GROWTH AND CHARACTERISATION OF IMIDAZOLE POTASSIUM SULPHATE – A SEMIORGANIC NLO CRYSTAL

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Abstract

A new semiorganicnonlinear optical crystal of Imidazole Potassium Sulphate (IPS) single crystalswas grown by slow evaporation solution growth technique from an aqueous solution. The unit cell parameters and the crystal structure were determined by single crystal X-ray diffraction study. The powder X-ray diffraction pattern of the grown IPS has been indexed.The presence of various functional groups in the crystal was confirmed by fourier transform infrared spectral (FTIR) analysis. The optical transmission window of the IPShas been analysed by UV - Vis - NIR spectral analysis. Thermal studies reveal that the crystal is stable up to 432^{o}C.The microhardness analysis revealed that the grown crystal belongs to hard material category.The relative second harmonic generation (SHG) efficiencymeasurements reveal that the IPS is a highly efficient nonlinear optical material.

Key words: Crystal growth; Single crystal; Characterization; FTIR; UV-Vis-NIR; TG/DTA; Microhardness; SHG

1. Introduction

Over the past two decades nonlinear optical (NLO) materials have been intensely investigated for their application in optical communications and optoelectronics [1–3]. The search of new and efficient NLO materials has resulted in the development of a new class of materials called semiorganics, which has the potential for combining high optical

nonlinearityand chemical flexibility of organic materials with the thermal stability and mechanical robustness of inorganic materials. In this new class of materials, high-efficiency optical quality organicbased NLO materials form compounds on which polarizable molecule is stoichiometrically bonded to an inorganic host.

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. The new development technique for the fabrication and single crystal growth of nonlinear optical materials has dramatically contributed to this evolution. On account of the large flexibility for molecular design and higher nonlinear optical efficiency, there has been much progress in basic research on semiorganic NLO materials.

Imidazole is an aromatic heterocyclic compound and its derivatives with delocalized π-electron systems are designed to enhance the molecular hyper polarizability and result in high bulk optical nonlinearities [4,5]. Several nonlinear semiorganic large size good quality single crystals such as bis(glycine) lithium molybdate, glycine sodium nitrate, thiourea cadmium sulphate, L-alanine cadmium chloride, Potassium Boro-oxlate, L-Histidine chloride monohydrate, bis thiourea cadmium chloride were successfully grown by this method [6-12]. In the present work, high quality single crystals of IPS was successfully grown by slow evaporation technique and were characterized with different techniques.

2. Experimental section

2.1 Material synthesis

IPS was synthesized by taking analargrade Imidazole and Potassium sulphate in 1:1 molar ratio in de-ionized water according to the following reaction.

$$C_3H_4N_2+K_2SO_4 = C_3H_4N_2K_2SO_4$$

Calculated amount of Imidazole was first dissolved in de-ionized water. Potassium sulphate was then added to the solution slowly by stirring in a magnetic stirrer attached with a hot plate at 50^{o}C. The prepared solution was allowed to dry at room temperature and the salts were obtained by evaporation technique. The product was further purified by successive recrystallization process.

2.2 Solubility

The solubility of the synthesized salt is determined by gravimetrical method [13]. The solubility of IPS in de-ionized water was estimated as a function of temperature in the range 30^o -50^{o}C. Fig.1 shows the solubility curve of IPS. From the graph it is observed that the solubility of IPS increases linearly with temperature exhibiting a high solubility gradient and positive temperature coefficient, which reveal the fact that slow evaporation technique is the appropriate method to grow single crystals of IPS.

