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Growth and characterization of new centrosymmetric 2-Aminopyridine potassium chloride single crystal for NLO Applications

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ABSTRACT

A new centrosymmetric semi organic crystal of 2-amino pyridine potassium chloride (2-APKC) was grown by slow evaporation solution growth technique at room temperature for the first time. Powder XRD study reveals the crystalline natures of the grown sample. Single crystal XRD study shows that the grown crystal is cubic systems of a= b= c= 6.19 Å; and α = β = γ = 90˚ with cell volume 237Å^3. FTIR spectral study identifies the chemical composition and their corresponding functional groups of the grown crystal 2-APKC. UV–visible NIR spectral study confirms the absorption band in the range 250-800 nm with lower cutoff wave length at 320 nm. Thermal, dielectric and photoconductivity studies of grown crystals were done and discussed. SHG efficiency of the as-grown centrosymmetric crystal is confirmed first time by the Kurtz powder technique.

Introduction

The search for nonlinear optical (NLO) material has been of great interest in recent years due to their widespread applications such as high speed information processing, optical communication and optical data storage [1, 2]. Organic molecular crystal possesses high polarizable conjugated systems suitably packed to build up a non-centro symmetrical structure. To achieve the strong mechanical and high thermal stabilities, highly delocalized π- electron complex of organic and inorganic molecules based on acid – base interaction, in which hydrogen bonded nonlinear organic molecules (highly polarizable cation) are linked to the inorganic molecules (anion). Hence highly delocalized π- electrons easily move between electron donor and electron acceptor groups on opposite sides of the molecule and inducing molecular charge transfer [3, 4]. In general highly polarizable cation of organic molecules (aromatic nitro systems), which is responsible for NLO properties, linked to the polarizable inorganic anions yields, non-centrosymmetric structural systems. Bonding energy present in the hydrogen bonds between organic and inorganic molecules [5] increase the SHG activity by counteracting the dipole moment paring in anti parallel fashion. In recent years growth of semiorganic complexes crystals have attracted considerable attention (6, 7). The structure of 2-amino pyridine has already been studied and known for a long time (8). Crystal growth of 2-amino pyridine complex (semiorganic) in the field of NLO is closely linked to the latest development in communication technology, such as ultra-fast phenomena, optical communication, optical storage devices, frequency doublers, optical modulators and color display units (9,10). Optical properties of 2-aminopyridine complexes and their suitability for optoelectronic devices have been reported (11-16). Optical, dielectic and NLO properties of 2-aminopyridine bisthiourea zincsulphate crystals (2-APTZS) have been 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 of light. Very few reports are available in the literature, which show that the centrosymmetric crystals also exhibit NLO properties [18-20]. SHG from centrosymmetric supermolecular assembly crystals having centrosymmetric structure possesses stable asymmetrical distribution of π-electron cloud and intramolecular charge transfer mechanism of organic crystal has been reported by Guo Wensheng et al [21]. Second harmonic generation has been reported from the surfaces of centrosymmetric particles in bulk isotropic solution for the first time [22]. Depends upon the crystal orientation, second harmonic generation in centrosymmetric silicon and germanium semiconductors were reported [23]. Strong second harmonic generation from centrosymmetric dyes, in which centrosymmetric molecules aggregate in non-centrosymmetric manner and hence bulk susceptibilities from intermolecular charge transfer have been reported [24]. Contributions of magnetic-dipole and electric- qudarapole in centrosymmetric media have been detailed [25]. Second harmonic generation in centrosymmetric media at boundaries and interfaces have been detailed by describing the surface susceptibility tensor [26-28]. Symmetry breaking in first few atomic and molecule monolayer on either sides of active nonlinear centrosymmetric thin slab interface, responsible for second harmonic generation have been explored [29,30]. Experimental demonstration of SHG sensitivity at the interface between two centrosymmetric media and theoretical equations that govern SHG from surfaces in a reflection geometry have been reported [31, 32]. In this view, a new type of semiorganic centrosymmetric single crystals of 2-aminopyridine potassium chloride (2-APKC) was grown by slow evaporation technique and its various physical properties have been discussed in this present paper for the first time.

