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# Growth, Dislocations and Hardness studies of a nonlinear Optical Crystal-Glycinium Oxalate

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### Abstract

Single crystals of glycinium oxalate (GOX) were grown from aqueous solution by employing slow evaporation method at room temperature. Bulk crystals of good quality with dimensions 16 mm x 15mm x 4mm were grown by suitable growth conditions. The grown crystals were confirmed by X-ray diffraction studies and Fourier transform infrared spectra. Dislocation density of the grown samples was estimated using chemical etching technique. The UV-Vis transmittance spectrum indicates that the material has wide optical transparency (62%) in the entire visible region. The Kurtz powder test indicates the second harmonic generation efficiency of GOX is 75% that of KDP crystal. The mechanical strength of these crystals has been studied by using Vicker's microhardness tester. The load independent hardness value is 42 kg/mm<sup>2</sup>.

Keywords: Crystal growth; Defects; Microhardness.

## Introduction

Nonlinear optical (NLO) materials have been playing a vital role in industrial applications. These materials show a significant impact on laser technology, optical communications and optical data storage etc<sup>1</sup>. Crystals of amino acid complexes with the simple inorganic salts<sup>2</sup> exhibit interesting physical properties from the application point of view. Hence in the recent years much of the work has been aimed at synthesizing semi-organic NLO crystals in particular glycine complexes, with better chemical stability, SHG efficiency, laser damage threshold, thermal and mechanical properties. Some of these complexes viz. tri glycine sulphate<sup>3</sup>, bis glycine manganese chloride dehydrate<sup>4</sup>, tri glycine selenate<sup>5</sup> and glycine silver nitrate<sup>6</sup> are known to have ferro-electric properties. Further, it is reported in the literature that glycine combines with Li<sub>2</sub>SO<sub>4</sub><sup>-7</sup>, HCl<sup>8</sup>, HF<sup>9</sup>, LiCl<sup>10</sup> exhibiting NLO properties. A comprehensive literature survey suggests that there are only two reports<sup>11,12</sup> on the growth and characterization of glycinium oxalate (GOX) crystal. The present communication emphasises the growth, thermal, UV-Vis. transmittance and hardness studies. We are presenting a brief report on dislocation studies with several etchants.

# Methodology

GOX was synthesised by taking glycine and oxalic acid in equimolar ratio1:1 [11] as follows.  $C_2H_5NO_2 + H_2C_2O_4 \rightarrow C_2H_6NO_2^+ \cdot C_2HO_4^-$  The composition was thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature. Good quality crystals of 16 mm x 15mm x 4mm dimensions were obtained over a period of 13days as shown in figure 1. The average growth rate of these crystals along <110> was found to be 0.323mm per day.



Figure-1 As-grown crystals of GOX

There is meagre information on solubility of this compound, the solubility data has been prepared at the temperature ranging from 30 to 55 °C (interval of 5°C) by employing the following procedure<sup>13,14</sup>. At each temperature 50 mL of slightly undersaturated solution is prepared by adding known amount of the synthesized salt (M1) dissolved in deionized double distilled water. A seed crystal of known mass is introduced into the growth cell<sup>15</sup> and observed continuously under a microscope. Initially the crystal starts dissolving and after some time when equilibrium is reached, recovery starts. At this stage, the crystal is withdrawn and again its mass is determined. The difference in the initial and final masses gives the amount dissolved in the solution (M2). Now, the mass of the salt (M1) plus the amount of mass of the crystal dissolved in the solution (M2) give the solubility. For each temperature, the above process is repeated 4 to 5 times and the average value is taken as the solubility at that temperature. The solubility data has been prepared by the above process and the solubility diagram for GOX is shown in figure 2.



Solubility curve of GOX

#### **Results and Discussion**

Confirmation studies: Powder X-ray diffraction (PW 1830 Philips analytical powder X-ray diffractometer with CuKa radiation of wavelength 1.5418 Å) and Fourier transform infrared (Perkin-Elmer BX I system spectrometer in the middle IR region (400-4000 cm<sup>-1</sup>) studies were made on the crystals to know the structure and functional groups respectively. These reports were well in good agreement with the earlier reports<sup>11</sup>.

Dislocation studies: To study the dislocation density on these crystals chemical etching technique has been employed. In view of the meager information on etching studies, a number of etchants were tried on these crystals as shown in table-1. Good etching action was observed with formic acid (etching time of 60

sec.) and methanol (etching time of 120 sec.). Figure 3 (a and b) shows the etch pattern observed with these etchants on (110) faces of GOX crystal. The etch pits are more or less elongated triangular in shape. The pits are not uniformly distributed, with a higher density at the edges. The average density of dislocations is found to be about  $4 \times 10^{5}$ /cm<sup>2</sup>. Figure 3c shows the polishing action of GOX crystal surface with orthophosphoric acid.

