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Process Development and Characterization of 2-Aminopyridine Potassium Dihydrogen Orthophosphate (2APKDP) Crystal

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***Abstract*—** A good optical quality bulk size defect free crystal of 2-aminopyridine potassium dihydrogen orthophosphate (2APKDP) was successfully grown from aqueous solution by slow evaporation solution growth technique at room temperature. The presence of functional groups in synthesized compound was identified by FT-IR analysis. Powder XRD pattern of 2APKDP crystal confirms the crystalline nature and (h k l) values are indexed. Single crystal X-ray diffraction analysis shows that the 2APKDP crystal crystallizes in tetragonal crystal system with noncentrosymmetric space group I4. Grown crystals has lower cut off wavelength 290 nm which is confirmed by UV- visible absorption studies and optical band gap was calculated using UV-vis-NIR spectrum data. The mechanical strength of the grown crystals was tested by Vicker's microhardness tester. The second order nonlinear optical property of the grown sample was analyzed by Kurtz-Perry powder technique. As grown 2APKDP crystal has high SHG efficiency which is 1.2 times that of known KDP. The dielectric constant and dielectric loss of grown 2APKDP crystal has been studied. A laser damage threshold study was carried out for 2APKDP crystal.

***Keywords*—** *Solution growth; non-centrosymmetric crystal; Band gap; SHG efficiency; LDT.*

I. 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 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 ligand complexes 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 amino acid , 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-Aminopyridine metal 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 on synthesis, growth and physicochemical properties of 2-Aminopyridine Potassium Di-hydrogen Orthophosphate crystal. 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.

II. EXPERIMENTAL PROCEDURE

A. 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 scheme of 2APKDP was shown in Figure 1.

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

2-aminopyridine + Potassium dihydrogen orthophosphate → 2APKDP

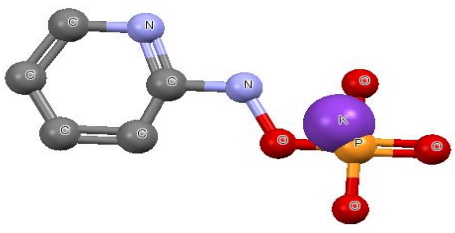

Figure 1. Molecular scheme of 2APKDP

B. Solubility of 2APKDP

The purity of the synthesized salt was further improved by successive recrystallization process. The solubility of the synthesized salt was carried out at various temperature from 30 ºC to 60 ºC in 5 ºC intervals by dissolving the solute in de-ionized water in an airtight container. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same procedure was repeated and the solubility curve for different temperatures was drawn. Figure 2 shows the solubility curve for 2APKDP in aqueous solution.

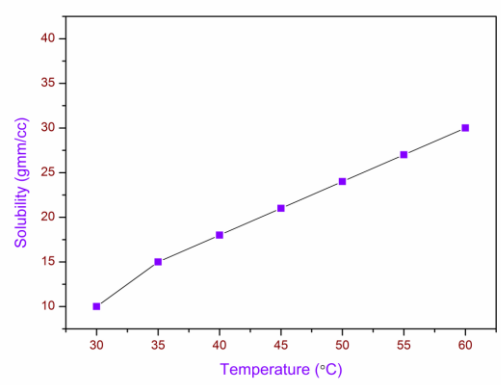

Figure 2. Solubility curve of 2APKDP

B. Crystal Growth of 2APKDP

The synthesized solution of 2APKDP was stirred for 4 hours 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 size filter paper. This synthesized clear solution was poured into 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 2APKDP is shown in Figure. 3 and Morphology of 2APKDP crystal is shown in Figure 4.

Figure 3. Photography of as grown crystal of 2APKDP

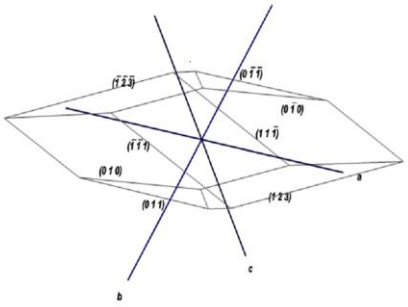

Figure 4. Morphology of 2APKDP Crystal

III CHARACTERIZATION TECHNIQUES

A. Fourier Transform Infrared analysis

In order to analyze the synthesized compound qualitatively for the presence of functional groups in the molecule, the FTIR spectrum is recorded between 500-4000 cm^{-1} using KBr pellet technique by Brukker IFS 66V Fourier transform infrared spectrometer. The spectrum obtained is shown in Figure 5 and the band assignments are shown in table 1.

