Studies on the Structural, and Hardness in Bis Glycine Maleate Crystal

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Abstract: ***A single crystal of bis glycine maleate have been grown from aqueous solution by slow evaporation method by optimizing the growth parameters within a period of 45 days. From the x-ray diffraction the crystal was found to be crystallize in hexagonal structure with a=7.402 Å, b=7.04 Å, c= 5.48 A and α=β=90 °,γ =120 °.The functional group was confirmed in FTIR analysis. Values of work hardening coefficient were determined from micro hardness studies and confirmed that the grown crystals belong to the category of soft materials. The results have been discussed in detail.***

Keywords: Solution growth method, X-ray diffraction, FTIR, Microhardness.

1. Introduction

Since 1961, when the nonlinear optical (NLO) phenomenon was observed for the first time, NLO frequency conversion materials have played more and more important role in many fields, such as laser technology, optical communication, optical data storage etc. [1]. In the context of NLO, organic materials have advantages such as large NLO coefficients and structural diversity or flexibility, compared to the inorganic counterparts [2]. They also have some inherent drawbacks, for example, poor physico-chemical stability and low mechanical strength. As a result, the quest for new frequency conversion materials is presently concentrated on semi-organic crystals due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [3–5].

Semi-organics include organic–inorganic salts and metal–organic coordination compounds [6]. Among the organic materials amino acids constitute a family in which glycine is the simplest of all the amino acids. It has been reported that some complexes of amino acids with simple inorganic salt may exhibit ferroelectric properties [7–9]. Some complexes of glycine with CaCl2 [10], BaCl2 [11], H2SO4 [12] and CoBr2 [13] form single crystals but none of these are reported to have nonlinear optical property. Single crystals of glycine sodium nitrate [14], glycine lithium sulphate [15] and benzoyl glycine [16] showed non-centrosymmetry and their quadratic nonlinear coefficients were examined.

In the present investigation, a new organic compound of glycine with maleic acid, a dicarboxyclic acid with relatively large π- conjugation was synthesized in the alkaline medium of 10% ammonium hydroxide solution. The bulk single crystals of BGM have been grown by slow cooling method and the grown crystals were subjected to structural, Optical and mechanical property studies.

2. Experimental Procedure

The analytical-grade glycine and maleic acid in the molar ratio 2:1 were taken as the starting materials for synthesizing BGM. The calculated amount of glycine was first dissolved in the alkaline medium of 10%ammonium hydroxide solution. Then, maleic acid was added to the solution slowly with continuous stirring at a temperature slightly more than the room temperature. The prepared solution was left to dry at room temperature. The BGM salt was obtained after two days. The purity of the synthesized salt was improved by successive recrystallization process. The reaction mechanism of the chemical synthesis is as follows.

$$2(NH_2CH_2COOH) + COOH - CH = CH - COOH \rightarrow HOOC - H_2C - NH_3^{+}COO^{-} - C$$

Bis Glycine   Maleic acid

$$= CH - COO^{-}NH_3^{+} - CH_2 - COOH$$

Bis Glycine maleate

Ammonium hydroxide was found to be a better solvent for growing single crystals of BGM because of its high solubility and low evaporation rate. Good quality crystals were obtained within 45 days as shown in Fig: 1.

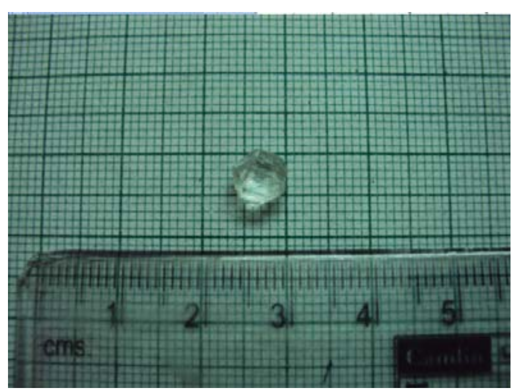

Figure 1: Grown BGM crystal

3. Characterization

3.1. X-Ray Diffraction Studies

Single crystal X-ray diffraction study was carried out on the BGM single crystal with ENRAF NONIUS CAD4 diffractometer. From this study, the lattice parameter values of BGM crystal were found to be a=7.402 Å, b=7.04 Å, c= 5.48 Å and $\alpha=\beta=90°$, γ =120° .This indicates that BGM crystallizes in hexagonal system. X-Ray diffractogram of the crystal was recorded on the XPERT-PRO diffractometer using CuKα radiation (λ=1.540598). Hence, the single crystal of BGM satisfies the prime requisite for the material to possess nonlinear optical properties

