Article

Synthesis, Growth and Optical Properties of 2-Aminopyridine Potassium Di-hydrogen Orthophosphate Crystal in Additive of Cadmium Chloride and Lithium Chloride

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Abstract:. A good optical quality crystal of 2-aminopyridine (2AP) metal complex crystals was grown by slow evaporation technique at room temperature. The transparent and defect less bulk size of 2-aminopyridine potassium dihydrogen orthophosphate metal complex crystals have been grown by solution growth method. The molecular structure and morphology of grown crystals was drawn and planes are indexed using WINXMORPH software. A optical absorption spectrum, the UV cut-off wavelength, Band gap (Eg), Reflectance (R), Refractive Index (n), Extinction coefficient (K) and Electrical susceptibility (χ_c) are calculated for 2AP metal complex crystals.

Keywords: Synthesis; Crystal growth; Optical band gap; electrical susceptibility

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1.Introduction

Optical materials with many significant achievements have occurred in the field of nonlinear optics because of the development of laser technology and new nonlinear optical materials of both inorganic and organic types [1, 2]. Second order nonlinear optical (SONLO) materials are proved to be interesting candidates for number A good optical quality crystal of 2-aminopyridine (2AP) metal complex crystals was grown by slow evaporation technique at room temperature. The transparent and defect less bulk size of 2-aminopyridine potassium dihydrogen orthophosphate metal complex crystals have been grown by solution growth method. The molecular structure and morphology of grown crystals was drawn and planes are indexed using WINXMORPH software. A optical absorption spectrum, the UV cut-off wavelength, Band gap (Eg), Reflectance (R), Refractive Index (n), Extinction coefficient (K) and Electrical susceptibility (χ_c) are calculated for 2AP metal complex crystals.of applications like second harmonic frequency conversion, electro-optic modulation and optical parametric amplification [3, 4].

The organic nonlinear optical materials with aromatic ring have been attracting much attention because of their high nonlinearity [5-7]. Purely inorganic materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of lack of π-electron delocalization [8].

Aminopyridine ligandcomplexes are class of compounds well known for a long time [9]. In recent years metal organic complexes have attracted considerable attention owing to their application in second and third harmonic generation, optical bistability, laser remote sensing, optical data storage, laser driven fusion, medical and spectroscopic image processing, color display and optical communication [10-12]. The major limitations in organic nonlinear optical (NLO) devices are low laser damage threshold, low optical transparency, and lack of the bulk size crystals. The inorganic NLO crystals possess relatively modest optical nonlinearity due to the lack of extended π-electron delocalization.

In semiorganics, polarizable organic molecules are stoichiometrically bound within an inorganic host; the NLO properties of semiorganic complex products of thiourea have attracted great interest because these metal-organic complexes combine the high optical nonlinearity and chemical flexibility of organics with the physical simplicity of inorganic [13, 14]. When an organic material mixed with aminoacid , NLO property was found to be increased due to the zwitterionic nature associated with enhanced transparency range[15,16]. KDP crystal plays an important role in the field of NLO and is used in quantitative x-ray analysis [17].

Amino acid contains a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH_3^+). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidate for NLO applications [18-20].

In recent years, research in engineering of 2-Aminopyridine complex crystal is very interesting for optical applications. The crystal structure of 2-aminopyridine is monoclinic and it has been reported earlier [21]. 2-Aminopyridine is used in the synthesis of pharmaceuticals especially for antihistamines, antiflammatories and other drugs. It is also used as a monomer for polymerization. At present, the investigation on 2-Aminopyridinemetal complex is of great interest for optoelectronic applications [22].

One of the obvious requirements for a non linear optical crystal is that it should have excellent optical quality. Potassium dihydrogen orthophosphate, KH2PO4 (KDP) is a good nonlinear crystal material due to its interesting electrical and optical properties, structural phase transitions and its easy crystallization [23]. The study of KDP is of great interest because of its unique non linear optical properties and vast applications in the field of high power laser systems. Potassium dihydrogen orthophosphate is a model system for a non linear optical device application. Large single crystal of KDP is used for frequency conversion and as parts of large aperture optical switches in the laser fusion systems [24]. In this present research we report that basically the 2-aminopyridine crystal crystallizes in centrosymmetric crystal system, but in addition of potassium dihydrogen orthophosphate the crystal crystallizes in non-centrosymmetric crystal system. The 2-Aminopyridine Potassium Di-hydrogen Orthophosphate crystals have many applications in optoelectronics.

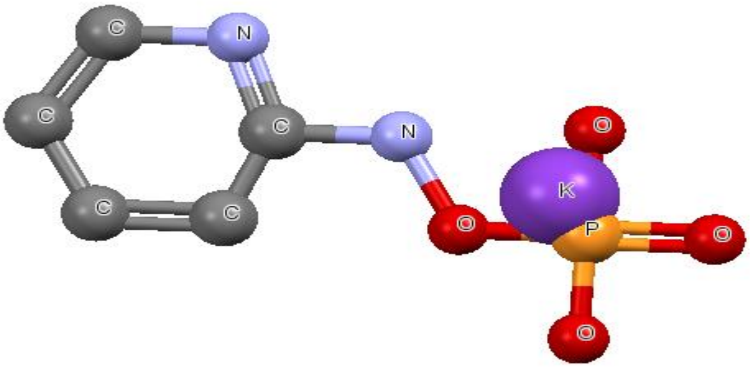
2. Experimental Procedure

2.1. Material Synthesis of 2APKDP

An analytical reagent grade of 2-aminopyridine and potassium dihydrogen orthophosphate was synthesized in equimolar ratio 1:1 using double distilled water as a solvent by using slow evaporation technique.at room temperature. The chemical reaction of synthesized compound was given below and the molecular structure of 2APKDP was shown in scheme 1.

$$C_5H_6N_2 + KH_2PO_4 \rightarrow C_5H_6N_2\ KH_2PO_4$$

2-aminopyridine + Potassium dihydrogen orthophosphate → 2APKDP



Scheme 1. Molecular scheme of 2APKDP.