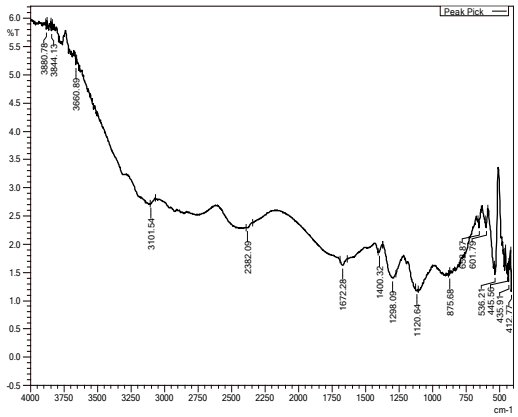

Figure 5. FTIR spectrum of 2APKDP crystal

Table 1. Assignments of IR band frequencies (cm^{-1}) for 2APKDP crystal

Wave number cm^{-1}	Assignments
3880	O-H stretching
3844	O-H stretching
3660	O-H bending
3101	NH_3^+ Stretching
2382	NH stretching
1672	P-O-H stretching
1400	O-H stretching
1298	P=O stretching
1120	P-O stretching
875	P-O-H stretching
653,601	COO^- bending
536	P-OH deformation / K-O stretching
445	Presence of Metal ion
435	Presence of Metal ion

C. Powder X-ray diffraction analysis

The crushed fine powder sample of 2APKDP was subjected to powder X-ray diffraction analysis by using BRUCKER, Germany (model D8 Advance) X-ray diffractometer with cuk_{alpha} (wavelength=1.5405A^0) radiation. The powder sample was scanned over the range 10– 80^o at a scan rate of 1^o / min. The well defined Bragg peaks are obtained at specific 2θ an angle which reveals that the grown crystal has good quality and high crystalline nature. The Powder XRD patterns 2APKDP crystal is obtained and (h k l) values are indexed using INDX software. The powder XRD pattern of grown crystal 2APKDP is shown in Figure 6.

D. Single crystal X-ray diffraction analysis

As grown crystal was 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 crystal are a = 7.53 Å, b = 7.53 Å, c = 7.02 Å and volume V = 398 $Å^3$, which shows that the grown crystal 2APKDP belongs to tetragonal crystal system with non-centrosymmetric space group I4.

2-aminopyridine crystallizes in monoclinic crystal system with centrosymmetric but incorporation of potassium di-hydrogen orthophosphate (KDP) the 2APKDP crystal crystallizes in non-centrosymmetric shown in Table 2.

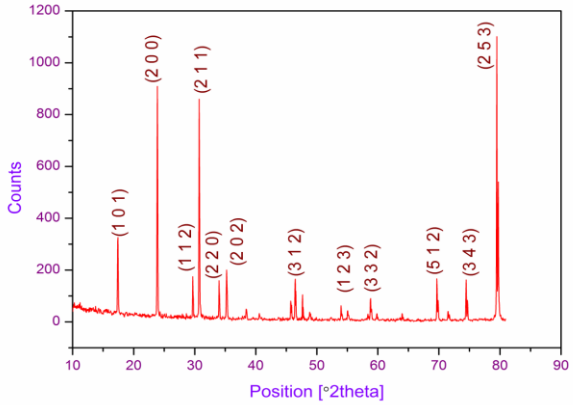

Figure 6. Powder XRD pattern of 2APKDP crystal

Table 2. Crystal system of 2AP and 2APKDP crystal

	2AP [21]	2APKDP
a Å	11.70	7.53
b Å	5.67	7.53
c Å	7.59	7.02
Volume Å^3	503	398
Structure	Monoclinic	Tetragonal
Space goup	$P2_1/c$	I4

***Present work**

E. UV-vis-NIR spectroscopy study

An optically polished 2APKDP single crystal was subjected to UV-vis-NIR spectrometer analysis using SHIMADZU UV-160 Spectrometer to find the transmission and absorption range about the suitability of this grown crystal for optical applications. The UV absorption spectrum was scanned in the range of 200 nm to 800 nm for 2APKDP crystal shown in Figure 7. A strong absorption and the UV cut off wavelength lies at 290 nm for 2APKDP crystal, and it reveals the good optical quality. High transmission in the entire visible region proves the suitability of grown crystal as UV tunable laser and in second harmonic generation (SHG) device applications.

