Growth, optical, thermal and dielectric studies on 2-Aminopyridine potassium thiocynate glycine (2-APKSNG) crystal for NLO applications

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A metal organic non-linear optical crystal of 2-Amino pyridine potassium thiocynate glycine (2-APKSNG) was grown at room temperature by slow evaporation technique. Crystalline nature and lattice parameters have been studied by powder and single crystal X-ray diffraction analysis. FTIR spectral study of the grown crystal confirms the chemical composition and their corresponding functional groups. UV–visible NIR spectral study confirms the transmission band from 200 nm to 900 nm with lower cutoff wave length at 250 nm. Thermal and dielectric studies of as grown crystals were studied and discussed. The SHG efficiency of the grown crystal was confirmed by the Kurtz powder technique.

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Keywords: Crystal growth, Metal organic, NLO crystal, X-ray diffraction, Thermal studies, Dielectric studies

1. Introduction

The search for nonlinear optical (NLO) material are of great interest in recent years due to their widespread applications, such as high speed information processing, optical communication and optical data storage [1]. In recent years, attention has been paid to develop novel organic NLO materials with large nonlinear optical coefficient. One of the advantages in working with organic materials is that the organic materials possess high polarizability conjugated system suitably packed to build up a non-centro symmetrical structure and properties for desired nonlinear optical applications [2, 3]. To achieve the strong mechanical and high thermal stabilities in NLO crystals, the complex of organic and inorganic molecules based on acid–base interaction, in which hydrogen bonded nonlinear organic molecules (cation) are linked to the inorganic molecules (anion) [4,5]. In this complexion, highly delocalized π electrons are made to easily move between electron donor and electron acceptor groups on opposite sides of the molecule inducing molecular charge transfer [6,7]. In acid-base interaction of organic and inorganic molecules, there are high polarizable cations, which are responsible for NLO properties, derived from aromatic nitro systems, linked to the polarizable inorganic anions through hydrogen bond network yielding non-centrosymmetric structural systems [8-10]. In recent years metal organic complexes have attracted considerable attention because these materials possess good second harmonic generation efficiency, hence rich demand in optical storage devices, color display and optical communication systems [11-13]. 2-Amino pyridine complexes are class of compounds well known for a long time [14-16]. Growth aspects of 2-Amino pyridine complex crystals in nonlinear optics (NLO) are closely linked to the rapid advancement in technology, such that ultra-fast phenomena, optical communication and optical storage devices, optoelectronic devices and fabrication were reported [17]. Recent investigations focus on the design of new materials that attain second order optical processes, as well as the strong interaction with the oscillating electric field. Materials based on the mixture of amino acids with ionic salts have been investigated and recognized as promising nonlinear optical properties [18,19]. Metal-organic compounds based on amino acids mixed with inorganic complexes have been realized to be useful for second harmonic generation (SHG) process [20–23]. Thiocynate ligand with S and N donors are capable of combining with metal to form stable complexes through coordination bond. These complexes show ligand to metal charge transfer by an electron movement from ligand to metal and metal to ligand in addition to π-π* conjugation [24, 25]. This paper deals with the study of synthesis, growth and characterization of 2-APKSNG crystals. The grown crystal have been subjected to powder and single crystal X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, Nuclear magnetic resonance (NMR) spectroscopy, ultraviolet-visible-near infrared (UV-vis-NIR) analysis, Thermo gravimetric (TG) and differential thermal analysis (DTA), dielectric studies and nonlinear optical studies by Kurtz-Perry powder technique.

2. Experiment

2.1 Crystal growth

2-APKSNG salt was synthesized by taking analytical reagent grade 2-aminopyridine, potassium thiocynate and glycine in 1:1:1 stachiometric ratio with Millipore water (18.2 mega-ohm cm resistivity) as a solvent.

$$C_5H_6N_2 + KSCN + NH_2CH_2COOH \rightarrow \{ [K]^+ [[C_5H_6N_2][COO]^- CH_2NH_2][SCN]^- \}$$

This solution was stirred vigorously for 4h using magnetic stirrer and allowed for slow evaporation. Supersaturation of the prepared solution was achieved by slow evaporation. High degree of purification of synthesized salt was achieved by successive recrystalization process. Synthesized saturated solution of 2-APKSNG was filtered using filter paper of micron pore size. This filtered solution of 2-APKSNG was poured into Petri dish and covered by porous paper for slow evaporation with pH value of 5.0. After super saturation with the time span of 30 days, quality crystal of size 19mm x 10 mm x 5 mm were harvested. As grown crystals of 2-APKSNG are shown in Fig. 1.