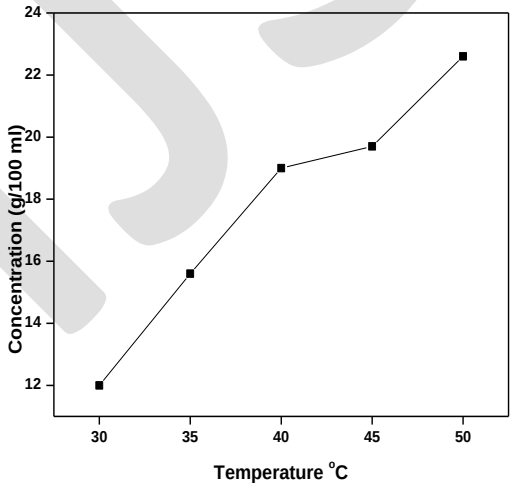

Fig 1. Solubility curve of IPS crystal

2.3 Crystal growth

Single crystals of IPS were grown from a saturated aqueoussolution containing AR grade Imidazole (Merck) and potassium sulphate (Merck) in 1:1 ratio respectively. The synthesized salt was dissolved in de-ionised water at room temperature. The solution was filtered by Whatman filter paper. The filtered solution was transferred to crystal growth vessels followed by slow evaporation at room temperature. Good transparent, colourless crystals were obtained in a period of 25 days. The as-grown single crystal of IPS is shown in Fig. 2.

Fig. 2 As grown crystal of IPS

3. Results and discussions

3.1 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction study was carried out to reveal the crystal structure and for confirming the grown crystal as a single crystal using ENRAF-NONIUS CAD4 diffractometer with CuKα radiation in the wavelength 1.540Å. Reflections from a finite number of planes were collected. This study revealed that the grown IPS crystal belongs to orthorhombic system which is recognized as noncentrosymmetric, thus satisfying one of the basic and essential

material requirements for the SHG activity of the crystal [14]. The crystallographic data is presented in table 1.

Table 1

Crystallographic data for IPS crystal

Identification code	IPS
Chemical formula	$C_3H_4N_2K_2SO_4$
Molecular weight	242.35 g/mol
Crystal color	colourless
Symmetry	Orthorhombic
Space group	P222
a	5.786Å
b	7.502A^o
c	10.091A^o
α	90^o
ß	90^o
γ	90^o
Volume	438.0 Å^3
Z	4
Diffracto meter	ENRAF-NONIUS CAD- 4
Radiation, wavelength	CuK_α, 1.540Å

3.2 Powder XRD

The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to powder X-ray diffraction using a Rich Seifert Powder X-ray diffractometer. The CuK_{α} radiations (λ = 1.5406 Å) from a copper target were used. The specimen in the form of a thin film was scanned in the reflection mode in the 2θ range 10-80^{o} with five decimal accuracy. Fig 3 represents the powder diffractograph for the grown IPS crystals. The peaks are indexed using indexing software.

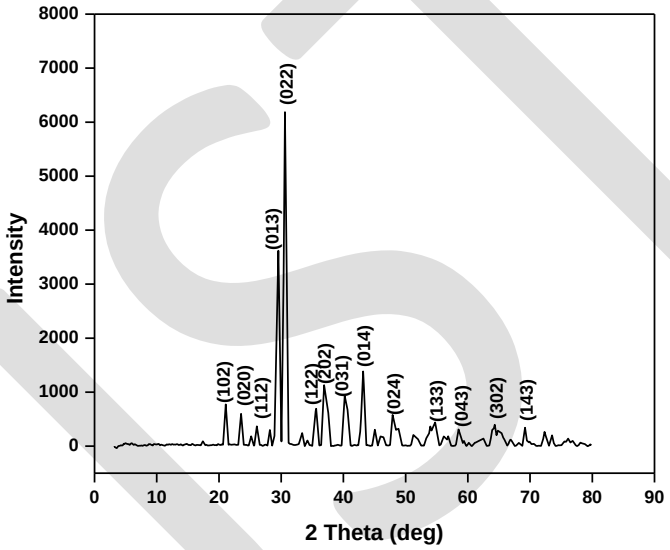

Fig. 3. Powder XRD spectrum

3.3 Fourier transform infrared (FTIR) analysis

FTIR spectrum is an important evidence that provides more information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency. The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The most important range (4000-400 cm^{-1}) is of prime importance for the study of semi organic compound by

spectral analysis [15]. In the present study, FTIR spectrum was recorded in the range of 4000-400 cm^{-1} for the grown IPS ingot using SHIMADZU spectrophotometer with KBr pellet technique and is presented in Fig.4.