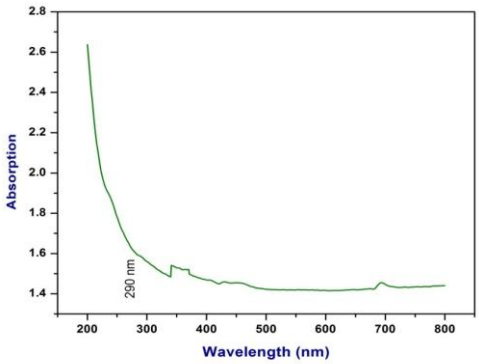

Figure 7. Optical absorption spectrum of 2APKDP

F. Optical band gap of 2APKDP crystal

The dependence of optical absorption coefficient on photon energy helps one to study the band structure and the type of transition of electrons [25]. 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 (hυ).

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

Where Eg is the optical band gap of the crystal and A is a constant. The plot of variation of $(\alpha.h\upsilon)^2$ versus hν is shown in Figure 8 for 2APKDP crystal. Optical band gap was evaluated by extrapolation of the linear part [26,27]. The band gap (Eg) is found to be 4.64 eV for 2APKDP crystal. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [28]. The Tauc's gap is often used to characterize practical optical properties of materials.

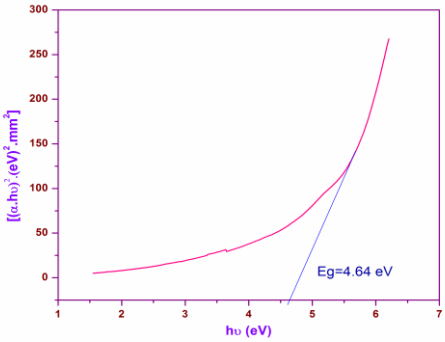

Figure 8. Tauc's plot of 2APKDP crystal

G. Nonlinear optical study

A Q-switched Nd: YAG laser emitting 1.06μm with power density up to 1 GW/cm^2 was used as a source of illuminating the powder sample of 2APKDP for calculating SHG efficiency. The sample was prepared by sandwiching the graded crystalline powder with average particle size of about 90μm between two glass slides using copper spices of 0.4 mm thickness. A laser was produced a continuous laser pulses repetition rate of 10Hz. The experimental setup uses a mirror and 50/50 beam splitter. Here well known NLO crystal KDP is taken as a reference material.

The fundamental beam was splitted into two beams by the beam splitter (BS); one of them was used to illuminate the powder under study and the other constituted the reference beam of power Pω. Half-wave plate (HW) placed between two parallel polarizers (P) and was used to pump the beam power. The input power was fixed at 0.701 J and the output power was measured as 10.72 mJ, which was compared to output 8.91 mJ of standard KDP. The diffusion of bright green radiation of wave length λ=532 nm ($P_2\omega$) by the sample confirms second harmonic generation (SHG). The powder SHG efficiency of 2APKDP crystal was about 1.2 times of KDP. The good second harmonic generation efficiency indicates that the grown crystals can be used as a suitable material for non-linear optical devices

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H. Vickers Microhardness study

The Vickers hardness indentations were made on the cut and polished grown crystal of 2APKDP at room temperature with load range of 25, 50 and 100 g using Vickers hardness

tester fitted with Vickers diamond indenter and attached to an incident light microscope.. The Vickers micro hardness number is evaluated using the formula $Hv=1.854\ P/d^2$ (kg/mm^2), Where Hv is the Vickers hardness number in (kg/mm^2), P is the applied load in g and d is the diagonal length of the indentation impression in μm and 1.854 is a constant of a geometrical factor for the diamond pyramid. From Figure 9, it is observed that initially the hardness increases with increase of load. At the low loads the indenter pierces only top surface layers resulting in increase of hardness and thereafter becomes load independent. Beyond the load of 100 g, a significant crack developed around the indentation mark, which may be due to the release of internal stresses generated at the corners of the indentation. The initial increase in microhardness (Hv) with increasing load is in agreement with the reverse indentation size effect (RISE).

