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OPTICAL AND MECHANICAL CHARACTERIZATION OF SOLUTION GROWN SEMI ORGANIC NLO CRYSTALS.

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ABSTRACT

The present fascinating field of research is to synthesize, grow and characterize semi organic NLO crystals. Here an attempt has been made to synthesize and grow number of NLO semi organic crystals. The semi organic crystals posses both the good qualities of host organic material and additive-inorganic material. The crystals grown are amino acid- γ-Glycine with additives namely, Potassium Nitrate, Sodium Nitrate, barium Nitrate, Ammonium Oxalate and Ammonium Chloride. Good crystals were obtained in a period of 3-4 weeks. Most of the crystals were transparent. The SHG efficiency has been tested by the Kurtz powder technique using Nd: YAG laser, and KDP sample has been used as a reference material. Since hardness play a key role in device fabrication and NLO materials are expected to play a major role in photonics as well as optical information processing, the present work pertains to mechanical characterization and SHG studies. The smooth surfaces of grown crystals were subjected to Vicker's hardness for duration of 5-10seconds indentation time at room temperature. Load ranging from 5gms to 20gms were applied over a fixed interval of time. The micro hardness H and Mayer's index n has been estimated. The value of Meyer's index for various samples investigated falls below 1.6 suggests that crystals are hard or moderately soft. This behavior has increased with additives. Also, SHG efficiency for the grown crystals and laser damage threshold studies have been carried out using Q switched Nd: YAG laser for 10 nano seconds laser pulse width at a wavelength of 1064nm. The value obtained for laser damage threshold is due to lower/ moderate hardness seen by Vicker's measurements. Plots of Hv, Mayer's index n, as a function of load P, are shown graphically.

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Key words: SHG, Laser damage, Semi organic, NLO, Micro hardness.

INTRODUCTION

Non linear optical materials are expected to play a major role or prominent role in the technology of photonics including optical information processing and frequency conversion [1, 2, 3]. Most of the organic non linear optical crystals usually have poor mechanical and thermal properties. They are susceptible for damage during the processing even though they have large NLO efficiency. In the present study we have made an attempt to grow number of semi organic non linear crystals of γ-Glycine with Potassium Nitrate, Sodium Nitrate, Barium Nitrate, Ammonium Oxalate and Ammonium Chloride as an additive by aqueous solution method. Mechanical characterization, SHG and laser damage studies have been carried out.

Crystal growth and characterization

Analytical reagent (AR) grade samples were used. Salts were taken in their molar mass, separately and then mixed together. Supersaturated solutions of the mixed salts were kept for slow evaporation in beakers covered with filter paper at room temperature.

The selected combinations are:
Glycine+ Potassium Nitrate (GPN Crystal)
Glycine + Sodium Nitrate (GSN Crystal)
Glycine + Barium Nitrate (GBN Crystal)
Glycine + Ammonium Oxalate (GAO Crystal)

Glycine + Ammonium Chloride (GAC Crystal)

Most of the crystals were transparent. Good transparent crystals were obtained in a matter of 3 to 4 weeks shown in figures 1 to 5. The crystals were characterized on the basis of XRD, FTIR, UV-Vis- IR optical measurements. Also, the above crystals have responded well for second harmonic generation (SHG) efficiency.

Fig.-1: GPN Crystal

Fig.-2: GSN Crystal

Fig.-3: GAOCrystal

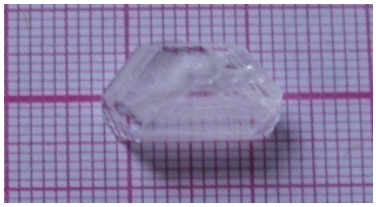

Fig.-4: GBN Crystal

Fig.-5: GAC Crystal

RESULTS AND DISCUSSION

SHG efficiency

Kurtz and Perry [4] powder method is an important tool for researchers searching for organic/semi organic/inorganic NLO material. The experimental setup used in the present investigation was similar to the generic one devised by Kurtz[5]. It consisted of a Q-switched Nd: YAG laser, the output of which was filtered through 1064nm narrow pass filter.

