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PHYSICS

SYNTHESIS, GROWTH AND CHARACTERIZATION OF SEMI-ORGANIC NONLINEAR OPTICAL CRYSTAL: GLYCINE ZINC CHLORIDE

M. Iyanar[1] and C. Muthamizhchelvan[2*], S. Ponnusamy[2] and J. Thomas Joseph Prakash[3]

[1]*Department of Physics, National College (Autonomous), Tiruchirappallli-620 001, India*
[2]*Department of Physics, SRM University, Kancheepuram-603 203, India*
3Department of Physics, H.H. The Rajah's College (Autonomous), Pudukkotai-622 001 India

Abstract

Semi-organic single crystals of glycine zinc chloride (GZC) have been grown by slow evaporation solution growth technique. The crystal system has been identified and lattice dimensions have been measured from the single crystal X-ray diffraction analysis. FTIR analysis was used to estimate qualitatively the presence of the functional groups in the grown crystal. Its linear optical character has been assessed by UV-visible analysis and found that there is no absorption in the entire visible region. Second harmonic generation (SHG) conversion efficiency were investigated to explore the NLO characteristics. The thermal behavior of the crystals has been investigated by TG/DTA analyses.

Keywords: Crystal growth; Solution growth; Nonlinear optical material

Introduction

Second order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [1,2]. Materials with large second-order optical nonlinearities, short transparency cutoff wavelengths, and stable physico-thermal performance are needed to realize many of these applications. The search for new frequency conversion materials over the past decade has concentrated primarily on organics. It has been demonstrated that organic crystals can have very large nonlinear susceptibilities compared with inorganic crystals, but their use is impeded by low optical transparency, poor mechanical properties, low laser damage threshold, and the inability to produce and process large crystals [3,4]. Purely inorganic nonlinear optical (NLO) materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended π-electron delocalization. In semi-organics, polarizable organic molecules are stoichiometrically bound within an organic host [5]. In recent years, the NLO properties of semi-organic complex products have attracted great interest because these metal-organic complexes combine the high optical nonlinearity and chemical flexibility of organics with physical ruggedness of inorganics [6,7]. Nowadays amino acids are noticeable materials due to its component nonlinear optical efficiency. Some complexes of amino acids with inorganic salts have already been reported by many researchers [8,9], and that has proven to be a good candidate for nonlinear optical applications. In this service, we have successfully synthesized the semi-organic nonlinear optical material of glycine zinc chloride and the single crystals have been grown by slow evaporation solution growth technique and the detailed discussions are given in the subsequent sections.

Experimental

Material synthesis

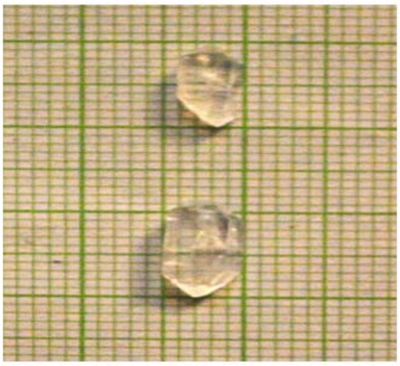
The GZC salt was synthesized using high purity zinc chloride and glycine in a stoichiometric ratio of 1:3. The calculated amounts of zinc chloride and glycine were dissolved in deionized water. This solution was kept for slow evaporation to dryness at room temperature. The purity of the synthesized salt was improved by a successive recrystallization process.

Crystal growth

The pure form of synthesized salt was used as the raw material for the preparation of the saturated solution. Then the solution was filtered using a WHATMAN filter paper. The filtered solution was tightly closed with thin plastic sheet, so that the rate of evaporation could be minimized and then housed in a vibration free place. Good transparent single crystals were harvested from the solution after a time span of one month. Fig.1 shows the as-grown single crystal of GZC. The grown crystal was subjected to different characterization analyses in order to know its suitability for device fabrication.

