Article

Growth, dislocations, optical and microhardness studies on bisglycine hydrogen chloride – A nonlinear optical crystal

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Abstract

Single crystals of bisglycine hydrogen chloride (BGHC), a semiorganic nonlinear optical crystal, of dimensions 13×4×4 mm^3 were grown in a period of 10 days. The grown crystals were confirmed by powder XRD, FTIR and DSC studies. For the first time, the defect content present in the crystals was estimated by chemical etching studies. The results indicate that the average dislocation density is about $3.1\times10^3/cm^2$. The UV-Vis. studies indicate that the crystal has a wide transmission range. The optical band gap, extinction coefficient and refractive index were estimated from the optical transmission data. The Kurtz powder test indicates that the second harmonic generation efficiency of BGHC is almost comparable to that of KDP. The load-hardness curves for BGHC were studied over the load range 10-120 g. The anisotropy in hardness was studied using Knoop indentation studies. The mechanical properties of BGHC viz. fracture toughness, brittle index number, Young's modulus and yield strength were also estimated for the first time.

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Introduction

Second harmonic generation (SHG), frequency mixing, electro-optic modulators, optical switches etc. are found to be the some of the important applications of non-linear optical crystals [1-4]. In the recent period many researchers have been aiming to grow such nonlinear optical (NLO) crystals to fulfill the requirements for above applications. Semiorganic single crystals have become potential materials because they possess the advantages of both organic [5] and inorganic materials [6]. In addition to these, they offer high resistance to laser induced damage. Recently, the growth and characterization of bisglycine hydrogen chloride (BGHC), a semiorganic NLO crystal, have been studied [7,8]. It crystallizes in orthorhombic system with space group $P2_12_12_1$ [7]. The main purpose of this communication is to present the results on growth, chemical etching, hardness and efficiency of second harmonic generation of BGHC and to the best of our knowledge there are no reports on chemical etching and load variation of hardness of BGHC.

Crystal growth

Glycine and hydrochloric acid have been dissolved in deionized double distilled water in stoichiometric ratio 2:1. The solution has been stirred well for 5 h at room temperature to remove unwanted nuclei [7]. The prepared saturated solution has been allowed for slow evaporation using a constant temperature bath by transferring it into beakers. Good quality tiny crystals obtained have been used as seeds to grow at a constant temperature 35 ^{o}C. Figure. 1 shows as-grown crystals of dimensions 13×6×4 mm^3 in a period of 10 days with an average growth rate of 1.3 mm/day along the longer edge of the crystal. Further, the grown crystals have been characterized by powder XRD and FTIR. The obtained results are in conformity with earlier reports [7].

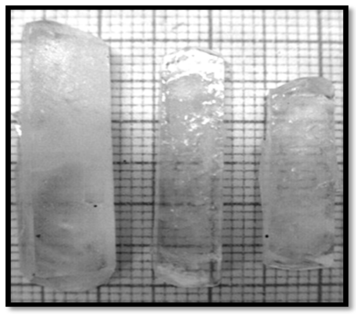

Figure 1. As-grown crystals of BGHC

Results and discussion- Dislocation studies

To study the density and distribution of dislocations in BGHC chemical etching technique has been employed using a Magnus MLX microscope fitted with Motic (1000) camera. As there are meager reports on chemical etching of these crystals several chemical etchants have been tried and formic acid is found to be capable of revealing dislocations. Figure 2 shows the etch pit pattern on (0 1 2) face of BGHC. The shape of the etch pits is elongated rectangular, whose longer sides are parallel to the longer edge of the crystal.

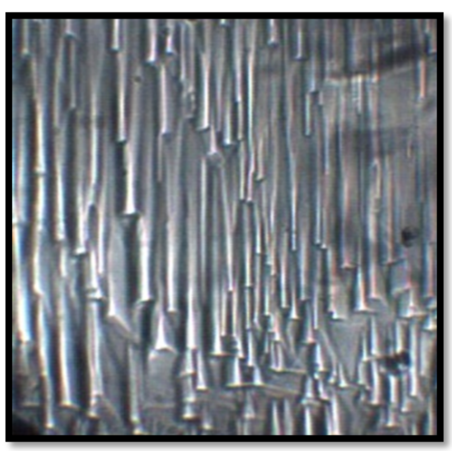

Figure 2. Etch pit pattern with formic acid (90 s) on (0 1 2) face of BGHC

Further, a careful observation on a number of crystals suggests that the distribution of etch pits is not uniform, the density is more at the edges than at other regions of the crystal surface. As BGHC crystals have different faces, they possess growth sector boundaries and also it is known that dislocations can originate from these growth sector boundaries [9]. Perhaps, this may be the reason for more density of etch pits at the edges. The average density of dislocations is about $3.1\times10^{3}/cm^{2}$.

Thermal studies

The thermal studies on BGHC crystals have been carried out using Mettler Toled (DSC 822 e) in the temperature range 25 to 500 ^{o}C at a heating rate of 10^{o}/min in N_2 atmosphere. The DSC thermogram of BGHC is shown in Figure 3. An endothermic peak observed in it at 259.76 ^{o}C can be attributed to the decomposition of the crystal, which is in confirmation with the earlier reports [7]. Further, prolonged heating up to 500 ^{o}C does not produce any significant peaks.