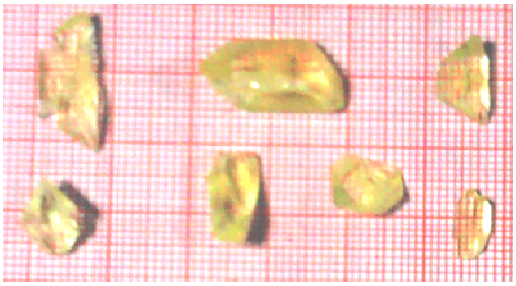

Fig. 1. The photograph of as grown crystals of 2-APKSNG.

3. Characterization

Single crystal and Powder XRD analysis were carried using a PHILIPS X PERT MPD system. The various functional groups present in the grown crystal was identified by FTIR analysis using PERKIN ELMER SPECTRUM RX1. ^{1}HNMR and ^{13}C NMR spectroscopic study were done by a Bruker Advance III 500MHz FTNMR spectrometer using D_2O as solvent to identify functional groups. The transmission behavior of the sample was studied by using LAMBDA-35 UV-vis-NIR Spectrometer. Thermal studies of TGA and DTA experiments were carried out on 2-APKSNG crystal using NETZSCA STA 409 instrument with a heating rate of 20°C min^{-1} from 50 to 500°C. The variation of dielectric constant as a function of frequency with different temperature was carried out by using HIOKI 3532 HiTESTER LCR meter. The NLO efficiency of the grown crystal was measured by Kurtz and Perry powder technique using ND:YAG laser of wave length 1064nm.

4. Results and discussion

4.1 Single and powder crystal XRD analysis

The rhombohedral crystal structure of the as-grown APKSNG single crystal was confirmed by using a single crystal X- ray diffraction analysis. The calculated cell parameters of the 2-APKSNG crystal are a = b = 12.08 Å; c = 16.28 Å; α = β = 90°; γ = 120° and the unit cell volume (V^3) is 2058 Å^3.

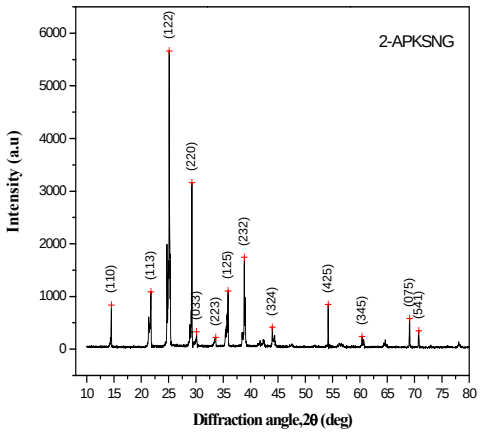

Fig. 2. Powder XRD pattern of 2-APKSNG.

Powder XRD pattern of grown 2-APKSNG crystal is shown in Fig. 2. The powdered sample wasscanned over the range of 10-80° at a rate of 1° per min. The sharp peaks observed in the powder XRD without any broadening confirm that the grown sample possess good crystallinity.

4.2 Fourier transform infrared analysis

The Fourier transform infrared spectral analysis can be effectively used to study the molecular structure and chemical bonding of the synthesized compound. Every chemical compounds have their own IR spectral lines [26, 27]. The FTIR spectrum of 2-APKSNG crystal was recorded in the range 4000 - 450 cm^{-1} by KBr pellet technique. The recorded FTIR spectrum is shown in Fig. 3. The frequencies of the vibrational mode of the crystal and their assignments are given in Table 1.

