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GROWTH AND CHARACTERIZATION OF PURE AND SODIUM SULPHATE DOPED CRYSTALS OF GLYCINE POTASSIUM SULPHATE

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Abstract:

Single crystals of undoped (pure) glycine potassium sulphate (GPS) and sodium sulphate doped glycine potassium sulphate have been grown by the free evaporation method and the grown crystals have been characterized by various studies. Effect of sodium sulphate on the properties of glycine potassium sulphate (GPS) has been investigated here. X-ray diffraction analysis indicates the structure of the crystals as orthorhombic. The functional groups have been identified using Fourier transform infrared spectral analysis. The UV –Vis-NIR spectral analysis shows that these crystals have their cut off wavelength around 200 nm. Second Harmonic generation (SHG) measurement shows that the grown crystals are NLO crystals. Microhardness measurement was carried out for samples. Solubility was measured for both the samples at different temperatures. LDT of the samples have been determined. Due to doping, there is an increase in optical transparency, microhardness, LDT and solubility of the GPS crystals.

Key Words: Semiorganic NLO, Doping, Crystal Growth, XRD, SHG, Microhardness & Solubility

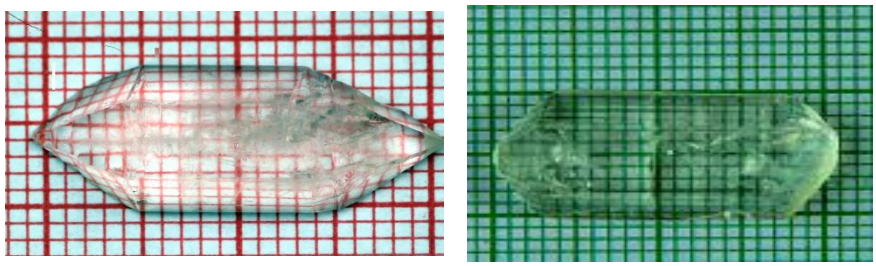
1. Introduction:

Nonlinear optical (NLO) materials for optical second harmonic generation (SHG) have received much attention owing to their practical application in the domain of optoelectronics and photonics. Crystalline semiorganic salts of amino acids have recently attracted considerable interest among researchers. The amino acid group materials have been mixed with inorganic salts to form adducts or complexes in order to improve their mechanical, thermal and NLO properties.[1-3]. Glycine is an organic material and it is a simple amino acid having three polymorphic forms, viz., α, β and γ forms. .Both α and β forms crystallize in centrosymmetric space group $P2_1/c$ [4, 5]. γ-glycine crystallizes in non-centrosymmetric space group $P3_1$ [6,7] making it a candidate for piezoelectric and NLO applications. New electronic materials of glycine can be synthesized from solutions containing specific ratios of the components. Some complexes of glycine with inorganic salts have already been reported to be promising materials for SHG such as glycine sodium nitrate[8], glycine silver nitrate[9], glycine hydrogen nitrate[10], glycine hydrogen phosphate[2], glycine potassium sulphate[11], glycine lithium sulphate [12], glycine zinc sulphate[13], glycine zincchloride[14], diglycine manganese chloride[15], triglycinefluoro beryllate [16]etc. It is generally understood that materials with wide range of optical properties are required for practical applications. In order to satisfy this requirement, it is necessary either to discover new materials or to modify the existing materials. In an attempt to discover new crystalline materials for industrial applications, in the present study, we have made an attempt to combine glycine with potassium sulphate to form glycine potassium sulphate (GPS) single crystal. Also, we have investigated the effect of sodium sulphate as an impurity on the physical properties of GPS single crystals. The results obtained are reported herein and discussed.