Experimental Procedure

Material synthesis

2-APKC salt was synthesized at room temperature by taking analytical grade 2-aminopyridine and potassium chloride in 1:1 stoichiometric ratio with Millipore water (18.2 mega-

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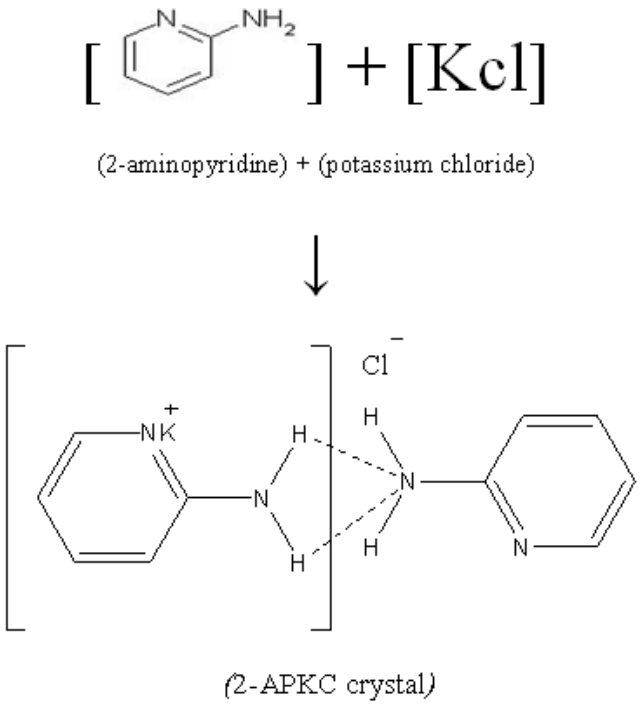
ohm.cm resistivity) as a solvent. 2-APKC salt has been obtained by the following chemical reactions. Reactant and products of the synthesis is shown in scheme 1.

$C_5H_6N_2 + KCl + \rightarrow [(K)^+ C_5H_6N_2 (Cl)^-]$

[(2-aminopyridine) + (potassium chloride)] → [(2-APKC)]

Scheme 1.



Crystal Growth

The prepared solutions were stirred vigorously at RT for 4h using magnetic stirrer. Continuous stirring with slight heating ensures homogeneous mixing of solutions. High degree of purity of synthesized salt was achieved by successive recrystalization process and filtration. Watman filter paper of micron pore size was used for filtration. The filtered solution was poured in to petri dishes of different sizes and covered with pores paper and housed for slow evaporation of the solvent at room temperature. After a time span of 15 days, good quality bulk 2-APKC crystals of size 10mm x 8mm x 3mm were harvested from the petri dishes. As-grown crystals of 2-APKC is shown in fig 1. In 2-APKC compound, potassium ion is coordinated to 2-aminopyridinium ion through nitrogen atom of aromatic ring (intramolecular charge transfer as LMCT), by leaving chloride ion as such and amino group hydrogen atoms form hydrogen bonding with aminogroup nitrogen of neighboring 2-aminopyridine ring molecule (intermolecular charge transfer).

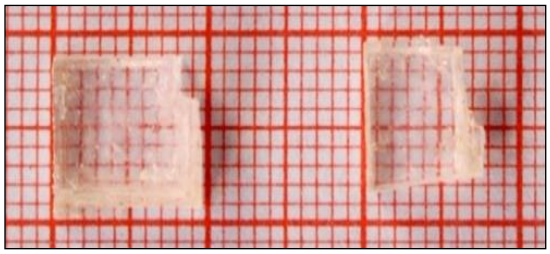


Fig 1. As- grown crystals of 2-APKC by slow evaporation solution growth technique

Characterization of 2-APKC single crystals

The grown crystal of 2-APKC was subjected to FTIR analysis using PERKIN ELMER SPECTRUM RX1 Fourier Transform infrared spectrometer. The transmission behavior of the grown crystal was studied by using LAMBDA-35 UV-vis-NIR Spectrometer. Powder and single crystal XRD analysis of the grown crystal were obtained on a PHILIPS X PERT MPD and APEX2 v 2.0.2 systems respectively. Thermal analysis (TGA and DTA) were carried out on NESTA STA 409 instrument heating rate of 20°C min^{-1} from 50°C to 500°C. Dielectric studies have been carried out by using HIOKI 3532 HiTESTER LCR meter. Photoconductivity study of the grown crystal was done by using Keithley 485 Picoammeter. The NLO efficiency of the grown crystal was tested by KURTZ powder technique using ND: YAG laser of wavelength 1064 nm.