2.1.1. Crystal Growth of 2APKDP

The synthesized solutionof 2APKDP was stirred for 4hours continuously using magnetic stirrer to ensure homogeneous mixing of solutions. High degree of purification of synthesized salt was achieved by successive recrystallization process. The saturated solution was filtered two times with micron pore sizefilter paper. This synthesized clearsolution waspoured in to a beaker and covered with pores paper, and housed for slow evaporation of the solvent. After 124 days the solvent was evaporated and good quality 2APKDP crystals of size 53mm x 38mm x 10mm were harvested. The grown crystal was optically transparent. As-grown crystal of 2APKDPis shown in Figure.1 and Morphology of 2APKDP crystal is shown in Figure 1a.

Figure 1. Photography of as grown crystal of 2APKDP.

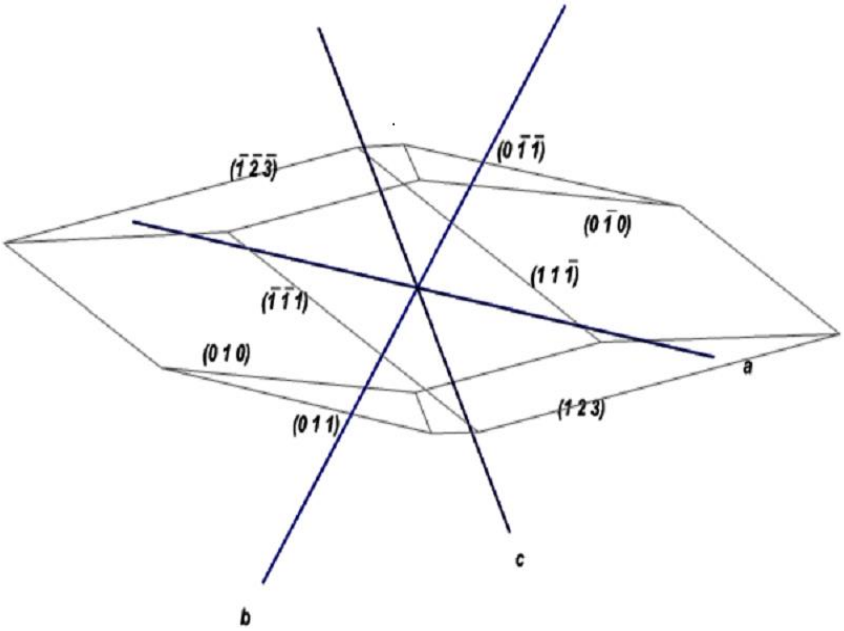


Figure 1a. Morphology of 2APKDP Crystal.

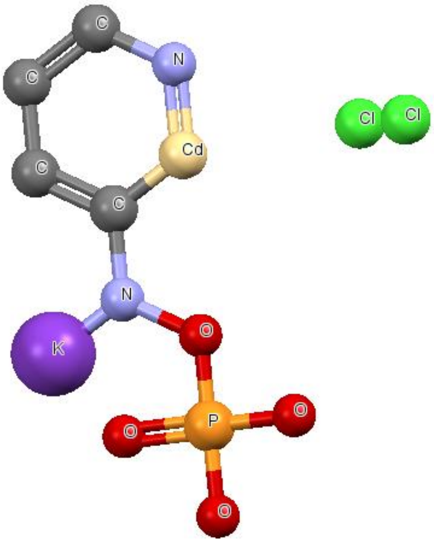
2.2. Material Synthesis of 2APKDPC

The product 2APKDPC was synthesized by using analytical reagent grade of 2-aminopyridine, Potassium di-hydrogen orthophosphate and Cadmium chloride in equimolar ratio 1:1:1 using double distilled water as a solvent by using slow evaporation technique at room temperature. The chemical reaction of synthesized compound was given belowand the molecular structure of 2APKDP was shown in scheme 2.

$$C_5H_6N_2 + KH_2PO_4 + CdCl_2 \rightarrow Cd[C_5H_6N_2\ KH_2PO_4]Cl_2$$

2-aminopyridine + Potassium dihydrogen orthophosphate

+ Cadmium chloride→ 2APKDPC



Scheme 2. Molecular scheme of 2APKDPC.

2.2.2. Crystal Growth of 2APKDPC

The synthesized solutionof 2APKDPC was stirred for 6 hours continuously using magnetic stirrer to ensure homogeneous mixing of solutions. High degree of purification of synthesized salt was achieved. The saturated solution was filtered with micron pore sizefilter paper. This synthesized clearsolution waspoured in to a beaker and covered with pores paper, and housed for slow evaporation of the solvent. After98 days the solvent was evaporated and good quality 2APKDPC crystals of size 23mm x 20mm x 4mm were harvested. The shape of the crystal confirms the additive of Cadmium chloride in 2APKDP.

The grown crystal was optically transparent. As-grown crystal of 2APKDPCis shown in Figure 2and Morphology of 2APKDPC crystal is shown in Figure 2a. .

Figure 2. Photography of as grown crystal of 2APKDPC.

