Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(5):177-185

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Growth, NLO, Z-scan and impedance studies of glycine potassium sulphate crystals grown by aqueous solution technique

N. Rathna[a], V. S. John[b], T. Chithambarathanu[c] and P. Selvarajan[d]

[a]*Department of Physics, Chandy College of Engineering, Tuticorin-628005, Tamil Nadu, India*
[b]*Department of Physics, T. D. M. N. S. College, T. Kallikulam-627113, Tamil Nadu, India*
[c]*Physics Research Centre, S. T. Hindu College , Nagercoil-629003, Tamil Nadu, India*
[d]*Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, India*

ABSTRACT

Semiorganic and third order nonlinear optical crystals viz. Glycine Potassium Sulphate (GPS) crystals with high degree of transparency were grown from aqueous solution of glycine and potassium sulphate mixed in 1:1 molar ratio at room temperature by slow evaporation solution growth technique. Solubility of the sample was determined at different temperatures. The grown crystal was subjected to X-ray diffraction method to identify the crystal structure. The obtained compound is observed to be crystallizing in orthorhombic structure with the space group Pnma. *The Second Harmonic Generation (SHG) relative efficiency of the grown crystal was checked by Kurtz and Perry powder technique. The third order nonlinear optical property of GPS crystal was analyzed by Z-scan experiment and the values of nonlinear absorption coefficient, nonlinear refractive index and third order nonlinear susceptibility were calculated. The real and imaginary parts of impedance and electric modulus were investigated for the GPS crystal as a function of frequency and temperature.*

Key words: Semiorganic NLO; Crystal growth; Solution method; XRD; EDAX; SHG; Z-Scan; Impedance

---

INTRODUCTION

The nonlinear optical (NLO) properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades [1]. Among the organic crystals for NLO applications, amino acids display special features of interest such as molecular chirality which secures acentric crystallographic structure. 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 centro symmetric space group $P2_1/c$ [2,3]. γ-glycine crystallizes in non-centro symmetric space group $P3_1$[4,5] making it a candidate for piezoelectric and NLO application. 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[7], glycine silver nitrate[8], glycine hydrogen nitrate[9], glycine hydrogen phosphate[6], glycine potassium sulphate[10], glycine lithium sulphate [11], glycine zinc sulphate[12], glycine zincchloride[13], diglycine manganese chloride[14], triglycinefluoro beryllate [15]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. This paper deals with the growth and various studies of GPS crystals. The aim of this paper is to present the results of XRD, EDAX, SHG, Z-scan and impedance studies.

EXPERIMENTAL DETAILS

2.1 Synthesis, Growth and Solubility

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. The prepared solution was filtered and kept undisturbed in a constant temperature bath maintained at a temperature of 30 ^{o}C. When evaporation takes place slowly, supersaturation is activated. As a result, transparent and colourless single crystals of glycine potassium sulphate (GPS) were formed in a period of about 25 days.

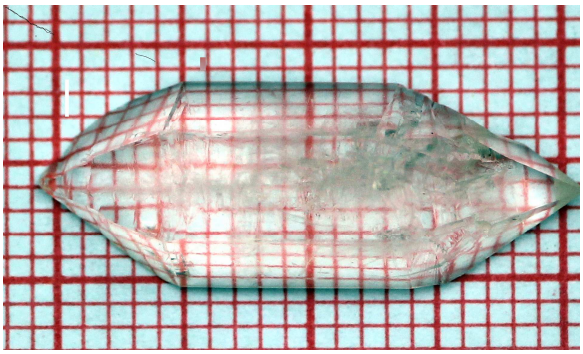

Fig.1: The grown glycine potassium sulphate single crystal

The solubility study of GPS salt was carried out in a solvent of double distilled water at five different temperatures (30, 35, 40, 45 and 50 ^{o}C). The solubility was determined by dissolving GPS salt in 100 ml of double distilled water at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The variation of solubility with temperature is shown in Fig.2. The results indicates that the sample has positive temperature coefficient of solubility because the solubility increases as the temperature increases.

