Growth, UV and IR Characterization of Tri- Glycine Potassium Sulphate [$NH_2CH_2COOH-K_2SO_4$] single [GPS] crystal

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ABSTRACT

Studies on dislocation & reactivity in organic crystalline materials play an important role in crystal growth, plasticity, crystal strength, ionic conductivity, electric conductivity & diffusion properties. The presence of dislocation governs or modifies a number of phenomenons. Etching behavior helps to understand surface characteristics & direction bonding. Studies on dislocations provide the information of ferroelectrics for the formation of domains. The interaction between domains and dislocation is not fully understood in organic ferroelectrics. Keeping this in view, crystalline materials were tried starting with amino acid having zwitter ions characteristics. In the present article Tri- Glycine Potassium Sulphate [$NH_2CH_2COOH-K_2SO_4$] single [GPS] crystal has been used for the study.

Keywords: *Crystal growth, ferroelectrics, IR, Surface Topology, UV.*

1. Introduction:

The factors affecting crystal growth [1] includes the presence of impurities, changing temperature and the pH of the solution to grow good crystal for investigation of mechanical, physical and electrical properties [2]. The crystal for water soluble components can be grown in laboratory by separation from aqueous solution. Though the crystallization [3] from a solution is of good quality than those obtained by other methods, the uniformity of the growth depends on the fact that slower the growth of the atoms, ions or molecule, have to pack together to form an ideal crystal. The ideal crystal is one in which space lattice continues from side to side. The excessive super cooling is avoided by rapid stirring of cooling solution to ensure that the crystal which forms first at the evaporating surface are distributed throughout the solution and the uniform growth in all directions will result [4,5].

In recent years, hybrid material [6] has attracted considerable attention for crystal growth. The inorganic derivatives of protein amino acids are often attributed to symmetric groups [7] without an inversion centre mostly to polar symmetry groups. These crystals have properties whose symmetry is described by odd -rank tensors such as pyro-electric effect, spontaneous electric polarization, piezoelectric effect, generation of second optical harmonics [8,9]. Tri- Glycine Sulphate (TGS) is a well-known ferroelectric and pyroelectric material. The ferroelectric crystals find important applications in opto electronics such as capacitors, non-volatile memory devices, actuators, high-performance gate insulators, etc. All ferroelectric materials are pyroelectric, however, not all pyroelectric materials are ferroelectric. Below Curie temperature, ferroelectric and pyroelectric materials are polar and possess a spontaneous polarization or electric dipole moment. However, this polarity can be reversed through the application of an electric field with ferroelectric materials.

2. Materials and Methods:

A) Synthesis and crystal growth of TGPS:

Single crystals of Tri- Glycine Potassium Sulphate crystals (TGPS), a semi organic nonlinear optical material was grown from solution by slow evaporation at ambient temperature [10]. Among these, the crystals with different proportion i.e. 1:1 and 3:1 were grown from aqueous solution by slow evaporation technique at room temperature. The pH of the solution at super-saturation was kept at 6.0. The solution was filtered and transferred to a petri dish for crystallization. This compound was re-crystallized twice for attaining purity.

Crystals of good quality appeared after about two weeks & crystals of appreciable size were obtained within six to eight weeks' time. The chemical composition of the grown crystals was determined by the FT-IR spectra. The structure is built from alternate layers of Glycine organic molecules and inorganic layers consisting of K^+ ions and SO_4^- ions. The grain size was found to be 5 microns.

Applications of various experimental techniques were employed depending on the factors like basic principles involved, advantages and limitations of each method. The fully grown crystals of GPS-1 & GPS-2 are shown in Fig. 1 a & 1 b.

Fig. 1a:Crystals of GPS - 1

Fig. 1b:Crystals of GPS - 2

This method was extensively used for obtaining single crystal of organic & inorganic materials. The factors affecting crystal growth are pH of solution, presence of impurities, temperature changes. The pure samples of seed crystals were characterized for UV, IR & other properties.

The pellets of TGPS were subjected to infrared light in range 4000 -500 cm^{-1} which is usually used for organic crystals. FT-IR 1600 Perkin Elmer was used for IR analysis. The etched and dried crystal face was mounted on glass plate using sand clay and then it was examined under a metallurgical "METZER" universal trinocular metallurgical research microscope [METZ-780]. "METAPHOT" was used for the topographical and dislocation studies on crystals. The absorption spectrum for the title crystal was recorded using JASCO corp., V-570, UV-VIS spectrometer in the region 190-2500 nm.

