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Synthesis, growth and structural perfection of nonlinear optical material of glycine hydrofluoride (GHF)

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Abstract In the present communication, we have successfully synthesized the efficient NLO material of glycine hydrofluoride (GHF) by conventional chemical reaction, and grown the single crystal by adopting slow evaporation solution growth technique. In order to know its suitability for device fabrication, different characterization analyses have been performed. The lattice constants have been determined from powder X-ray diffraction (PXRD) method and found that it crystallizes in orthorhombic crystal system. Its crystalline perfection was evaluated by high-resolution X-ray diffraction technique (HRXRD) and the value of FWHM indicates the presence of low angle structural grain boundaries. Its luminescence behaviour has been analysed by photoluminescence (PL) analysis and found maximum luminescence in the lower wavelength region. Its relative second harmonic generation efficiency was evaluated from Kurtz powder technique. The phase matching angle of GHF was determined by using Nd:YAG laser as a source. Its thermal, mechanical and electrical properties were examined by TG/DTA, Vickers microhardness tester and dielectric measurements, respectively.

Introduction

Nonlinear optical (NLO) materials are mainly used in the field of photonic and optoelectronic technologies [1, 2]. For the past few decades materials explored for NLO applications were mostly inorganic. However, its nonlinear optical coefficients and laser damage threshold are fairly low in comparison with organic and semi-organic materials [3, 4]. By considering all the parameters, material scientists focuss their attention on the growth of technologically important materials of organic and semi-organic types. Presently semi-organics are gaining attention because it is sharing the properties of both organic and inorganic materials, e.g., higher second order nonlinear optical efficiency, good laser damage threshold and mechanical properties etc. [5, 6].

Nowadays amino acids are noticeable materials due to its competent nonlinear optical efficiency. Some complexes of amino acids with inorganic salts have already been reported by many researchers [7–9], and that has proven to be a good candidate for nonlinear optical applications. In this series, we have successfully synthesized the semi-organic nonlinear optical material of glycine hydrofluoride, and the single crystals have been grown by slow evaporation solution growth technique and the results have been reported. It crystallizes in orthorhombic crystal system with noncentrosymmetric in nature. It comprises a molecular formula of $C_2H_5NO_2HF$ having the molecular weight of

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106.08 g/mol. Its relative second harmonic generation efficiency is 6.3 times higher than that of standard potassium dihydrogen phosphate (KDP). Even though some reports are available for the growth of GHF [10], in this communication we are reporting its structural and optical properties of the compound. Its laser damage threshold and luminescence behaviours have also been analysed and the detailed discussions are given in subsequent sections.

Experimental

Crystal growth

In general, the purity of the commercially available materials lies in the range 95–99%. Impurities may create the defects during the formation of single crystals. So, in the present study, the purity of the raw material was improved by repeated recrystallization processes using double distilled water as the solvent. The calculated amounts of glycine and hydrofluoric acid were taken [10] in a separate beaker and dissolved thoroughly. Then they have been mixed together using a hot plate attached motorized magnetic stirrer. In order to complete the chemical reaction, the temperature of the hot plate was maintained around 60 °C. Then the solution was filtered and kept in a hot oven for complete dryness. The saturated solution was prepared using the dried salt and filtered using a WHATMAN filter paper (no. 1001 125). The filtered solution was tightly closed with thin plastic sheet, so that the rate of evaporation could be minimized and then housed in a constant temperature bath (CTB) with a setting temperature of 32 °C. Good transparent single crystals were harvested from the mother solution after a time span of 2 months ($14 \times 13 \times 3$ mm^3) (Fig. 1). The grown single crystal was subjected to different characterization analyses in order to know its suitability for device fabrication.