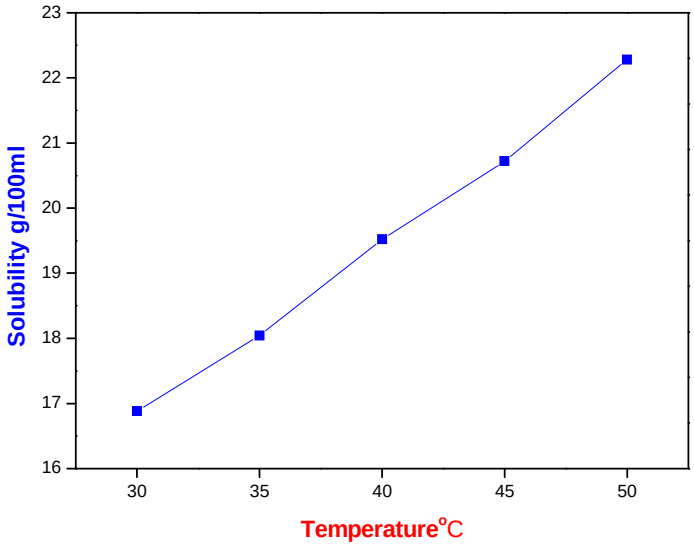

Fig.2: The solubility curve for GPS crystal

RESULTS AND DISCUSSION

3.1 XRD studies

The X-ray diffraction analysis on the grown GPS crystal was used to confirm the crystalline nature and identification of the unit cell parameters. The study for GPS crystal was carried out using Bruker4 SMART KAPPA APEX II CCD diffractometer using graphite monochromatized MoKα radiation (λ= 0.71073 Å). It is observed that the GPS crystal belongs to orthorhombic structure with centrosymmetric space group Pnma. The obtained single crystal XRD data are given in the table 1.

Table 1: Single crystal XRD data for GPS crystal

Unit cell dimensions	a = 7.4725(3) Å, alpha = 90 deg.
	b = 5.7668(3) Å, beta = 90 deg.
	c = 10.0640(5) Å, gamma = 90 deg.
Volume	433.684(4) $Å^3$
Z, Calculated density	4, 2.561 g/cc
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pnma

For the confirmation of the crystal structure obtained by single crystal XRD studies, powder X-ray diffraction studies were also carried out using a powder X-ray diffractometer in reflection scan mode. The powder XRD of the grown crystal is shown in Fig 3. The well defined Bragg's peaks at specific 2-theta angles show the high crystallinity of the sample. The diffraction peaks were indexed for the orthorhombic system. The software packages such as INDEXING and UNITCELL were used for the analysis of the powder XRD data.