Table-1	
Action of various etchants on (110) face of GOX crysta	al

Etchant	Action
Methanol	Well-defined etch pits
Ethanol	No etching
Acetic acid	No etching
Formic acid	Well-defined etch pits
Acetone	No etching
Orthophosphoric acid	Polishing action

Microhardness studies: The mechanical strength of a material is usually determined by indentation microhardness test, which provides information on the strength and deformation characteristics<sup>16</sup> and yield stress<sup>17</sup>. Traditionally microhardness is defined as the ratio of applied indentation load to the contact (or projected) area of the resultant indentation impression. Now a days, it is well accepted as the resistance offered by the crystal lattice to the motion of dislocations, deformation or damage under an applied stress<sup>18</sup>. With the development of new material for industrial applications particularly in semiconductors, optoelectronic devices etc. the study of hardness has become quite essential.

In view of this Vickers hardness  $(H_v)$  measurements were made on (110) face of GOX crystals,  $H_{\nu}$  is calculated by following equation:

$$H_{\rm v} = 1854.4 \, (P/d^2) \, {\rm Kg/mm}^2$$
 (1)

Where 'P' is load applied in 'g' and 'd' is the diagonal length of the impression in microns  $(\mu)$ . The variation of hardness with the applied load is shown in figure-4a. In the figure initially hardness value increases up to a load of 35 g and attains a load independent value of 42 Kg/mm<sup>2</sup>. This shows the reverse indentation size effect (reverse ISE) of the crystals. The relation between applied load and the diagonal length can be represented by Mayer's law as follows; Р

$$P = ad^n$$
 (2)

Where n is the Mayer index number. n value is evaluated by drawing linear regression plot between  $\ln P$  and  $\ln d$  shown in figure-4b. From the careful observations of Onitsch<sup>19</sup> and Hanneman<sup>20</sup> on various materials, pointed out that 'n' lies between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials. The value of 'n' obtained for GOX is 1.788. Hence GOX belongs to softer material category.





C Figure-3 Etch pit pattern on (110) face of GOX with a) Formic acid (e.t.~60 sec.) b) Methanol (e.t.~120 sec.) and c) Orthophosphoric acid (Polishing action)





Plots of a) variation of Vickers hardness with load and b) ln *P* against ln *d* for (110) GOX crystals

**Second Harmonic Generation (SHG) studies:** GOX crystal nonlinear optical property was carried out by Kurtz SHG test. Fine powder sample of the crystal is densely packed between two transparent glass slides and is irradiated with Nd:YAG laser beam of wavelength 1064nm. The emission of green radiation from the sample confirms the second harmonic generation in the crystal. The second harmonic generation efficiency of GOX was compared with KDP. The SHG output of KDP was 31 mV where as for GOX it is observed to be 25 mV at given pulse energy of 2.5 mJ/s.

**Differential scanning calorimetry:** Differential scanning calorimetry (DSC) study was performed using Mettler Toledo in the temperature range 25-500°C at a heating rate of 10 °C/min in the Nitrogen atmosphere. Sample of 12.71 mg was placed in an alumina crucible. The GOX crystal is stable upto its melting point 177.58 °C and no phase transition was observed upto this temperature as shown in figure-5.

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**UV-Vis Studies:** UV-Vis studies were recorded in the range of 200 -650 nm by Perkin-Elmer (Lambda 25) spectrophotometer. Figure-6 shows the transmittance spectra of GOX crystal. From the figure, it can be observed that the conventional grown GOX crystal has transmittance up to 62 % in the higher wavelength region, with a lower cut off wavelength at 230 nm.



Figure-6 UV-Vis. Spectra of GOX crystal

# Conclusion

GOX single crystals of dimensions 16 mm x 15mm x 4mm were grown over a period of 13 days with average growth rate of 0.323 mm/day by slow evaporation method. Dislocation studies indicate that the etch pits are not uniformly distributed. The average dislocation density is  $4 \times 10^5$ /cm<sup>2</sup>. The load independent value on (110) face of GOX is 42 Kg/mm<sup>2</sup> and the Mayer Index (n=1.788) confirms GOX to be a soft material. The SHG efficiency of GOX is 75% that of KDP crystal. Sample is stable upto 177.58  $^{\rm o}C$  which is the melting point of the crystal. The transmittance percentage of GOX crystal was found to be 62 %.

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