Characterization analyses

The lattice dimensions have been calculated from the powder X-ray diffraction analysis using D8 Advanced powder X-ray diffractometer (Bruker make) at a scanning speed of 1.2°/min. The crystalline perfection was assessed by National Physical Laboratory (NPL)-developed high-resolution X-ray diffractometer using a well-collimated and monochromated MoKα_1 beam. Its phase matching angle was determined by using a high intensity Nd:YAG laser as a source. Its relative second harmonic generation efficiency was examined by Kurtz powder technique with reference to KDP. Its thermal, mechanical and electrical properties have been studied by using Mettler Toledo Star simultaneous DTA/TGA analyser, Vickers microhardness tester and PSM 1735 NUMETRIQ LCR meter, respectively. The observed results and the significant discussions are given in the following sections.

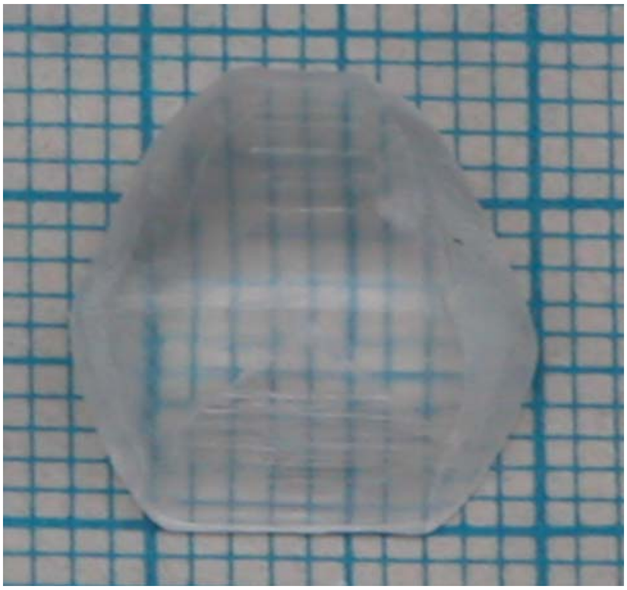

Fig. 1 As grown single crystal of GHF

Results and discussions

The powdered form of the GHF specimen was subjected to powder X-ray diffraction analysis and scanned between the ranges 10–50°. The recorded PXRD spectrum is shown in Fig. 2. The lattice dimensions were calculated by TREOR programme using the observed two theta values. From this measurement one can comprehend that the title compound crystallized in orthorhombic system have the lattice dimensions of $a = 5.4732$; $b = 7.6487$; $c = 8.5458$ Å. The formation of functional groups and the purity of the synthesized compound were identified from the Fourier transform infra-red (FTIR) analysis. The spectrum was recorded in the wavenumber region between 400 and 4000 cm^{-1} and is shown in Fig. 3. The region 2600–311 cm^{-1} is assigned to N–H stretching of the primary ammonium group. The peaks observed in the region 1590–1610 is interpreted to asymmetric and symmetric NH$_3$ bending vibration. Whereas the peak observed at 1660 cm^{-1} is due to carboxylate ion.

In the present study, the crystalline perfection of the as-grown single crystal of GHF was characterized by HRXRD by employing a multicrystal X-ray diffractometer developed at NPL [11]. The well-collimated and monochromated MoKα_1 beam obtained from the three monochromator Si crystal sets in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The schematic representation of the experimental set up and the detailed