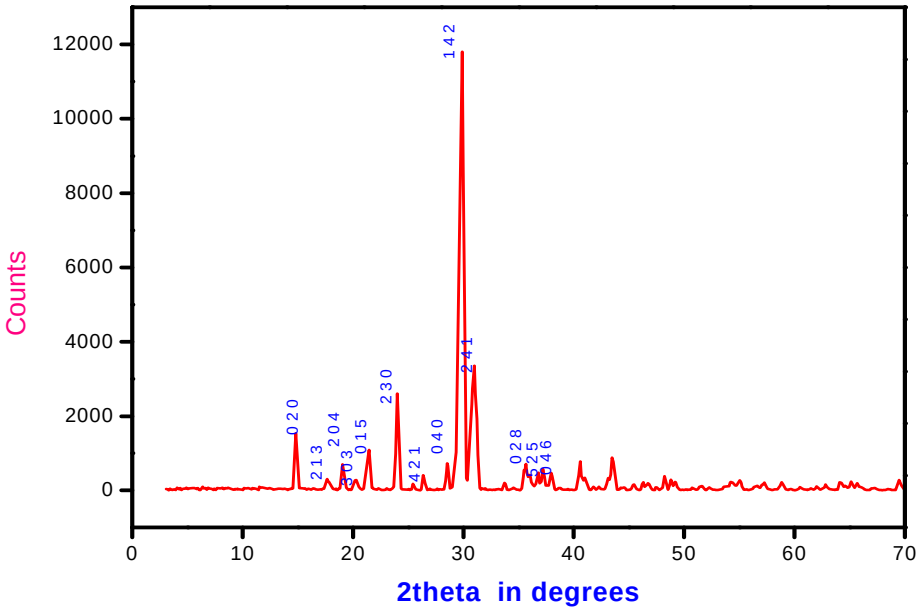

Fig.3: Powder XRD pattern of the grown GPS crystal

3.2 EDS analysis

Energy dispersive spectroscopy (EDS) is an analytical technique used for the elemental analysis of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. The EDS detector measures the relative abundance of emitted X-rays versus their energy. The detector is typically lithium drifted silicon, solid state device. EDS studies were performed using the EDS detector (Oxford Instruments, INCA Penta FETx3). The recorded EDS spectrum for the grown GPS is shown in the figure 4. From the spectrum, it is clear that the elements such as C, O, N, S and K were present in the crystal.

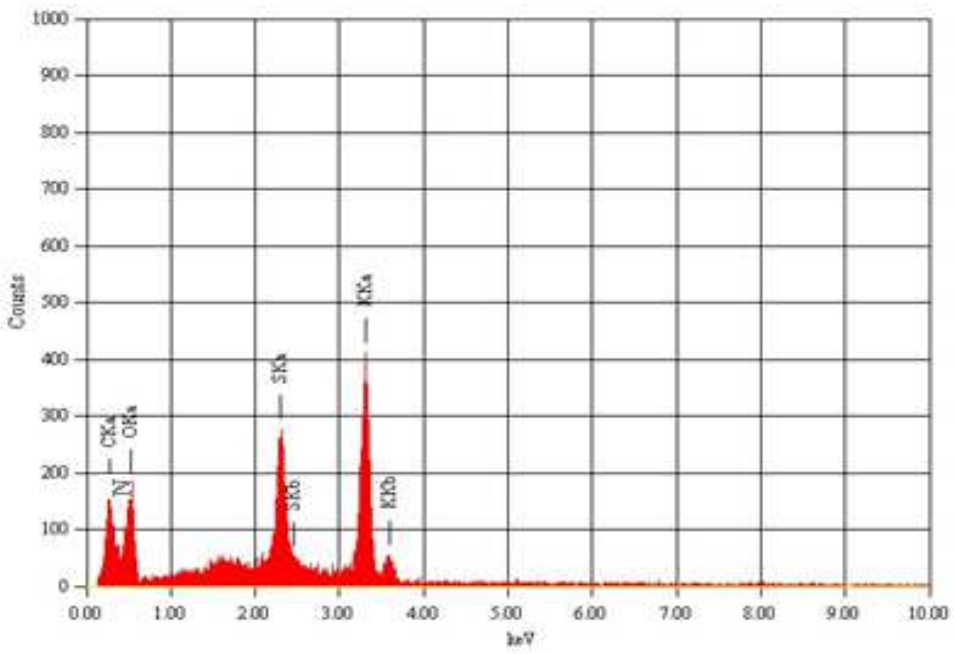

Fig.4: EDAX spectrum of the grown GPS crystal

3.3 Second Harmonic Generation (SHG)

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 sample. The method used here is Kurtz and Perry method [16]. The SHG output from the sample was compared with that from KDP. From the experiment, is is noticed that there is no green light is emitted from the sample and this gives the conclusion that the grown crystal gives zero second order susceptibility coefficient and hence GPS crystal is a centrosymmetric crystal.

