

## Growth and Characterization of Lithium Potassium Phthalate (LiKP) Single Crystals for Third Order Nonlinear Optical Applications

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Single crystals of lithium potassium phthalate (LiKP) were successfully grown from aqueous solution by solvent evaporation technique. The grown crystals were characterized by single crystal X-ray diffraction. The lithium potassium phthalate  $C_{16}H_{12}KLi_3O_{11}$  belongs to triclinic system with the following unit-cell dimensions at 298(2) K;  $a = 7.405(5) \text{ \AA}$ ;  $b = 9.878(5) \text{ \AA}$ ;  $c = 13.396(5) \text{ \AA}$ ;  $\alpha = 71.778(5)^\circ$ ;  $\beta = 87.300(5)^\circ$ ;  $\gamma = 85.405(5)^\circ$ ; having a space group  $P\bar{1}$ . Mass spectrometric analysis provides the molecular weight of the compound and possible ways of fragmentations occurs in the compound. Thermal stability of the crystal was also studied by both simultaneous TGA/DTA analyses. The UV-Vis-NIR spectrum shows a good transparency in the whole of Visible and as well as in the near IR range. Third order nonlinear optical studies have also been studied by Z-scan technique. Nonlinear absorption and nonlinear refractive index were found out and the third order bulk susceptibility of compound was also estimated. The results have been discussed in detail.

**Key Words :** Single crystal X-ray diffraction, FTIR, UV-Vis-NIR, Nonlinear optical material, Z-scan method

### Introduction

Search for new materials with high optical nonlinearities has been the important task, because of their practical applications in harmonic generation, amplitude and phase modulation, switching and other signal processing devices.<sup>1-3</sup> An ultimate goal for designing the molecules with large third order nonlinearities is to incorporate them into devices for optical signal processing.<sup>4,5</sup> Non-linear optical absorption (NOA) has shown its potential application in optical information storage, optical logic gates, laser radiation protection and for mode locked lasers. In the recent past, the interest in searching for NOA materials has been gradually increased.<sup>6</sup> Especially; organic molecules have been the subjects of great attention due to their chemical configuration which is more favorable for all further applications. Indeed, the potential use of organic device materials in optoelectronics is now a very serious matter.<sup>7</sup>

We have been pursuing a programme of X-ray studies on crystalline complexes involving phthalic acids and alkali metals at the atomic resolution. Lasers are increasingly used for high-speed recording/storage and for the information transmission & processing. Many electro-optical devices rely on the use of nonlinear materials in particular those with the capability of frequency conversion second harmonic and third order harmonic generations. Organic materials provide good electro-optic figure of merit as they are made up of higher polarisable molecules and possess higher refractive index. There are situations, where the electro-optic devices are expected to match refractive index of air, glass or optical fibers. Hence, it is necessary to investigate the electro-optic

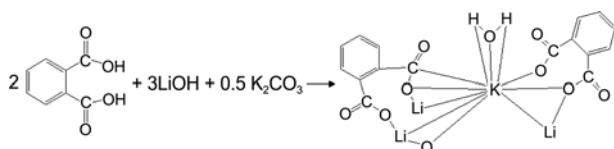
material with lower refractive index that can match specific range of refractive index. Potassium acid phthalate popular known as KAP is a relatively old and efficient nonlinear optical material used principally in SHG applications at the UV region. It has a large nonlinear optical coefficient, wide transparency range and high chemical inertness.<sup>8-10</sup> It is a biaxial crystal that can meet the requirements of a good electro-optic modulator. It is widely used as an X-ray monochromator and as well as X-ray analyzer. KAP is extensively studied for its crystal morphology.<sup>11-14</sup> Belyaev and his co-workers<sup>11,15</sup> conducted studies on its growth, dielectric behaviour, piezoelectric and non-linear optical properties. The electro-optic co-efficient of KAP is comparable to the urea crystal.<sup>16,17</sup> Its electro-optical dispersion properties were also studied by Kejalakshmy and Srinivasan.<sup>17</sup> Its higher chemical stability and economical viability with good kinetic growth properties have made to pay attention on them in past decades.

In pursuance of the fascinating properties of the above alkali types of crystals, we describe the synthesis, characterization, spectroscopic and thermal analyses of a new alkali phthalate complex of lithium hydroxide mixed potassium carbonate and phthalic acid. The grown crystals were subjected to single-crystal X-ray diffraction, fourier transform infrared (FTIR) spectroscopy, mass spectrometry, thermal studies and third order nonlinear optical Z-scan measurements.