By Meyer's law the size of indentation and the load are related as

$$P=k_1d^n$$

Where k_1 is the material constant and n is Meyer's index.

$$\text{Log } P=\log k_1+ n \log d$$

The plot of log P vs. Log d fitting data before cracking gives a straight line, which are in good agreement with Meyer's law (Figure 10). The slope of the graph gives the value of 'n'. The slope of the linear fit is the Meyer's index, and observed to be n = 0.32. According to Onitsch and Hanneman [29], 'n' should lie below 1.6 for comparatively hard materials, whereas it is above 1.6 for softer ones. Thus 2APKDP crystal belongs to hard materials category.

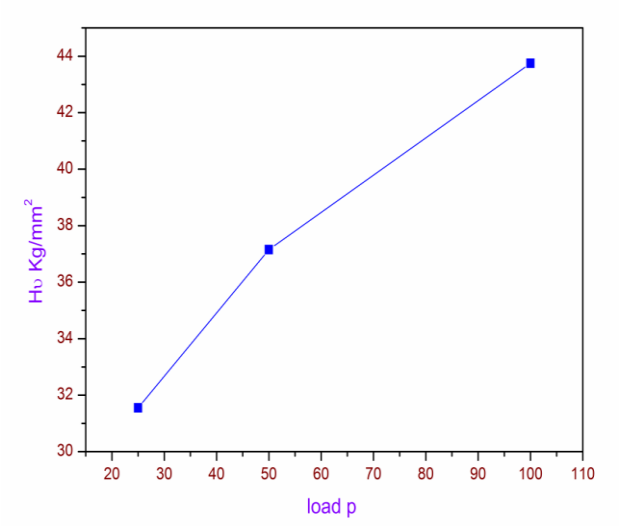

Figure 9. Variation of load p versus Hv of 2APKDP crystal

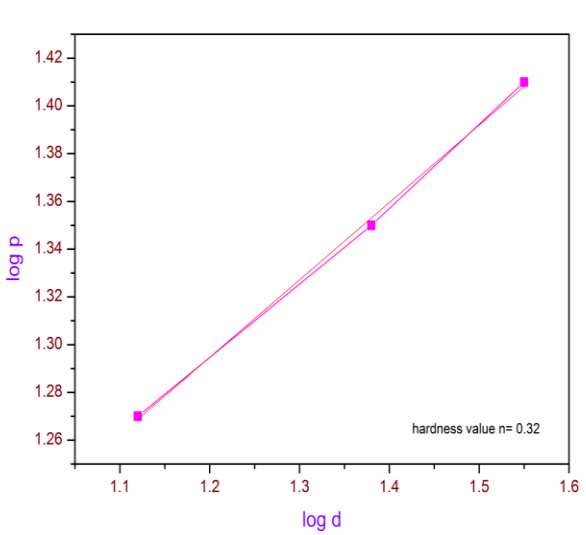

Figure 10. Plot of log d versus log p of 2APKDP crystal

I. Dielectric studies

Dielectric study was most important to know the electro-optic coefficient of the crystals and hence the dielectric properties for technical applications [30]. Optically good quality 2APKDP crystal was selected for dielectric measurements using HIOKI 3532-50 LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil. Silver paint was applied on the both faces to make a capacitor with the crystal as dielectric material. Both dielectric constant and dielectric loss were measured for 2APKDP crystal. Crystals were carefully selected with high transparency and defect-free surface (without any pit or crack or scratch on the surface). As the frequency increased, both the dielectric constant and the dielectric loss values were found to be decreased exponentially which is shown in Figure 11. . The dielectric constant (ε_r) at low frequencies depends on the excitation of bound electrons, lattice vibrations, dipole orientation and space-charge polarization (atomic or electronic). At very low frequencies all four contributions may be active, so it has a high value. The lower value of the dielectric constant at higher frequencies explains the higher SHG conversion efficiency of the as-grown crystal and this is in agreement with the Miller rule [31].