3.4 Z-scan studies

Z-Scan technique was originally introduced by Sheik Bahae *et al.* [17].This technique is used to measure the magnitude of both real and imaginary part of third order nonlinear susceptibility. There are two Z-scan methods namely open and closed aperture used for the measurement of nonlinear absorption coefficient and nonlinear optical refraction for optical materials. A He–Ne laser (λ = 632.8 nm) was used as the light source and focused by a lens of 22.5 cm focal length. The light intensities, transmitted across the sample, are measured as a function of sample position in the Z-direction with respect to the focal plane either through a closed aperture (CA) or open aperture (OA) in order to resolve the nonlinear refraction and absorption coefficients. The beam was focused using a convex lens and the focal point has been taken as Z=0. By placing the sample in different positions with respect to the focus of the beam, the corresponding normalized transmission to the grown GPS crystal was measured. The diagrams for open aperture and closed aperture Z-scan curves are presented in the figures 5(a) and 5 (b). The Z-scan curves are characterized by a prefocal transmittance maximum (peak) followed by a postfocal transmittance minimum (valley) intensity. The transmission difference between peak and valley, linear transmittance aperture, the third-order nonlinear refractive index (n_2) of the crystal, the nonlinear absorption coefficient (β) and the third order nonlinear optical suceptibility ($\chi^{(3)}$) were determined as the procedure given in the literature [18]. The figures show curves between the normalized transmittance and the distance Z along the lens axis in the far field in open and closed aperture modes. As seen from the closed aperture Z-scan curve the prefocal transmittance peak is followed by the post focal valley which is the negative nonlinearity. The calculated value of the nonlinear refractive index n_2 is -1.23×10^{-10} cm^2/W. As the material has a negative nonlinear refractive index, it results in self-defocusing nature of the material. The value of nonlinear absorption coefficient (β) estimated from the open aperture Z-scan curve is 5.85×10^{-4} cm/W and the third order susceptibility is 7.36×10^{-7} esu.