2. Experimental Details:

2.1 Synthesis and Growth of Crystal:

An aqueous solution was prepared by dissolving analytical grade chemicals of glycine and potassium sulphate in 1:1 molar ratio with continuous stirring using a magnetic stirrer for five hours at room temperature. To obtain the sodium sulphate doped sample, 1 mol% of sodium sulphate (Na_2SO_4) was added to the solution of GPS. The prepared solution was filtered and kept undisturbed in a constant temperature bath maintained at a temperature of 30 ^oC. When evaporation takes place slowly, supersaturation is activated. Initially, small crystal nuclei are formed in the supersaturated solution and due to slow evaporation, the crystal nuclei are converted into big-sized crystals. Transparent and colourless single crystals of undoped and sodium sulphate doped glycine potassium sulphate were harvested within a period of about 25 days. The harvested crystals are shown in the figure 1.



(a) (b)

Figure 1: The grown (a) undoped and (b) sodium sulphate doped GPS crystals

2.2 Measurement of Solubility:

. Solubility of the material in a solvent decides the amount of the material which is available for growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and if too low, it restricts the size and growth rate of the crystals. Solubility gradient is another important parameter which dictates the growth procedure. Solubility study was carried out using a constant temperature bath (CTB) by gravimetrical method. The salt of the prepared sample was added step by step to 20 ml of double distilled water in an air-tight container kept in the CTB and the stirring was continued till a small precipitate was formed at 30 ^{o}C. Then, 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of the samples water was determined. The same procedure was followed to find solubility of sample at other temperatures using the constant temperature bath. Figure 2 shows the solubility curves for undoped and sodium sulphate doped GPS crystals. From the graph, it is observed that the solubility of the sample in water increases with temperature, exhibiting a high solubility gradient and it has positive temperature coefficient of solubility. In this figure, there are three regions namely, supersaturated region above the curve, saturated region along the curve and undersaturated region below the curve. It is observed that the solubility is more when GPS crystals are doped with sodium sulphate and this indicates that the solution accommodates more solute in the case of doped sample.

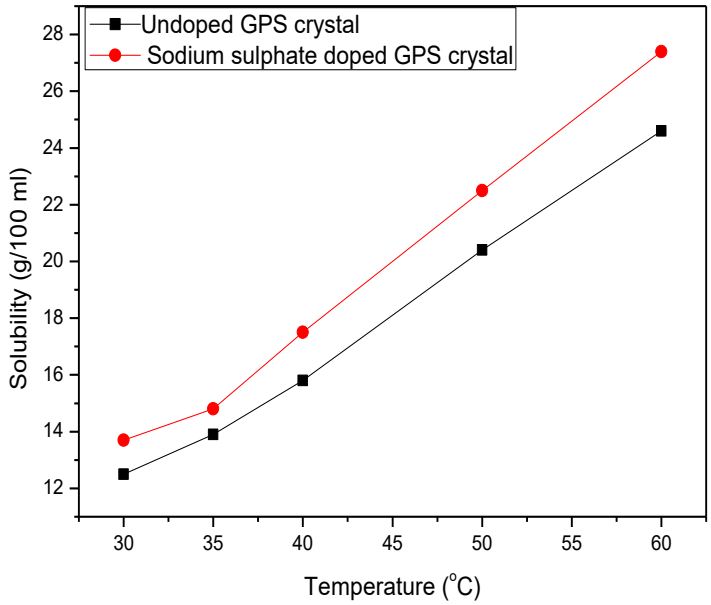


Figure 2: The solubility curves for undoped and sodium sulphate doped GPS crystals

2.3 Analysing Techniques:

The grown single crystals of pure and sodium sulphate doped GPS were subjected to single crystal XRD studies using a BRUKER KAPPA APEX II diffractometer with CuK_{α} radiation (λ = 1.54056 Å). X-ray powder diffraction analysis was carried out for the crystal grown using an automated X-ray powder diffractometer (PANalytical) in the 2θ range 10-70° with CuK_{α} radiation (λ = 1.54056 Å).The reflection data were indexed following the procedures of Lipson and Steeple [17]. Fourier transform infrared (FTIR) spectra were recorded by the KBr pellet method for the crystal grown in the wave number range 400-4000 cm^{-1} by using a SHIMADZU spectrometer. The UV-Vis-NIR absorption spectra were recorded in the wavelength range 190-1100 nm for the crystals grown by using a Lambda-35 spectrophotometer. The NLO property of the grown

crystals was tested by passing the output of Nd-YAG Quanta ray laser (with fundamental radiation of wavelength 1064 nm) through the crystalline powder sample [18].The SHG output from the sample was compared from KDP. Vickers hardness measurements were carried out on the grown crystals by making indentations on the large area faces using a SHIMADZU HMV2 microhardness tester.