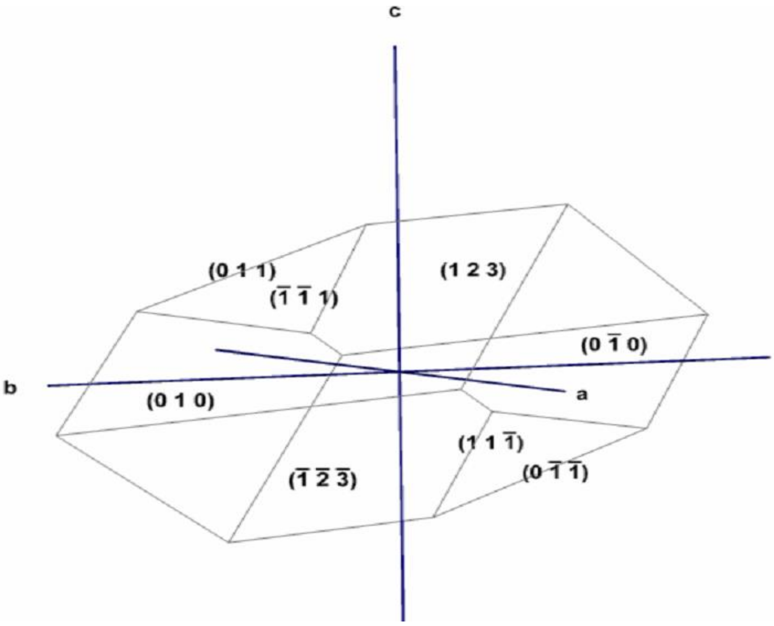


Figure 2a. Morphology of 2APKDPC Crystal.

2.3. Material synthesis of 2APKDPL

Aoptical quality crystal of 2APKDPL was synthesized by using 2-aminopyridine, Potassium di-hydrogen orthophosphate and Cadmium chloride [AR grade, LOBA] in equimolar ratio 1:1:1, a double distilled water was used as a solvent by slow evaporation technique at room temperature.

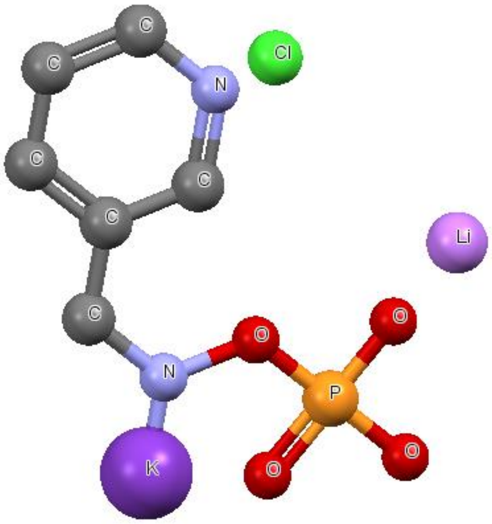
doi:10.20944/preprints201807.0220.v1

The chemical reaction of synthesized compound was given below and the molecular structure of 2APKDP was shown in scheme 3.

$$C_5H_6N_2 + KH_2PO_4 + LiCl_2 \rightarrow Li[C_5H_6N_2\ KH_2PO_4]Cl_2$$

2-aminopyridine + Potassium dihydrogen orthophosphate

+ Lithium chloride→ 2APKDPL



Scheme 3. Molecular scheme of 2APKDPL.

2.3.1. Crystal Growth of 2APKDPL

The synthesized product 2APKDPL was stirred for 4 hours continuously using magnetic stirrer to form homogeneous mixing of solutions. High degree of purification of synthesized salt was achieved. The saturated solution was filtered with micron pore sizefilter paper. This synthesized clearsolution waspoured in to a beaker and covered with pores paper, and housed for slow evaporation of the solvent. After 75 days the solvent was evaporated and good quality 2APKDPl crystals of size 9mm x 4mm x 2mm were harvested. The shape of the crystal confirms the additive of Lithium chloride in 2APKDP. The grown crystal was optically transparent. As-grown crystal of 2APKDPLis shown in Figure 3and Morphology of 2APKDPL crystal is shown in Figure 3a.   .

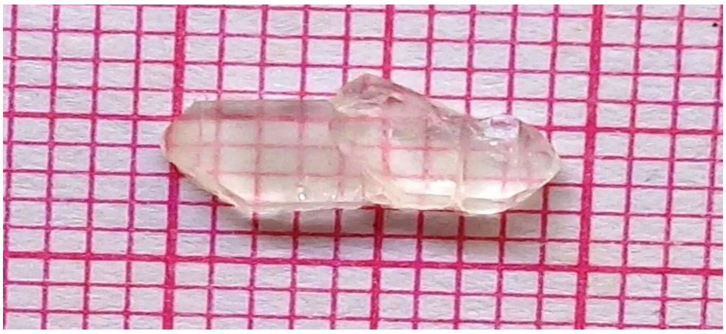


Figure 3. Photography of as grown crystal of 2APKDPL.

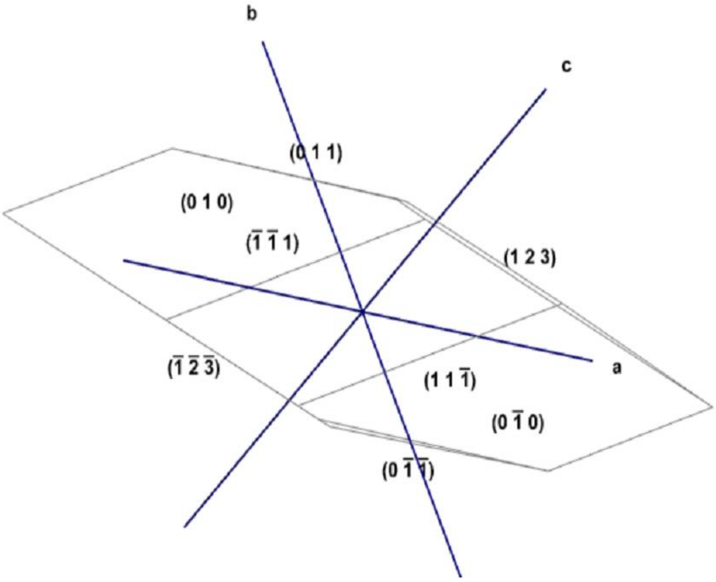


Figure 3a. Morphology of 2APKDPL Crystal.