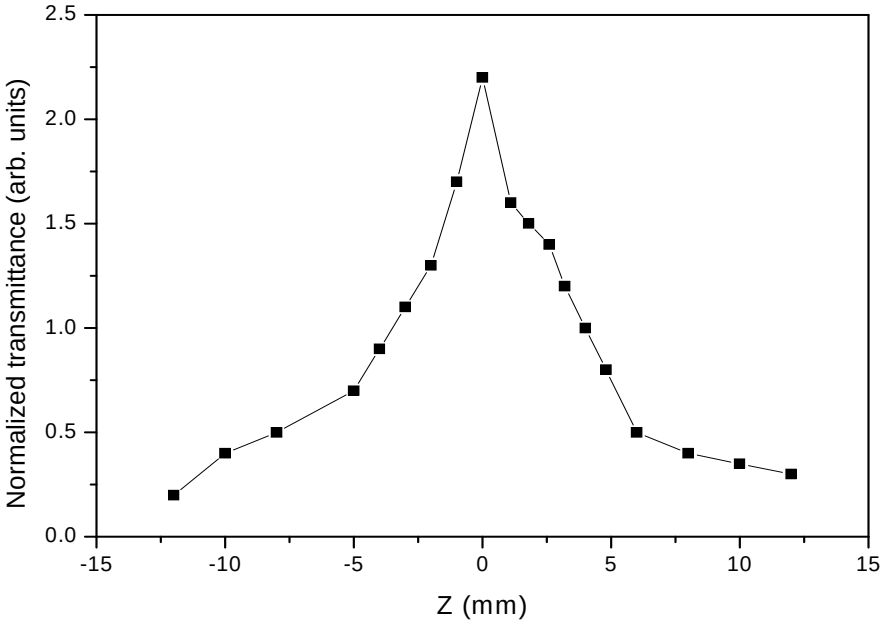

Fig.5(a): Open aperture Z-scan curve for glycine potassium sulphate crystal

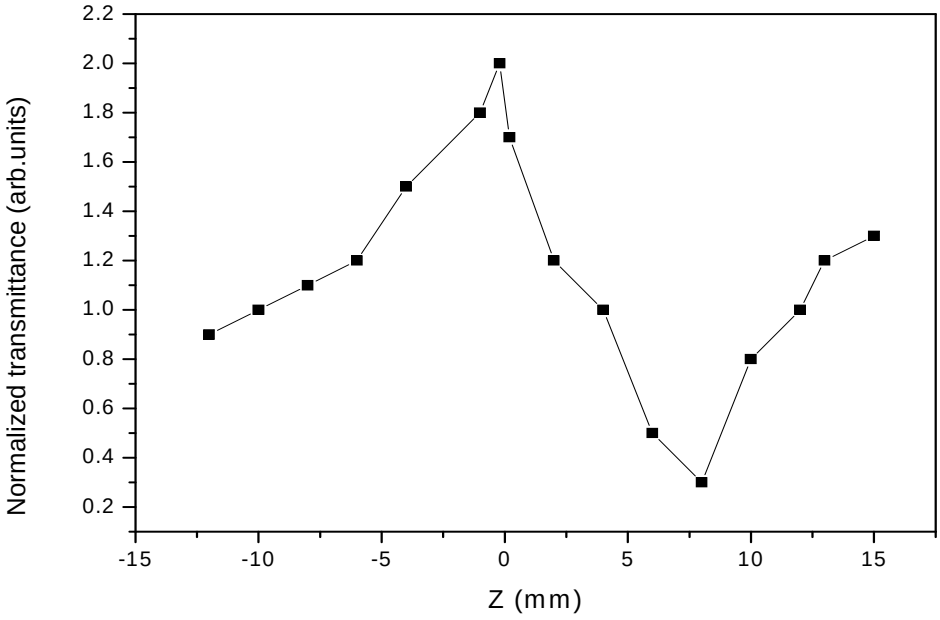

Fig.5(b): Closed aperture Z-scan curve for glycine potassium sulphate crystal

3.5 Impedance studies

The electrical properties have been studied by complex impedence spectroscopy over a range of frequencies and temperatures**.** The frequency dependent properties of a material are often represented as complex impedence Z^* and which is related as $Z^*(\omega)=Z' - jZ''$ where Z' and Z'' are the real and imaginary components of impedance. The variation of real part of impendance (Z')and imaginary part of impedance (Z'') with frequencies at temperatures 30, 50, 70, 90, 110 ^oC are shown in the figures 6 and 7. From the result it is observed that the real and imaginary part of impedance decreases with the increase in temperature and frequency. This decrease of impedance gives an indication of negative temperature coefficient of resistance behavior like that of an insulators. The high value of impedance at low frequency indicates low ionic mobility in the grown GPS crystal. The peaks in the plots of impedance versus frequency are corresponding to relaxation process and the peak frequency is equal to relaxation

frequency. The peak broadening on increasing temperature suggests the presence of temperature dependent relaxation processes in the sample. It may be due to the presence of immobile species at low temperature and defects at higher temperature.

