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Thermal, optical, mechanical, and electrical properties of a novel NLO active Glycine potassium sulphate single crystals

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ABSTRACT

Semi-organic single crystals of glycine potassium sulphate were synthesized by a slow evaporation technique. Good quality single crystals with size 6.02mm x 2.63mm x 1.81mm were grown in 32 days. Single crystal and powder XRD analyses confirmed the orthorhombic crystal structure. Vibration spectrum was recorded to determine the symmetries of molecular vibrations. The TGA, DTA shows that the material has good thermal stability; the UV-Vis spectrum shows the transmitting ability of the crystal in the entire visible region. The dielectric constant and dielectric loss were calculated by varying frequencies at different temperature. The microhardness test reveals that the crystals possess good mechanical strength.

Keywords: NLO, dielectric constant, micro hardness

INTRODUCTION

The search for nonlinear optical (NLO) materials has been of great interest because of their significant impact on laser technology, optical communication and data storage technology. The synthesis of new and efficient frequency conversion materials has resulted in the development of new semi organic materials. Semi organic system provides many structure and bonding schemes for the molecular engineering of new materials. Semi organic nonlinear optical (NLO) crystals are attracting a great deal of attention due to their high NLO coefficient, high damage threshold and high mechanical strength compared to organic NLO crystals. Materials with large second order optical nonlinearities, transparency at all wavelengths involved and stable physiochemical performance are needed in order to realize many applications [1,2]. Recently, complexes of amino acid have been explored. The importance of amino acid in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in non-centro-symmetric space groups [3]. Many number of natural amino acids are individually exhibiting the nonlinear optical properties because they are characterized by chiral carbons, a proton- donating carboxyl (-COOH) group and the proton accepting amino ($-NH_2$) group the crystal The crystal structures of amino acids and their complexes have provided a wealth of interesting information to the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties [4].

Glycine is the simplest amino acid. It has no asymmetric carbon and is optically inactive. Potassium sulphate K_2SO_4 belongs to orthorhombic system In this paper we report the studies on solubility, growth, XRD, optical transmittance

properties, vibration, mechanical, dielectric, nonlinear optical properties and thermal properties of the grown glycine potassium sulphate crystal.

MATERIALS AND METHODS

2.1. Synthesis

Recrystallised salts of (analar reagent grade) glycine and potassium sulphate (K_2SO_4) and de-ionized water are used in the present crystal growth experiment. Saturated aqueous solutions were prepared at room temperature following the known solubility data. The solubility of glycine and potassium sulphate in de-ionized water (100ml) at room temperatures is 25gm and 14gm respectively. The solutions are mixed in the volume ratio 1:1 for about 5 hours using a magnetic stirrer with 520rpm to ensure a homogeneous temperature and concentration through out the volume of the solution. The pH value of the solution is found to be 7. The saturated solution is filtered using whattmann filter paper and then covered with perforated transparent polythene paper and left undisturbed for slow evaporation. The solvent evaporates slowly leading to supersaturation which in turn initiates the nucleation and the crystal grows. Good quality single crystals were grown in 32 days and are shown in figure 1.

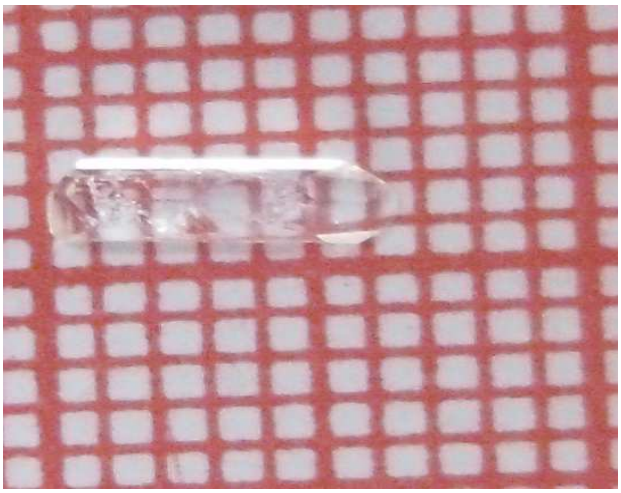

FIG. 1. Glycine Potassium Sulphate Crystal

2.2 Solubility

In solution growth technique the size of a crystal depends on the quantity of the material available in the solution which in turn is decided by the solubility of the material in that solvent. The solubility of the synthesized material was determined by adding water maintained at constant temperature to a known quantity of the material till the material is completely dissolved. Using this technique, we evaluated the magnitude of the solubility of glycine potassium sulphate at various temperatures between 25ºC and 45ºC and the variation of solubility with temperature is shown in fig 2. Glycine potassium sulphate crystal has a positive temperature coefficient of solubility. Thus slow cooling of aqueous solution of glycine potassium sulphate crystal could be attempted to grow bulk crystals [5].