The band at 3678.55 and 3577.31 cm^{-1} are due to O-H stretching vibrations. The band observed at 2992.02 cm^{-1} arises from C-H stretching vibrations. The broad band at 2803.99 cm^{-1} corresponds to NH_3^+ stretching band. C-H out of plane summation bands are observed at 1706.69 cm^{-1}. The band at 1112.73 cm^{-1} corresponds to S=O stretching vibrations. The COO^- stretching vibration was observed at 611.324 cm^{-1}.

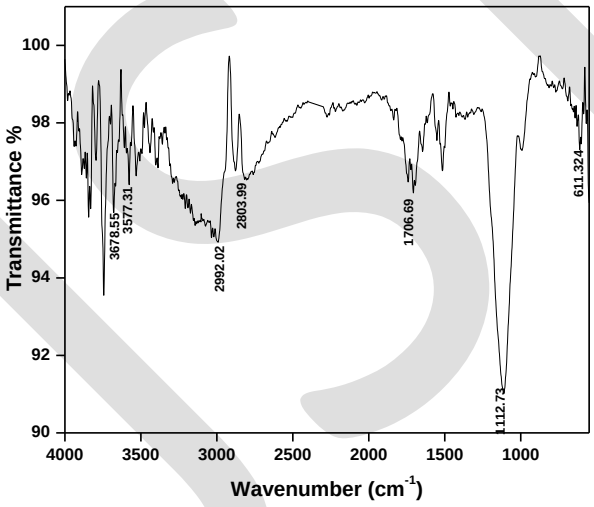

Fig. 4. FTIR spectrum

3.4 UV- Vis- NIR spectral studies

The optical transmission spectrum gives valuable information about the atomic structure of the molecules because the absorption of UV and visible light involves the promotion of electrons from the ground state to higher energy state. This is one of the desirable properties of the crystals for the device fabrication. In this study, the transmittance process was recorded at room temperature. The transition occurs at 200 nm which indicates the lower cutoff wavelength

of the IPS single crystal. From Fig. 5, it is observed that the crystal has increased 67% of transmittance in the (200–2500 nm) visible region.This is one of the most desirable properties of the crystals for the device fabrication [16]. The wide transparency and lower cutoff is one of the additional key requirements for having efficient NLO character [17] Using the formula $E_g = 1240/\lambda$ the optical band gap energy (E_g) was determined to be 6.2 eV for the grown IPS crystal. It showed that the transmittance increases while the band gap becomes wider.

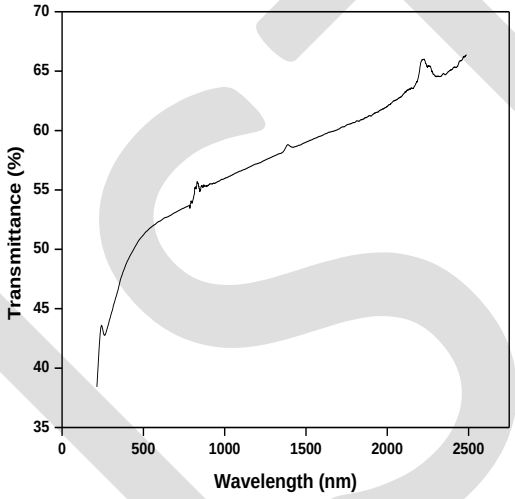

Fig. 5. Optical transmission spectrum

3.5 Thermal studies

The thermal properties of the IPS crystal are studied using thermo gravimetric analysis (TGA)/differential thermal analysis (DTA). Powdered sample of 13.840 mg is analyzed in Nitrogen atmosphere by using Perkin Elmer Diamond TGA/DTA equipment. The analysis is carried out simultaneously in air at a heating rate of 10°C/min for a temperature range of 26°C to936^{o}C. The TGA/DTA curve is shown in Fig.6. From the curve it is observed that the first

mass change occurs at 432^{o}C and the material is stable up to this temperature. There is no weight loss at 100^{o}C is due to the absence of water in the crystal. The next mass change occurs at 451^{o}C. The endothermic peak appearing at this temperature indicates the melting point of the crystal. The gradual mass change occurs at 468^{o}C which may be due to the decomposition of the sample.