Results and discussion

Fourier Transform Infrared analysis

The FTIR analysis of 2-APKC was carried out by KBr pellet technique in the wave length range 500-4000 cm^{-1}. In the recorded absorption spectrum NH_2, C=C, N-H and C-H functional groups of 2-APKC are identified and shown in fig 2. The vibrational frequencies assigned to the functional groups are shown in Table 1.

Table 1. Vibration frequencies and their assignments of as-grown 2-APKC crystal

Frequency in wave number (cm^{-1})	Assignment of vibration(2-APKC)
1611.64	NH_2 Bending
1485.13	C=C Stretching
1440.27	N-H Plane bending
770.08	Aromatic C-H Out of plane pending
530.51	(NH_3^+) Torsional oscillation
487.98	(N–C–N) Bending vibration

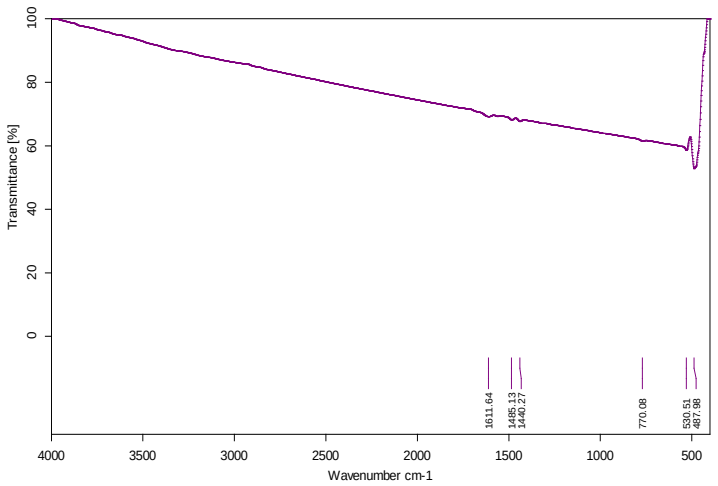


Fig 2. FTIR spectrum of 2-APKC crystal

UV- Visible spectral analysis

UV-visible absorption spectrum of 2-APKC recorded in the wave length ranges 250-800 nm was shown figure 3. The absorption spectrum shows the grown crystal has lower cut off wave length 330 nm. The grown crystal has good transmission in UV and visible region. This cut off wave length is compared with 2-aminopyridine complexes 2-aminopyridine bisthiourea zincsulphate (2-APTZS) [17], 2-aminopyridinium 4-nitrophenolate 4-nitrophenol (2APNP) [33], 2-aminopyridinium-4aminobenzoate (APAB) [13] and glycine complexes Glycine potassium chloride (GPC) [42], Diglycine picrate (DGP) [20], Glycine potassium sulphate (GPS) [35]. This wide range of absence of absorption shows that the as-grown 2-APKC crystal is potential candidate for the optoelectronic applications and also can be used as a sensor material (43).

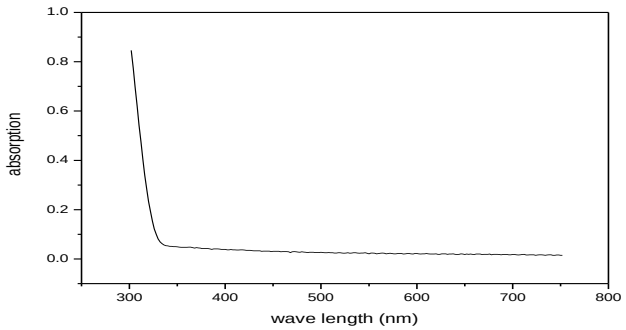


Fig 3. UV-Visible absorption spectrum of as-grown 2-APKC crystal

Table 2.