3.Results and Discussion

3.1. Single crystal X-ray diffraction analysis of 2APKDP in Additive of Cadmium Chloride and Lithium Chloride

As grown crystals were subjected to X-ray diffraction analysis using ENRAF NONIUS CAD 4 diffractometer with MoKα radiation λ= 0.71073Å. The calculated unit cell parameters of 2APKDP, 2APKDPC and 2APKDPL were shown in table 1. In addition of cadmium chloride and lithium chloride in 2APKDP there is a slight variation in lattice parameters without change in crystal system. But when compared to pure 2AP there is a change in crystal structure because of metal ions.

Table 1. Crystal system of 2AP complexes.

S.No.	Crystal Name	a Å	b Å	c Å	Volume Å^3	Structure
1.	2AP	11.70	5.67	7.59	503	Monoclinic
1.	2APKDP	7.53	7.53	7.02	398	Tetragonal
2.	2APKDPC	7.49	7.49	7.03	394	Tetragonal
3.	2APKDPL	7.45	7.45	7.04	390	Tetragonal

3.2. Optical Properties of 2APKDP in Additive of Cadmium Chloride and Lithium Chloride

The optical absorption spectrum gives, valuable information about the atomic structure of the molecules because the absorption of UV and visible light involves the promotion of σ and π orbital electron from the ground state to higher energy state. This is the one of the desired property of the crystals for the device fabrications.

In this study, the UV-visible spectrum of grown crystal 2APKDP, 2APKDPC and 2APKDPL has been recorded using DOUBLE BEAMUV-Vis spectrophotometer:2202. The absorption spectrum was recorded for grown crystals in the wavelength range200- 1000 nm and the absorption spectrum is shown in the Figure 4, Figure 5 and Figure 6. Here, the polished grown crystal of 2APKDP, 2APKDPC and 2APKDPL with 2 mm thick was subjected to this absorption measurement. The UV-vis-NIR absorption spectrum indicates that the complete transparent character of the material in the entire UV-vis-NIR region.

From the absorption spectrum it is evident that grown crystals has UV lower cut-off wavelength at 290 nm for 2APKDP, 237 nm for 2APKDPC and 262 nm for 2APKDPL. The change in cutoff wavelength indicates that the incorporation of cadmium and lithium ion in 2APKDP and the transparency in the entire visible region for this crystal suggests its suitability for second harmonic generation.

The wide transparency and lower cut-off wavelength are the important requirements for having efficient NLO character. The cutoff wavelengths for grown crystals are given in table 2.

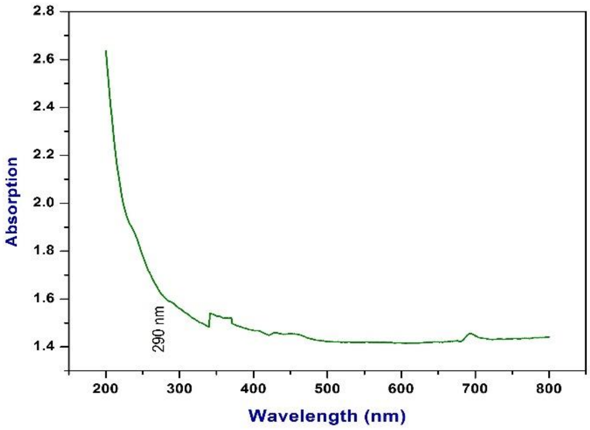


Figure 4. Optical absorption spectrum of 2APKDP.

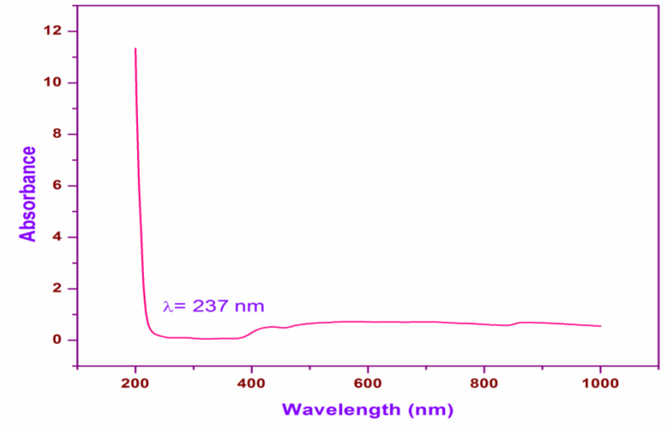


Figure 5. Optical absorption spectrum of 2APKDPC.

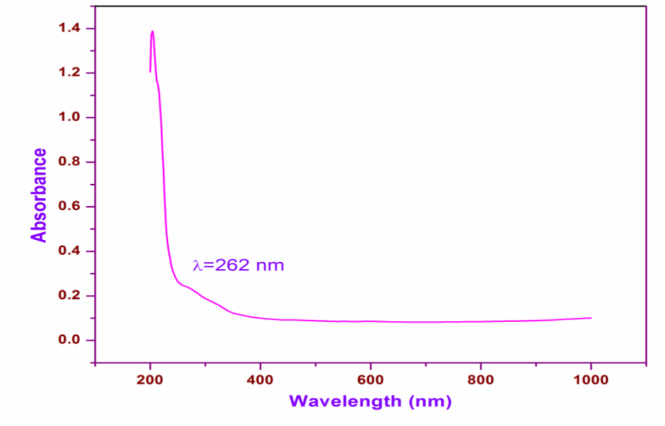


Figure 6. Optical absorption spectrum of 2APKDPL.