### Experimental Section

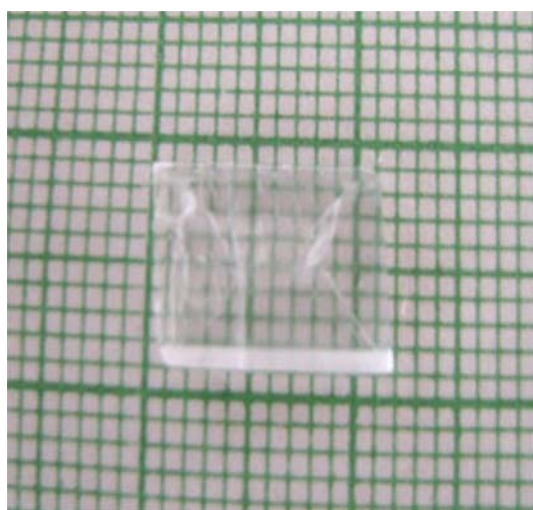
Lithium potassium phthalate (LiKP) single crystals were synthesized by the reaction between phthalic acid (Merck

99%), lithium hydroxide (Merck 99%) and potassium carbonate (Merck 99%) taken in molar ratio 2:3:0.5 respectively. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer for a homogeneous mixing of solution. Then, the solution was allowed to evaporate at room temperature which yielded transparent crystalline salt of LiKP. The process of re-crystallization was carried out to purify the synthesized salt. The reaction mechanism of LiKP is given in Scheme shown below 1.



Saturated solution of 100 mL prepared at 35 °C using recrystallized LiKP salt was filtered with microfilters and taken in a glass beaker of 250 mL capacity. Then, the beaker was hermetically sealed and placed in a constant temperature bath having an accuracy of  $\pm 01$  °C. The growth process was initiated with the saturated temperature and the temperature of the solution was periodically reduced @ 0.1 °C/day. After a typical growth period of 15-20 days, well-developed optically transparent LiKP crystal has been grown and it is shown in Figure 1.

The unit cell dimension and X-ray intensity data of LiKP was obtained on a Enraf Nonius CAD 4 Bruker Kappa APEX II single crystal X-ray diffractometer equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). The FTIR spectrum of the title crystal was recorded in the frequency range 400-4000  $\text{cm}^{-1}$  using a Perkin Elmer Spectrum One FTIR spectrometer by KBr pellet method to identify the various functional groups present in the title crystal. Optical absorptions properties of the crystals were studied using a Varian Cary 5E UV-Vis-NIR spectrophotometer. The emission spectrum of the crystal was recorded using JPBIN YVON Spectrofluorometer. Mass spectral analysis was also carried out for LiKP



**Figure 1.** LiKP single crystals grown from slow evaporation technique.

using a JEOL GC mate mass spectrometer for the confirmation of the formation and successive fragmentations of the crystallized compound. Simultaneous thermo gravimetric (TGA) and differential thermal analyses (DTA) were carried out using TGA Q500 V20.10 Build 36 Thermal Analyzer. Third order nonlinear optical measurement of the LiKP crystal has been studied using versatile Z-scan technique.

## Results and Discussion

The unit cell dimension and X-ray intensity data of lithium potassium phthalate (LiKP) was obtained on a Bruker apex 2 single crystal X-ray diffractometer equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å)<sup>18</sup> and  $\omega/2\theta$  scan mode was employed for data collection. The dimension of the crystal used for the measurements was  $0.30 \times 0.20 \times 0.20$  mm<sup>3</sup>. A total of 15388 reflections were measured out of which 2999 were found unique and its limiting indices were  $-8 \leq h \leq 8$ ,  $-11 \leq k \leq 11$ , and  $-15 \leq l \leq 15$ . For the structure solution and refinement, the lattice parameters were refined then for all collected reflections. Integrated intensities were reduced for Lorenz, polarization and decay corrections. Absorption correction was employed based on psi-scan mode.<sup>19</sup> The maximum and minimum transmission factors were 0.93 and 0.86 respectively. The crystal structure was solved by direct method using SIR92 (WINGX) and refinement was done by use SHELXL97.<sup>20</sup> The hydrogen atoms of phthalic ring are located by difference Fourier map and are refined with isotropic thermal parameters. Non-hydrogen atoms were refined with anisotropic displacement parameters. Other hydrogen atoms were fixed at meaningful positions and were given riding model refinement. The refinement was continued until maximum shift/esd was zero. The final R factor was 0.0610.

Single crystal data and details of the data collection for the crystal structure determination are listed in supplementary Table 1. Atomic coordinates and equivalent isotropic displacement parameters are given in supplementary Table 2. The bond lengths and bond angles are given in supplementary Table 3. Anisotropic displacement parameters are listed in Supplementary Table 4. Hydrogen coordinates and isotropic displacement parameters are listed in supplementary Table 5. Torsion angles are listed in supplementary Table 6.

