GROWTH AND CHARACTERIZATION OF PROMISING NONLINEAR OPTICAL GTFA SINGLE CRYSTAL

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ABSTRACT
This work investigates the growth of promising nonlinear optical single crystal of semi organic optical material Glycine Trifluoro Acetate (GTFA) with the molecular formula CH₂NH₂COOH.CF₃COOH (C₃H₄F₃NO), which has synthesized by slow evaporation technique at constant room temperature. Spectral, thermal and optical techniques have been employed to characterize the new material. The lattice parameters and the crystal system of the crystal was observed by Powder X-ray diffraction method, and identified as Tetragonal. Functional groups present in the sample were identified by FTIR spectral analysis. The optical transmission study shows that the crystal is transparent in the entire visible region with a cutoff wavelength of 327 nm. The optical band gap was found to be 4.1 eV. The Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of GTFA was determined from the TGA/DSC response curve. The second harmonic generation (SHG) of the GTFA crystal was demonstrated by Kurtz Perry method using Nd: YAG laser and the result confirm that the grown crystal is 60% as that of KDP.

Keywords: Crystal growth, X-ray diffraction, optical properties, Second harmonic generation.

INTRODUCTION
NLO has emerged as one of the most attractive fields of current research in view of its vital applications in the areas like optical modulation, optical switching, optical logic, frequency shifting, and optical data storage in telecommunications and signal processing. One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Among NLO materials, Organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals, but exhibit low damage threshold and poor processibility. But semi organic materials are having a specific interest since the NLO response in this board class of material is microscopic in organ, providing an opportunity in the use of theoretical modeling coupled with synthetic flexibility to design and produce novel materials. Another important advantage in working semi organic materials is that they permit one to fine-tune the chemical structures and properties for the desired nonlinear optical properties. Apart of this, they have large structural diversity. The properties of semi organic compounds can be refined using molecular engineering and chemical synthesis.

Hence, there is a need to search new advanced NLO materials and study their structural, physical, thermal and optical properties in numerous disciplines of science and development of many new technologies. NLO materials capable of generating the second harmonic frequency play their potential applications in the domain of optoelectronics and photonics. NLO crystals have come upon the materials science scene and are being studied by many research groups around the world. These materials operate on light in a way very analogous to the way of semiconductors which operate on electron to produce very fast electronic switching and computing circuits.
However, most of the organic NLO materials are constituted by weak vander walls and hydrogen bonds with the delocalized electronic structure of conjugated π organic compound offers a number of provoking opportunities in applications as NLO materials. So they are very soft in nature and difficult to polish and these materials also have intense absorption in UV region.

In this paper the growth of Glycine Trifluoroacetate (GTFA) crystal by slow evaporation method has been reported. The grown crystal has been investigated by powder crystal XRD technique to calculate the lattice parameters. Functional groups and the modes of vibration have been distinguished by FT-IR analysis. The optical transmission study is carried out by UV-Vis-NIR spectroscopy. The thermal endurance of the grown crystal is validated by TGA-DSC analysis. The powder samples are subjected to SHG test to affirm its NLO properties.

**EXPERIMENTAL**

**Synthesis and crystal growth**

Glycine trifluoroacetate was synthesized by the reaction between 2 mol of glycine (Merck, AR) and 1 mol of Trifluoroacetic acid (Sigma- Aldrich CAS Number 76-05-1) in 100 ml demineralised water (resistivity 18 MΩ.cm). The continuous stirring of the solution for 12 hours at constant temperature using temperature controlled magnetic stirrer yielded the precipitate of crystalline substance of GTFA and the solution was filtered using a high quality Whatmann filter paper (Cat no. 1001-042). The prepared solution was taken in a glass vessel and it is kept at room temperature in a dust free and vibration free compartment. The induction period for nucleation is 3-4 days. The solvent was evaporated and the solution became super saturated and the tiny unit cell was found. The nucleated crystals were allowed for further growth at room temperature and the crystal size 15 mm× 10 mm× 5 mm was harvested. Repeated crystallization and filtration processes were applied for the purification of the synthesized compound. The grown crystal of GTFA is shown in Fig.-1.

![Fig.-1: Photograph of GTFA single crystal.](image)

**Characterization Studies**

The grown single crystal of GTFA was confirmed by powder XRD analysis using PANalytical, Xpert PRO powder X-ray diffractometer. The functional group identification of the compound and its purity were studied using Perkin-Elmer Spectrum-RXI FT-IR spectrometer in the range of 400- 4000 cm⁻¹. The transmission properties of the crystals were examined between the ranges of 180 - 1100 nm using Perkin-Elmer Lambda 35 UV-Vis-NIR spectrometer. The Thermo gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out for the crystal by TA Instruments Q 600 V20.9 Simultaneous Thermal Analyzer. The NLO property of the crystal was confirmed by Kurtz and Perry powder technique using Nd: YAG laser.
RESULTS AND DISCUSSION

Powder X-ray diffraction studies
The unit cell parameters and the structure of GTFA were determined using powder X-ray diffraction data obtained from PANalytical, XPert PRO powder X-ray diffractometer with CuKα radiation (λ= 1.5418 Å) using a tube voltage of 40kV and current of 30 mA at room temperature (300 K). The sample was scanned over the range of 20-80° at the rate of 1°/min. Powder XRD pattern of the crystal is shown in Fig.-2. The lattice parameters and the cell volume have been calculated using Winplotr 2013 software package. We observed that the grown crystal belongs to Tetragonal system with noncentro symmetric space group of P4/mmm and Volume of the unit cell was calculated to be 637.29 Å³.