2.3. Analyzing techniques

The grown crystal was confirmed by single crystal x-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. Powder x-ray diffraction (XRD) had been recorded using XPERT PRO diffractometer with CuKα radiation (λ=1.5405 Å). The crystal was characterized by SPECTRUM ONE CPU 32 spectrophotometer, using KBr pellet technique. The optical properties of the grown crystals were studied using LAMDA 35 spectrophotometer in the wavelength region from 200nm to 1100nm. The dielectric study on glycine potassium sulphate single crystal is carried out using the instrument, HIOKI3532-50 LCR HITESTER Thermal stability and physiochemical changes of the sample were analyzed by recording the TG and DTA spectrum in the temperature range 30ºC to 1000ºC in nitrogen atmosphere at a heating rate of 10ºC/ min. Second Harmonic generation (SHG) test for the grown glycine potassium sulphate crystal was performed by the powder technique of Kurtz and Perry using a pulsed Nd:YAG laser (Model: YG501C, λ=1064nm). The microhardness measurement of the crystal was carried out by a REICHERT MD 4000E ultra microhardness tester with a diamond pyramidal indenter.

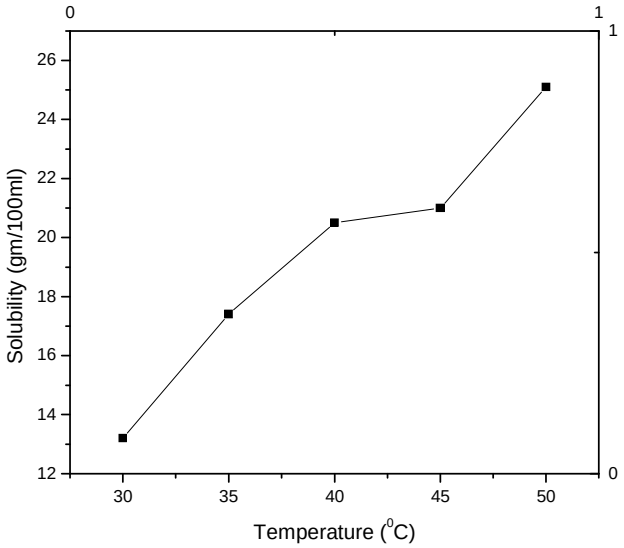

Figure 2 Solubility curve of GPS

RESULTS AND DISCUSSION

3.1. Single crystal diffraction

Single crystal X-ray diffraction analysis for the grown glycine potassium sulphate crystal is carried out to confirm the crystalline nature and also to identify the unit cell parameters using ENRAF Nonius CAD4 single crystal x-ray diffractometer. The calculated lattice parameters are a= 5.77Å b=7.54 Å c=10.04 Å and α=β=γ= 90 and volume V= 436Å^3 and the crystal system is found to be orthorhombic.