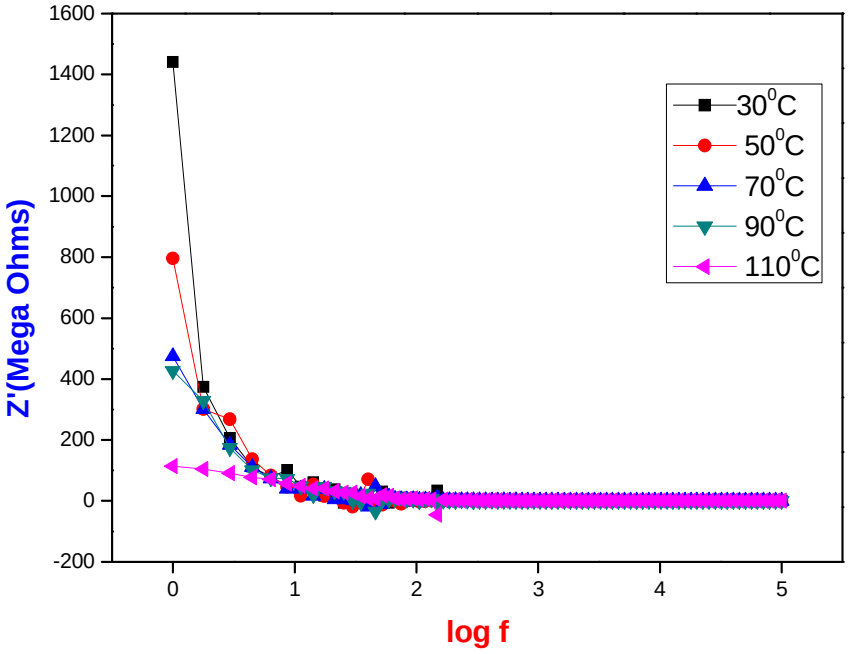

Fig.6:Plots of real part of impedance versus frequency for GPS crystal

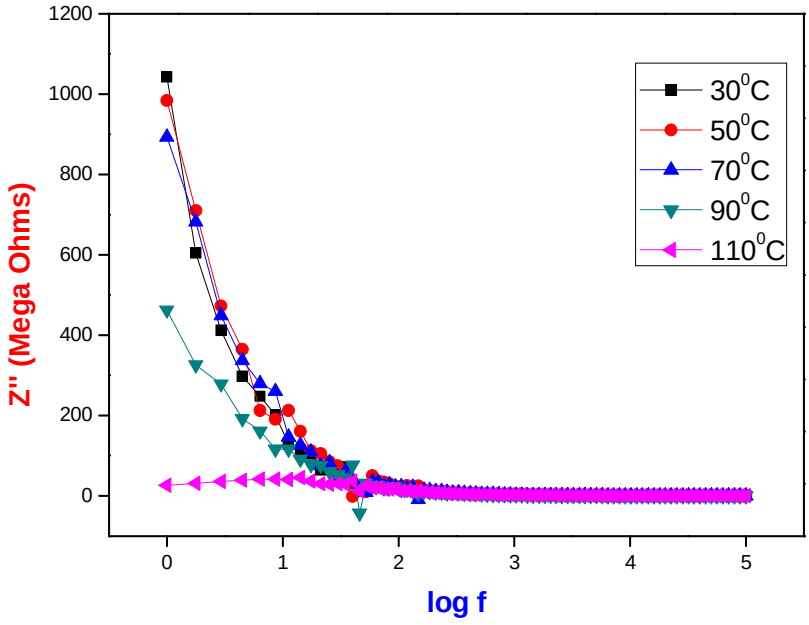

Fig.7:Plots of imaginary part of impedance versus frequency for GPS crystal

The Nyquist plots for the grown GPS crystal have been drawn between real part and imaginary part of impedance at different temperature and they are presented in figure 8 .The graph shows the transport response function characteristically, one semicircular arcs and spikes and these plots reveal the presence of bulk effect, grain boundary effect of the sample. Semicircular at low frequencies are considered due to the grain boundary whereas the semicircles at higher frequencies depict the bulk effect. The bulk effect arises due to the parallel combination of bulk resistance (R_b) and bulk capacitance (C_b) of the sample. The real part and imaginary part of electric modulus for

GPS crystal at different frequencies and temperatures are shown in the figures 9 and 10. The results show the modulus peak shift towards higher frequency side on increasing temperature. The asymmetric broadening of the peak indicates the spread of relaxation with different time constant and the relaxation in the GPS crystal is of non-Debye type [19,20].