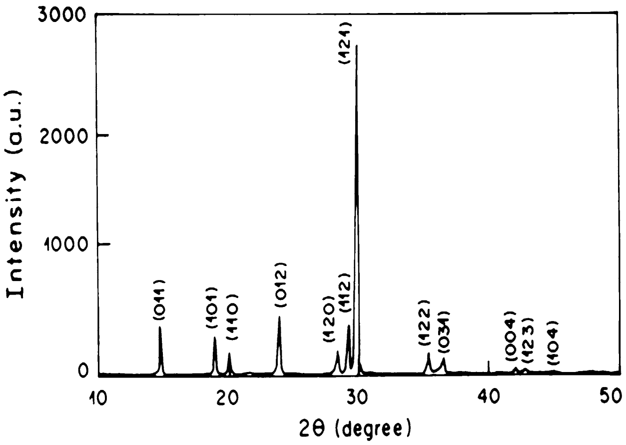

Fig. 2 PXRD pattern of glycine hydrofluoride

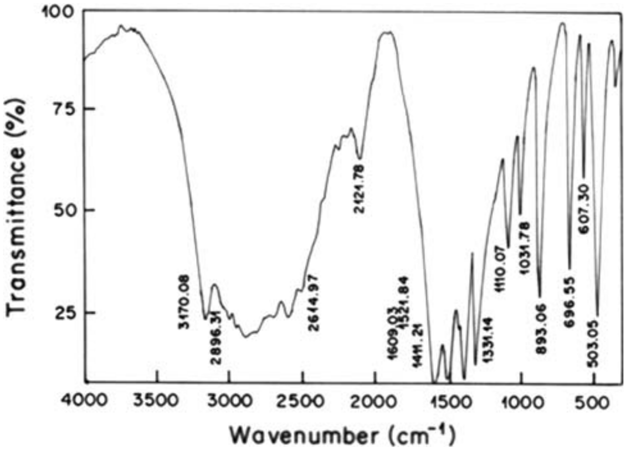

Fig. 3 FTIR spectrum of glycine hydrofluoride

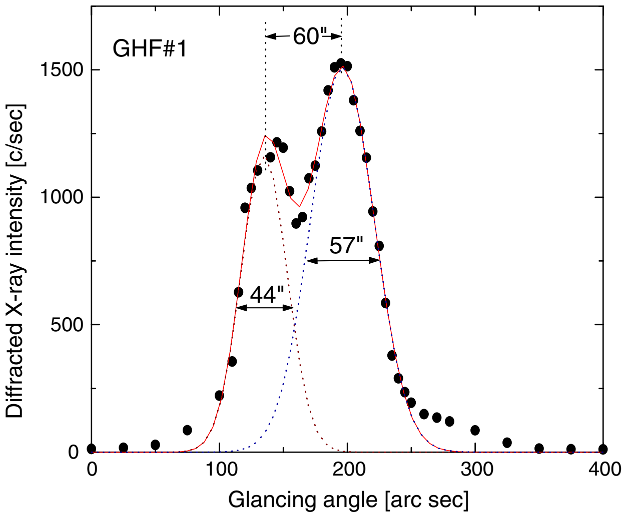

Fig. 4 High-resolution X-ray diffraction curve recorded for (121) diffracting planes using MoKα_1 radiation in symmetrical Bragg geometry

discussions were reported in our earlier article [12]. Before proceeding the analysis, the specimen was prepared by grinding and lapping, and then chemically etching with water and acetone solution in 1:1 ratio. Figure 4 shows the high-resolution diffraction curve recorded for (121) diffracting plane. As seen in figure, an additional peak at an angular distance of 60 arc sec away from the main peak towards the lower diffraction angle side indicates a very low angle structural grain boundary which might be formed by a little quantity of solvent entrapped inside the crystalline matrix during the growth process. The half widths of the main peak and the peak due to *very low* angle boundary are, respectively, 57 and 44 arc sec, which show that the crystalline quality of the specimen is quite good. Such types of boundaries are commonly observed in solution grown crystals [13, 14].

The relative second harmonic generation efficiency was determined by modified Kurtz powder technique [15] at Indian Institute of Science (IISc), Bangalore. It is an important and well accepted tool to evaluate the conversion efficiency of a nonlinear optical material. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1064 nm, generating about 1.3 mJ and pulse of width 8 ns was used for the present experimental study. The input laser beam was passed through an IR reflector and then incident on the powdered form of the GHF specimen, which was packed in a glass capillary tube. The output energy was detected by a photodiode detector integrated with oscilloscope assembly. Second harmonic signal was confirmed when the laser beam was passed through GHF specimen. The second harmonic generation efficiency was measured with respect to KDP (with same particle size as that of the specimen, i.e. 120–125 μm). From this measurement we found that the relative SHG efficiency of glycine hydrofluoride is 6.3 times higher than that of standard potassium dihydrogen phosphate. Its phase matching angle was determined by adopting high intensity Nd:YAG laser having the wavelength of 1064 nm. The phase matched angle is 26.2° in XZ plane for second harmonic generation of 1064 nm wavelength.

