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Growth and characterization of Glycyl L-Alanine single crystals for NLO devices

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ABSTRACT

The crystalline material of Glycyl-LAlanine (GLA) was synthesized and the single crystals of the title compound grown by slow evaporation solution growth technique. The powder was characterized through XRD and FTIR techniques. EDAX studies indicated the presence of elements in the grown GLA crystals. The UV-Vis- NIR spectral studies were carried out to analyze the optical absorption of the grown crystals and was found that the absorption is very low in the wavelength region between 250-1000nm. The thermal stability of the crystals was studied using TG/DTA analyses techniques. The second harmonic generation (SHG) of the material was confirmed by using Nd:YAG laser. The dielectric constant and dielectric loss of the grown crystal was measured.

KEYWORDS

Non linear material;
EDAX;
UV-Vis-NIR;
TGA/DTA;
Dielectric studies.

INTRODUCTION

The NLO materials play pivotal role in SHG, laser technology, optoelectronics, optical communications, optical data storage and optical signal processing[1-5]. Thanks to the extremely high optical non linearity possessed by the organic molecular crystals, they steal a march over the inorganic analogues in the potential areas of applications akin to electro optic modulations, frequency doubling of lasers, etc. The former class of -comprehensive properties. Amino acid crystals are widely used and thoroughly studied NLO crystals. L-alanine is one of the 20 proteinogenic amino acids and has been currently recognized as one of the most abundant amino acids in natural proteins[6] L-Alanine (CH_3CHNH_2COOH), the simplest acentric member of the amino acid family was first crystallized by Bernal[7] and later by Simpsonet. al[8] and Destroet.al[9], who refined the structure (a=6.032 Å, b=12.343 Å, c=5.784Å) and assigned it the $P2_12_12_1$ space group. Many researchers have tried to modify the properties and the growth rates of the amino acid crystal by either changing the growth conditions or by adding different impurities. This paper reports the synthesis, growth aspect, optical, thermal, and electrical properties of dipeptide Glycyl-L-Alanine crystal whose SHG efficiency has been estimated to be 18% that of KDP.

EXPERIMENTAL

Crystal structure

The unit cell for crystalline GLA contains four molecules. The lattice is composed of columns of molecules in which both the amine (N1) hydrogen and the amide

(N2) hydrogen are oriented towards the terminal carboxyl oxygen (O2/3) in order to facilitate hydrogen bonding. Molecules within the column exist in layers and forms head – to – tail hydrogen bonds. Each molecule is connected via hydrogen bonds to seven neighboring molecules. The peptide carboxyl projects into a hydrophobic cavity with no strong hydrogen bonds within a 4 radius around it. The lattice structure and hydrogen bonding in GLA is shown in Figure 1.

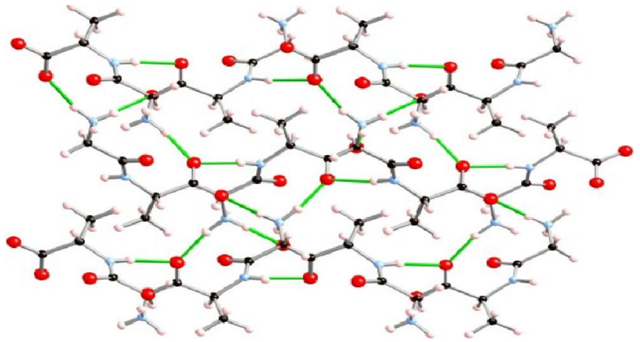

Figure 1 : Lattice structure and hydrogen bonding in GlyAla.

Crystal growth

The recrystallized salts of Glycine and L-Alanine (AR grade chemicals from E- Merck India Ltd) were used in the present crystal growth experiment. The seed crystals were prepared by slow evaporation of GLA in millipore water at room temperature. Good size and optical quality of GLA are grown in a period 50-52 days. The temperature of the growth solution was maintained at 36°C using a constant temperature controller. In this present work, two drops of hydrogen peroxide were added to the solution of Glycyl L-Alanine to inhibit the growth of micro organisms[10,11]. The growth solution was stirred continuously during the growth of the crystal to maintain homogeneity. Figure 2 shows photographs of as grown crystals of Glycyl L-Alanine crystals.