3. Results and Discussion:

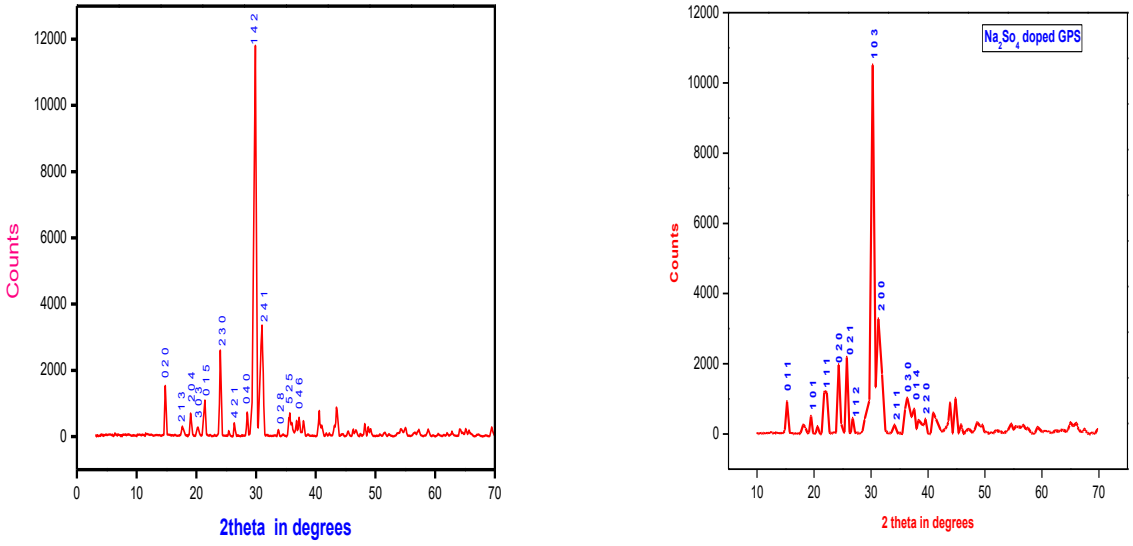
3.1 X-Ray Diffraction Studies:

X-ray diffraction (XRD) method is used to find the crystal structure of the crystals. The lattice parameters of pure and Na_2SO_4 doped GPS crystal obtained through single crystal XRD analysis are presented in Table 1.The study reveals that pure and Na_2SO_4 doped GPS crystallize in the orthorhombic structure. The observed difference in lattice volume is very small to have any lattice distortion in the GPS crystal due to doping. This confirms that the dopant atoms have entered into the GPS crystal matrix but not distorted the regular structure of the GPS crystal. There is a slight changes in lattice parameters have been noticed for the sodium sulphate doped GPS sample compared to that of a pure GPS sample. The changes are mainly due to the incorporation of Na_2SO_4 in the lattice of GPS crystal. The presence of dopant in a GPS crystal may produce lattice strain, which leads to change of unit cell parameters in a Na_2SO_4 doped GPS crystal. The recorded powder XRD patterns of the grown crystals are shown in Figure 3. Appearance of sharp and strong peaks confirms the crystalline nature of the samples. The diffraction peaks were indexed for the orthorhombic system. It is noticed that there is a slight shift in diffraction peaks and change in the intensity of the powder XRD pattern of doped sample compared to that of a pure sample and this shift is mainly due to the doping of sodium sulphate into the lattice of pure GPS crystal. It is observed that the unit cell parameters obtained from powder XRD analysis are almost same as the values obtained from single crystal XRD studies.

