

Growth and characterization of Imidazole Potassium Chloride – A semiorganic NLO Crystal

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Abstract: A new semiorganic nonlinear optical single crystal of Imidazole Potassium Chloride (IPC) has been grown successfully by slow evaporation method. Colourless, transparent IPC crystal of dimension 5 x 5 x 2 mm³ has been grown within a period of 21 days. The grown crystal was subjected to single crystal X-ray diffraction (XRD) analysis to determine the lattice parameters. The powder X-ray diffraction pattern of the grown crystal has been indexed. The presence of functional groups in the grown crystal was confirmed by fourier transform infrared spectroscopy (FTIR) analysis. The optical transmission property of the grown crystal was analysed using UV-Vis- NIR spectral analysis. The mechanical strength of the crystal was found out using Vickers microhardness test. The second harmonic generation (SHG) has been tested using Kurtz powder technique.

Key words: Solubility, Crystal growth, XRD, FTIR, UV-Vis-NIR, Microhardness, SHG

1. Introduction

The fast growing development of optical fibre communication systems has stimulated the search for highly nonlinear materials capable of fast and efficient processing of optical signals. Nonlinear optical materials play a major role in the field of telecommunication, optical information storage and optoelectronic technologies. The most popular nonlinear optical materials used to generate the SHG signal so far have been inorganic bulk crystals with rather small second order nonlinear optical susceptibilities, such as potassium dihydrogen phosphate, lithium triborate, potassium niobate etc., [1]. But due to its lower SHG efficiency and laser damage threshold, scientist focused their attention on organic materials because they possess large second order nonlinear optical susceptibilities due to delocalized π -electrons.

The large nonlinearity in organic materials arises from the strong charge transfer and high polarizability. One major difference between inorganic and organic crystals is that only relatively weak vanderwalls forces are hydrogen bonding, resulting in rather poor mechanical properties often couples the molecules in pure organic crystals. Hence the molecules being held together by comparatively weak dispersive forces, the molecular identity in organic crystal is preserved. Accordingly, the molecular absorption will control the absorption spectrum of the crystal. Hence, organic materials are perceived as being structurally more diverse and are believed to have more long-term promise than inorganic [2].

The organic materials have an enormous array of exciting properties that are almost continuously “tunable”, telecommunications, frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability and other applications. The oriented nonlinear optical fields will be strengthened by the production of new nonlinear optical materials [3,4]. The large second order optical nonlinearity originates from

organic π conjugated molecules having an electron acceptor group at one end and donor group at the opposite end [5-7]. It is well established that donor-acceptor compounds with their large differences between ground state and excited state and dipole moments as well as large transition dipole moments can exhibit large molecular second order nonlinearities [8-11].

In 1987, a new type of semiorganic materials was discovered. It was the combination of both organic and inorganic materials [12,13]. The search for new and efficient NLO materials has resulted in the development of a new class of materials called semiorganics. Semiorganic materials are metal-organic-coordination complexes in which the organic ligands plays a dominant role for the NLO effect. They have gained considerable attention due to their excellent properties for frequency doubling, high laser damage threshold, wide transparency range, less delinquency and high nonlinear optical coefficient [14-17]. The advantage of semi organic materials is that the crystal can be grown from aqueous solutions and they form three-dimensional crystals which can be easily cut and polished [18]. The low-temperature solution growth is an important technique because large size nonlinear optical crystals can be grown by this technique.

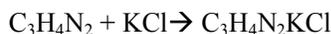
Imidazole is an aromatic heterocyclic compound and its derivatives with delocalized π -electron systems are designed to enhance the molecular hyper polarizability and result in high bulk optical nonlinearities [19,20]. Several nonlinear semiorganic large size good quality single crystals such as bis(glycine) 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 [21-27]. In the present work, high quality single crystals of Imidazole Potassium Chloride (IPC) was successfully grown by slow evaporation technique.

A survey of the literature shows that no reports on the crystal growth and characterization of IPC are available. This paper reports the synthesis, solubility, growth and characterization of the title compound. The X-Ray diffraction studies shows that IPC belongs to cubic system with space group P23. FTIR study reveals the functional groups of the grown crystal. The optical and mechanical properties of the crystals were studied. The SHG efficiency has been estimated to be 0.75 times that of potassium dihydrogen phosphate.

2. Experimental Section

2.1 Material synthesis

IPC was synthesized by taking analar grade (Merck) Imidazole and Potassium chloride in 1:1 stoichiometric ratio in de-ionized water according to the following reaction.