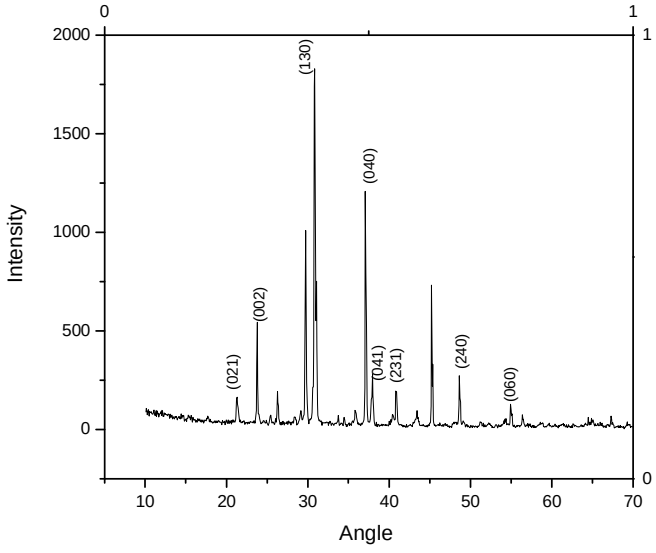

Figure 3. Powder xrd pattern of glycine potassium sulphate

3.2 Powder X-ray diffraction

The grown single crystal of glycine potassium sulphate has been subjected to powder X-ray diffraction. Powder form of the above mentioned crystal is taken for the analysis using XPERT PRO diffractometer. The indexed

powder x-ray diffraction pattern of the grown crystal is presented in fig 3. The lattice parameters obtained from the data of powder XRD pattern using UNITCELL software package are a = 5.788 Å, b = 7.532 Å and c = 10.00372 Å cell vol=436.11Å^3 and are found to be in good agreement with the literature [6].

3.3 Optical transmission spectra

A transmission spectrum is very important for any NLO materials, because a nonlinear optical material can be of any practical use if it has a wide transparency window. In the present study, we have recorded the UV-Vis NIR transmission spectrum in the range of 190nm-1100nm is shown in fig 4 and the instrument used in the analysis is LAMBDA-35 UV-Vis spectrophotometer. From the spectrum, it is seen that the crystal has a lower cut-off wavelength of 384nm. The spectrum further indicates that the crystal has a wide optical window from 385nm to 1100nm. The crystal is transparent in the visible and infrared spectral regions. Optical transmittance of about 100% is observed for 1.5mm plates of glycine potassium sulphate crystals and is sufficiently good for SHG [7].

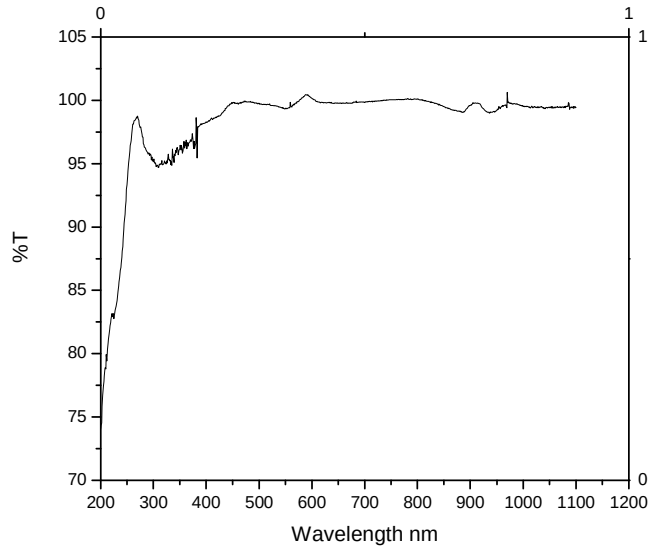

Figure 4. UV-Vis NIR Spectrum of glycine potassium sulphate crystal

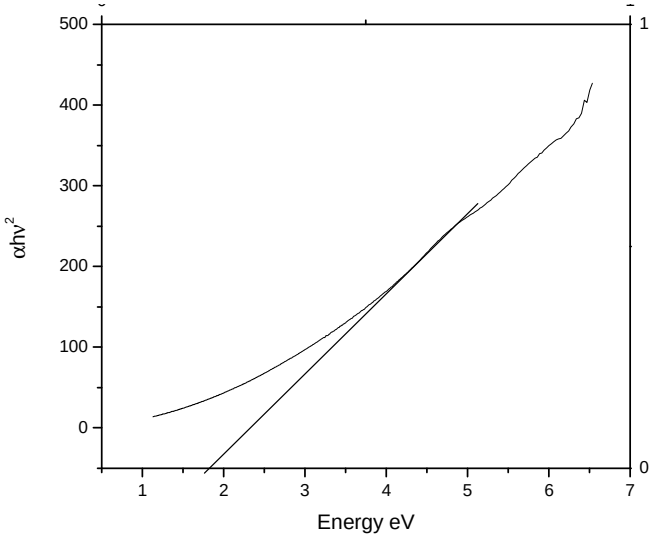

Figure 5 Plot of energy versus (αhυ)^{2}of glycine potassium sulphate

The measured transmittance (T) is used to calculate the absorption coefficient (α) using the formula α = 2.303log (1/T) /t where t is the thickness of the sample. The optical band gap (E_g) is evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by [8]