Table 2. The cutoff wavelength of grown crystals.

S.No.	Name of the Grown Crystal	UV-vis-NIR Cutoff Wavelength
1.	2APKDP	290 nm
2.	2APKDPC	237 nm
3.	2APKDPL	262 nm

4. Determination of Optical Bandgap and Optical Constants

4.1. Optical band gap (Eg)

In solid-state physics, a band gap, also called an energy gap, is an energy range in a solid where no electronstates can exist. In graphs of the electronic band structure of solids, the band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current.

If the valence band is completely full and the conduction band is completely empty, then electrons cannot move in the solid; however, if some electrons transfer from the valence to the conduction band, then current can flow (carrier generation and recombination).

Therefore, the band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors either have very small band gaps or none, because the valence and conduction bands overlap.

The dependence of optical absorption coefficient on photon energy helps one to study the band structure and the type of transition of electrons [21]. The optical absorption coefficient (α) was calculated from transmittance using the following relation.

$$\alpha = \frac{(2.3026 \log(1/T))}{t}$$

Where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν).

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

Where Eg is the optical band gap of the crystal and A is a constant. The plot of variation of $(\alpha.h\nu)^2$ versus hν is shown in Figure 7 for 2APKDP crystal, Figure 8 for 2APKDPC crystal and Figure 9 for 2APKDPL crystal. Optical band gap was evaluated by extrapolation of the linear part [21]. The band gap (Eg) is found to be4.64 eV for 2APKDP crystal, 5.66 eV for 2APKDPC crystal and 4.86 eV for 2APKDPL crystal. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [22].

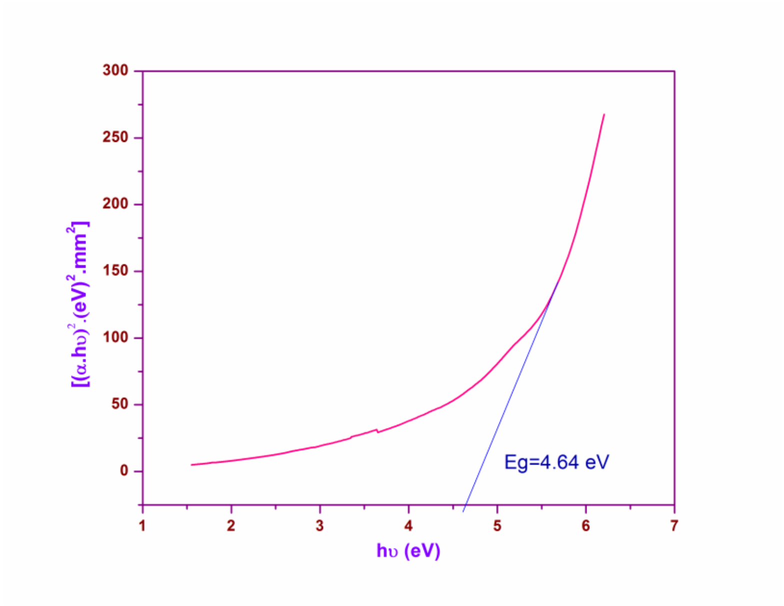


Figure 7. Tauc's plot of 2APKDPcrystal.

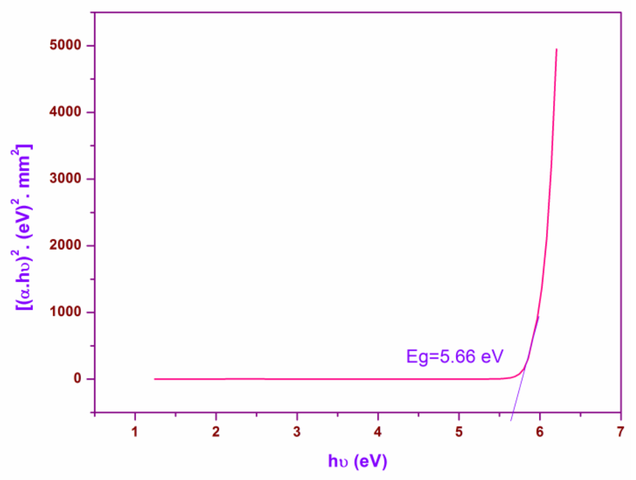


Figure 8. Tauc's plot of 2APKDPCcrystal.

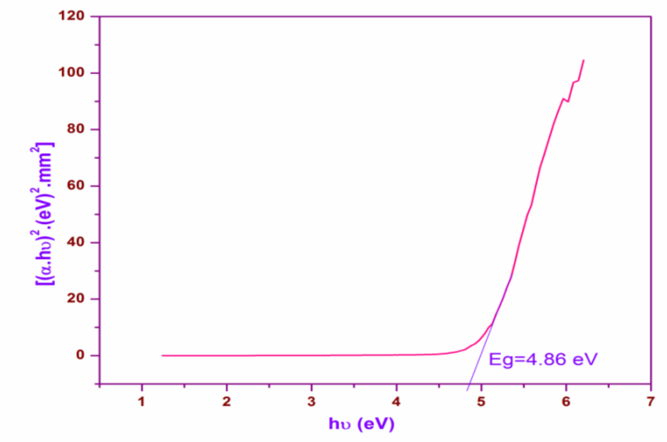


Figure 9. Tauc's plot of 2APKDPLcrystal.

