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Structural, Spectral and Mechanical Studies of Picric Acid-Doped Glycine Lithium Sulphate Crystals

KEYWORDS: Glycine complex; single crystal; solution method; solubility; XRD; SHG

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ABSTRACT *This paper deals with the growth and characterization of undoped and picric acid doped glycine lithium sulphate crystals. Growth of the crystals was carried out by solution method with slow evaporation technique. Solubility studies were carried out for the samples at various temperatures ranging from 30 oC to 50 oC. XRD studies reveal the structural properties. The functional groups of the sample were identified by FTIR studies and the optical band gap was calculated using the transmission spectra. The microhardnes characterization was performed for samples to understand the mechanical strength. Nonlinear optical activity for the grown crystals has been checked by carrying out second harmonic generation (SHG) studies.*

1. Introduction

In recent years, the need of nonlinear optical (NLO) materials is much more than other materials because of their applications in optoelectronics and photonics [1]. Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [2,3]. The research of combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semiorganic materials. In semiorganic materials, the organic ligand is ionical1y bonded with inorganic host, because of this, the new semiorganic crystals are having higher mechanical strength and chemical stability. The semiorganic crystals possess several attractive properties such as high damage threshold, wide transparency region and high nonlinear coefficient [4-6]. Glycine lithium sulphate (GLS) is a semiorganic NLO crystal which is formed by mixing glycine and lithium sulphate and in this work picric acid doped GLS crystal was prepared using picric acid as the dopant. The aim of this work to grow undoped and picric acid-doped glycine lithium sulphate crystals and to discuss the results obtained from various studies.

2.Experimental

2.1. Growth and solubility

Glycine lithium sulphate (GLS) was grown from aqueous solutions of AR grade glycine and lithium sulphate taken in 1:1 molar ratio. The evaporation of the solution yielded GLS crystals. To obtain picric acid-doped GLS, 1 mole% of picric acid was added the solution of GLS. The key factor for successful growth of any crystal is the proper selection of solvents. To find out the suitable solvent, the solubility test was carried out by gravimetrical method [7] and here water was found to be the suitable solvent for growing crystals. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined. The solubility curves for undoped (pure) and picric acid doped glycine lithium sulphate samples were plotted and they are shown in figure 1. It is observed that solubility increases with temperature for both the samples. When picric acid was doped into GLS crystal, it is noticed that the solubility increases leading to dissolution of more solute in the same amount of solvent.

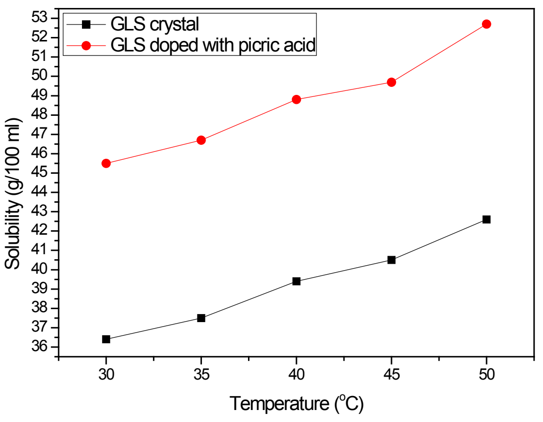

Fig.1: Solubility curves for undoped and picric acid-doped GLS crystals

2.2 Characterization techniques

The grown GLS crystal was subjected to various characterization techniques like single crystal X-ray diffraction, FTIR technique, microhardness and second harmonic generation (SHG). The crystal system and lattice parameters were calculated with the help of single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoKα (α= 0.71069 Å) radiation. The functional groups were identified from FTIR analysis recorded using a SHIMADZU 8400s spectrometer by the KBr pellet technique in the range of 400-4000 cm^{-1}. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm [8]. Microhardness hardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface were selected and subjected to this study for both pure and picric acid doped GLS crystals. Indentations were made for various loads and several trials of indentation were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers microhardness number was calculated using the relation H_v = 1.8544 P/d kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression [9].