$h\upsilon\alpha = A(h\upsilon - E_g)^{1/2}$

where A is a constant, E_g the optical band gap, h the Plank's constant and υ the frequency of the incident photons. The band gap of the grown crystal is estimated by plotting $(\alpha h\upsilon)^2$ versus hυ as shown in Fig5 and extrapolating the linear portion near the onset of absorption edge to the energy axis. From Fig.5 the value of band gap is obtained as 1.8eV.

The reflectance R in terms of the absorption coefficient is given by the relation [9]

$R= \exp(-\alpha t)\pm\beta\sqrt{(\exp(-\alpha t)T-\exp(-3\alpha t)T+\exp(-2\ \alpha t)T^2)} / \exp(-\alpha t)+ \exp(-2\ \alpha t)T$

The refractive index (n) can be determined from reflectance data using

$n= - (R+1) \pm 2\sqrt{R} / (R-1)$

Figure 6 shows the energy dependence of n in the range 400-1100nm for UKS crystal. The refractive index decreases on increasing the wavelength. The refractive index (n) is 1.0237 at 1000nm for the grown crystal.

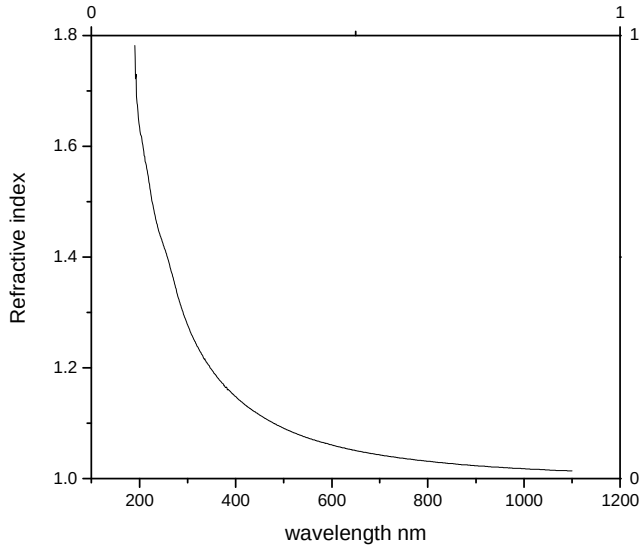

Figure 6. Plot of wavelength versus refractive index of glycine potassium sulphate

3.4. FTIR analysis.

The FTIR spectral analysis (fig 5) for the grown crystal is recorded in the range 400-4000cm^{-1} using SPECTRUM ONE, CPU 32 spectrophotometer using the KBr pellet technique.

Glycine exists as a zwitter ion in the crystalline state both in the free molecule and in the sandwich complex. The $-CH_2$ group frequencies are not affected since they are not metal sensitive. The peak at 3433 cm^{-1} is due to the NH_2 asymmetric stretching which is associated with a broad peak. The broadness of the peak 2900 cm^{-1} to 3700 cm^{-1} is due to the intermolecular hydrogen bonding. The peak at 1628 cm^{-1} is due to C=O stretching. The COO^- is confirmed by the peak at 1388 cm^{-1}. The peak at 1115 cm^{-1} is due to NH_2 rocking. The presence of sulphate ion is confirmed at 1115cm^{-1} and 619 cm^{-1}.

