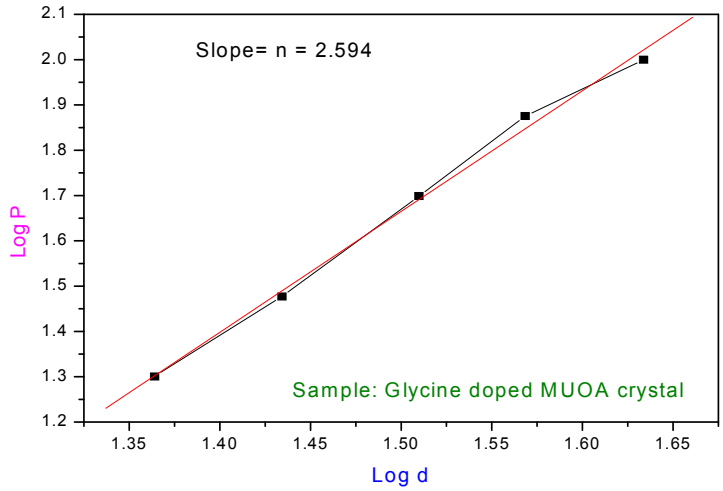

Fig.6. Plot of log P versus log d for glycine doped MUOA crystal

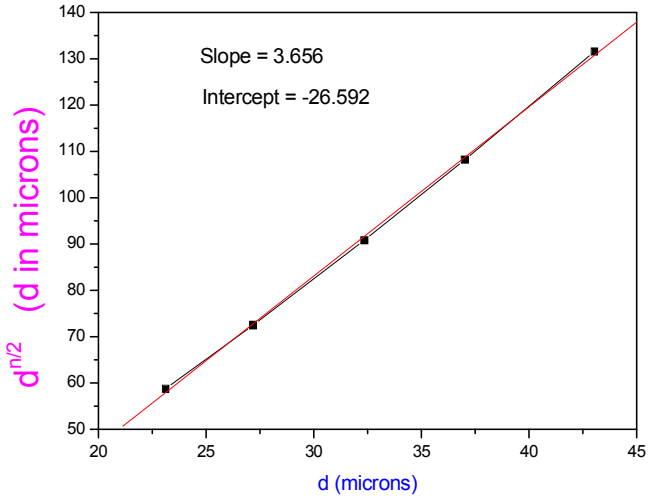

Fig.7. Plot of $d^{1/2}$ versus d for glycine doped MUOA crystal

Table 2: Values of n, k_1, k_2 and x for glycine doped MUOA crystal

Work hardening coefficient (n)	k_1 (10^6 kg/m^2)	k_2 (10^6 kg/m^2)	x (μm)
2.594	95.382	1.271 x 10^3	- 7.267

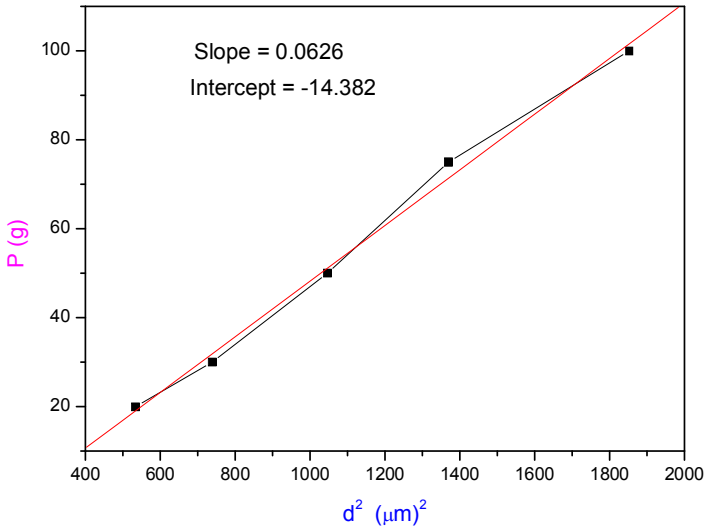

Fig.8. Plot of P versus d^2 for glycine doped MUOA crystal

CONCLUSIONS

Glycine doped mono-urea oxalic acid (GMUOA) crystals were grown by solution method. Single crystal XRD method was used to find the crystal structure as monoclinic. SHG efficiency of GMUOA crystal is

found to be 0.71 times that of KDP sample. The cut-off wave length of the sample is found to be 244 nm and using the Tauc's plot the optical band gap was estimated to be 5.09 eV. The absorption coefficient and extinction coefficient of the sample were determined using the UV-visible spectral studies. Using the microhardness studies, the hardness is found to be increasing with increase of the applied load and hence the sample exhibits reverse indentation size effect. Using the Meyer's law and Kick's law, the work hardening coefficient, the correction factors of the sample were estimated. Using the Hays-Kendall's approach, the resistance pressure and the load-independent constant of GMUOA crystal were found.

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REFERENCES

1. D.F. Eaton, Science 253 (1991) 281.
2. P.V. Kolinsky, Opt. Eng. 31 (1992) 1676.
3. K. Meera, R.Muralidharan, R. Dhanasekaran, PrapunManyum, P. Ramasamy, J. Crystal Growth 263 (2004) 510-516.
4. K. Ambujam, K.Rajarajan, S. Selvakumar, J. Madhavan, Gulam Mohamed, P. Sagayaraj, Optical mater.29 (2007) 657-662.
5. D. Sajan, N. Vijayan, K. Safakath Reji Philip, Hubert Joe, Jr. Phys. Chem. A. 115 (2011) 8216 -8220.
6. F. Q. Meng, M.K. Lu, Z. H. Yang, and H. Zeng, Mat. Let. 33 (1998) 265-268.
7. E. De Matos Gomes, V. Venkataramanan, E. Nogueira, M. Belsely, E. Proenca, A. Criado, M.J. Dianez, M.D. Estrada, S. Perez-Garrido, Syn. Metals 115 (2000) 225- 228.
8. S. Krishnan, C. Justin Raj and S. Jerome Das, Jr. Cry. Grow. 310 (2008) 3313-3317.
9. S. Harkema and J.H.M. Jer Brake, Acta Cryst. B35 (1979) 1011-1-13.
10. S. Harkema, J.W. Bats, A.M.Weyenberg, D.Feil, Acta Cryst. B28 (1972) 1646.
11. B.J. Mc Ardle, J.N. Sherwood, A.C. Damask, J. Cryst. Growth. 22 (1974) 193.
12. M. Arivanandhan, K. Sankaranarayanan, K. Ramamoorthy, Sanjeeviraja, P. Ramasamy, Thin Solid Films 477 (2005) 2.
13. S. Ayers, M.M. Faktor, J. Mater. Sci. 7 (1972) 31.
14. M.D. Aggarwal, R.B. Lal, Rev. Sci. Instrum. 54 (1983) 772.
15. S.K. Kurtz, T. Perry, J. Appl. Phys. 39 (8) (1968) 3798–3813.
16. J.Tauc, Amorphous and Liquid Semiconductors Plenum, New York (1974).
17. Abu El-Fad A, Soltan I A S and Shaalan N M, Cryst. Res. Technol., 42 (2007) 364.
18. E.Meyer, Z.Ver, Dtsch.Ing.52 (1908) 645-654.
19. F.Kick, Das Gesetzder, Proportionalen Widerstande Und Science Anwendung, Felix, Leipzig (1885)
20. C. Hays, E.G. Kendall, An analysis of Knoop microhardness, Metallography, 6(1973) 275–282.