Synthesis, Crystal Growth, Spectral, Optical and Thermal characterization of Di-(L-Serine) Phosphate monohydrate(DLSP) Crystal

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Abstract: Di-(L-Serine) phosphate monohydrate (DLSP) material was synthesis and single crystals DLSP were successfully grown by slow evaporation solution growth technique. The single crystal XRD analysis was carried out on DLSP to estimate the lattice parameter.The various planes of reflection were identified from the powder XRD pattern. The functional groups and positions of protons and carbons were studied using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral analyses respectively. The UV-Visible spectrum was recorded to discern the transparency in visible and near infrared (NIR) region. The thermal behavior of the material was analyzed using TGA-DTA. The nonlinear optical (NLO) behavior of DLSP was studied by measuring its second harmonic generation (SHG) efficiency using Kurtz - Perry powder technique.

Keywords: ***nuclear magnetic resonance, nonlinear optics, slow evaporation, solution growth, second harmonic generation, X-ray diffraction***

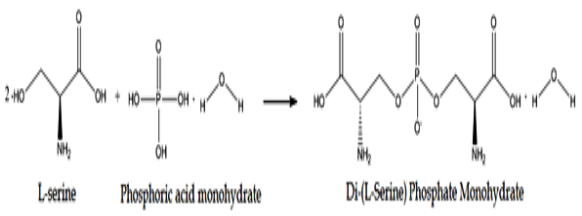
I. INTRODUCTION

The field of crystal growth involves controlled phase transformation with the development of materials for technological applications. The nonlinear optical (NLO) materials are of great interest due to their significant impact on laser technology, optical communication, optical data storage and optical data processing. Convincingly, efforts are being made in recent times to combine amino acids with different organic and inorganic salts and acids to synthesize excellent NLO materials [1]. Development in the field of nonlinear optics play a vital role in applications such as laser frequency conversion, optical information processing, telecommunication, integrated optics, optical disc data storage, optical computing, laser remote sensing, color displays and medical diagnostics[2]. L-serine, one of the basic amino acids is consideredas the most important building blocks of proteins, since the molecules ofL-serine can combine with anionic, cationic and overall neutral constituents [3], [4]. On the other hand, the highly polar natured phosphoric acid is a sequestering agent which binds many divalent cations. Motivated by the stimulating nonlinear properties of these materials, an attempt has been made for synthesize and growth of Di-(L-Serine) Phosphate monohydrate (DLSP) crystals. These grown crystals are subjected to various studies such as spectral, thermal and opticalstudies and the results are discussed in details.

II. EXPERIMENTAL ANALYSIS

A. Synthesis and growth technique

The starting material was synthesized by taking L-Serine (Aldrich-AR grade) and Phosphoric acid monohydrate (Aldrich-AR grade) in a 2:1 stoichiometric ratio. The required amount of starting materials for the synthesis of Di-(L-Serine) phosphate monohydrate crystal was calculated according to the following reaction.



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The calculated amount of L-Serine was first dissolved in deionized water and then the taken amount of Phosphoric acid monohydrate was added to the same solution. The solution was agitated with a magnetic stirrer continuously for 10 hours and filtered after the complete dissolution of the starting materials. The prepared solution was allowed for slow evaporation at room temperature till the crystals were obtained. The purity of the synthesized crystals was further improved by successive recrystallization process thereby single colorless crystals of good optical quality were obtained in 40 days. The as grown crystals of are shown in Figure 1.

III. RESULT AND DISCUSSION

A. Single crystal XRD analysis

The grown transparent single crystal of DLSP was analyzed by single crystal XRD using Bruker axis (Kappa Apex2) diffractometer. The observed values of lattice parameters are given in Table 1. This confirms that the crystal belongs to monoclinic system with space group $P2_1$. The lattice parameters agree well with the reported literature [5].

Table 1. Lattice parameters of DLSP crystal

Sample	Lattice parameters						Volume ($Å^3$)
	a (Å)	b (Å)	c (Å)	α (˚)	β (˚)	γ (˚)	
DLSP	4.642	13.352	9.852	90	98.65	90	603.68

Powder XRD analysis: The powder XRD analysis has been carried out to confirm the crystallinity and also to identify the lattice parameters. The sample was scanned over the range 10-50º at a rate of 2ºmin^{-1}. The resulted powder XRD pattern is shown in Figure 2. The Miller indices of the planes of the DLSP have been calculated and their corresponding Bragg's peaks have also been indexed.The sharp and well defined peaks confirmed the good crystallinity of the grown crystals.

B. FT-IR spectral analysis

The FT-IR spectrum of DLSP crystals was recorded in the range of 4000-400 cm^{-1} employingBRUKER IFS 66v by KBr pellet technique. The FT-IR spectrum is shown in Figure 3. The formation of the intermolecular charge transfer complex is strongly evident by the presence of the characteristic IR bands of the donor and acceptor molecules in the spectrum. The presence of amine in the DLSP grown single crystal was evident by the absorption at 3349cm^{-1}.The NH_2 peakswere observed at 1571 cm^{-1} and 1623cm^{-1}. The P-O stretching frequency and deformation of phosphoric acid was identified at 1030cm^{-1}and 493cm^{-1} respectively. The C-H peaks were observed at 2888 cm^{-1} and 2960 cm^{-1} [6]. The CH_3 anti-symmetric deformation absorption peak was found at 1480 cm^{-1}.