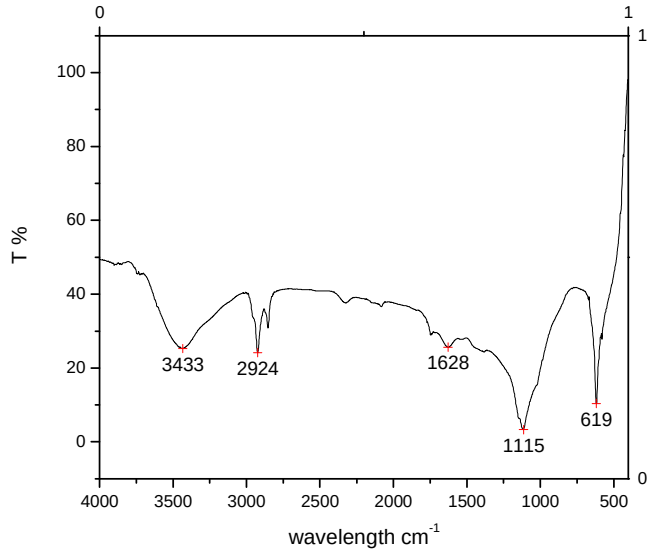

Figure 7 FTIR spectrum of glycine potassium sulphate

3.5. Thermal Analysis

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. We have carried out simultaneous TGA and DTA for the grown crystals in the temperature range of 30ºC to 1000ºC with a heating rate of 10K / min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in fig.10. The weight loss around 100ºC is due to the presence of water of crystallization in the molecular structure. The endothermic peak at 259ºC is assigned to the melting point of the crystal. The decomposition starts at 259ºC and major weight losses occur which is due to the liberation of volatile substances like carbon mono oxide and ammonia. The initial mass of the sample was 7.6mg and about 6.6mg of the sample is retained at 1000ºC which shows the thermal stability of the crystal system.

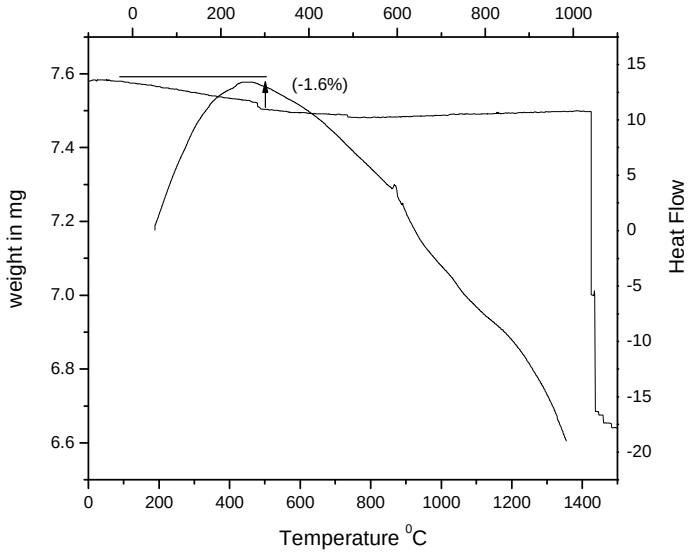

Figure 8 TG-DTA Curves of Glycine Potassium Sulphate crystal

3.6. Microhardness Studies

The mechanical properties of crystals are evaluated by mechanical characteristics. The fastest and simplest type of mechanical testing is hardness measurement. Among the different testing methods, the Vickers hardness test is more commonly used. Microhardness measurements are made using a Leitz microhardness tester fitted with a diamond pyramidal indentor. Single crystal of glycine potassium sulphate crystal is subjected to microhardness on (001) orientation. The applied load is varied from 25 to 200 g for a constant indentation period of 10s. the Vicker's hardness number H_v is calculated using the relation $H_v = 1.8544P/d^2$ Kg/mm^2 where P is the indenter load in kg and d is the diagonal length of the impression in mm[10].The variation of H_v with applied load is shown in Fig11. It is evident from the plot that the microhardness of the crystal increases on increasing the load. For loads above 200g cracks developed on the surface of the crystal due to the release of internal stress generated locally by indentation.