Lithium potassium phthalate crystallizes with four carboxylate anions, three lithium and one potassium cations in the symmetric unit with space group of P-1 of the triclinic crystal system. The protonated cations and deprotonated anions are linked by number of intermolecular O-H $\cdots$ O hydrogen bonds to form a three dimensional network stabilizing the crystal package. An ORTEP (50% probability) diagram of LiKP molecule is shown in Figure 2. The unit cell packing of the crystal is shown in Figure 3.

The potassium ion is surrounded by four 'O' atoms of the phthalate ions. The coordination of both Li and O ions around this K<sup>+</sup> ion is clearly shown in the ORTEP representation. The O atoms present in both water molecules act as the acceptors of hydrogen through O(11)-H(11A) $\cdots$ O(9).

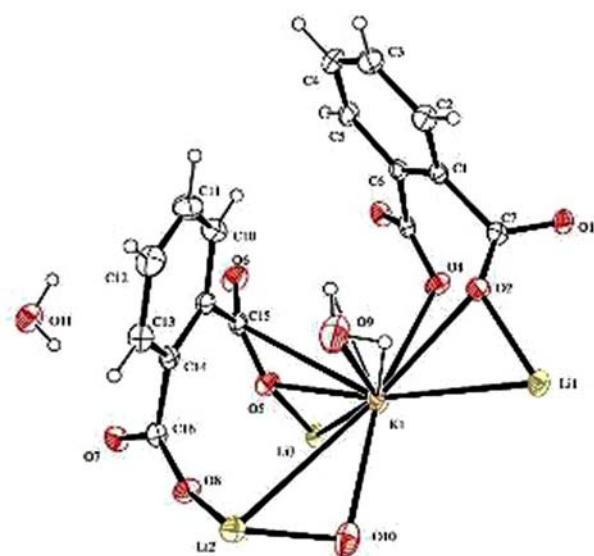


Figure 2. A view of the LiKP molecular complex.

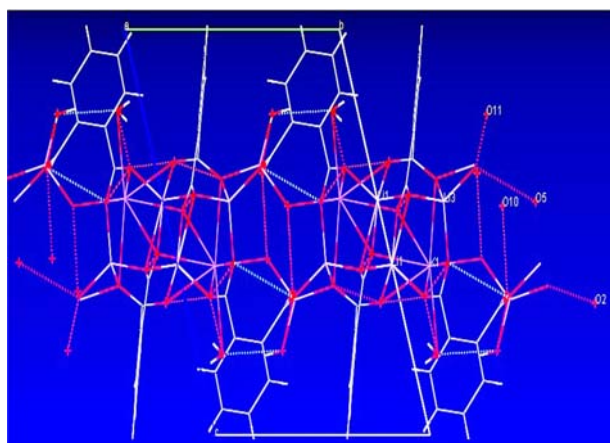


Figure 3. A view of the crystal packing of LiKP.

Data pertaining to the geometry of the water molecules and the hydrogen bonds are given in the supplementary Table 7.

The first water molecule [O(9), H(9A) and H(9B)] is hydrogen bonded to O(6) and O(11) and the other [O(11), H(11A) and H(11B)] bonded to O(7). The oxygens of carboxylate group present with phthalate ions namely O(5) and O(8) & O(4) and O(2) are co-ordinated with centred  $K^+$  ion while the lithium ions are connected with central metal ion via the oxygen's of above carboxylate group. The cations of both phthalates show normal aromatic C-C bond length values except for the [C(1)-C(6)=1.400 Å] which are slightly greater than the other C-C bond length. This lengthening is due to the stretched OH group attached with the  $K^+$  ion, which in turn gives strong intermolecular interaction with the nearby cations and anions. The bond lengths of O(4)-K(1), O(2)-K(1), O(5)-K(1), and C(15)-K(1) are 2.726(2) Å, 2.7491(2) Å, 2.708(3) Å and 3.327(3) Å respectively.

The hydrogen bonded networks of LiKP are determined by a network of three bonded O-H...O hydrogen bonds. In LiKP, the hydrogen phthalate anions form along b-axis

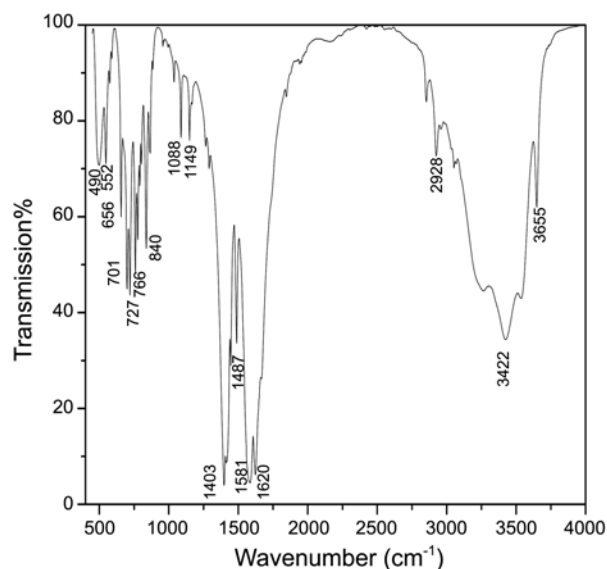


Figure 4. FTIR spectra of LiKP single crystal.