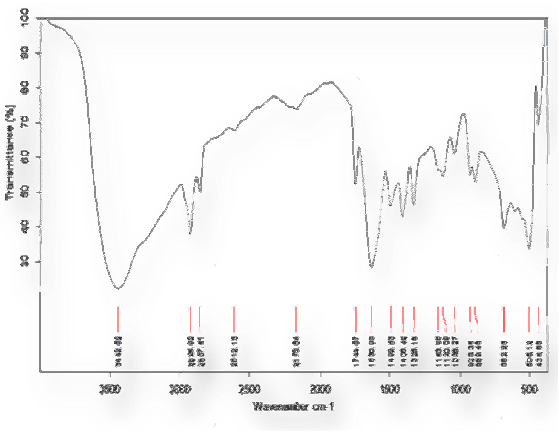

Fig. 3. FTIR spectrum of the grown 2-APKSNG crystal.

Table 1. Frequency and their assignments.

Frequency in wave number [cm^{-1}]	Assignment of vibrations
3442.52	O-H Stretching
2925.92	C-H Aliphatic Stretching
2857.51	C-H Aliphatic Stretching
2612.13	N-H Stretching
2170.84	N-H Multiple and over tone bond
1744.57	O–C = O-Ester bond
1630.90	N-H Bending
1492.63	$COO^{\square}$ Symmetric Stretching
1406.42	-C=S Symmetric Stretching
1328.15	C-H Twisting
1120.09	N-H Bending
926.35	C-H Rocking
889.48	C-C-N Symmetric stretching
682.26	$COO^{\square}$ Bending
505.12	N-H Torsion
435.68	COO^{-} Rocking

4.3 UV- VISIBLE NIR spectral analysis

The UV-Vis-NIR absorption spectrum of 2-APKSNG recorded in the wave length range 200-900 nm with high resolution is shown in Fig. 4. The absorption spectrum shows that the grown crystal have lower cut off wave length at 250 nm. The grown 2-APKSNG crystal has good transparency in UV-Visible and IR region. Hence the crystal can be used as a sensor material from down to UV, Visible and in the IR regions [28]. This wide range of transparency conforms that the grown 2-APKSNG crystal is a potential candidate for the optoelectronic application.

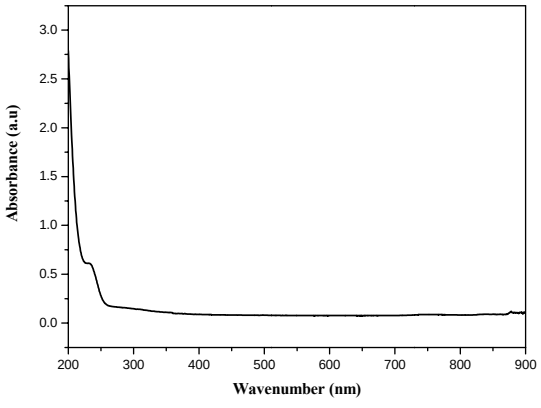

Fig. 4. UV-VIS Absorption spectrum of 2-APKSNG.

4.4 Thermal analysis

Thermo gravimetric (TG) and differential thermal (DTA) analysis derives information regarding phase transition, water of crystallization and different stages of decomposition of the crystalline sample [29]. The TGA and DTA spectra of the grown crystal are shown in Fig. 5. Samples were weighed in an Al_2O_3 crucible with a microprocessor-driven temperature controller.TG and DTA spectra of 2-APKSNG crystals were recorded in nitrogen atmosphere between 50 and 500°C. TGA spectrum shows that there is no weight loss up to 228.1°C. This indicates that there is no inclusion of solvent in the crystal lattice, which was used for crystallization. Hence the 2-APKSNG crystal is thermally stable up to 228.1°C. The thermogram reveals that the major weight loss [28.88%] starts at 228.1 ˚C and continues up to 484.0˚C. The nature of weight loss indicates the decomposition of the material. Below 484.0˚C, no weight loss was observed. A major weight loss [28.88%] occurs between 228.1˚C and 484.0˚C and 1.388mg [71.12%] was obtained as residue. DTA curve shows the decomposition point of as grown 2-APKSNG crystal 264.5˚C. This was compared with decomposition point of pure gamma glycine crystal of 246˚ [10].