C. NMR spectral analyses

The NMR technique is used to detect the presence of particular nuclei in a compound and also the position of carbons for a given nuclear species. It is also an important tool for the identification of molecules and the examination of their electronic structure [7]. The ^{1}HNMR and ^{13}CNMR spectrawere recorded using a JEOL: GSX 500 instrument in D_2O as the solvent.

^{1}HNMR: The^{1}HNMR spectrum (Figure 4) of DLSP with D_2O as solvent shows well resolved characteristic peaks of different protons and chemical environment. The doublet at 3.52 ppm is due to the -CH proton attached to COOH group. The triplet at 4.64 ppm corresponds to -CH_2 carbon present in the amino acid. The sharp singlet's at 5.00 ppm and 11.0 ppm correspondto amine and carboxyl acid protons respectively.

^{13}CNMR:The^{13}CNMR spectrum (Figure 5) of DLSP shows three characteristic peaks corresponding to three different carbon environments in the compound. The peak absorbed at 69.2 ppm is due to the H_2C asymmetric carbon and peak at 74.6 ppm is the characteristic of -CH_2 carbon. The peak appeared at 174.58 ppm confirms the presence of carbonyl carbon of -COOH group.

D. UV-Vis-NIR spectral analysis

The UV-Vis-NIR spectrum of DLSP crystal was recorded in the wavelength region of 200-1000 nm using UV-Vis-NIR spectrophotometer in order to identify the suitability of the crystals for optical applications. The obtained transmittance spectrum shows (Figure 6) the cut off region at 252 nm. The spectrum also shows the presence of a wide precision window in the entire visible region. Hence, from the analysis of absorption spectrum, it is evident that the grown crystal is transparent in the entire visible region without any absorption peak, which is a major prerequisite for any nonlinear optical crystal having applications in second harmonic generation, parametric oscillations, etc. [8].

E. TG/DTA analysis

The thermogravimetric (TG) and differential thermal analyses (DTA) gives information about the phase transition and different stages of decomposition of the crystal. The thermal behavior of DLSP was studied using a PERKIN ELMER DIAMOND instrument at a heating rate of 10^{o}C.min^{-1} in the temperature range 20 ^{o}C- 800 ^{o}C in Nitrogen atmosphere. From the TGA curve (Figure7) it is observed that the DLSP crystal was stable up to 251^{o}C and then decomposed immediately after melting. The results of DTA specify that the sharp endothermic peak observed at 251°C is attributed to the melting point of DLSP. All other

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endothermic peaks are assigned to degradation of DLSP. From the results of DTA, no transformation in the structure is observed before melting.

F. NLO test

The Second harmonic generation (SHG) efficiency of DLSP crystals was determined using the Q-Switched Nd:YAG laser by Kurtz-Perry [9] powder method as it is a fast preliminary screening for the noncentrosymmetric structures to check whether they are useful for the NLO applications. In the present investigation, the samplewas exposed to the fundamental Q-switched Nd:YAG laser beam with wavelength of 1064 nm, input power of 3.2 mJ, pulse depth of 8 ns and pulse rate of 10 Hz.The second harmonic signal emission wavelength of 532 nm (green light) was generated. It was also observed that the DLSP crystal had SHG efficiency 3 times greater than that of KDP. The high efficiency of the material elucidates the strong future aspect of DLSP crystal for NLO applications.

IV. CONCLUSION

Optically clear single crystal of Di-(L-Serine) Phosphate monohydrate (DLSP) has been grown by slow evaporation technique. The powder XRD confirmed the crystallinity and the lattice parameters and crystal structure were obtained by the single crystal XRD analysis. The presences of various functional groups were confirmed byFT-IR and NMR (^{1}H and ^{13}C) spectral analysis. The UV-Vis-NIR spectrum showed that DLSP crystal is suitable for photonic applications. The thermal analysis confirmed that the grown DLSP single crystals are stable upto 251^{o}C.The Kurtz-Perry powder test confirmed the SHG efficiency is 3 time higher than that of the KDP.