* Corresponding Author, *Email*: selvancm@gamil.com, Mob: 9940036004, Fax: 91-44-27452343

Fig. 1. As-grown single crystals of GZC



Characterization

Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was carried out using an Enraf CAD-4 diffractometer with MoK_α (λ=0.1770Å) radiation. From this analysis it was observed that the crystal belongs to orthorhombic crystal system having non-centrosymmetry with $Pna2_1$ space group. Lattice parameters have been determined as: a=15.224, b=11.171 and c=15.538 Å; α=β=γ=90 which are in good agreement with the reported values [10].

FTIR spectral analysis

The FTIR spectrum of GZC crystals was recorded in the range 400-4000cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method to study the metal organic cooridination. Fig.2 shows the recorded FTIR spectrum of the grown crystal of GZC. The vibrational frequency of various functional groups of GZC and the tentative frequency assignment [11] are presented in Table 1. The absorption due to carboxylate group of free glycine is observed at 504, 892 and 1593 cm−1. In GZC these peaks are shifted to 511, 912 and 1641 cm−1 respectively. Similarly the absorption peaks due to$NH3^+$ group of free glycine are absorbed at 1113, 1131 and 1502 cm−1 respectively. These are shifted to 1098, 1143 and 1560 cm^{-1} respectively.

Fig. 2. FTIR spectrum of GZC crystal

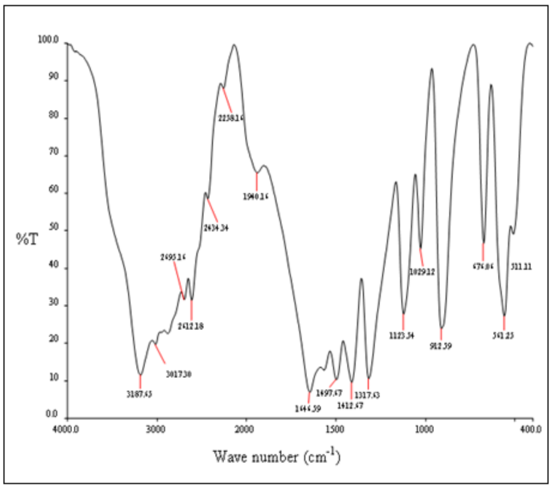


Table 1: Vibrational band assignments of GZC

Wave number (cm^{-1})	Band assignments
3187	NH2 asymmetric stretching
3017	NH2 symmetric stretching
1644	C=O asymmetric stretching
1497	CH2 bending
1412	C=O symmetric stretching
1317	-
1123	NH2 deformation
1029	C–N stretching
912	CH2 rocking
676	NH2 deformation
561	-
511	COO rocking

Optical assessment

Linear properties of the grown crystals of GZC were studied using Lambda-35 UV-visible spectrophotometer. Optical transmission and absorption spectra were recorded using a crystal of thickness 2mm. The recorded spectra are shown in Fig. 3(a) and Fig. 3(b). From the spectra, it is evident that GZC crystal has UV cut off below 230nm, which is sufficient for SHG laser radiation of 1064nm or other application in the blue region. It further indicates that the crystal has wide transparency window between 300nm and 1100nm. The wide transparency in the entire visible region is one of the additional key requirements for having efficient NLO character [12].

Fig. 3(a) UV-visible absorption spectrum of GZC

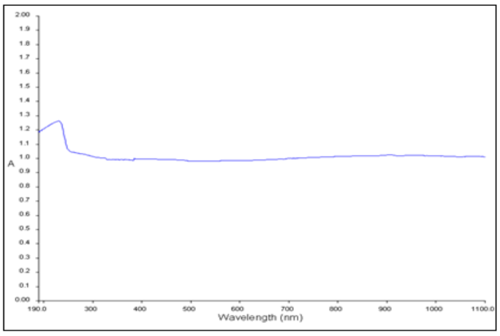
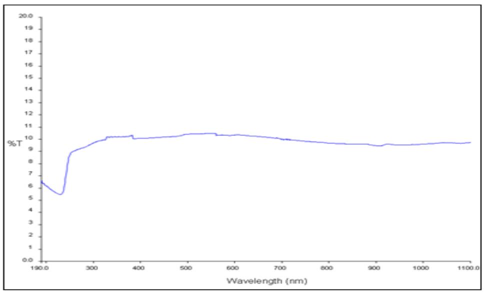