In order to identify the laser resistive power of GHF, laser damage threshold (LDT) has been carried out using Q-switched Nd:YAG laser having the wavelength of 1064 nm. The details of the experimental set up and the schematic representation have already been reported [16]. The energy density was calculated using the relation, ED = E/A GW/cm^2, where E is the input energy and is measured in milli-joules and A is the area of the circular spot size. The laser damage threshold value of the title compound was found to be 2.12 GW/cm^2, whereas the lower value of laser damage threshold (LDT) was observed, when the crystal is subjected to multiple shots. From these measurements we have observed that the single shot laser damage threshold is higher than that of multiple shot damage threshold. Boomadevi et al. [17] described that apart from thermal effect, multi-photon ionization is the important cause of laser-induced damage. From this analysis we found that the laser damage threshold is nearly 11 times higher than inorganic crystal of potassium dihydrogen phosphate (KDP). The laser damage threshold of some NLO crystals is given in Table 1 [18]. The higher value of LDT is very much useful to make the frequency conversion or laser devices.

The as-grown well tested inclusion-free single crystal of GHF was scanned between 500 and 700 nm using Ar^+ ion laser operating at 488 nm and 5 mW for excitation in all measurements. In the present investigation, the excitation wavelength is 490 nm. The recorded emission spectrum is shown in Fig. 5. For 490 nm excitation wavelength, the observed emission band lies between 500 and 800 nm. The maximum intensity peaks are observed in the region from 520 to 620 nm. These peaks are due to carboxylic acid and amino groups, which arise by the donation of protons from carboxylic acid to amino group, and lead to luminescence nature for the GHF specimen and may be useful for optical data storage applications.

Its thermal properties have been analysed by TG/DTA analyses. The spectrum was recorded in the nitrogen atmosphere at a scan rate of 10 °C/min. The recorded spectrum is shown in Fig. 6. From the TG curve one can see that there is a single stage weight loss starting at about 225 °C. No weight loss is observed below 225 °C. The material is moisture-free and stable up to 225 °C. In order to examine the physico-chemical change, the differential thermal analysis (DTA) was also performed in the range 20–400 °C. DTA curve contains a sharp endothermic peak at 255 °C. It is attributed to the melting point of the title compound. Below this endothermic peak, no exothermic or endothermic peak was observed, indicating the absence of any isomorphic transition. Hence GHF is thermally stable up to its melting point. The sharpness of the endothermic peak shows its good crystallinity [19], which is also evidenced from the high-resolution X-ray diffraction analysis.

Table 1 LDT value of the GHF specimen along with other important NLO crystals

Compound	Laser damage threshold (GW/cm^2)
KDP (potassium dihydrogen phosphate)	0.20
Urea	1.50
BBO (beta-barium borate)	5.0
LAP (L-arginine phosphate)	10
GHF (present study)	2.12