4.2. Extinction coefficient (K)

Extinction coefficient (K) can be obtained from the following equation

$$K = \lambda\alpha/4\pi$$

The extinction coefficient as a function of absorption coefficient (α) is shown in Figure 10 for 2APKDP crystal, Figure 11 for 2APKDPC crystal and Figure 12 for 2APKDPL crystal.

The transmittance (T) is given by

$$T = ((1-R)\hat{}(2\ )\ \exp(-\alpha t))/(1-R\hat{}2\ \ \exp(-2\alpha t))$$

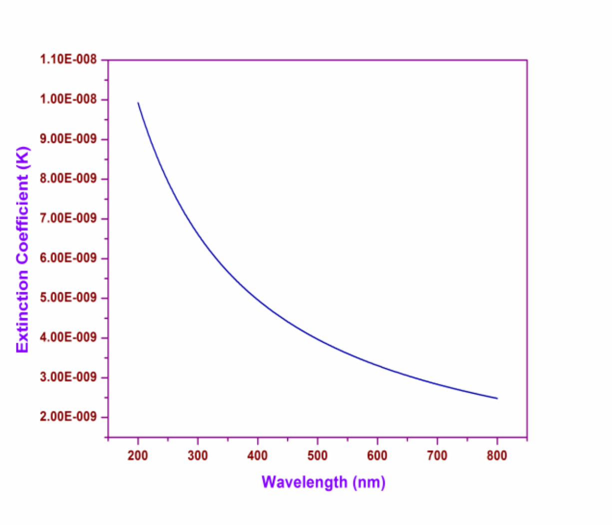


Figure 10. A plot of Wavelength Vs Extinction coefficient of 2APKDP crystal.

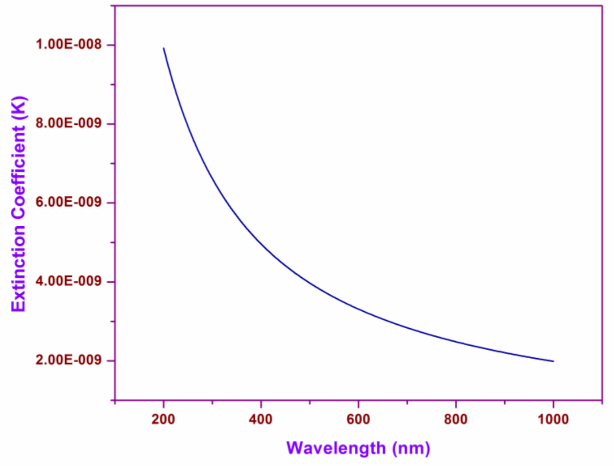


Figure 11. A plot of Wavelength Vs Extinction coefficient of 2APKDPC crystal.

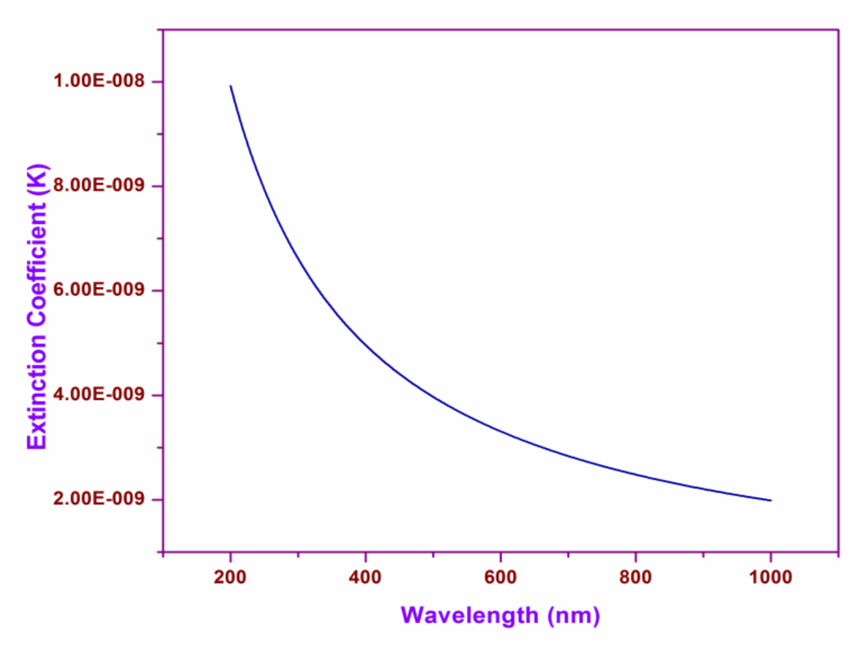


Figure 12. A plot of Wavelength Vs Extinction coefficient of 2APKDPL crystal.

4.3. Reflectance (R)

Reflectance of the surface of a material is its effectiveness in reflecting radiant energy. It is the fraction of incident electromagnetic power that is reflected at an interface. The reflectance spectrum or spectral reflectance curve is the plot of the reflectance as a function of wavelength.

The reflectance (R) in terms of the absorption coefficient can be obtained from the above equation. Hence,

$$R = \exp\left((-\alpha t) \pm \sqrt{\exp(-\alpha t)\,T} - \exp(-3\alpha t) + \exp(-2\alpha t)\,T^{2}\right)/\left((\exp(-\alpha t) + \exp(-2\alpha t)T\right)$$

The absorption coefficient versus reflectance is shown in the Figure 13for 2APKDP crystal, Figure 14 for 2APKDPC crystal and Figure 15 for 2APKDPL crystal.