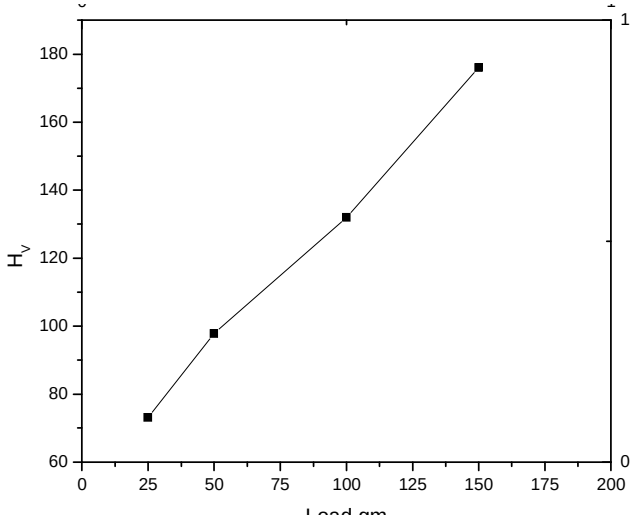

Figure 11 Variation of microhardness number with load for GPS crystal

Mayer's law [11] relates load and size of indentation as $P=a\ d^n$ where a and n are the constants. The plot of log d versus log p is drawn (fig11) and from plots, the hardening coefficient (n) is determined. The value of n is found to be 1.001. According to Onitsch, n should be below1.6 for hard materials and above 1.6 for softer ones [12]. Hence glycine potassium sulphate crystals belong to hard materials.

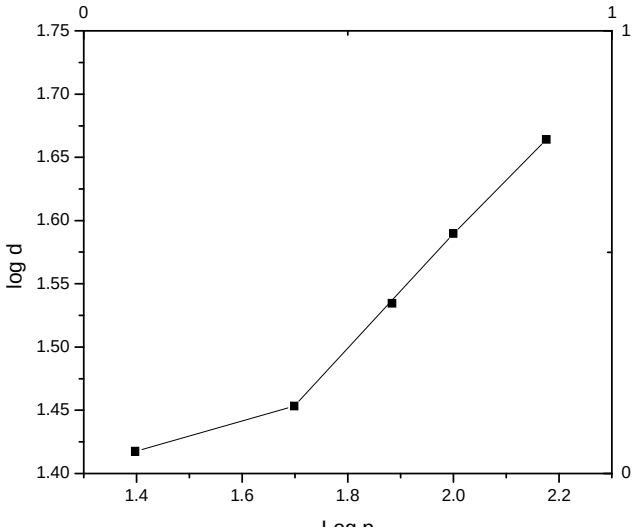

Figure12. Plot of Log p versus log d

3.7. Dielectric Studies

Dielectric properties are correlated with electro-optic property of the crystals [13]. The dielectric constant is the measure of how easily a material is polarized in an external electric field [14]. The dielectric study on glycine potassium sulphate single crystal is carried out using the instrument, HIOKI3532-50 LCR HITESTER. A sample of dimension 5*2.6*2 mm^3 having silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed [15]. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation $\varepsilon_r = Cd/A\ \varepsilon_0$ and is shown in fig8.

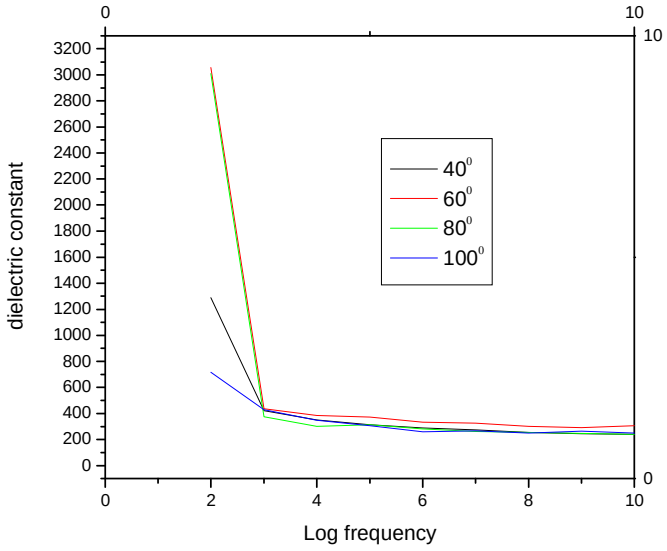

Figure 13 Plot of Log frequency versus dielectric constant

The larger values of dielectric constant at lower frequencies are due to the impedance to the motion of charge carriers at the electrodes, space charge and macroscopic distortion results [16]. The dielectric constant is low at high frequencies. This is due to the fact that at higher frequencies the ionic and electronic polarizations are active [17]. According to Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of the SHG coefficient [18].