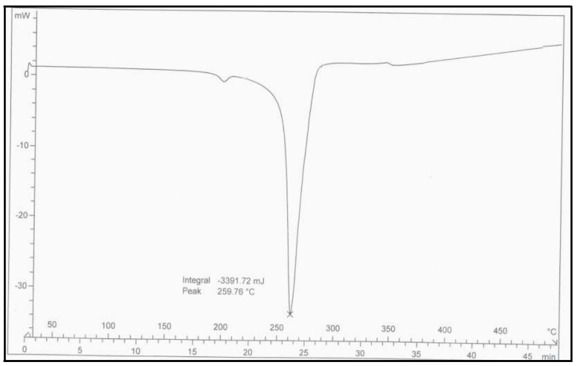

Figure 3. DSC curve of BGHC

Optical studies

The optical transmittance of BGHC has been carried out in the wavelength range 200 to 650 nm using UV-Vis. spectrophotometer. The crystal has a transmittance of 70% in the higher wavelength region with a lower UV cut off at 245 nm as can be seen from Figure 4.

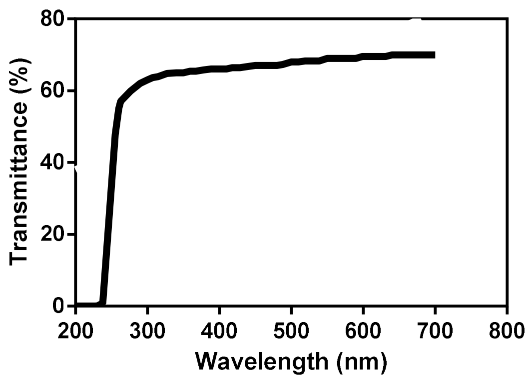

Figure 4. UV-Vis. Spectra of BGHC

To determine the SHG efficiency of BGHC, the output from Q-switched Nd: YAG laser (1064 nm) has been focused on the powdered sample. The pulse energy has been 2.5 mJ/s with a pulse width of about 10 ns. A bright green flash emission from the sample has been observed which indicates the NLO behaviour of the material. The SHG efficiency of BGHC has been found to be almost two times that of KDP [7].

Hardness Studies

The mechanical strength of a material is usually determined by indentation microhardness test, which provides information on the strength and deformation characteristics [10]and yield stress [11]. Microhardness measurements have been made using Leitz-Wetzlar (miniload 2) microhardness tester equipped with a Vickers diamond pyramidal indenter. For these studies, samples with smooth plane surfaces of BGHC on (0 1 2) face were chosen. 10 to 100 g loads have been used with a constant indentation time of 15 sec in all cases. The values of hardness H_v have been estimated using the following expression.

$$H_v = 1.854\ P/d^2 \quad (1)$$

where P is the applied load in kg and d the diagonal length in μm. The load variation of hardness on as-grown faces of BGHC crystal is shown in Figure 5.The figure interprets that hardness initially increases upto 25 g which shows reverse ISE of the crystals. At initial loads, generation and easy propagation of dislocations results in a low value of hardness. The gradual increase of hardness with load may be due to dislocation interaction which slows down the motion of dislocations. The hardness value slightly decreases as the load is increased (beyond 25 g), which may be due to the activation of slip systems [12] resulting in the easy glide of dislocations. Due to the mutual interaction or rearrangement of dislocations,the hardness reaches a load independent value (57 kg/mm^2) at higher loads (>75g).

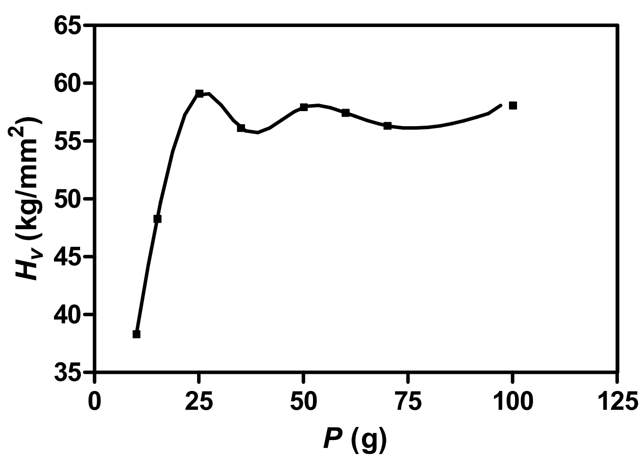

Figure 5. Load-hardness curve for BGHC

CONCLUSIONS

The average growth rate is 1.3 mm/day along the longer edge of the BGHC crystal. Formic acid is found to be the best of all the tried etchants to reveal the defects and the average dislocation density is $3.1\times10^3/cm^2$. The melting point of BGHC is found to be 259.76 ^oC. The load-hardness curve for BGHC indicates that the crystal exhibits reverse ISE and the possible reasons have been discussed. The hardness reaches a load independent value of 57 kg/mm^2. In the higher wavelength region the crystal has a transmittance of 70%. The Kurtz powder test indicates that the SHG efficiency of BGHC is almost two times that of KDP.

Acknowledgments

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