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3.2. FT-IR Spectral analysis

The infrared spectral analysis is effectively used to understand the chemical bonding and it provides information about molecular structure of the synthesized compound. Each and every one chemical compounds have their own typical IR spectrum [17].The FTIR Spectrum of the title material was recorded using the PEFTIR Spectrometer in the wave number range 600-4000 cm^{-1} by KBr pellet method and is shown in the Fig: 2 The intense absorption band at 3107 cm^{-1} is difficult to assign for the overlapping frequencies of (O –H)and (N –H).Because O –H vibrations of water molecule and hydrogen bonds extend to the region near 3200 cm $^{-1}$ .The broad band in the higher energy region between 2169 and 1594cm^{-1} is due to $NH3^{+}$ Bending vibrations. The peaks at 1527 cm^{-1} corresponds to NH3 $^{+}$symmetric stretching. These results confirm that the glycine exists in zwitter ionic form in the grown crystal. The involvement of NH3 $^{+}$ in hydrogen bonding is evident from the fine structure of the band in the lower energy region. The absorption bands occur at 885 cm $^{-1}$ corresponding to C –C stretching. On investigation of the absorption bands below 1000 cm^{-1} , COO bending COO rocking are identified at 685 and 502 cm^{-1} ,respectively [18].

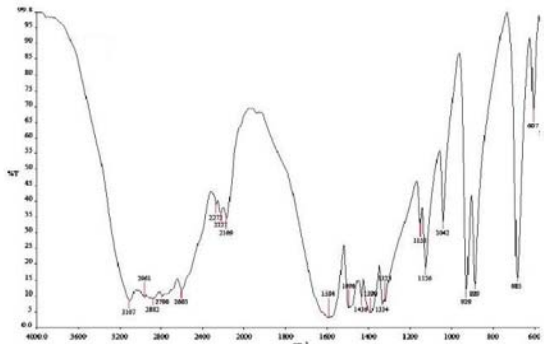

Figure 2: FT-IR Spectrum of BGM crystal

3.3. Microhardness

Mechanical strength of a crystal was studied by measuring micro-hardness and it plays an important role in the fabrication of opto-electronic devices. The hardness of a material is a measure of its resistance to plastic deformation. The permanent deformation can be achieved by indentation, bending, scratching or cutting. This is due to normal indentation size effect (ISE) [19]. It was observed that micro-hardness number increases with increase in load up to 200 g and further increase in load causes cracks formation which leads the decrease in hardness value. This may be due to the release of internal stress.

The plots between log P against log d for BGM crystals are shown in the Fig: 5. The slope of the straight lines of the figure gives the work hardening coefficient (n). The work hardening coefficient (n) for BGM crystal is found to be 1.85 which is in good agreement. According to Onitsch [20], if n is greater than 1.6, the microhardness number increases with increase in load. Since the obtained values of BGM is more than 1.6, the grown crystals of this work belong to the category of soft materials and hardness number increases with the load and it is useful for non-linear optical applications

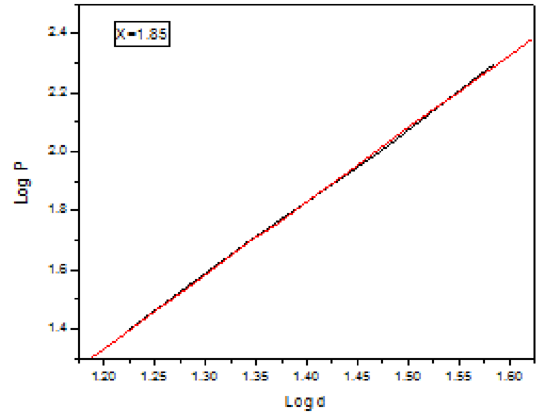

Figure 5: Plots of Log d versus Log P for BGM crystal

4. Conclusion

Optically transparent nonlinear optical BGM single crystal was grown by temperature lowering method from aqueous solution containing glycine, maleic acid and ammonium hydroxide. The single crystal X-ray diffraction studies revealed that the grown crystal of BGM belongs to a hexagonal system. FTIR spectrum confirms the presence of various functional groups of bis glycine maleate and the existence of glycine in zwitter ionic form in the grown crystal has also been identified. The work hardening co-efficient value was calculated to be 1.85, which ensures the good mechanical stability of the grown crystal and it is a soft material which is best used for the non linear optical applications.

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