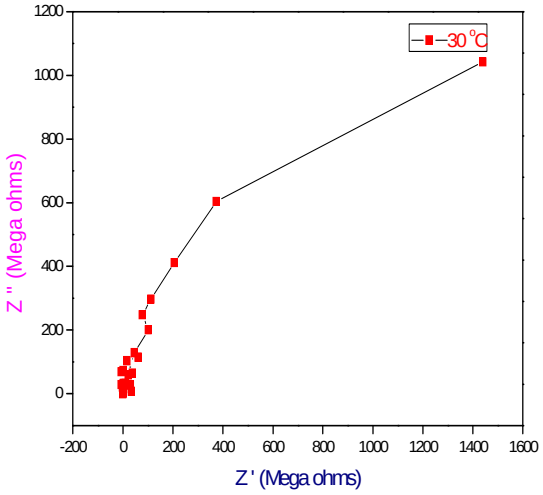

Fig. 8 (i) : Nyquist plot for GPS at 30 ºC

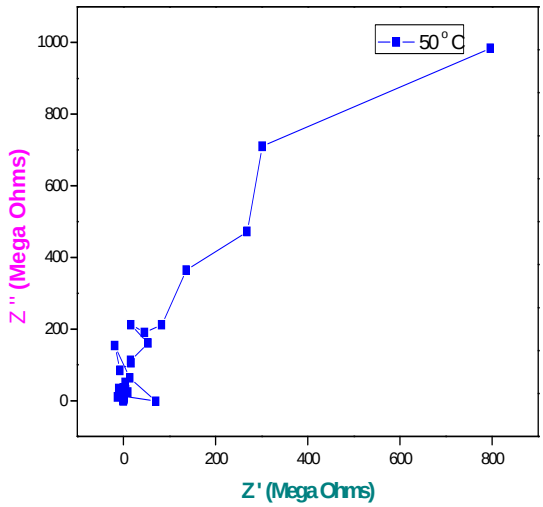

Fig.8 (ii) : Nyquist plot for GPS at 50 ºC

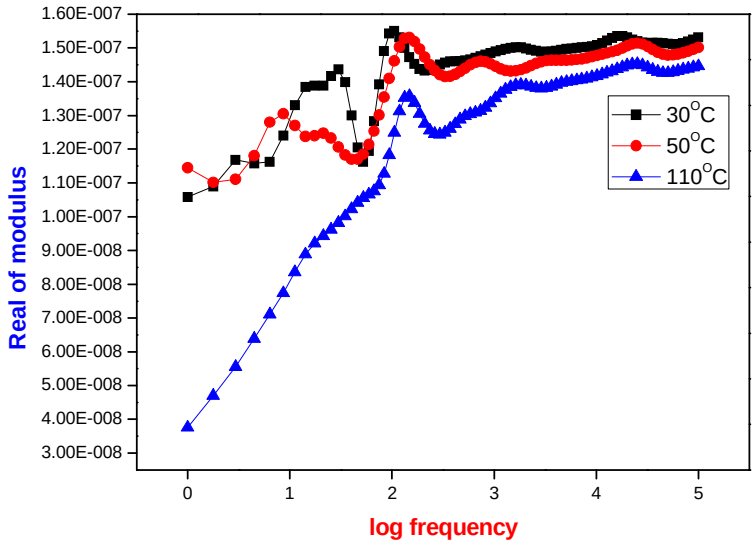

Figure 9: Variation of real part of the electric modulus with frequency at different temperatures for GPS crystal

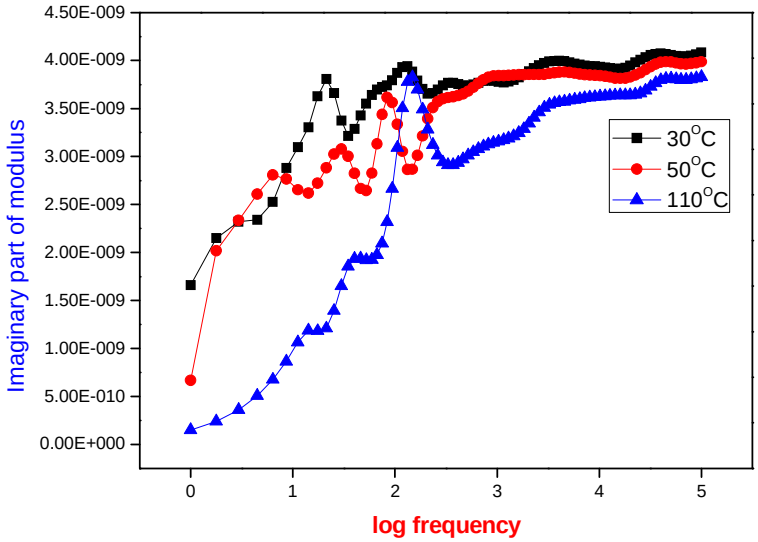

Figure 10: Variation of imaginary part of the electric modulus with frequency at different temperatures for GPS crystal