Table 1: Single crystal XRD data for pure GPS and sodium sulphate doped GPS crystal

$\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$

Crystal	Lattice parameters			Volume of the unit cell ($Å^3$)
	a (Å)	b(Å)	c(Å)	
Pure GPS	7.4725(3)	5.7668(10)	10.0640(7)	433.684 (5)
Na_2SO_4 doped GPS	7.4947(10)	5.7789(11)	10.0534(9)	435.420(12)



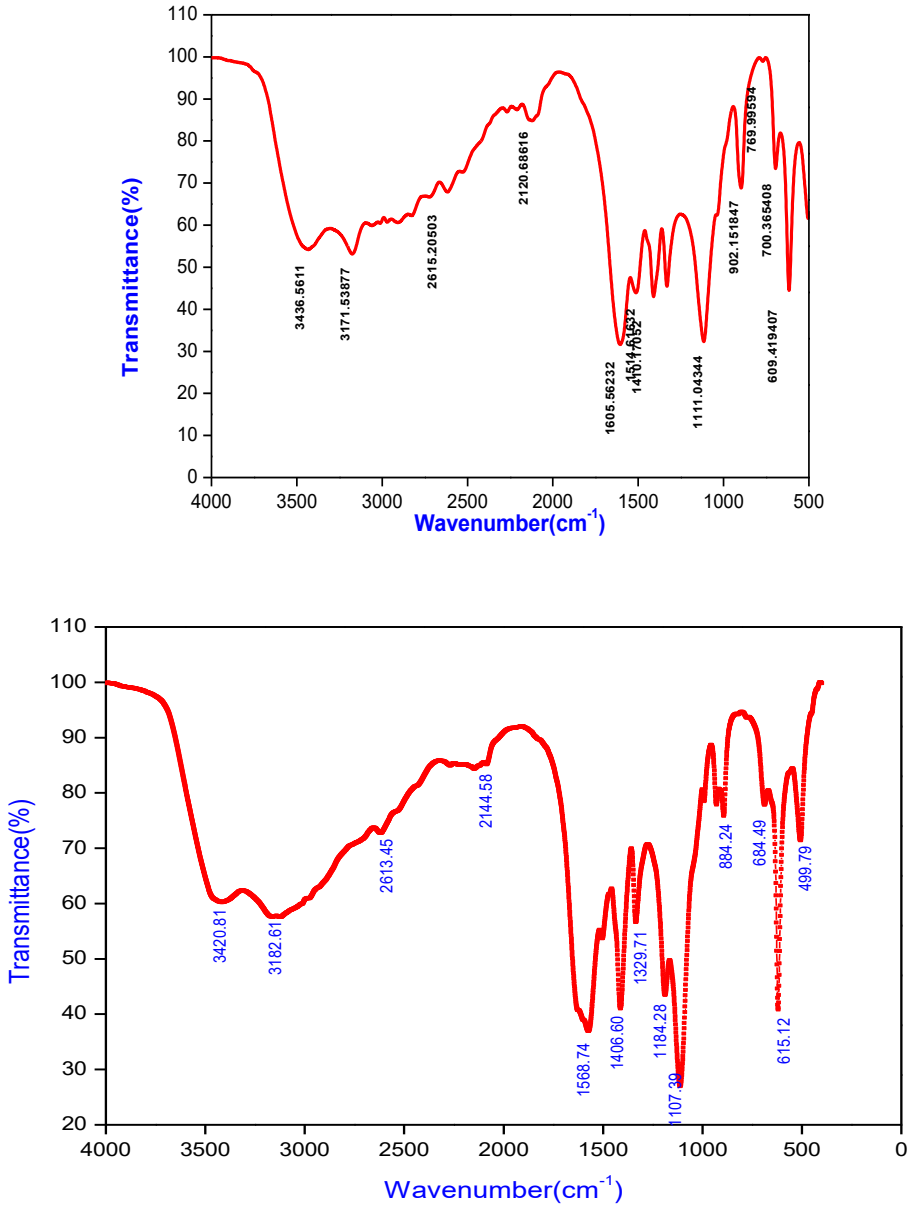
(a) (b)