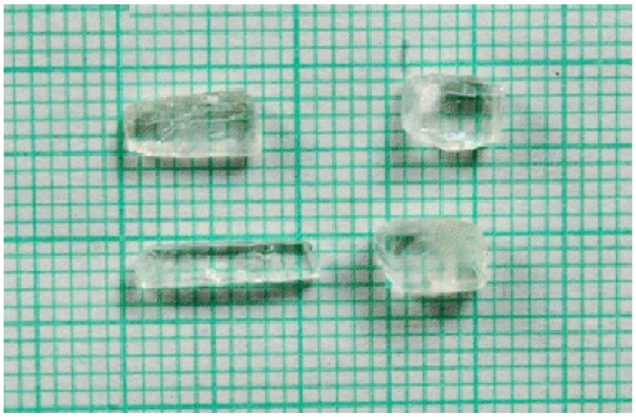

Figure 2 : Photographs of as grown GLA single crystals

CHARACTERIZATION

Single crystal X-ray diffraction (XRD) analysis of Glycyl L-Alanine was carried out using Enraf- Nonius CAD4 X-ray diffractometer with MoKα (λ=0.71073Å) radiation. The FTIR spectra of the materials in the wavenumber range of 400-4000cm^{-1} was recorded on a KBr pellet technique. The percentage of all the elements in the grown crystals has been confirmed by INCA 200 energy dispersive X- ray analyzer (EDAX). The optical absorption spectrum of grown crystals was taken using Perkin Elmer UV-Vis-NIR spectrophotometer in the range 200-1200nm. Thermal studies (TGA/DTA) was carried out simultaneously in the temperature range between 25º-1200ºC at a heating rate of 10º C using the instrument NETSZCH STA 409C/CD. The SHG efficiency was measured with respect to KDP by Kurtz and Perry powder technique using a Q-switched Nd:YAG laser with first harmonic output of 1064nm. Dielectric measurement was carried on GLA using the instrument HIOKI 3532-50 LCR Hitester.

Single crystal x-ray diffraction

The physical properties of the single crystal may change when the defects are created during growth. Also, the quality of the crystal highly depends on the method and material used for the growth. The mechanical damages are more viable in the case of organic crystals because of their soft nature. Single crystal X-ray diffraction studies have been carried out to confirm the crystalline and to calculate the lattice parameters of the grown crystals. It is observed that Glycyl L-Alanine crystals crystallize in the orthorhombic system and belong to $P2_12_12_1$ space group which is recognized as non centrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals[12]. The lattice parameter values were calculated as a = 9.695 Å, b = 9.564 Å, c = 7.437Å and compared with the literature values[13].

FT IR spectrum

The FT-IR Spectrum of Glycyl L-Alanine crystal is shown in Figure 3. N-H stretching frequencies of amino group are found between 3100 cm^{-1} and 2600 cm^{-1} for LA crystal. The LA compound shows absorption at 1618 cm^{-1} indicating the presence of primary amino group. The characteristic absorption for the -NH group in the aromatic ring is observed at 1306 cm^{-1} for LA. The broad absorption around 3080 cm^{-1}indicates the co presence of C=O stretching and O-H stretching. The broad envelope between 2150 cm^{-1} and 3900 cm^{-1} includes overlapping of stretching modes due to N-H and C-H. The peaks at 1568 cm^{-1} and 1454 cm^{-1} are due to the symmetric and asymmetric stretching modes of NH_3^+ and COO^-. respectively. The FTIR spectra and the corresponding band assignment clearly indicate the presence of functional groups in the grown sample. Moreover the presence of absorption peak at 1620 cm^{-1} confirms the presence of peptide bond between L-Alanine and Glycine[14]. The wave numbers observed from the recorded spectra are found to be in close agreement with the literature values[15-17].

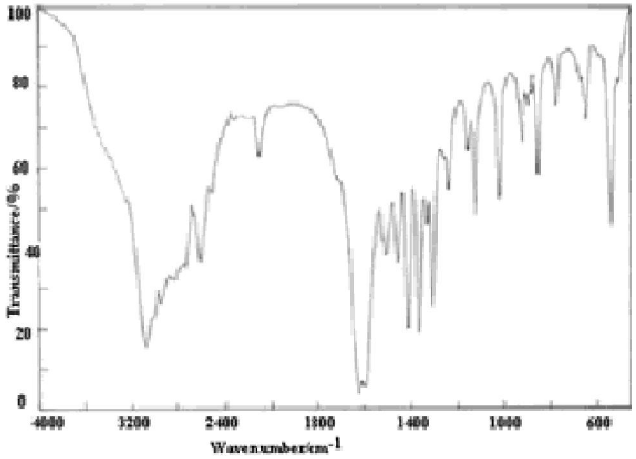

Figure 3 : FTIR of GLA single crystal

EDAX analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals. The results obtained in EDAX of the doped crystal are shown in Figure 4 with its quantization values as given in TABLE 1. This confirms the presence of all the elements in the grown sample.