Crystals Name	Cutoff wave length(nm)
2-APTZS	240
2APNP	480
APAB	367
2-APKC	**330**
GPC	295
DGP	450
GPS	384

Powder XRD studies

Uniform fine powder form of the as-grown crystal 2-APKC was subjected to powder X-ray diffraction study to reveal crystalline perfection of the compound. The observed sharp and intense peaks confirm the high crystallinity of the grown crystal. The recorded powder X-ray diffraction pattern of 2-APKC crystal is shown in Figure 4.

Single crystal XRD Studies

Single crystal XRD study confirms the unit cell parameters of the 2-APKC crystals as a= b= c=6.19 Å; α = β = γ = 90˚; and volume of the unit cell is found to be V= 237 Å^3. Hence the crystal is cubic in structure. The cell parameters of the as-grown crystal is compared with well known potassium chloride cell parameters (a= b= c=6.3 Å; α = β = γ = 90˚; and volume V= 250Å^3). Same values of α, β and γ of 2-APKC and KCl indicates that there was no change in cubic crystal systems.

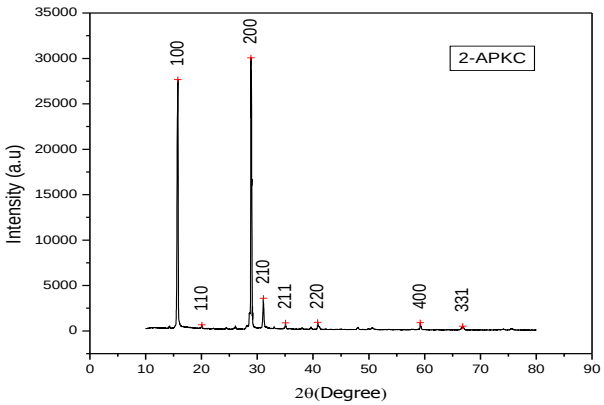


Fig. 4 Powder XRD of grown crystal 2-APKC

Influences of additives on the crystal habit of potassium chloride have been reported [34]. Comparison of lesser cell volume of 2-APKC (237Å^3) with cell volume of KCl (250Å^3), confirms the inclusion of 2-aminopyridine in to the KCl crystal lattice, without changing the crystal structure and only change in the crystal habit (physical property). The coordination of 2-aminopyridine with metals complexes yield lesser cell volume are tabulated in table 3.

Table 3.

Crystal name	a (Å)	b (Å)	c (Å)	α	β	γ	Volume (Å^3)	Crystal system
ZTS [41]	11.126	7.773	15.491	90°	90°	90°	1339.7	Orthorhombic
2-APTZS [17]	6.45	9.57	13.25	90°	90°	90°	818	Orthorhombic
KCl [34]	6.3	6.3	6.3	90°	90°	90°	250	Cubic
2-APKC (present work)	*6.19*	*6.19*	*6.19*	*90°*	*90°*	*90°*	*237*	Cubic

Thermal studies

The thermal decomposition path way of the 2-APKC complex crystal was shown in figure 5. Samples of 2-APKC crystals weighed in an Al_2O_3 crucible with a microprocessor driven temperature control. TG and DTA curves of 2-APKC crystals were recorded in nitrogen atmosphere between ambient temperatures to 450˚C. According to DTA analysis, 2-APKC crystal undergoes two stage decompositions. First stage decomposition was observed between 30˚C and 180˚C with exact decomposition temperature at 80˚C. As a second stage, the exact-decomposition temperature lies at 390˚C. The thermo gravimetric spectrum reveals that the gradual weight loss up to 430˚C indicates the decomposition of the material.