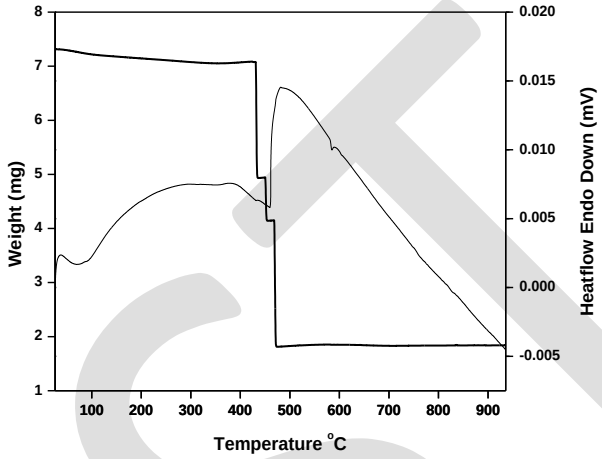

Fig.6 TG/DTA spectrum

3.6 Evaluation of microhardness, yield strength and stiffness constant

The Vickers hardness is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps of bulk crystals in the fabrication of devices. Mechanical properties of the IPS crystal were studied by making indentations on the selected plane using Vicker's microhardness tester fitted with a diamond pyramidal indenter and the indentation time was fixed as 5 s. The hardness values $H_v$were calculated usingthe relation,

$H_{v\_} = 1.8544P/d^2$ (kg/mm^2)

where P is the applied load in kg andd is the diagonal length of the indentation impression in mm. Fig. 7 shows the variation of H_v as a function of applied load ranging from 25 to 100 g on the face for IPS crystal. It isvery clear from the Fig. 7 that $H_v$decreases with increase of load. On

further increase of the load beyond 100 g, cracks developed on the surface of the crystal. It may be due to the release of internal stress generated locally by indentation. The relation connecting the applied load and diagonal length 'd' of the indenter is given by Meyer's law [18],

$$P = kd^n$$

where k is the standard hardness value and n is the Meyer's index or work hardening coefficient. This is calculated from the plot of logP vs logd (Fig. 8). Onitsch [19] and Hanneman [20] pointed out that 'n' lies between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials. The value of 'n' obtained for IPS is 1.4. Hence IPS belongs to hard material category[21].