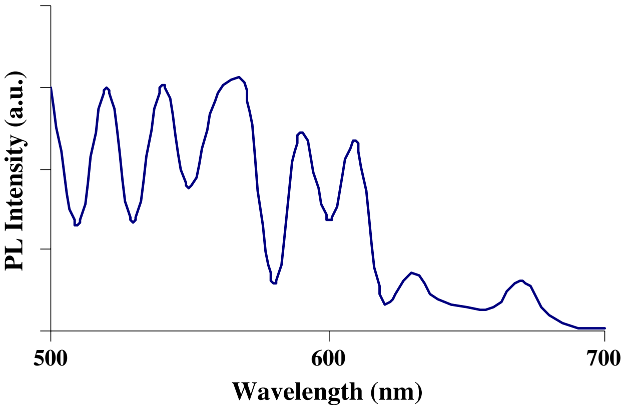

Fig. 5 Emission spectrum of GHF crystal

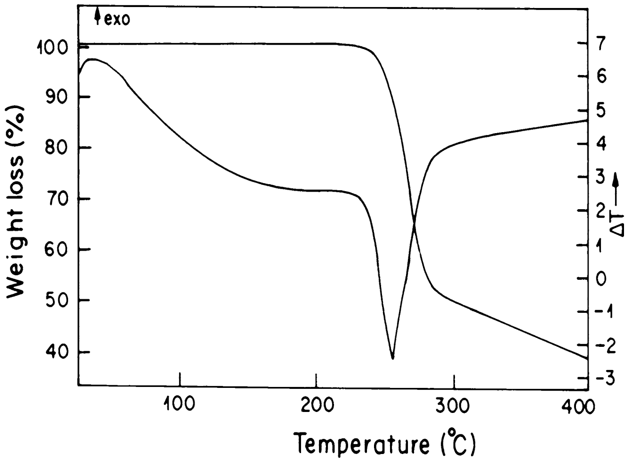

Fig. 6 TG/DTA spectrum of GHF

The mechanical properties of the grown specimen were assessed by Vickers method using Leitz Weitzler microhardness tester fitted with a diamond indenter. The smooth and polished surface of the (121) plane was subjected to the analysis. The measurements have been carried out from 10 to 100 gm and the indentation time was kept at 5 s for all the measurements. Three measurements have been done for each load, and the average Vickers hardness number (VHN) value was used for the calculation. The calculated VHN value is moderately higher than the other nonlinear optical materials of L-arginine tetrafluoroborate and methyl *p*-hydroxybenzoate [20, 21]. The Meyer's index number (*n*) or work hardening coefficient has been calculated from the slope of log *p* vs. log *d* plot and found to be 1.13. From careful examination on different materials, Onitsch and Hanneman [22, 23] suggested that, *n* lies in the range 1–1.6 for hard materials and is higher than 1.6 for soft materials. In the present study, the estimated work hardening coefficient (*n*) of GHF is 1.13, suggesting that the title compound belongs to hard material category and its yield strength was found to be 17.54 GPa. Its dielectric constant and dielectric loss have been measured at different temperatures (from

291 to 423 K) using PSM 1735 NUMETRIQ analyser. The cut and polished specimen was coated with silver paste on both sides in order to get the proper electrical contact during the measurement, and the temperature of the furnace was controlled by Eurotherm temperature controller with an accuracy of 0.01 °C. The recorded data suggested that the dielectric constant is higher in the lower frequency regions and it decreases with increase in frequency. The same behaviour was also observed in the higher temperature regions. This may be due to considerable contribution from ionic polarizability, whereas in the lower frequency regions all the polarizations may be prominent. The lower value of dielectric loss at higher frequency regions implies that the grown specimen was free from defect and other boundaries. The detailed investigation of the effect of swift heavy ion irradiation on GHF single crystal will be reported in due course of time.

Conclusions

The title compound, glycine hydrofluoride has been successfully synthesized and the single crystals have been grown by solvent evaporation method at room temperature. It crystallizes in noncentrosymmetric space group and belongs to orthorhombic crystal system. The crystalline perfection was found to be reasonable as evidenced from the high-resolution X-ray diffraction analysis. Its relative second harmonic generation efficiency and laser damage threshold were found to be higher than KDP single crystal. The higher value of luminescence was observed in the lower wavelength region and that may due to donation of protons from carboxylic acid to amino group of glycine. From the thermal analysis we observed a sharp endothermic peak around 255 °C, which is assigned to the melting point of the specimen, and such a sharp peak suggests that the crystallinity of the specimen is good. Its mechanical and electric properties have been analysed. Hence, we conclude that the title compound is suitable to make some nonlinear devices like frequency doublers, SHG generators, etc.

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