The variation of dielectric loss vs. log frequency is shown in Figure 12. From the graph, it is found that the dielectric loss decreases with increase in frequencies. The value of dielectric loss is high at lower frequencies and it is low at higher frequency region. The low values of dielectric loss imply that the sample possesses enhanced, optical quality with lesser defects and this parameter indicates that the material can be useful for NLO applications [32].

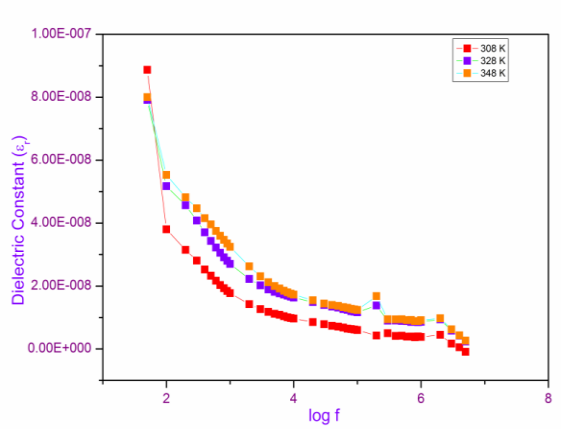

Figure 11. Variation of log f versus Dielectric constant (ε_r)

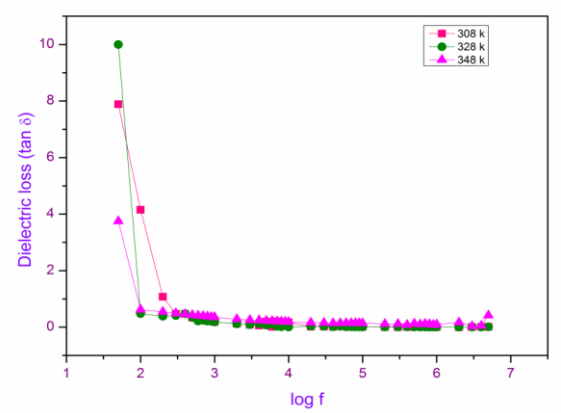

Figure 12. Variation of log f versus Dielectric loss (tan δ)

J. Laser damage threshold study

The laser damage threshold of an optical crystal is an important factor affecting its applications. If the material has a low laser damage threshold it severely limits its applications, even though it has many excellent properties like high optical transmittance and high SHG efficiency [33-35]. The present study is of great interest to find out the influence of combining an organic 2-aminopyridine with potassium di-hydrogen orthophosphate and find out the modification in the laser induced damage and thereby to prescribe the maximum permissible laser power for the newly formed semiorganic crystals. A Q-switched high energy Nd:YAG was used to generate pulses at 1064 nm fundamental radiation at a frequency of 10 Hz and pulse duration of 6 ns. The laser beam of diameter 1 mm was focused on the 2mm of 2APKDP crystal. The sample was placed at the focus of a Bi-convex lens of focal length 20 cm. The pulse energy of each shot was measured using the combination of phototube and oscilloscope.

The measured multiple shot laser damage threshold value is 74 mJ for 1064 nm wavelength of Quantum Nd:YAG laser radiation.

IV CONCLUSION

A new NLO material 2APKDP has been synthesized and crystal was grown by slow evaporation method at room temperature. The presences of functional groups have been identified from FT-IR analysis. The crystalline nature of the grown 2APKDP crystal was confirmed by well defined sharp peaks from powder X-ray diffraction analysis. The lattice parameter values have been evaluated by single crystal XRD analysis. From the XRD analysis, we confirm that the crystal 2APKDP belongs to tetragonal crystal system with non-centrosymmetric space group I4. UV-visible-NIR analysis was carried out to determine the lower cut off wavelength at 290 nm and optical band gap Eg=4.64 eV was determined from UV-vis-NIR spectrum data. The SHG behavior was confirmed from the emission of bright green radiation (532nm) and the SHG efficiency was found to be 1.2 times greater than that of KDP, so it is a good NLO material for several NLO applications. A Vickers hardness test was carried out and the hardness number was found to be 0.32 confirm that the 2APKDP crystal belongs to hard category. The dielectric studies of 2APKDP crystal establish as the frequency increased, both the dielectric constant and dielectric loss values were found to be decreased exponentially. Laser damage threshold value was found to be 74 mJ, which evident that the 2APKDP material has more optical applications.

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