B) Characterization:

i. **IR Studies:** From the IR studies, it was concluded that the presence of potassium makes absorption more sharp with decrease in concentration of potassium. Linear variation of band shift is observed. Glycine is seen to exist in Zwitter ionic form. Fundamental characteristic variations are mostly achieved showing molecules having lack of centre of symmetry. The presence & absence of water of crystallization is confirmed by peaks in 3400 cm^{-1} in IR region. Fig.2a and 2b represent the IR spectra for GPS-1 & GPS-2 crystals respectively.

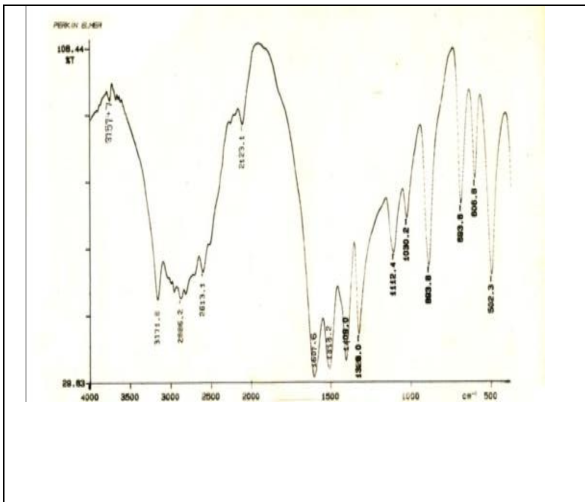

Fig.2a : IR Spectra of TGPS -1

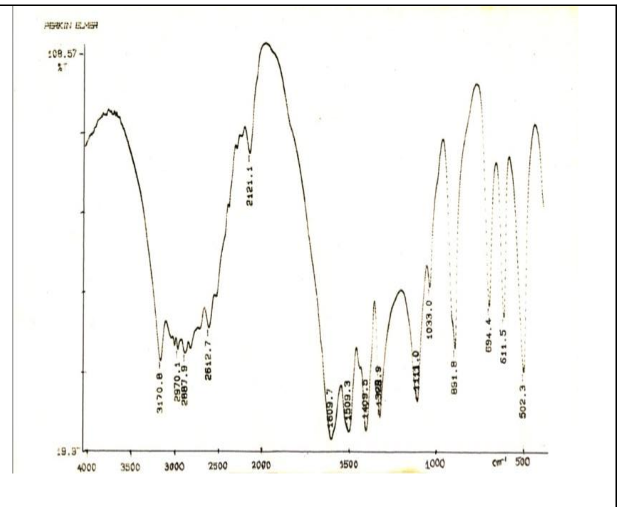

Fig.2b : IR Spectra of TGPS- 2

Table 1 depicts that both spectra exhibits strong acid stretch and then weak and continuous N-H stretch in 2500 -3500 cm^{-1} region. The -COO bands for both crystals are in the frequency range 502- 694 cm^{-1} and anti symmetric stretch at 1409 cm^{-1} is clearly seen to split C-CN band are observed from 891-1033 cm^{-1} region. NH_3 deformation are observed from 1509-1609 cm^{-1} amino acid absorption, the bands attributable to NH_3^+ groups and COO^- groups exhibit absorption maximum indicating the glycine molecule exist as zwitterionic.

Table 1: Frequency assignments for GPS-1 and GPS-2 crystals

Sr.No	GPS-1 (cm^{-1})	GPS-2 (cm^{-1})	Band assignments
1	502.3	502.3	N asymmetrical stretching
2	611.5	606.8	COO- scissoring
3	694.4	693.6	COO- rocking
4	891.8	893.8	CCN symmetrical stretching
5	1033.0	1030.2	CCN asymmetrical stretching
6	1111.0	1112.4	NH_3 rocking
7	1323.9	1328.0	NH_2 twist
8	1409.5	1409.0	COO^- symmetrical stretching
9	1509.3	1513.2	NH_3^+ symmetrical stretching
10	1609.7	1607.6	NH_3 deformation
11	2121.1	2123.1	Characteristic amino acid comb. band
12	2612.7	2613.1	N-H hydrogen bonded
13	2887.9	2886.2	CH_2 symmetrical stretching
14	2970.1	2971.0	C-H stretching
15	3170.8	3171.8	NH_3^+ stretching

ii. UV – Visible Spectra studies:

The optical absorption spectra of Tri- Glycine Potassium Sulphate crystals (TGPS) were recorded in the range 190–2500 nm using Varian Carry 5E spectrophotometer. The absorption spectra obtained for grown samples with highly transparent single crystal of TGPS of thickness 3.2 mm is shown in Fig. 3.