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3. Results and Discussion
3.1 Single crystal XRD studies

Single crystal XRD data of undoped and picric acid-doped glycline lithium sulphate were collected from a single crystal X-ray diffractometer with graphite monochormated MoK_a radiation. The obtained crystallographic data for undoped glycine lithium sulphate (GLS) and picric acid doped GLS crystals are a= 5.027(2) Å, b=7.632(3) Å, c= 16.394(1) Å, α = 90°, β= 90° γ=90° and a= 5.052(4) Å, b=7.6292(2) Å, c= 16.534(2) Å, α = 90°, β= 90° γ=90° respectively. From the data, it is observed that both the grown crystals crystallize in orthorhombic crystal systems. The number of molecules per unit cell (Z) for both crystals of this work is found to be 4. The changes in the lattice parameters are due to incorporation of picric acid in the lattice of GLS crystal. The presence of dopant in GLS crystal may produce lattice strain which leads to change of unit cell parameters in the picric acid doped GLS sample.

3.2 FTIR Study

The FTIR spectrum of picric acid doped GLS crystal is shown in Fig. 2. In the molecular packing diagram of the sample, the NH_3^+ acts as a donor for hydrogen bond formation, whereas the oxygen atom of carboxyl and sulphate groups acts as acceptors. The broad and intense peak is due to NH_3^+ stretching vibrations appeared as strong absorption band in the range 2950–3300 cm^{-1}. The peak at 1665 cm^{-1} corresponds to the COO^{-1} stretching vibration. The absorption band at 2200 cm^{-1} corresponds to CH_2 stretching vibration. The stretching vibrations are due to SO_4^- group appeared at 895 and 645 cm^{-1}. The characteristic absorption band at 998 cm^{-1} is attributed to C–N stretching vibration.

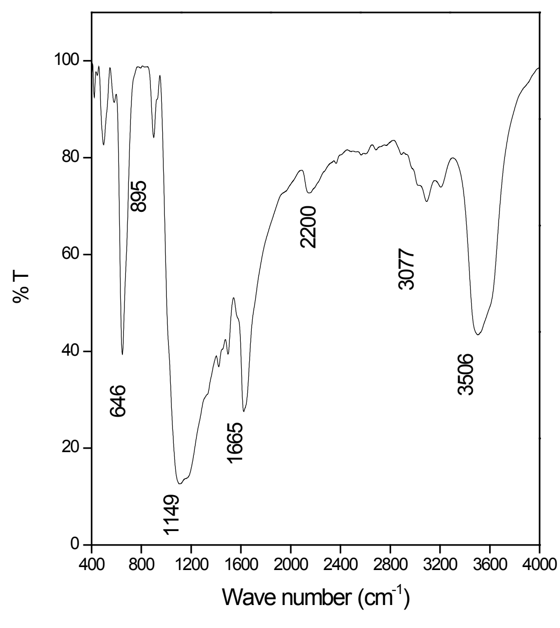

Fig.2: FTIR spectrum of picric acid doped GLS crystal

3.3 UV-visible spectral study

UV-Visible-NIR transmittance spectrum of picric acid-doped GLS crystal in the wavelength range 200-1100 nm is shown in figure 3. The study of the 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 spectrum, it is noticed that picric acid doped GLS crystal has high transmittance in the entire visible-NIR region of the spectrum and this property enables the materials for optoelectronic applications and second harmonic generation [10]. Absorption at 390 nm is due to yellow colouration of the sample. The cut-off wavelength is observed to be at 285 nm and this arises from electronic transitions associated within the sample. Using the formula $E_g = 1240 / \lambda$□ (nm), the band gap is calculated to be 4.35 eV.

