Growth and Characterization of Semi organic nonlinear optical Crystal

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Abstract--- Triglycine Potassium Sulphate (TGPS) is one of the potential materials for Non-linear optical property applications. Single crystals of Triglycine potassium Sulphate (TGPS) with very high degree of transparency were grown from aqueous solution by slow evaporation technique. The optical absorption study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 300 nm. A wide transparency window useful for optoelectronic applications is indicated by the UV studies. The mechanical properties were studied using Vickers microhardness tester. Using Nd-YAG laser (1064 nm), the optical second harmonic generation (SHG) conversion efficiency of TGPS is found to be 1.13 times that of standard KDP.

Keywords--- Slow evaporation technique, Optical Absorption, Microhardness, Second harmonic generation

I. INTRODUCTION

A n organic material Glycine, a simple amino acid has three polymorphic forms, viz., α, β and γ. Both α and β forms crystallize in Centro Symmetric space group P2₁/c[1,2], γ glycine crystallizes in non-Centro Symmetric space group P3₁[3,4] making it a candidate for Piezo electric and NLO application. Glycine is the simplest amino acid. It has no asymmetric carbon and is optically inactive; Potassium sulphate belongs to orthorhombic system. A new semi-organic nonlinear material Triglycine potassium sulphate(TGPS) has been synthesized from alpha-glycine and crystals have been grown and characterized.

In this paper we report studies on growth, XRD, Optical transmittance properties, vibration, mechanical, dielectric, and non linear properties of the grown TGPS crystal.

II. CRYSTAL GROWTH

A solution of Triglycine Potassium Sulphate was prepared by dissolving Analytical grade chemicals of Glycine and Potassium Sulphate in 3:1 molar ratio with continuous stirring using a magnetic stirrer for six hours at room temperature. The prepared solution was filtered and kept undisturbed in a constant temperature bath maintained at a temperature of 30°C. When evaporation taken place slowly, super saturation is activated. As a result, crystals with dimensions 12 × 11 × 5 mm³ were harvested in a period of 40 days.

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III. POWDER X-RAY DIFFRACTION

The grown single crystal of Triglycine potassium sulphate has been subjected to powder X-ray diffraction. Powder form of the crystal is taken for the analysis using X-ray diffractometer. The lattice parameters obtained from the data of powder XRD pattern (Fig.2) using UNITCELL software package are a=5.811 Å, b=7.499 Å and c=10.1001 Å and are found to be in good agreement with the literature [5]. Using Debye-Scherrer’s equation particle size is calculated and the average particle size is found to be 111.8 nm.

IV. UV-VIS-NIR SPECTRAL ANALYSIS

The determination of optical transmission range and the transparency cutoff are important for any NLO material.
because a non linear 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 200nm-1100nm using the LAMBDA-35 UV-Vis spectrophotometer. The transmission spectrum of TGPS crystal is shown in the Fig.3. It can be seen from the transmission curve that the lower cutoff wavelength lies below 300nm. The material is found to be transparent to all radiations in the wavelength range 300-1100nm. The absence of absorption in the visible region clearly indicates that TGPS crystals can be used as window material in optical instruments [6].

VI. MICROHARDNESS STUDIES

Hardness is a measure of the resistance to plastic deformation. The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material. The hardness tests for TGPS crystal was carried out by Zwick micro hardness tester fitted with a Vickers diamond pyramidal indenter. The diagonal length of the indentation for various applied loads in gm is measured for a constant indentation period of 10 sec. The hardness values were calculated from the formula $H_v = \frac{1.8544P}{d^2}$, P is the applied load in Kg, d is mean diagonal length of the indentation in mm [7].

Graph (Fig.5) shows that the hardness increases with the increase of load due to the release of internal stress generated by indentation. The phenomenon of dependence of microhardness of a solid on the applied load, at low level of testing load is known as indentation size effect. Meyer’s law [8] relates load and size of the indentation as $P = ad^n$ where a and n are constants for a given material. The work hardening coefficient was found to be 0.4062 by taking a slope in the straight line of the graph (Fig.6 ) drawn between logP and logd. According to Onitsch and Hanneman ‘n’ should lie in the range of 1.0 - 1.2.
between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials [9]. The ‘n’ value observed in the present studies is around 0.4062 suggests that the grown TGPS crystal belongs to harder material category.

VII. DIELECTRIC STUDIES

Dielectric properties are correlated with electro-optic property of the crystals [10]. The dielectric constant is the measure of how easily a material is polarized in an external electric field [11]. The dielectric study on TGPS single crystal is carried out using the HIOKI3532-50 LCR HITESTER. A sample of dimension 2x2 mm² having a silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation

$$\varepsilon_r = \frac{C d}{A \varepsilon_0}$$

where C is the capacitance of the sample, d the thickness of the sample, A the area of the face in contact with the electrode, $\varepsilon_0$ the permittivity of free space and is shown in the Fig.7.

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. 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. According to Miller rule, the lower values of dielectric constant are suitable for the enhancement of the SHG coefficient [12].

VIII. SECOND HARMONIC GENERATION

The Powder SHG measurement of TGPS crystals were carried out using Kurtz and Perry technique [14]. An Nd:YAG laser beam of wavelength 1064nm with input energy of 3.3 mJ per pulse is used for the present work. KDP was used as the reference material. The powder sample was taken in the capillary. The laser light was made to fall directly on the samples. The green signal was obtained by monochromator after separating the 1064nm beam with an IR-blocking filter. The measured amplitude of second harmonic signal for TGPS is 6.9mv and for the standard KDP was 6.2mv for the same input energy. Thus it is observed that the SHG efficiency of the grown single crystal is 1.13 times that of the standard KDP crystal.

IX. CONCLUSION

Transparent good quality single crystals of Triglycine Potassium Sulphate were grown by slow evaporation technique from a mixture of aqueous solution of Glycine and Potassium Sulphate at constant temperature of 30°C. Sharp peaks found in the powder XRD spectra reveals good crystallinity of the grown crystals. The UV-Vis-NIR absorption spectrum shows a wide transparency window making it a potential material for NLO applications. The presence of functional groups was confirmed by vibrational analysis. The relative SHG conversion efficiency of the grown Triglycine Potassium Sulphate crystals is about 1.13 times than that of KDP sample. 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 Triglycine 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.

REFERENCES

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