Optical absorption

In order to get an insight on the perfection and impurity content of Glycyl L-Alanine crystals, UV-Vis-NIR studies are carried out between 200nm-1200nm. The recorded absorption spectrum of GLA crystals is shown in Figure 5. It is seen from the spectra that for the grown crystal absorption is not observed between 400nm to 800nm (visible region). The absence of absorption of light in the visible region is an intrinsic property of all the amino acids[18]. The crystal is highly transparent in the entire range (250nm-1200nm) without any absorption peak, which is an essential parameter for NLO crystals. The maximum absorption lies around 250nm. This transparent nature of crystals in the UV-Vis-NIR region can be exploited for various NLO applications.

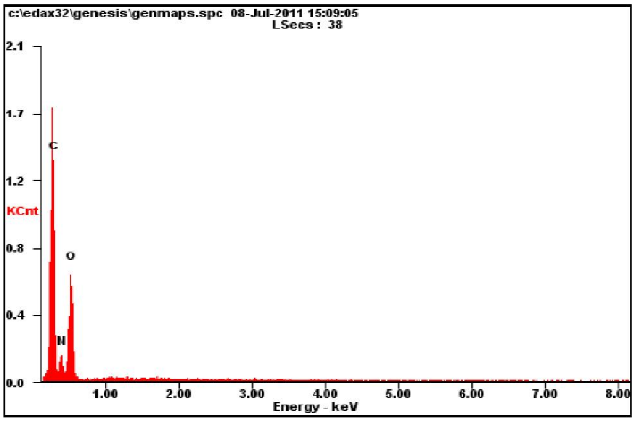

Figure 4 : EDAX spectra of GLA single crystal

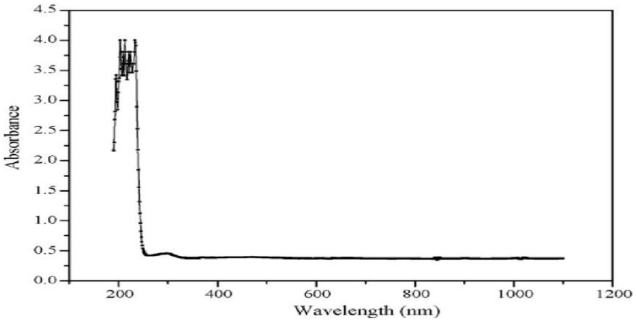

Figure 5 : UV-visible absorption spectra of GLA single crystal

Thermal analysis

The thermal behavior of GLA single crystal was studied in the temperature range from 100C° to 1400C° at a heating rate of 25/10(K/MIN0 /1400 IN THE Nitrogen atmosphere by using NETZSCH STA 409C/CD system. Figure 5 shows the TGA/DTA curves. The DTA curve indicates that the material has an exothermic peak at 235C° which represents the melting point respectively. The TGA curve of GLA indicates that the sample is stable from ambient up to 242 C° with a weight loss of 33.62%. A systematic weight loss was observed as the temperature further increases above the melting point. The total weight loss of the sample is 98.4% at 300C°. It is observed that there is no phase transition or decomposition up to the melting point (235C°) and also there is no mass reduction or decomposition up to 200C° indicating that one can crystallize this material by slow evaporation solution growth technique. The crystal is found to be stable in the Nitrogen atmosphere under normal humidity conditions. The stability of this crystal is a useful property for its possible NLO applications.