Fig. 3(b) UV-visible transmittance spectrum of GZC



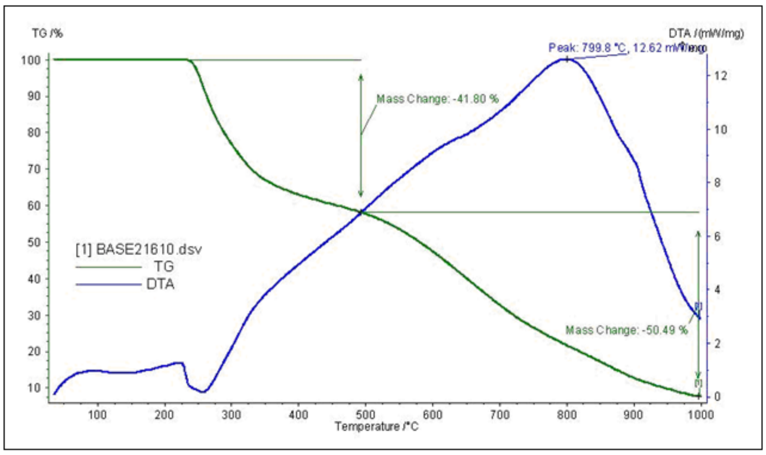
Second harmonic generation efficiency measurement

The SHG efficiency was estimated using the modified setup of Kurtz and Perry [13] at the Indian Institute of Science, Bangalore. A Q-switched Nd:YAG laser beam of 1064nm wavelength with 6.5mJ input power, 8ns pulse width and repetition rate 10Hz was used. In the present study, the grown single crystal of GZC was ground with particle size in the range 125-150µm and then packed in a microcapillary of uniform bore and exposed to laser radiation. The fundamental input radiation (1064nm) was separated or filtered by a monochromator and the output i.e. the intensity of second harmonic generation radiation of 532nm was measured. Second harmonic radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R5 109). SHG was confirmed by the emission of green light. Using the potassium dihydrogen phosphate (KDP) crystalline powder (having the same particle size as that of the GZC specimen) as reference material, the output of SHG signal was compared and found that the SHG conversion efficiency of GZC is 0.6times that of KDP.

Thermal studies

Thermogravmetric (TG) and differential thermal analysis of GZC crystals were carried out between 25˚C and 1200˚C in nitrogen atmosphere at a heating rate of 10˚C/min using NETZSCH STA 409 thermal analyzer. The TGA/DTA pattern recorded for the GZC is shown in Fig. 4. On a careful examination of TGA/DTA, there is no weight loss up to 250˚C. Hence the crystal is devoid of any physically absorbed water on it. From the DTA curve it is observed that an endothermic peak at 250˚C, which indicates the decomposition temperature. Hence it is concluded that GZC crystals can be used for device application till 250˚C.

Fig. 4. TGA/DTA trace of GZC



Conclusions

Single crystals of GZC, a semi-organic NLO material, have been grown from aqueous solution. Lattice parameters have been evaluated by Single crystal XRD analysis. The presence of various functional groups of the grown crystals has been identified by FTIR spectral analysis. It is observed that GZC has 0.6 times relative SHG efficiency than that of KDP. Its optical behavior has been assessed by UV-visible spectroscopy and found no absorption in the entire optical region. From the thermal analysis it is concluded that the grown crystal decomposes without melting at about 250˚C.

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