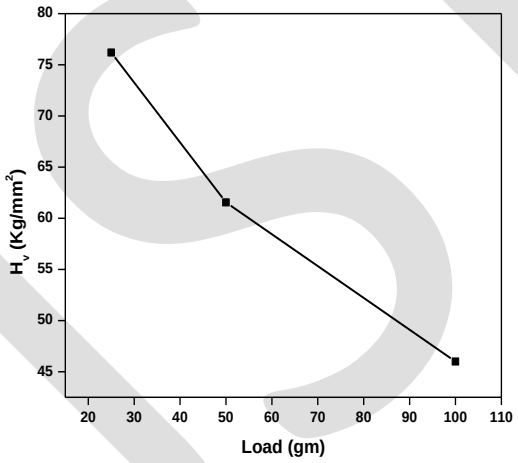

Fig. 7. Plot of H_v vs load P

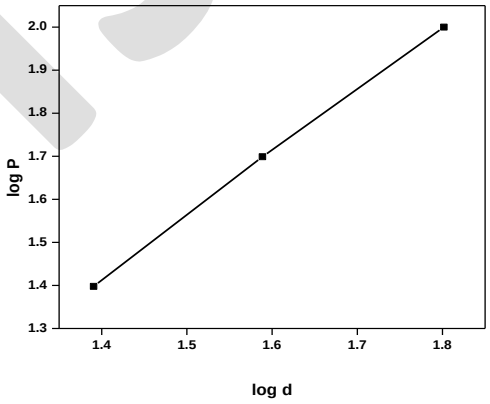

Fig. 8. Plot of log P vs log d

Elastic stiffness constant C_{11} is a measure of the ability of the material to resist deformation and it gives an idea about the tightness of bonding with the neighbouring atoms. The elastic stiffness constant for different loads are calculated using Wooster's empirical formula

$$C_{11}=H_v^{7/4}$$

and is shown in Table 2. Yield strength of a material is the minimum stress applied to the material for permanent deformation. Yield strength for different loads are calculated using the relation

$$\sigma_V= \underline{H_v}[1-(2-n)][\frac{12.5(2-n)}{1-(2-n)}]^{2-n} \quad 2.9$$

And is also shown in Table 2.

Table. 2

Load (g)	H_v	C_{11}(x10^{14} Pa)	σ_v(MPa)
25	76.2	3.8823	51.654
50	61.55	2.6424	41.559
100	46	1.5880	31.059

3.6 SHG conversion efficiency

The Kurtz–Perry powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation (SHG). Electron–phonon interactions including anharmonic ones play principal role in the nonlinear optical properties of semiorganic crystals [22,23]. The crystal was ground into a homogeneous powder of particles and compactly packed in a triangular cell and is kept in a cell holder. Second harmonic efficiency measurements were carried out using nanosecond laser flash photolysis (Applied photophysics, UK) and the instrument setup is shown in Fig. 9. The fundamental 1064 nm beam of a Q-switched Nd:YAG laser (Quanta-Ray, LAB 150, Spectra Physics, USA) with 8 ns pulse width and 200 mJ pulse

energy was used to strike the powder samples, which are placed in the triangle cuvette. The second harmonic signals from the sample were focused onto a Czerny–Turner monochromator using a pair of lenses. The signals were detected using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infiniium digital storage oscilloscope and the data were transferred to the computer for further analysis. The SHG efficiency is estimated to be 0.3times that of the reference KDP sample.

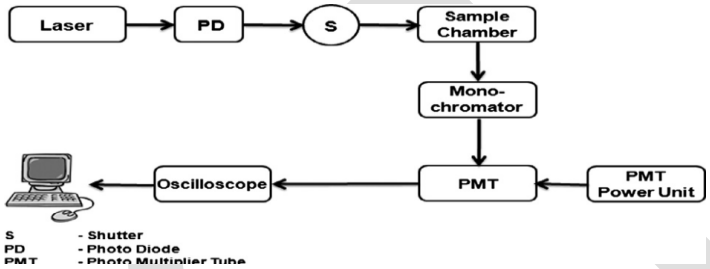

Fig. 9. Experimental setup ofSHG measurement

3.7 Conclusions

The bulk IPS single crystals have been grown successfully from slow evaporation solution growth technique. The unit cell parameters of IPS were confirmed by single-crystal X-ray diffraction analysis and the grown crystal crystallizes in the orthorhombic system with non-centrosymmetric space group P222. The functional groups were identified by FT-IR spectroscopic analysis. Optical studies reveal that IPS crystal has good transmission window with UV cut-off wavelength at 200 nm. Thermal studies indicate that the crystal is stable up to 432^{o}C. The Vickers microhardness value decreases with increasing load and the crystal develops cracks for loads above 100 g and the work hardening coefficient is less than 2. The SHG relativeefficiency of IPS was found to be of the order of KDP. Based on these observations we

can say that IPS can be a promising nonlinear opticalmaterial which possibly can be used for fabrication of NLO devices.

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