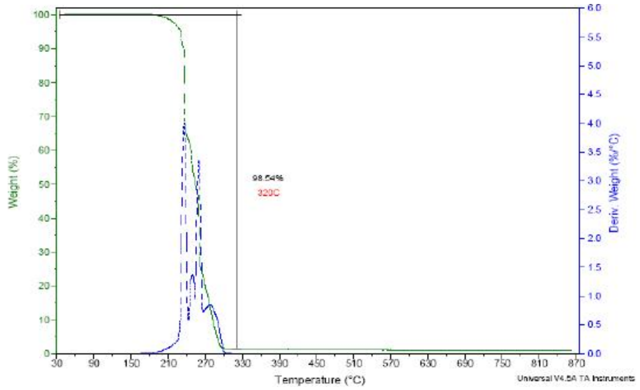

Figure 6 : TGA and DTA curves of GLA single crystal

Nonlinear optical studies

The SHG efficiency of grown samples was measured by using the Kurtz powder technique[19]. In this technique, the grown crystals were grounded into fine micro crystalline powder and densely packed between two transparent glass slides. The fundamental beam 1064nm from Q-switched Nd: YAG laser (Prolab 170 Quanta ray, pulse width 8ns, repetition rate 10 Hz) was made to fall normally on the crystalline powder densely packed in a micro-capillary tube. The bright emission of green light from the pure and doped samples (λ=532 nm) confirms the second harmonic generation behavior of crystals.

Dielectric studies

The cut and polished surface of GLA single crystal was mounted between the electrodes to measure the dielectric constant and dielectric loss. The capacitance was measured in the frequency range between 10^1 and 10^6 Hz for different temperatures (50K, 100K, and 150K). Figure 7 and 8 shows the dielectric constant and dielectric loss of GLA crystal for different temperatures and different frequencies. The dielectric constant of GLA is increasing in the lower frequency region and also the resonance effect is more in the lower frequency region. The dielectric constant of organic crystals shows resonance effect in the lower frequency region[20]. A similar effect is observed for GLA single crystals also. The larger values of dielectric constant at lower frequencies may be attributed to space charge polarization due to charged lattice defects[21]. The dielectric loss also decreases with increasing frequencies. The low value of dielectric loss indicates that the grown crystal is of good quality.

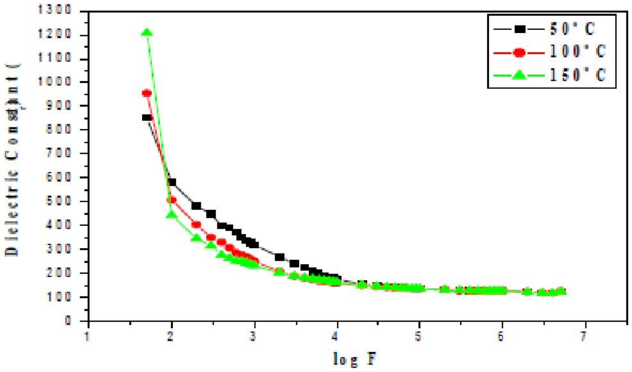

Figure 7 : Variation of dielectric constant with log frequency for GLA single crystal

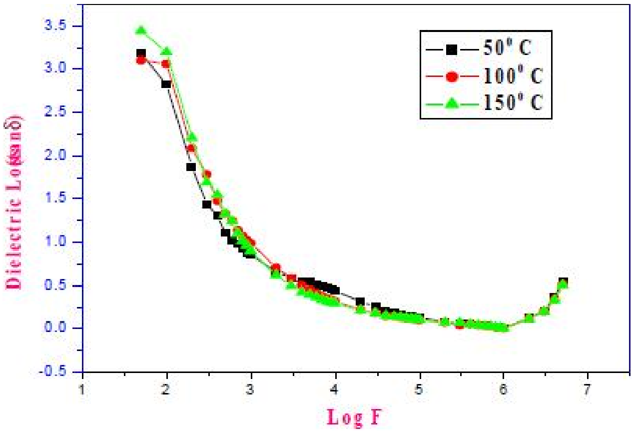

Figure 8 : Variation of dielectric loss with log frequency for GLA single crystal

CONCLUSIONS

Optically clear pure GLA crystals have been grown successfully by slow evaporation solution growth technique from aqueous solution. XRD and FTIR studies confirmed the identity of grown crystals. The EDAX studies suggest the presence of all the elements present in the crystal lattice. Optical assessment show that the grown crystal has a large transmission window and it may be used for frequency doubling and other NLO applications. The thermal behavior of the GLA crystal was analysed by TGA/DTA studies and the thermal stability of the material was determined. The powder SHG efficiency of GLA single crystals is 18% that of KDP. The lower value of dielectric constant from dielectric studies is a suitable parameter for the enhancement of SHG signals

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