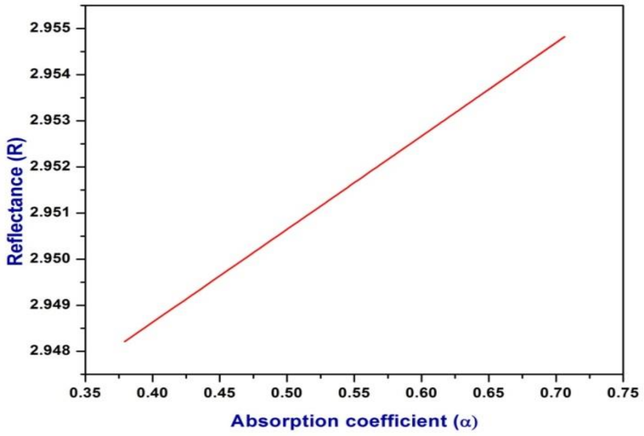


Figure 13. Absorption coefficient Vs reflectance for 2APKDP crystal.

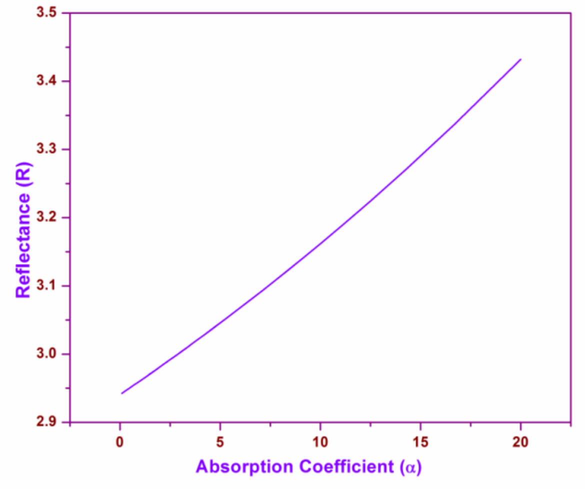


Figure 14. Absorption coefficient Vs reflectance for 2APKDPC crystal.

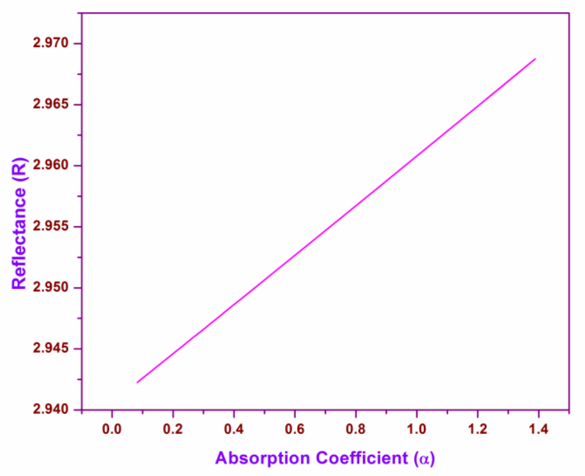


Figure 15. Absorption coefficient Vs reflectance for 2APKDPL crystal.

4.4. Refractive Rndex (n)

Refractive index, also called index of refraction, measure of the bending of a ray of light when passing from one medium into another.

The refractive index (n) can be determined from reflectance data using the equation.

$$n = (-(R+1) \pm 2\sqrt{R})/((R-1))$$

Figure 16for 2APKDP crystal, Figure 17 for 2APKDPC crystal and Figure 18 for 2APKDPL crystal, represents the variation of refractive index as a function of wavelength. The refractive index (n) decreases with increase in wavelength indicates that the grown sample absorbs at lower wavelength region.

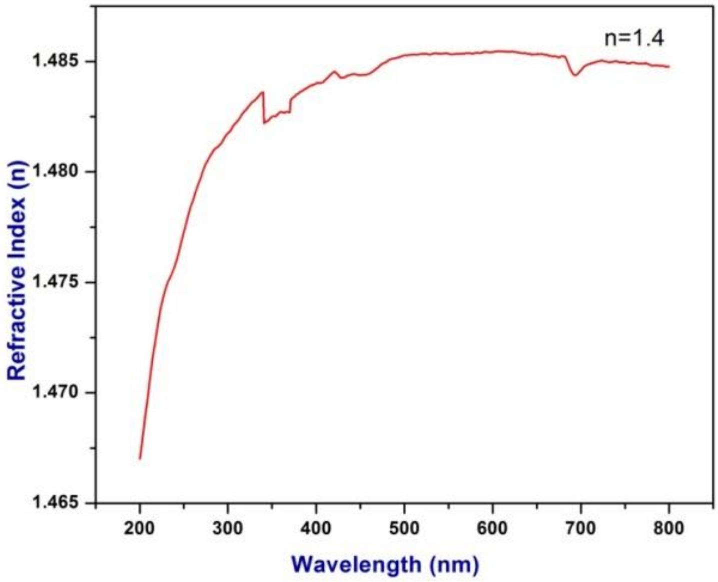


Figure 16. Plot of Wavelength Vs Refractive index of 2APKDP crystal.