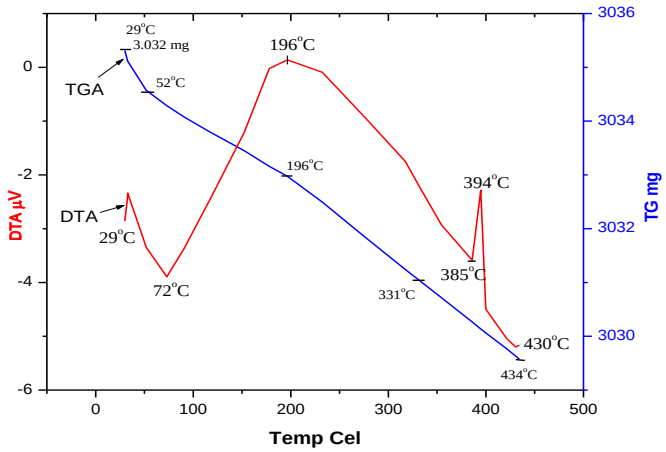


Fig 5. TG & DTA graph of 2-APKC crystal

Dielectric Studies

Different polarization mechanism can be understood by drawing graph between dielectric constant vs frequency. The samples dimensions of 5.11mm x 4.37mm x 1.36mm were used for measurement. Graphite was applied on opposite sides of the crystal and then the crystal was placed between two copper electrodes and thus parallel plate capacitor was formed. The capacitance of the crystalline sample was measured for various frequencies in the range 500H$_Z$ to 5MH$_Z$ at different temperatures. The variation of dielectric constant with frequency of the as-grown crystal 2-APKC at different temperature is shown in fig 6.The high dielectric constant value at low frequency region and then it decreases with the increase in frequency. Dielectric constant value (ε_r) reached the least value at the range of frequencies 700Hz and the value remains constant for further increase in frequency. A similar trend was observed for all the recorded temperature. This high dielectric constant value at low frequency was due to predominance of

electronic and space charge polarizations (37,38) . The sample (2-APKC) possesses enhanced optical quality due to low dielectric constant for higher frequency values.

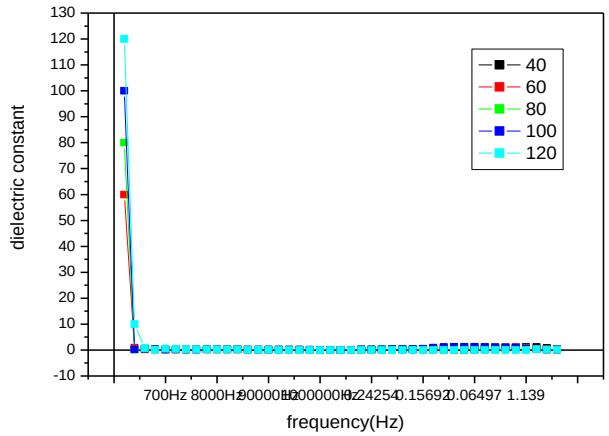


Fig 6. Dielectric studies of 2-APKC crystal

Lesser defects with low dielectric constant in higher frequency region are the essential criteria for different nonlinear optical materials and their applications [39].

Photoconductivity studies

The photoconduction studies of as-grown 2-APKC crystals were carried out by connecting the sample in series with a dc power supply and an ammeter at room temperature. The applied field increased from 100 to 800 v/cm and corresponding dark current without exposure of radiation was recorded. Photocurrent was recorded by exposing the sample with halogen lamp of power100w. The dependence of the dark current and photocurrent with respect to the applied field of same range were drawn on the same graph (Fig 7). It was observed from the graph that the dark current (I_d) always greater than the photocurrent (I_p), called negative photoconductivity. Thus, as-grown 2-APKC crystal exhibits negative photoconductivity. This may be attributed due to decrease in either the number of free charge carriers or their life time when subjected to radiation. According to Stockman model, the forbidden gap in the material contains two energy levels in which one is situated between the Fermi level and the conduction band while other is located close to the valence band. The second state has high capture cross section for electrons and holes. As it captures electrons from the valence band the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation. Thus the crystal is said to exhibit negative photoconduction effect [44].