Figure 3: Powder XRD patterns of (a) pure GPS and (b) Na_2SO_4 doped GPS

3.2 Fourier Transform Infrared (FTIR) Spectral Analysis:

FTIR spectra of the samples have been recorded using an FTIR spectrometer and it is shown in the figure 4. The absorption due to the carboxylate group of free glycine is normally observed in the region 607 and 1413 cm^{-1}, whereas in the case of GPS and doped GPS crystal, these peaks are shifted to 609, 1410 cm^{-1} and 684.49 ,1406.60 cm^{-1} respectively. Similarly the transmission peaks for the NH_3^+ group of free glycine are observed at 1110, 1507 and 3175 cm^{-1} respectively. In the GPS crystal and doped GPS crystal, NH_3^+ group of free glycine are shifted to 1111, 1514, 3171 cm^{-1} and 1107.39, 3182.61 cm^{-1} respectively. This observation confirms that glycine exists in the zwitterionic form and the involvement of NH_3^+ in hydrogen bonding is evident by the fine structure of the bond in the lower energy region. The peaks observed at nearly 1333 cm^{-1} correspond to the CH_2 group. Observation of peaks at nearly 884.24 and 1107.39 cm^{-1} can be assigned to the

SO_4^{2-} group. A less intense peak observed at nearly 2144.58 cm^{-1} may be due to the combination bond. Thus, with the help of available data on the vibrational frequencies of amino acids [19] all the molecular groups present in sodium sulphate doped GPS crystal could be identified.