Calculated amount of Imidazole was first dissolved in de-ionized water. Potassium chloride was then added to the solution slowly by stirring in a magnetic stirrer attached with a hot plate at 50°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

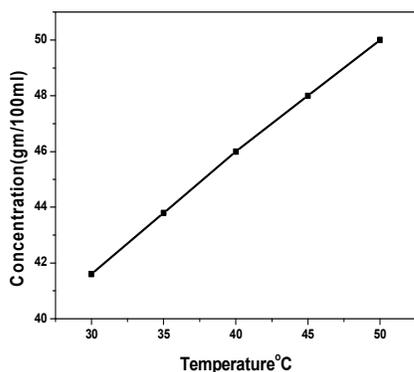


Fig.1. Solubility curve

The solubility of the synthesized salt is determined by gravimetric method [28]. The solubility of IPC in de-ionized water was estimated as a function of temperature in the range 30° -50°C. Fig.1 shows the solubility curve of IPC. From the graph it is observed that the solubility of IPC sample in water increases linearly with temperature exhibiting a high solubility gradient and positive temperature coefficient, which reveal the fact that's low evaporation technique is the appropriate method to grow single crystals of IPC.

2.3 Crystal growth

Single crystals of IPC were grown by solution method with slow evaporation technique at room temperature. In accordance with the solubility data, saturated solution of IPC was prepared by dissolving the synthesized salt in de-ionized water and stirred using a magnetic stirrer for three hours to obtain homogeneous solution. The saturated solution was then filtered using 4 micro whatmann filter paper to remove the impurities. The filtered solution was taken in vessels and closed with perforated covers and kept in dust free atmosphere for slow evaporation. A well developed crystal of size 5 x 5 x 2 mm³ was harvested within a period of 21 days. The grown crystal is shown in Fig.2 and is found to be transparent and colourless.

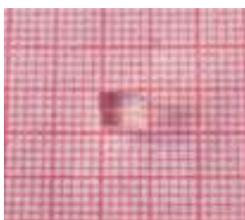


Fig.2 As grown crystal of IPC

3. Results and discussions

3.1 Single crystal X-ray diffraction analysis

Table 1 Crystallographic data for IPC crystal

Identification code	IPC
Chemical formula	C ₃ H ₄ N ₂ KCl
Molecular weight	142.63 g/mol
Crystal color	Colorless, transparent
Symmetry	Cubic
Space group	P23
a	5.98 Å
b	5.98 Å
c	5.98 Å
α	90°
β	90°
γ	90°
Volume	214 Å ³
Z	1
Diffractometer	ENRAFNONIUS CAD- 4
Radiation, wavelength	CuK _α , 1.540Å

The X-ray diffraction analysis on the grown IPC crystal was used to confirm the crystallinity and identification of the unit cell parameters. The grown IPC crystal has been subjected to single crystal X-ray diffraction using ENRAF NONIUS CAD4 diffractometer to obtain the crystallographic data. The calculated lattice parameters are a = b = c = 5.98 Å and α = β = γ = 90°. This reveals that the IPC crystal crystallizes in cubic structure. The obtained single crystal XRD data are provided in Table 1. The space group and the number of molecules per unit cell are observed to be P23 and 1 respectively.

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 REICH SIEFERT X-ray diffraction instrument using CuK_α (1.540\AA) radiation. The sample was scanned for 2θ in the range $10\text{--}80^\circ$ at a scan rate of $1^\circ/\text{min}$. The sharp peaks at specific 2θ values show high crystallinity of the crystal. The reflection planes are indexed using INDEXING software. The indexed powder X-ray diffraction pattern of the grown crystal is shown in Fig.3.