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FIGURES

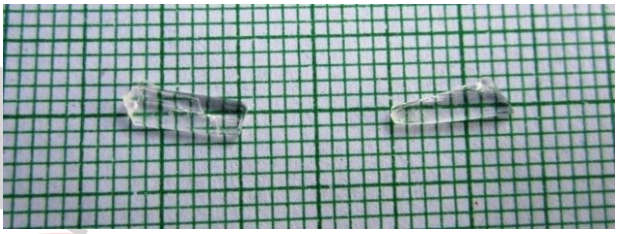

Figure1. As grown crystals of DLSP

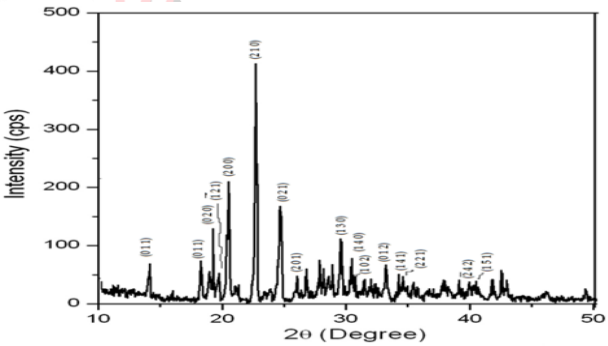

Figure 2. Powder XRD pattern of DLSP

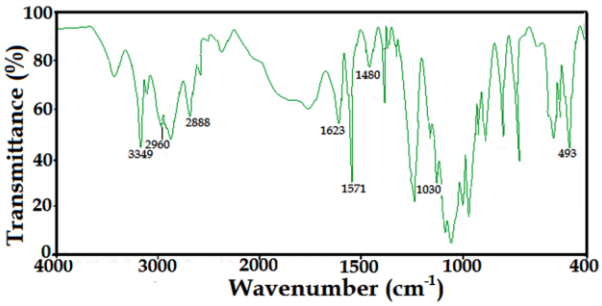

Figure 3. FT-IR spectrum of DLSP crystal

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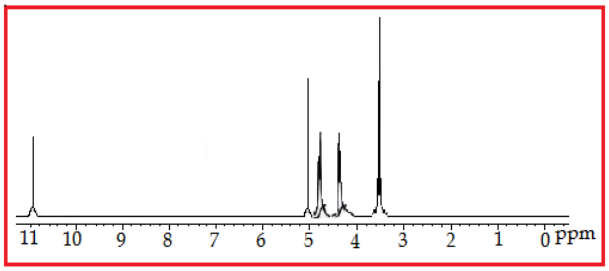

Figure 4. ^{1}HNMR spectrum of DLSP crystal

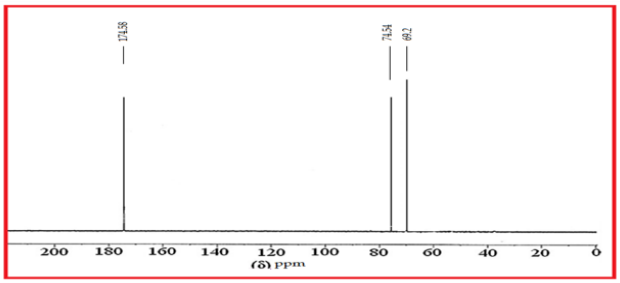

Figure 5. ^{13}CNMR spectrum of DLSP crystal

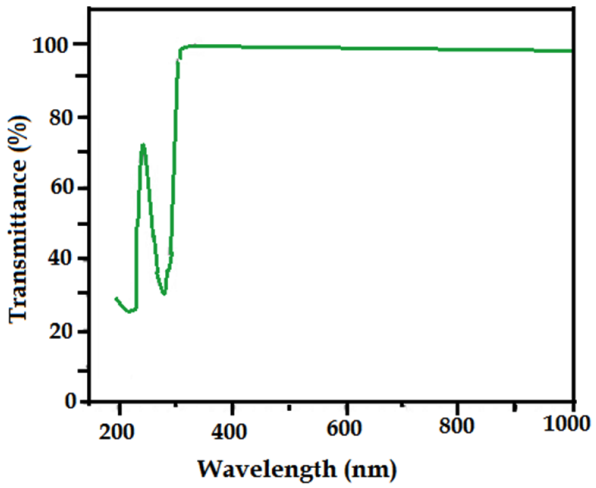

Figure 6. UV-Vis-NIR spectrum of DLSP crystal

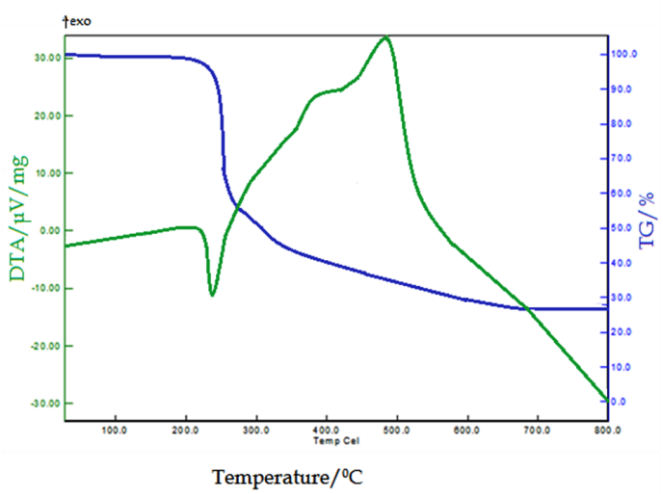

Figure 7. TGA/DTA curve of DLSP crystal

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