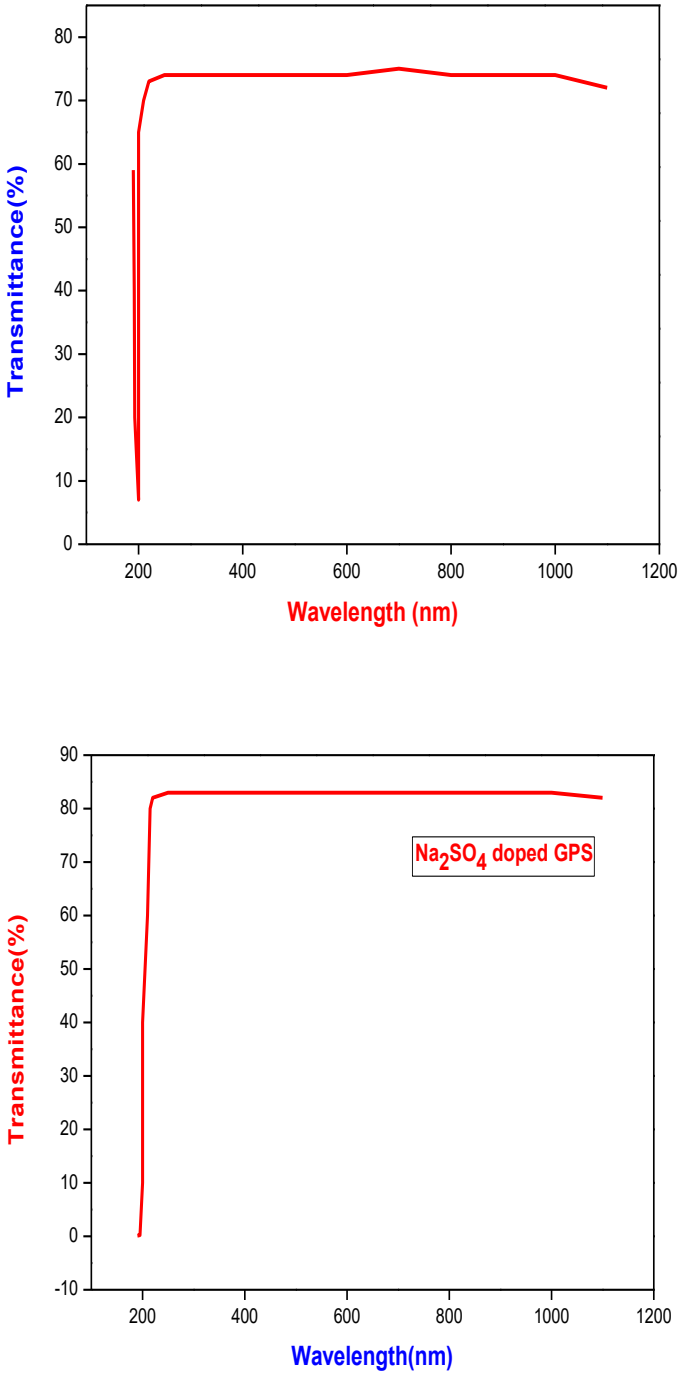


(a) (b)

Figure 4: The FTIR spectra of (a) pure GPS and (b) Na_2SO_4 doped GPS samples

3.3 UV-Vis-NIR Spectral Analysis:

UV-visible-NIR transmittance spectra of pure GPS and Na_2SO_4 doped GPS crystals in the wavelength range of 190 nm-1100 nm are shown in figure 5.This spectral study may be assisted in understanding the electronic structure of the optical band gap of the crystal. The study of absorption edge is essential in connection with the theory of electronic structure which leads to the prediction of whether the band structure is affected near the band extreme. From the transmittance spectra, it is noticed that sodium sulphate doped GPS crystals have high transmittance in the entire visible-NIR region of the spectra than the undoped GPS crystal. This property enables the materials for optoelectronics applications and second Harmonic generation from Nd-YAG laser. Efficient nonlinear optical (NLO) crystals have optical transparency and lower cut-off wavelengths between 200 and 400 nm[20].This indicates that the crystals grown in the present study can be considered as promising NLO crystals.



(a) (b)

Figure 5: Transmittance spectra of (a) pure GPS and (b) Na_2SO_4 doped GPS crystals

3.4 Mechanical Properties:

Mechanical property of the samples was studied by measuring microhardness number with various loads. The hardness of a material is a measure of its resistance to plastic deformation. The permanent deformation can be achieved by indentation, bending, scratching or cutting. In an ideal crystal the hardness value is independent of the applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect (ISE) as reported in the literature [21, 22]. The plot of Vickers microhardness number as a function of the applied load is shown in Figure 6. It is observed that the Vickers hardness number increases with increase in load. From the result, it is observed that the hardness of the GPS crystal increases when it is doped with sodium sulphate.

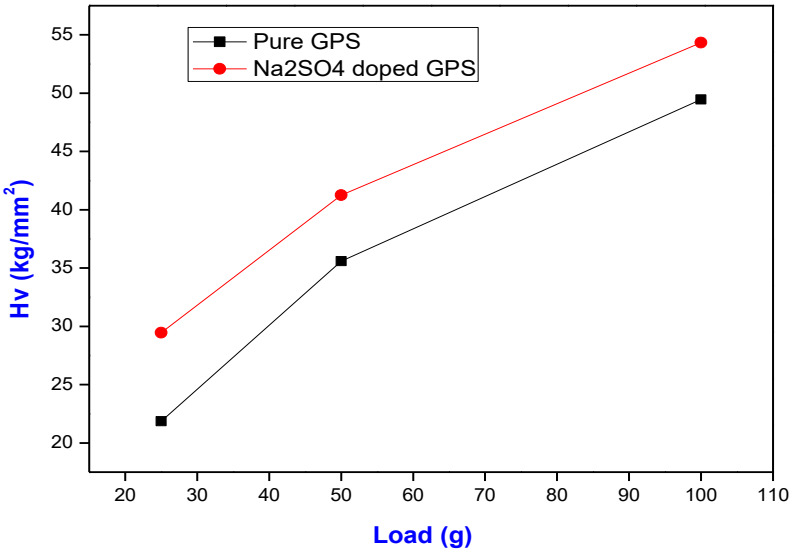


Figure 6: Plot of variation of hardness with load for GPS and Na_2S_4 doped GPS crystals