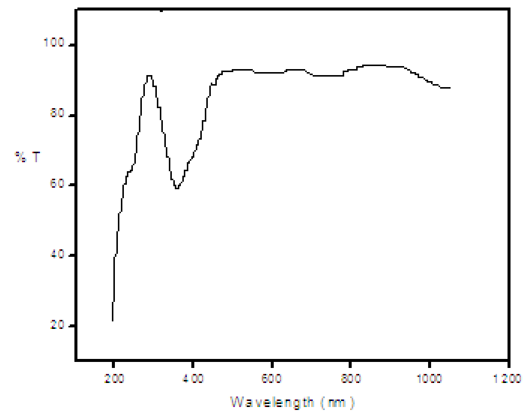

Fig.3: UV-visible spectrum of picric acid doped glycine lithium sulphate crystal

3.4 NLO activity

Second harmonic generation (SHG) test is important to check whether a sample is Nonlinear Optical (NLO) active or not and it was carried out by powder Kurtz and Perry technique. The crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q switched Nd:YAG laser beam of wavelength 1064 nm (pulse width 6 ns) was allowed to strike the sample cell normally. The SHG output (532 nm) was finally detected using a photomultiplier tube. Asample of powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement. The SHG efficiency for undoped GLS crystal is found to be1.94 times and for picric acid doped GLS crystal is observed to be 2.5 times that of KDP sample and hence the samples are the better candidates for NLO applications.

3.5 Microhardness test

Measuring microhardness gives an idea about the mechanical strength of a material. The hardness of a material is a measure of its resistance to plastic deformation. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect (ISE). The hardness number was measured for undoped and picric acid doped GLS crystals by applying different loads. The obtained values of hardness are 76.5,110.7, 132.4 for undoped GLS crystal and 80.7, 115.4, 139.5 for picric acid-doped GLS crystal for the applied loads of 25 g, 50 g and 100 g. It is observed that the hardness number for picric acid doped GLS crystal is more than those of undoped GLS crystal and hence the picric acid doped GLS crystal is more harder than the undoped sample. This increase in the hardness value of doped sample can be attributed to the incorporation of impurity into the lattice of GLS crystal. The addition of picric acid into GLS crystalline sample most probably enhances the strength of bonding with the host material and hence hardness number increases.

4. Conclusion

The grown picric acid doped GLS crystal is observed to be slightly yellow in colour and the undoped GLS crystal is colourless and both the crystals are transparent and non-hygroscopic. Both the crystals of this work crystallize in orthorhombic structure with non-centrosymmetric space groups. Good optical transparency is observed for the samples at the wavelengths of sources commonly used in nonlinear optical devices and it shows that the samples are very good materials for nonlinear optical applications. It is observed from microhardness studies that picric acid-doped GLS crystal is more harder than the undoped GLS crystal .

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REFERENCE

[1] J. Zyss , D.S. Chemla "Nonlinear optical properties of organic | molecules and crystals", Academic Press, London (1987). | [2] D.Eimerl, S.Velsko, L.Davis , F.Wang, G.Loicono, G. Kennedy, (IEEE), | J.Quantum Electron., 25 (1989) 179. | [3] M. Narayan Bhat, S.M. Dharmaprakash, J. Crystal Growth 243 (2002) 526. | [4] C. Krishnan, P. Selvarajan, S. Pari, Current Applied Physics 10 (2010) 664. | [5] Min-hua Jiang, Qi Fang, Adv. Mater. 11(1999) 1147. | [6] A.S.J. Lucia Rose, P. Selvarajan, S. Perumal Mater.Chem. Phys. 130 (2011) 950. | [7] D.Shanthi, P.Selvarajan, Ind. J.App.Res. 3 (2013) 565. | [8] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798. | [9]A Shanthi, C Krishnan and P Selvarajan Phys. Scr. 88 (2013) 035801. | [10] G. Bhagavannarayana, S.K.Kushwaha, S.Parthiban, | Subbiah Meenakshisundaram, J.Crystal Growth 311 (2009) 960. |