CONCLUSION

Single crystals of GPS were grown by slow evaporation method using the aqueous solutions of glycine and potassium sulphate. The crystal structure of the grown GPS was obtained by XRD studies and it reveals that GPS crystal crystallizes in orthorhombic structure. By Kurtz powder technique, it is observed that GPS crystal is a centrosymmetric crystal. Third order nonlinear optical properties of GPS crystal have been evaluated by Z-scan technique. The electrical properties such as impedance and electric modulus for GPS crystal were analyzed at different frequencies and temperatures. EDS method was used to check the presence of various elements in GPS crystal.

Acknowledgments
The authors like to thank the staff members of Sophisticated Test Instrumentation Centre (STIC), Cochin University, Cochin for providing the single crystal X-ray diffraction analysis test and extend our thanks to Dr. Basheer Ahamed, Professor of Physics, B.S. Abdur Rahman University, Vandalur, Chennai for providing the SHG analysis of the title compound. The authors also like to thank staff members of PSN College of Engineering, Tirunelveli for the impedance analysis of the sample.

REFERENCES

[1] N.Bloembergen *J Nonlinear Opt. Phys.Mater* 15(**1996**)1.
[2]G.Albrecht, R.B.Corey, *J.Am.Chem.Soc*.61, 1087(**1939**)
[3] E.Fischer, *Ber.Deutsch.Chem.Ges*.38, 2917 (**1905**)
[4] Y.Iitaka, *Acta.Cryst*.11, 25(**1958**)
[5] Y.Iitaka, *Acta.Cryst*.14, 1(**1961**)
[6] A.DeepthyandH.L.Bhat, *J.Cryst.Growth* 226 (**2001**) 287-293
[7] M.N.Bhat and S.M.Dharmaprakash, *J.Cryst.Growth236* (**2002**)376-380
[8] J.K.Mohan Rao and M.A.Vishwamitra, *ActaCrystallogr.B28* (**1972**)1484
[9] S.A.Martin Britto and S.Natarajan, *Mater.Lett.62* (**2008**)2633-2636
[10] Ra.Shanmugavadivu, G.Ravi and A.Nixon Azariah, *J.Phys.and Chem.Solids* 67(**2006**)1858-1861
[11] M.R.Suresh Kumar, H.J.Ravindra and S.M.Dharmaprakash, *J.Cryst.Growth* 306(**2007**)361-365
[12] T.Balakrishnan and K.Ramamurthi, *Spectrochim.ActaPart* A68 (**2007**)360-363
[13] T.Balakrishnan and K.Ramamurthi, *Mater, Lett.*62 (**2008**) 65-68
[14] R.Pepinsky, K.Vedam and Y.Okaya, *Phys.Rev*.110 (**1958**)1309-1311
[15] S.Hosino, T.Mitsui, F.Jona and R.Pepinsky, *Phys.Rev*.107 (**1957**)1255-1258 1915.
[16] S.K.Kurtz and T.T.Perry, *J. Appl.Crystallography* 9 (**1968**) 3798
[17] Bahae M.S., Said A. and Van Stryland E.W.,High, *Opt.Lett.*,**1989**,14,955-957.
[18] A. Shanthi, C. Krishnan, P. Selvarajan, *Spectrochimica Acta Part* A 122 (2014) 521–528.
[19] A.Shukla,R.N.P.Choudhary,*Curr. Appl.Phys*,11(2011)414.

[20] J.R.Macdonald, Impedence Spectroscopy,Wiley Interscience Pub.,Newyork (**1987**).