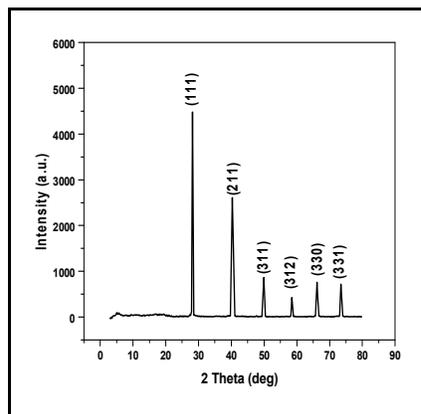


Fig.3. Powder XRD spectrum

3.3 Fourier transform infrared (FTIR) analysis

Infrared spectrometry involves examination of the twisting, bending, rotating and vibrational modes of atoms in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at specific wavelengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum that is uniquely a characteristic of the functional groups that make up the molecule and of the overall configuration of the molecule as well. FTIR spectrum of IPC was recorded from SHIMADZU spectrophotometer in the regions $400\text{--}4000\text{ cm}^{-1}$ using a KBr pellet and is shown in Fig.4. The sharp peak at 3454.62 cm^{-1} is due to N-H stretching vibration. The O-H stretching vibration was found at 2870.59 cm^{-1} . The C-H out of plane summation bands and C-C skeletal vibrations were found at 1641.26 cm^{-1} and 1495.33 cm^{-1} respectively. The NO_2 stretching vibration was observed at 1386.49 cm^{-1} . The C-H plane deformation is assigned at 1167.35 cm^{-1} and 1023.54 cm^{-1} . The band observed at 655.05 cm^{-1} can be attributed to Cl stretching vibration.

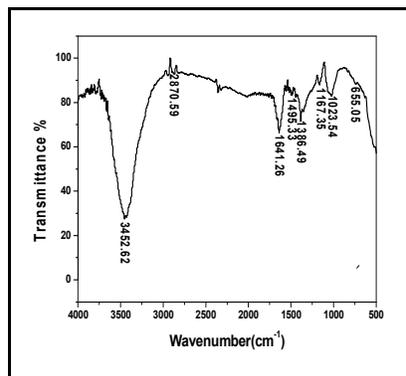


Fig.4. FTIR spectrum

3.4 UV- Vis-NIR spectral studies

The optical transmission spectrum of IPC single crystal was recorded in the wavelength region from 200 to 2000 nm using Perkin Elmer Lambda 35 UV/VIS spectrometer is shown in Fig.5. For optical fabrications, the crystal should be highly transparent in the considerable region of wavelength [29]. The transmission is found

to be nearly 90%. The good transmission property of the crystal in the entire visible region suggests its suitability for second harmonic generation [30,31]. The UV absorption edge for the grown crystal was observed to be around 205nm. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition electrons [32].

The optical absorption coefficient (α) was calculated from the transmittance using the following relation

$$\alpha = 1/t \log (1/T)$$

where T is the transmittance and t is the thickness of the crystal. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$):

$$\alpha = \frac{A (h\nu - E_g)^{1/2}}{h\nu}$$

where E_g is optical band gap energy of the crystal and A is a constant. The plot of variation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ is shown in Fig.6. E_g is evaluated by the extrapolation of the linear part to the x-axis. The band gap is found to be 4.97eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region[33].

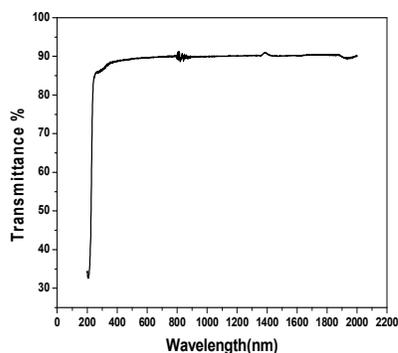


Fig.5. Optical transmission spectrum

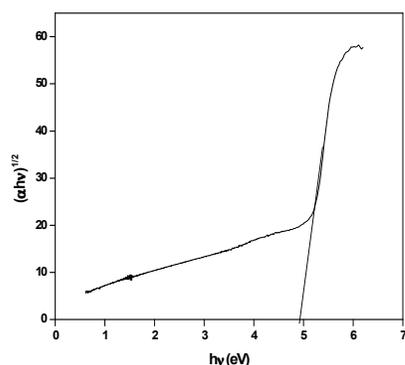


Fig.6. Plot of $(\alpha h\nu)^{1/2}$ vs Energy

3.5 Microhardness studies

Mechanical strength of the material plays a key role in device fabrication. It is a measure of resistance, the lattice offers to local deformation [34]. Selected smooth and flat surface of the grown crystal was subjected

to hardness test at room temperature using Vickers microhardness tester (LEITZ WETZLER) fitted with a diamond pyramidal indenter and attached to a incident light microscope. The indentation time was kept at 5s for all the loads. The Vicker's hardness number was calculated using the relation.