The power of the fundamental beam was monitored by a split beam technique, in one channel of the power meter. The sample was ground in the form of fine powder of known grain size and pressed between two glass plates. The sample size was kept larger than the beam cross section. The generated harmonic was passed through a 532 nm narrow pass filter and fed to other channel of the power meter. The ratio of the fundamental and harmonic intensities determines the efficiency of the sample. To eliminate the experimental error, urea sample of the same size was also tested in the same setup and the efficiency was evaluated as a ratio. The input power of the laser beam was measured to be 16.5 mJ/ pulse. Pure KDP was used as reference sample. Both the reference and test samples had uniform particle size of 130 to 150microns.The experiment was carried out in pure KDP and later in all the samples. Throughout the experiment the laser power was kept constant.

Table-1: SHG efficiency

Semi organic Crystal	SHG signal (mV)	Efficiency with respect to KDP
γ -Glycine+Potassium Nitrate	6.8	0.98
γ -Glycine + Sodium Nitrate	9	1.35
γ -Gycine + Barium Nitrate	0	0
γ -Gycine + Ammonium oxalate	10.2	1.48
γ -Gycine + Ammonium chloride	6	0.85

Results show that SHG efficiency of γ-Gylcine containing alkali nitrates answer for higher efficiency compared to KDP. To exhibit NLO activity, the additives present in the host material (γ-Glycine) have to be macroscopically aligned, then only there can be increase in efficiency, justified experimentally [6]. Among the samples studied, crystals namely Glycine with Sodium Nitrate, γ-Glycine with Potassium Nitrate have answered for higher efficiency. Whereas crystal containing ammonium oxalate has resulted in excellent efficiency taking KDP as reference. The best additive to organic material works out to be Ammonium Oxalate. Next in the series happens to be Sodium Nitrate. These additives are favoring SHG.
It is surprising that the additives namely Barium Nitrate is acting as poison, not favoring NLO efficiency. In the present study 1% of Barium Nitrate has been used. It is interesting to carry out the work at lower values to know exactly at what amount of the above material starts nullifying the SHG efficiency and making the host crystal lose the NLO property. Definite conclusion regarding the result requires further work on phase matched SHG efficiency of single crystal.

Mechanical properties: micro hardness studies

One of the methods to determine the mechanical behavior of the grown NLO crystals is micro hardness test. The polished surface of the crystals namely, γ-Glycine with Potassium Nitrate, Sodium Nitrate, Barium Nitrate Ammonium Oxalate and Ammonium Chloride were indented at different sites for the load 5gms to 20gms for 10 seconds and the average value of the hardness were found out using M H – 5 hardness tester. The diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope. The micro hardness is calculated using the expression [7]

$$H= 1.8544P/d^2 \text{ kg-mm}^2$$

Where P is the applied load in grams and d is the average diagonal length of the vicker's impression in mm after loading. The micro hardness and the diagonal length were calculated from the micro computer attached to the instrument. Plot of H vs P for the investigated samples are shown in figure 6. The non linear variation of H with load implies the presence of imperfection and voids. The imperfections are mainly impurity, dislocation or grain boundary diffusion.
The Meyers' index number n [8] gives the value of work hardening index. Materials are normally characterized by Meyers' index or work hardening index. The lower the value of the work hardening index better will be the hardness of the material [9, 10, 11]. The value of n comes to be 1 or 1.6 for hard material and more than 1.6 for soft material. The log-log plot between d and P yields almost straight line graph. The slope of the line gives the work hardening index n. The n value obtained for different samples are given in Table 2. These values of work hardening index suggest that materials are harder, whereas, in case of γ-Glycine with Ammonium Oxalate crystal work hardening index is 1.8 which implies that the material is softer.