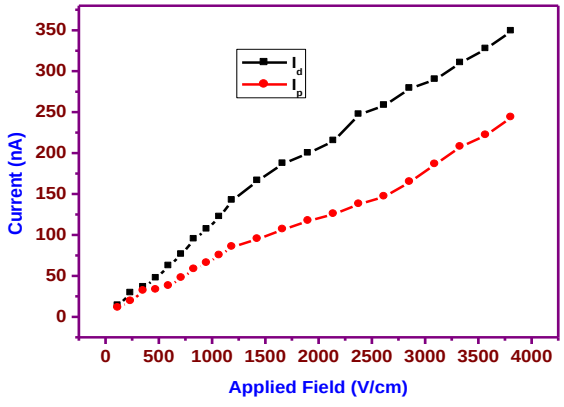


Fig 7. Photoconductivity of as-grown crystal 2-APKC

NLO studies

In the centrosymmetric structure of as- grown 2-APKC crystals, intramolecular charge transfer of 2-aminopyridine ligand to metal (LMCT), stable asymmetrical distribution of π-electron cloud density of 2-aminopyridine, hydrogen bonding between as- grown crystal 2-APKC to adjacent 2-aminopyridinium molecule network, paring of dipole moments in parallel fashion between inorganic potassium chloride and organic 2-Aminopyridine and symmetry breaking in first few atomic or molecule monolayer on the interfaces of 2-aminopyridinium potassium chloride grown crystal are responsible for second harmonic generation (SHC). In order to confirm the NLO property, powdered samples of the grown crystals arranged in an asymmetric manner such that a polar orientation maintained throughout the crystals, were subjected to KURTZ and PERRY techniques, which remains powerful tool for initial screening of materials for SHG [36]. The beam of fundamental wave length λ =1064nm (incident radiation) from Q-switched Nd: YAG laser (Quanta ray series) and coherent Molectron power meter, was made to fall normally on the calibrated powder form crystal sample, which was packed between two transparent glass slides. Here KDP taken as a reference material. The input power was fixed at 0.68 J and the output power was measured as 7.46 mJ, which was compared to output 8.8 mJ of standard KDP. Emission of bright green radiation of wave length λ=532 nm by the sample, after filtration of the incident (fundamental) radiation, confirms second harmonic generation (doubling of frequency). The powder SHG efficiency of 2-APKC crystal is about 0.85 times of KDP. The good second harmonic generation efficiency indicates that the centrosymmetric 2-APKC crystals can also be used in NLO devices. Some of the reported centrosymmetric crystals and their SHG efficiency are tabulated in table 4.

Table 4. Centrosymmetric crystals and their SHG efficiency

Crystal	Space group	SHG efficiency	Reference
(*p*–nitrophenol,hexamethylenetetramine, phosphoric acid and water) Superamolecular crystal	$P2_1/c$	4.1 times of KDP	[21]
Diglycine picrate (DGP)	$P2_1/c$	2.34 times of KDP	[20]
R,S-serine	$P2_1/a$	0.02 times of KDP	[40]
2-APKC	$P2_1/a$	0.85 times of KDP	Present work

Conclusion

The novel centrosymmetric 2-aminopyridine potassium chloride semi organic NLO single crystal (2-APKC) was grown successfully first time by slow evaporation solution growth technique. The grown crystal 2-APKC of size 10mm x 8mm x 3mm were subjected to various characterization studies. FTIR spectral study confirms the various functional groups presence in the as-grown crystal. UV –visible spectral study shows that it has the wide band transmission from 300nm to 900nm with cut off wave length 330nm. Powder XRD study reveals the good crystalline nature of the grown crystal. Single crystal XRD study shows that the 2-APKC crystal is centrosymmetric cubic system with lesser cell volume compared to potassium chloride cubic systems, indicating that incorporation of 2-aminopyridine ion with the KCl crystal lattice. The variations of dielectric constant as a function of frequency at different temperature are discussed. Photoconductivity study of the as-grown crystal carried out to measure dark current and photocurrent. Generation of stable asymmetrical distribution of π- electron cloud density structure by paring of dipole moments in parallel fashion between inorganic potassium chloride and organic 2-Aminopyridine,

inter and intramolecular charge transfer, symmetry breaking in first few atomic or molecule monolayer on either sides of the interfaces of 2-Aminopyridinium potassium chloride (as a physical change of lesser cell volume) and hydrogen bonding are responsible NLO property and their SHG efficiency is compared with standard KDP. This observed NLO property in a new type centrosymmetric crystal is an interesting remarkable experimental observation. Both theoretical and experimental analysis of the navel centrosymmetric 2-aminopyridine complex NLO crystals may yield many interesting research in future.

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