$$H_v = 1.8544 (P/d^2) \text{ kg/mm}^2$$

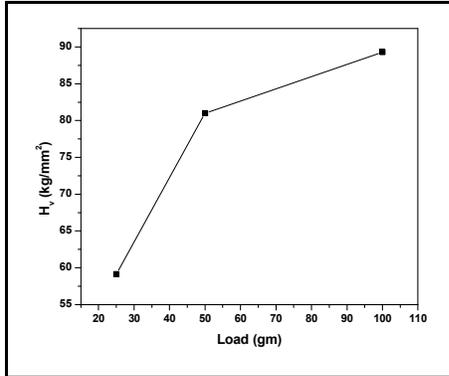


Fig.7. Plot of H_v vs load P

where P is the applied load in kg and d is the diagonal length of the indentation impression in mm. Variation of hardness value H_v with the load P is shown in Fig.7. From the graph, it is observed that the hardness increases with increase in load [15] satisfying reverse indentation size effect (RISE). The plot between log P and log d yields a straight line graph as shown in Fig.8 and its slope gives the work hardening coefficient n, which is found to be 2.81. According to Onistch concept, if n>1.6 H_v increases with increasing load. (Reverse indentation type) whereas for n<1.6, H_v decreases with increasing load. In our case, n>1.6 which shows that IPC crystal has the reverse indentation type and it satisfies the Onistch's concept, and it belongs to soft material category.

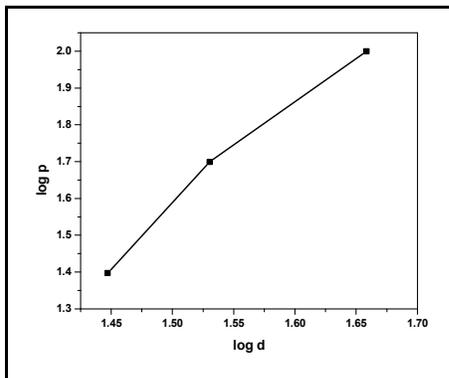


Fig.8. Plot of log P vs log d

Elastic stiffness constant C₁₁ 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

$$\sigma_v = H_v^3$$

and is also shown in Table 2.

Table. 2

Load (g)	H _v (kg/mm ²)	C ₁₁ (x10 ¹⁴ Pa)	σ _v (M Pa)
25	59.15	3.9053	19.72
50	81	6.7310	27
100	89.3	8.0452	29.77

From the table it is clear that the elastic stiffness constant and yield strength increases with load.

3.6 SHG conversion efficiency

SHG is a nonlinear optical process in which photons with the same frequency interacting with a nonlinear material are effectively “combined” to generate new photons with twice the energy and therefore twice the frequency and half the wavelength of the initial photons. The first and the most widely used technique for confirming the SHG from prospective second order NLO materials is the Kurtz powder technique [35] to identify the materials with noncentrosymmetric crystal structures. The SHG conversion efficiency of IPC crystal was studied using a 1064nm Nd:YAG laser. The crystalline samples were powdered into particle sizes in the range 125-150 μm. To make relevant comparisons with known SHG materials, KDP was also ground and sieved into the same particle size range. The powdered samples were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter. A Q-switched, Nd:YAG laser was used to generate about 0.68J/pulse at 1064nm as fundamental radiation. This laser device can be operated in two different modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multi-shot mode of 8 ns laser pulse with a spot radius of 1 mm was used. The input laser beam was allowed to pass through an IR reflector and then directed on the micro-crystalline powdered samples packed in a capillary tube. The photodiode detector and oscilloscope arrangements measure the light emitted in the sample. The SHG radiations of 532 nm (green light) emitted were collected by a photomultiplier tube (PMT-Hamamatsu-model R 2059). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 305213). The second harmonic signal of 6.6 mJ was obtained for an input energy of 0.68 J, while the standard KDP crystal gave a SHG signal of 8.8 mJ for the same input energy. The result obtained for IPC shows a powder SHG efficiency of about 0.75 times that of KDP crystal.

3.7 Conclusions

Good quality single crystals of IPC were successfully grown by slow evaporation solution growth method. Single crystal X-ray diffraction analysis confirms that the crystal belongs to cubic system with space group P23. The FTIR spectral analysis confirms the presence of functional groups present in the crystal. The UV-Vis-NIR study reveals the high transparency of the crystal with a short wavelength cut off at 205nm. The bandgap energy for the grown crystal was found to be 4.97 eV. Mechanical hardness studies reveal that Vicker’s hardness number increases with load satisfying reverse indentation size effect (RISE). The SHG efficiency of the crystal is found to be 0.75 times that of KDP. These studies confirm that the IPC crystals are considered as the potential material for the fabrication of optoelectronic devices.

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