4.5 Dielectric studies

The dielectric studies were carried out on the grown sample with dimension of 19.1 mm x 8.99 mm x 3.51 mm. Graphite was applied on opposite sides of the sample placed between two copper electrodes and thus forming a parallel plate capacitor. The capacitance of the crystalline sample was measured for various frequencies in the range $500H_Z$ - $5MH_Z$ at different temperatures. The dielectric constant was calculated using the formula,

$$\varepsilon_r = Ct/\varepsilon_O A$$

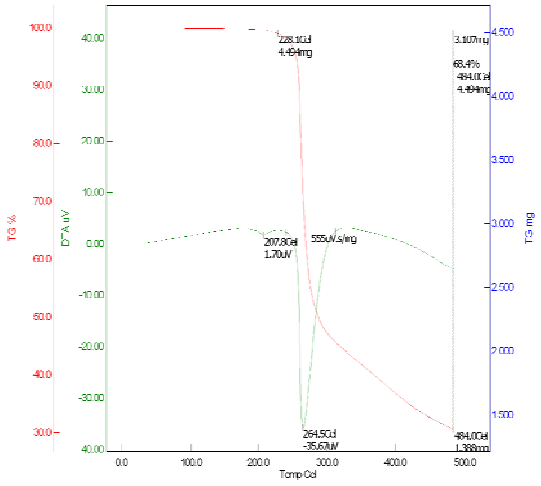

Fig. 5. TGA and DTA graph of 2-APKSNG crystal.

Where C is the capacitance; t, thickness of the sample; □o, the permittivity of the free space and A, the area of cross section of the sample. The dielectric values are obtained as a function of different temperatures (35°C to 55°C) for various frequencies (500Hz to 5MHz). The variation of dielectric constant with frequency of the grown crystal 2-APKSNG at different temperatures are shown in Fig. 6. Different polarization mechanism can be understood by ploting the dielectric constant vs frequency. The high dielectric constant value at low frequency region decreases with increase in frequency. From the figure the □$_r$ value reached the least value of about 25 at an applied frequency of 2.5 kHz and the value remains constant for further increase in the frequency. A similar trend was observed for all the recorded temperatures. Among the four polarizations, electronic and space charge polarizations are predominant in the low- frequency region [30]. The characteristic of low dielectric constant with high frequency of the sample suggests that the sample possesses enhanced optical quality with lesser defects and is most important for nonlinear applications [31].

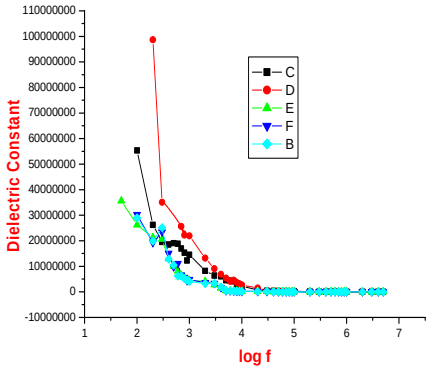

Fig. 6. Dependence of dielectric constant of 2-APKSNG crystal on frequency at different temperatures.

4.6 NLO studies

In order to confirm the NLO property, powdered samples were subjected to KURTZ and PERRY techniques, which remain the powerful tool for initial screening of materials for SHG [35]. The beam of wave length λ =1064 nm from Q-switched Nd:YAG laser was [Quanta ray series] incident normally on the prepared powdered sample, which was packed between two transparent glass slids. The SHG behavior was confirmed from the emission of bright green radiation [532 nm] by the sample. The measured amplitude of second harmonic green light for 2-APKSNG crystal is 4.42 mJ against 8.8 mJ for KDP and 8.9 mJ for urea crystals. It confirms the powder SHG efficiency of 2-APKSNG crystal is about 0.5 times of KDP and urea. The good second harmonic generation efficiency indicates that the 2-APKSNG crystals can be used in nonlinear optical devices.

5. Conclusion

Single crystals of 2-APKSNG were grown by slow evaporation technique. The crystallinity was confirmed by X-ray diffraction analysis and it was observed that the crystal belongs to rhombohedral crystal structures. FTIR and NMR spectral studies indentify the functional groups present in the entire region of UV-Vis-NIR. The 2-APKSNG is thermally stable up to 228 °C. Dielectric characterization shows the low value of dielectric constant at high frequencies. The powder SHG analysis reveals that the efficiency of this material is 0.5 times of KDP and urea. The promising crystal growth characteristics and properties of 2-APKSNG crystal reveal it as a potential material for photonic, electro-optic and SHG applications.

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