3.5 Second Harmonic Generation:

The NLO property of the grown crystal was tested by passing the output of Nd-YAG Quanta ray laser with fundamental radiation of wavelength 1064 nm through the crystalline powder GPS sample by Kurtz and Perry method [18]. It is noticed that there is no emission of green light from the sample and this gives the conclusion that GPS is not having SHG property. But sodium sulphate doped GPS crystal is subjected to NLO test and there is an emission of green radiation from the sample and it confirms the second harmonic generation in the crystal. SHG output from the sample was compared with that from KDP crystal. The SHG relative efficiency of sodium sulphate doped GPS crystal is about 0.41 times that of KDP.

3.6 EDAX Analysis:

An elemental analysis was carried out for sodium sulphate doped GPS crystals by employing energy dispersive analysis by X-ray in order to confirm the composition of elements in the doped crystals. Figure 7 shows the EDAX spectrum of sodium sulphate doped GPS crystal. From the spectrum, it is clear that the elements such as C, O, N, S, Na and K were present in the crystal.

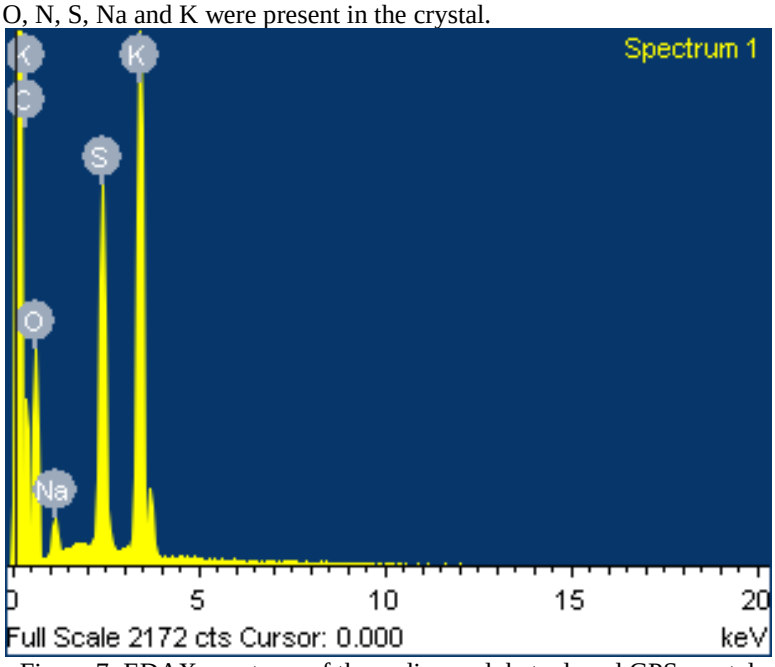


Figure 7: EDAX spectrum of the sodium sulphate doped GPS crystal

3.7 Measurement of LDT:

Laser damage threshold (LDT) testing is a method for quantifying the amount of electromagnetic radiation an optical component can withstand. Laser beams often contain high energies and are capable of damaging sensitive optical components. The type of damage induced to an optical component by a laser beam is