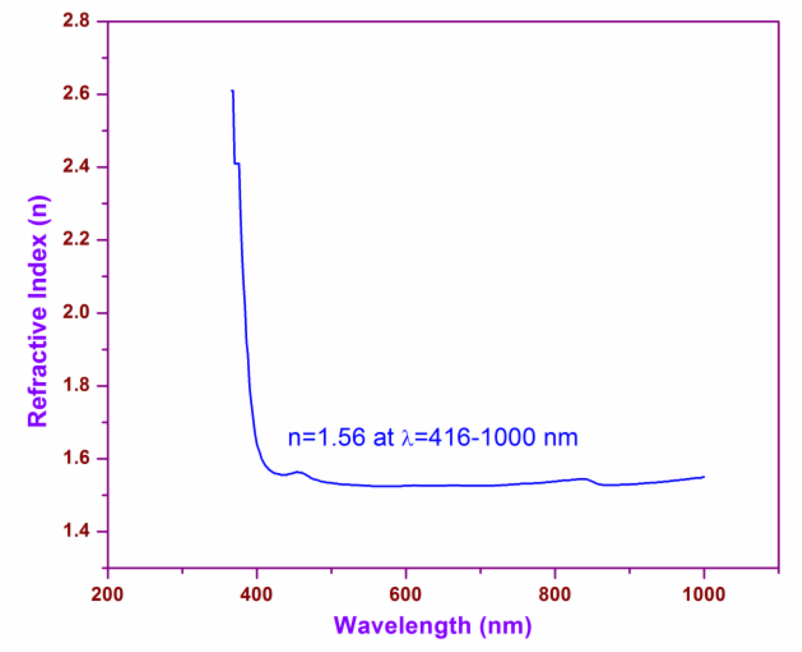


Figure 17. Plot of Wavelength Vs Refractive index of 2APKDPC crystal.

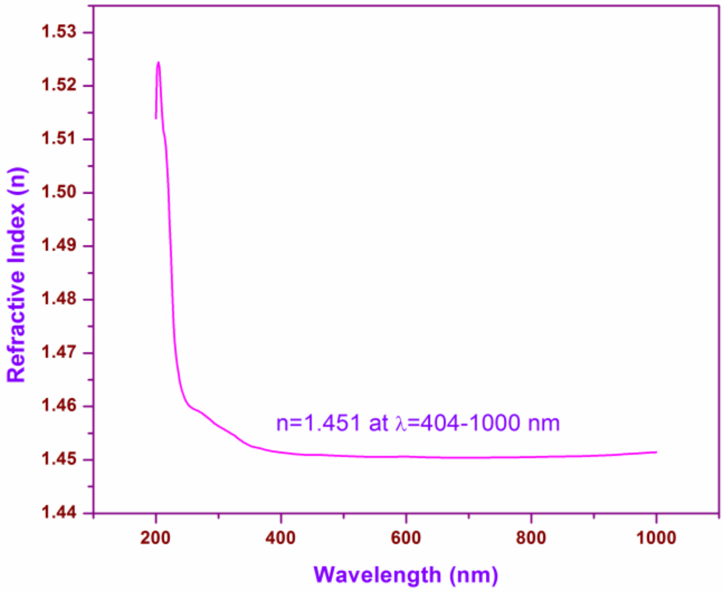


Figure 18. Plot of Wavelength Vs Refractive index of 2APKDPL crystal.

Refractive index has the large number of applications. It is mostly applied for identify a particular substance, confirm its purity, or measure its concentration. Generally it is used to measure the concentration of a solute in an aqueous solution. It is used to calculate the focusing power of lenses, and the dispersive power of prisms. Also it is applied for estimation of thermo physical properties of hydrocarbons and petroleum mixtures

4.5. Electrical Susceptibility

The variation of n and K values with respect to wavelength reveals the interaction of photon with electron. The refractive index 'n' is 1.4 at 800 nm for 2APKDP crystal, 1.56 at 1000 nm for 2APKDPC crystal and 1.451 at 1000 nm for 2APKDPL crystal.The refractive index is strongly dependent on wavelength. The electrical susceptibility (χ_c) can be calculated using the following relation,

$$\chi_c = \varepsilon_r - 1$$

$$\text{(or)} \quad \chi_c = n^2 - 1 \ (\text{i.e, } \varepsilon_r = n^2)$$

The calculated value of electrical susceptibility is shown in Table 2.

Table 3. Electrical susceptibility of 2AP complexes.

S.No.	Name of the Grown Crystal	Electrical Susceptibility (χ_c)
1.	2APKDP	0.96
2.	2APKDPC	1.43
3.	2APKDPL	1.10

The electrical susceptibility is lesser than 1 for 2APKDP crystal, but in additive of cadmium and lithium ion in 2APKDP crystal, the value of electrical susceptibility isgreater than 1 for 2APKDPC crystal and 2APKDPL crystal; the material can be easily polarized when the incident light is more intense.

5. Conclusion

A good optical quality of 2APKDP (53mm x 38mm x 10mm), 2APKDPC (23mm x 20mm x 4mm) and 2APKDPL (9mm x 4mm x 2mm)crystals was grown by slow evaporation technique at room temperature. The UV-vis-NIR absorption spectrum indicating the complete transparent character of the material in the entire UV-vis-NIR region. From the absorption spectrum it is evident that grown crystals has UV lower cut-off wavelength at 290 nm for 2APKDP, 237 nm for 2APKDPC and 262 nm for 2APKDPL crystals. The change in cutoff wavelength indicates that the incorporation of cadmium and lithium ion in 2APKDP and the transparency in the entire visible region for this crystal suggests its suitability for second harmonic generation. The band gap (Eg) is found to be4.64 eV for 2APKDP crystal, 5.66 eV for 2APKDPC crystal and 4.86 eV for 2APKDPL crystal. The refractive index 'n' is 1.4 at 800 nm for 2APKDP crystal, 1.56 at 1000 nm for 2APKDPC crystal and 1.451 at 1000 nm for 2APKDPL crystal. The electrical susceptibility is lesser than 1 for 2APKDP crystal, but in additive of cadmium and lithium ion in 2APKDP crystal, the value of electrical susceptibility isgreater than 1 for 2APKDPC crystal and 2APKDPL crystal.

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