![Fig.-2: Power X-ray diffraction pattern of GTFA crystal.](image)

FTIR spectral analysis
To analyze the presence of functional groups in GTFA, qualitatively, we record the FTIR spectrum in the range of 400-4000 cm⁻¹ using Perkin-Elmer Spectrum-RXI FT-IR grating infrared spectrometer. The recorded spectrum is shown in the Fig.-3. In the FTIR spectrum, it is noted that the band at 3752 cm⁻¹ and 2745 cm⁻¹ are attributed to the stretching vibrations of NH₃⁺ groups. The peak at 2960 cm⁻¹ corresponds to the CH₂ stretching. Asymmetric stretching vibration of COO⁻ is observed at 1699 cm⁻¹. The peak at 1420 cm⁻¹ is due to the symmetric stretching vibration of COO⁻. The IR spectrum exhibited absorption C-F stretching at 1282 cm⁻¹ and 1190 cm⁻¹ respectively which is the characteristic vibration peaks of CF₃ group. The band at 1030 cm⁻¹ is assigned to CCN stretching. The wagging and rocking vibrations of COO⁻ and CH₂ are observed at 925 cm⁻¹ and 681 cm⁻¹ respectively. The characteristic band, COO⁻ scissoring is observed at 725 cm⁻¹.

Optical studies
Optical transmittance properties of the GTFA crystals were examined between the range of 180-1200 nm with a crystal of thickness 5 mm using Perkin-Elmer Lambda 35 UV-Vis-NIR spectrometer and transmittance spectrum is shown in Fig.-4. The spectrum of GTFA crystal indicates that there is no remarkable absorption in the entire range from 327 to 1200 nm. Using optical absorption, the optical band gap was found to be 4.1 eV the lower cut-off near 327 nm in transmittance spectrum combined with the very good transparency, makes the usefulness of this material for optoelectronic and nonlinear optical applications. The absence of absorption in the entire visible region is sufficient for Opto-electronics applications like photovoltaic cell, infrared diode, IR sensor modules and Laser applications.
Thermal analysis
Thermal Analysis (TGA/DSC) was performed by using TA Instruments Q 600 V20.9 Simultaneous Thermal Analyzer in the temperature range of 20 - 500°C at the heating rate of 10°C/min in inert nitrogen atmosphere. TGA and DSC curve of GTFA were shown in Fig.-5. TGA curve indicates that there is a major weight loss (25.08%) of the sample starts from the region at 250°C and ending at 300°C. The following decomposition pattern is formulated for GTFA crystal.

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\text{CH}_2\text{NH}_2\text{COOH} + \text{CF}_3\text{COOH} \rightarrow \text{C}_3\text{H}_4\text{F}_3\text{NO} + \text{H}_2\text{O} + \text{CO}_2
\]
The weight loss can be occurred due to eliminating of volatile substance in the compound, probably the complete weight loss may due to the dehydration of carbon diode. This accounts for 59.95% mass loss observed in TG curve. The remaining portion of GTFA slowly decomposed up to 500°C. This high mass loss indicates the presence of Glycine in the sample. The thermo gravimetric study confirms the formation of the titled compound in the stoichiometric ratio and the decomposition pattern of GTFA. The DSC trace indicates a sharp endothermic peak starting at 259°C which concludes very well with the melting point of the sample. Also, it is found that there is no endothermic peaks are observed up to 250°C proving absence of the water of crystallization on GTFA crystal. The final residue obtained at 500°C is about 1 mg. This result indicates the thermal stability of GTFA up to 250°C and establishes its suitability to withstand at high temperatures in laser experiments.

SHG efficiency analysis GTFA crystal
The SHG efficiency of GTFA was measured by Kurtz and Perry powder technique. The second harmonic output was generated by irradiating powder samples by Nd: YAG laser emitted radiation of wavelength 1064 nm with pulse width 8 ns and a repetition rate of 10 Hz allowed to pass through the powdered sample in a capillary tube. The green output light of 43 mV was observed from the sample with wavelength 532 nm from an input energy of 2.149mJ/pulse. KDP sample was used as the reference material and the powder SHG efficiency of grown crystal was found to be 0.6 times that of KDP. The depressed SHG efficiency may be due to the disturbance of charge transfer between the particles.

CONCLUSION
In the present paper, we reported optically transparent NLO crystal of Glycine Trifluoroacetate grown from an aqueous solution by employing the slow evaporation technique and the crystal was subjected to powder XRD, functional group, optical and NLO studies. Powder XRD analysis confirmed that the crystal system as tetragonal. The FTIR spectrum reveals the modes of vibration of different molecular groups and protonation of amino groups are present in the titled compound. The optical transmittance of the crystal confirms the wide range of transparency of the crystal. TGA / DSC study shows that crystal is stable up to 250°C without any phase transition and its suitability to withstand at high temperatures in laser experiments. The powder SHG efficiency of grown crystal was found to be 0.6 times that of KDP.
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REFERENCES


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