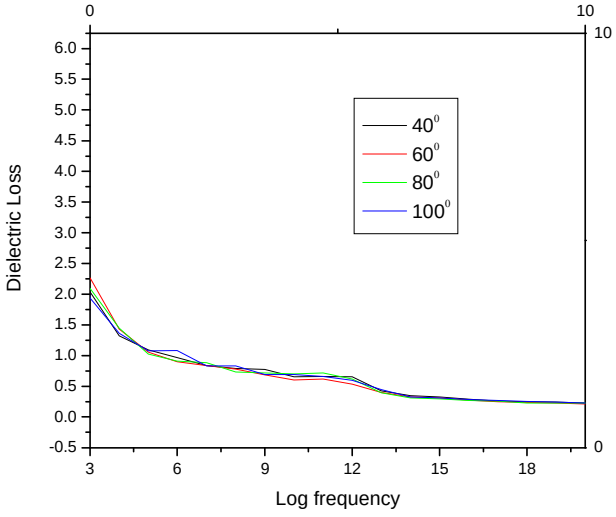

Figure 13. Plot of Log frequency versus dielectric loss

The dielectric loss versus log frequency is shown in fig13. The dielectric loss values are found to be high at low frequencies and low at high frequencies. The low dielectric loss at higher frequency of the sample indicates that the crystal posses lesser number of electrically active defects [19] and this parameter is of vital importance for nonlinear optical materials in their applications.

The AC conductivity (σ_{ac}) is calculated using the relation [20], $\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta$ where ε_0 is the permittivity of free space ($8.85*10^{-12}$ C^2 N^{-1} m^{-2}) and ω is the angular frequency ($\omega = 2 \pi f$) It is found to be $1.09x10^{-6}$ at 1000Hz and $2.5x10^{-7}$ at 1MHz.

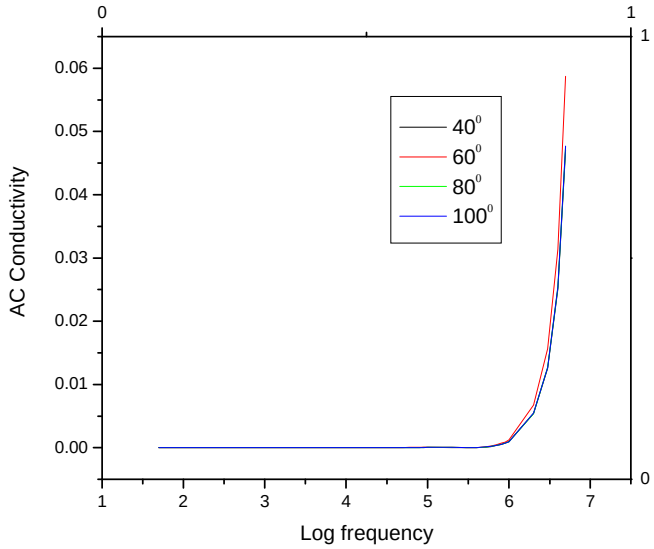

Figure 14.Plot of log frequency versus ac conductivity

3.8. Second harmonic generation

The second harmonic generation behavior of the powdered material is tested using the Kurtz and Perry [21] method. A high intensity Nd:YAG laser (λ=1064nm) with a pulse duration of 10 ns was passed through the powdered sample. The SHG behaviour is confirmed from the output of the laser beam having the green emission (λ=532nm). The second harmonic signal of 1.1mJ is obtained for GPS crystal. But the standard KDP crystal gave an SHG signal of 8.8mJ for the same input energy. Thus, it is observed that the SHG efficiency of the grown single crystal is 1/8 times that of the standard KDP crystal.

CONCLUSION

Optical quality crystals of semiorganic glycine potassium sulphate (GPS) can be successfully grown by slow evaporation method. The grown crystals were characterized using single crystal X-Ray diffraction analysis, which shows that the glycine potassium sulphate crystals belong to orthorhombic system. The presence of functional groups of glycine potassium sulphate has been confirmed by FTIR analysis. Optical studies show that the glycine potassium sulphate crystals have a wide transparency window in the entire visible region making it an ideal candidate for NLO device applications. The TG-DTA studies reveal that the crystal is thermally stable up to ~259ºC and the mechanism responsible for weight loss is discussed. Low dielectric constant and dielectric loss at high frequency suggest that the sample possesses enhanced optical quality with lesser defects. Hence it is concluded that optically good quality NLO active glycine potassium sulphate single crystals with good thermal and mechanical stability can be grown by slow evaporation technique and is suitable for the fabrication of various optoelectronic devices.

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