dependent on the wavelength, pulse length, polarization and spatial characteristics. During exposure to a continuous wave (CW) laser, failure can occur due to laser energy absorption and thermal damage or melting of the substrate material or the optical coating. The damage caused by a short nanosecond laser pulses is typically due to dielectric breakdown of the material that results from exposure to the high electric fields in the laser beam. Laser damage threshold (LDT) values for the sample was measured using an Nd:YAG laser (1064 nm, 18 ns pulse width). After exposure, the sample is examined by a microscope (~ 100 times magnification) for any visible damage. The number of locations that are damaged at a particular power/energy level is recorded. The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). LDT value is determined using the formula $P = E/ \tau \pi r^2$ where E is the energy in mJ, r is radius of the spot in mm and τ is the pulse width. The obtained value of LDT of the grown undoped glycine potassium sulphate crystal 0.647 GW/cm^2 and that for sodium sulphate doped GPS crystal is 0.735 GW/cm^2.

4. Conclusion:

Pure and sodium sulphate doped glycine potassium sulphate single crystals have been successfully grown by the free evaporation method and characterized. The solubility is observed to increasing when GPS crystals are doped with sodium sulphate. The unit cell parameters have been evaluated by single crystal XRD and powder XRD methods. The FTIR spectra were recorded for the samples and functional groups were identified. The UV-visible-NIR spectra show that the grown crystals have good optical transmittance window in the entire visible –NIR region. NLO property is confirmed by Kurtz and Perry technique. Microhardness studies of the samples have been carried out to understand the behavior of mechanical strength of the samples. The elements present in the sodium doped GPS crystal have been identified by EDAX analysis.

5. References:

1. M. N. Bhat and S. M. Dharmaprakash, J. Cryst. Growth 235 (2002)511-516 .
2. A. Deepathyand H. L. Bhat, J.Cryst.Growth226 (2001)287-293.
3. R. Rajasekaran, P. M. Ushashree, R. Jayavel and P. Ramasamy, J.Cryst.Growth229 (2001)563-567.
4. G. Albrecht, R. B. Corey, J.Am.Chem.Soc.61, 1087(1939)
5. E. Fischer, Ber.Deutsch.Chem.Ges.38, 2917 (1905)
6. Y. Iitaka, Acta.Cryst.11, 25 (1958)
7. Y. Iitaka, Acta.Cryst.14,1 (1961)
8. M. N. Bhat and S.M. Dharmaprakash, J. Cryst.Growth236 (2002) 376-380.
9. J. K. Mohan Rao and M.A. Vishwamitra, ActaCrystallogr. B 28 (1972) 1484.
10. S. A. Martin Britto and S. Natarajan, Mater. Lett. 62(2008) 2633-2636.
11. Ra. Shanmugavadivu, G. Ravi and A. Nixon Azariah, J.Phys. and Chem. Solids 67 (2006) 1858-1861.
12. M. R. Suresh Kumar, H. J. Ravindra and S. M. Dharmaprakash, J. Cryst. Growth 306 (2007) 361-365.
13. T. Balakrishnan and K. Ramamurthi, Spectrochim. Acta Part A 68 (2007) 360-363.
14. T. Balakrishnan and K. Ramamurthi, Mater. Lett. 62(2008) 65-68.
15. R. Pepinsky, K. Vedam and Y. Okaya, Phys .Rev. 110(1958) 1309-1311.
16. S. Hoshino, T. Mitsui, F. Jona and R. Pepinsky, Phys.Rev. 107(1957) 1255-1258.
17. H. Lipson and H. Steeple Interpretation of X-ray power Diffraction Patterns, MacMillan, New York, 1970.
18. S. K. Kurtz and T. T. Perry, J. Appl. Crystallography 9 (1968) 3798-3813.
19. R. S. Krishnan, K. Sankaranarayanan and K. Krishnan, J.Indian Inst. Sci. 55 (1973) 313.
20. U. Le. Fur, R. Masse, M. Z. Cherkaoui and J. K. Nicoud, Z. Kristallogr. 210 (1995) 856.
21. P. N. Kotru, A. K. Razdan, B. M. Wanklyn, J. Matter. Sci. 24 (1989)793.
22. J. B. Charles, F. D. Gnanam, J. Matter. Sci. Lett. 12 (1993) 1395.