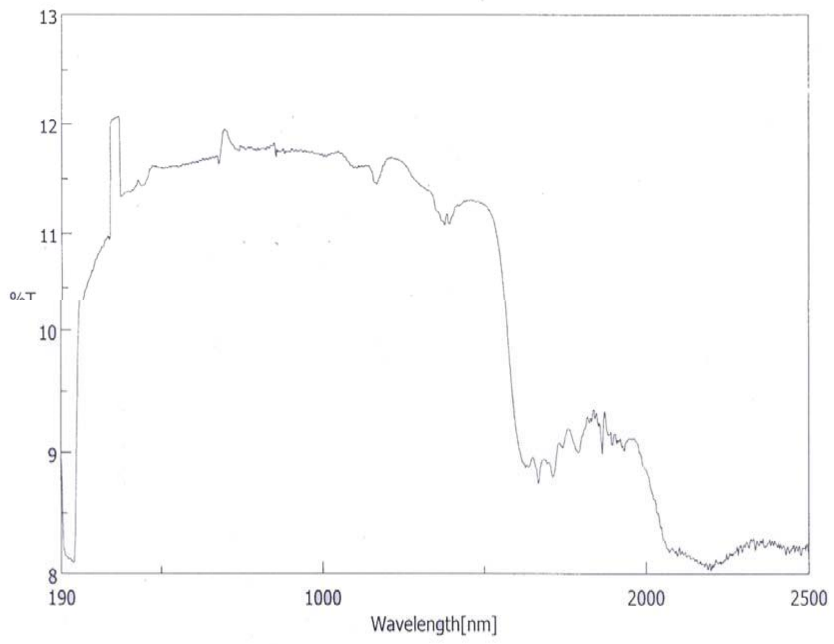

Fig.3. UV – Visible Spectrum of Tri- glycine potassium Sulphate Crystal

3. Result and Discussion:-

Geometry of grown crystals: The shape of number of crystals of various sizes has been studied. Crystal wi t h 18x15x3 mm^3 size shows the geometry as represented in Fig. 4 and 5.

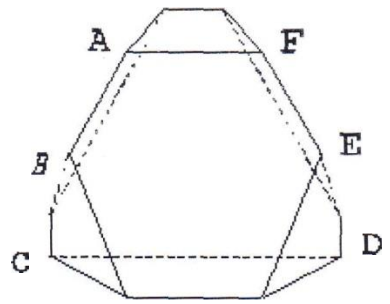	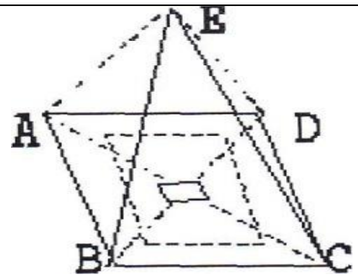
Fig.4: Development with triangular structure	**Fig. 5: Growth of periodical crystal**

But, the crystal geometry has been drawn using the dimensions of the grown crystals. Triangular faces with truncated corners in Fig. 4 represents [111] family plane, whereas the bottom face of crystals such as in Fig. 5 corresponds to [110] family as is evident from the crystal symmetry.

The pH of the solution is more important during the growth of crystal. After K_2SO_4 is added to glycine, the external growth features are changed. The external geometry of the crystal does not change while the physical nature of crystal is also same, as that of glycine when heated i.e. decomposition to brown colour.

In IR spectra, the presence of potassium makes the absorption sharper with decrease in concentration of potassium an overall linear variation of hand shifts is observed [11]. The presence of water of crystallization is confirmed by the peaks in 3400 cm^{-1} region. The symmetry of tri- glycine potassium sulphate is seen different than the symmetry of glycine crystal. This may be due to the high chemical reactivity of sulphate acid with glycine molecule as compared to that of potassium sulphate.

The topographical studies [12] on cleavage faces has been reported that (a) faint line having perfect crystallographic orientation are the ferroelectric domain walls as supported by evidence of formation of wedge. (b) Domain walls show the correspondence on matched faces but washed out after heavy etching (c) No dislocation etch pits are observed; it is very difficult to say that there is no co-ordination number between the domain and dislocation[13] interaction. (d) The crystals when heated beyond the transition temperature do not change the geometry. This conclusion is regarding domain dislocation interaction.

The UV absorption spectrum showed that the crystal is transparent in the range 280-1365 nm without any absorption peak, which is an essential parameter of nonlinear optical crystals. The absence of absorption of light in the visible region is the intrinsic property of the amino acids.

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