Table -2: Meyers' index number n

Grown Crystal	n Value
γ-Glycine+ Potassium Nitrate	0.567
γ-Glycine + Sodium Nitrate	0.653
γ-Glycine + Barium Nitrate	0.702
γ-Glycine + Ammonium Oxalate	0.876
γ-Glycine + Ammonium Chloride	1.82

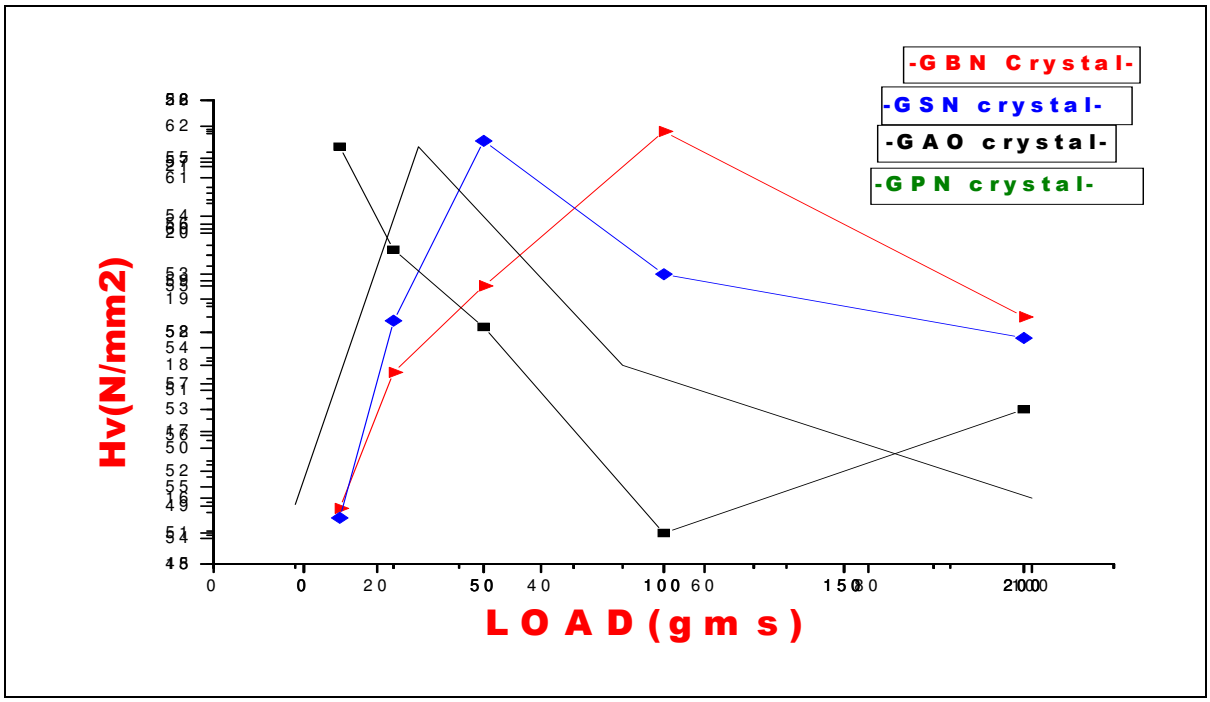

Fig-6: Plot of H vs P of GBN, GSN, GAO, GPN crystals.

Laser damage

The optical damage threshold of an optical crystal is an important factor that hinders its applications. Optical damage threshold studies have been carried out for the solution grown γ-Glycine with Potassium Nitrate single crystal using Q switched Nd: YAG laser of pulse width 10 nano seconds and repetition rate of 10Hz operating in (TEM_{OO}) mode, is used as the source. The laser beam was focused and the sample was moved step by step into the focus along the optical axis of the crystal. The energy density was calculated using the formula, energy density=E/A (GW/cm^2), where E is the input energy measured in milli joules and A is the area of the circular spot [12]. In the present study the laser damage threshold energy density for γ-Glycine Potassium Nitrate crystals was found to be 12.41 GW/cm^2.

CONCLUSIONS

Good quality crystals were obtained in a period of 3 to 4 weeks by slow evaporation method. XRD confirms crystalline nature. UV-Vis-IR spectrum confirming the transparent nature in the visible region. FTIR confirms the identity of the grown crystals. All the grown crystals have responded well for second harmonic generation efficiency (SHG). Amino acid- γ -Glycine with additives namely, Potassium Nitrate, Sodium Nitrate, Barium Nitrate, and Ammonium Chloride are hard materials whereas γ –Glycine with Ammonium Oxalate haven proven to be a soft material. Laser damage value reveals that the crystal is having moderate laser damage threshold.

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