through O(11)-H(11A)...O(9) and the hydrogen bonds running parallel to the (0 1 1) direction. The second hydrogen bonds viz O(9)-H(9B)...O(6) links the same chains in the opposite direction. Molecules are highly stabilized three-dimensional network of O-H-O hydrogen bonds.

The morphology of the lithium potassium acid phthalate single crystal is made up of various planes viz., (0 0 1) (0 1 1) (0 1 0) (-1 0 1) and (1 0 1) of which (0 0 1) is a prominent and wider one. The crystal possess a platelet morphology and (0 0 1) was found to be larger and optically transparent to other faces with a length to thickness ratio of 3:2 with reference to the bc-plane. The other planes designated in the diagram are Friedel pairs. Further, it also shows that the (0 0 1) is quite suitable for optical device applications. Since, molecule crystallizes in centrosymmetric space group; it may be much useful for the third order non-linear optical applications in the UV-Visible regime.

FTIR analysis has been carried out for the LiKP polycrystalline sample in the frequency region 400-4000  $cm^{-1}$ . The sample has been prepared by using KBr pellet technique and the FTIR spectrum obtained is shown in Figure 4. The O-H stretch of hydrated molecules produces a broad shoulder between 3200-3500  $cm^{-1}$  and it is assigned to the intermolecular O-H...O hydrogen bonding.

Ring structure stretching vibration of molecules gives IR absorption at 1581  $cm^{-1}$  and the C=C ring structure modes appear at 1487  $cm^{-1}$ . The ketonic C=O stretch due to carboxyl group appears at 1620  $cm^{-1}$  and the absorption at 656  $cm^{-1}$  may be due to the wagging C=O. The C-H out of plane bending mode is observed at 840  $cm^{-1}$ . Also, the Para disubstitute in the benzene ring mode could be evidenced from the peak observed at 766  $cm^{-1}$ . The other vibrations of the title compound are listed in the supplementary Table 8.

Mass spectrometry was carried out for LiKP in the  $m/z$  range 50-450 amu is shown in Figure 5. Since, the phthalic acid molecule contains aromatic rings, a molecular ion peak could be observed at  $m/z$  77.06. The base peak at  $m/z$  58.80

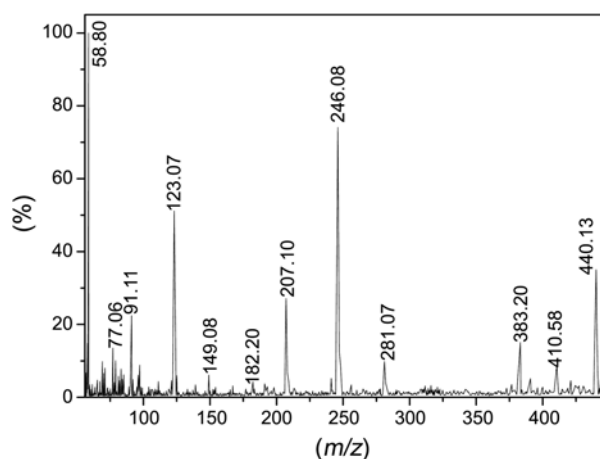


Figure 5. Mass spectra of LiKP single crystal.

corresponds to the  $C_3H_6O^+$  ion and it clearly shows that the preferential point of ionization occurs between fragmented bonds. It occurs exactly between the carbon atom of the phthalate ring with the caboxylate ion group and it is also found to be most abundance one. The peak associated with  $m/z$  123.07 is due to the fragmentation of  $C_6H_5COOH^+$  ion. The fragmentation observed at  $m/z$  207.10 is due to the removal of potassium acid phthalate group from the molecule ion  $C_6H_5COOH COOK^+$ . The deviation from the proposed molecular weight of the crystalline compound  $m/z$  at 440.13 may be attributed to the presence of fractional impurities in the crystal. The possible successive fragmentations of the molecular ion are clearly shown in the supplementary Table 9.

The thermal properties of the title LiKP crystal were studied by simultaneous TGA/DTA. The corresponding curves are presented in Figure 6 weight loss around 80 °C in TGA curve and small hump appear in the DTA trace reveal the hydrated nature of the compound. From the TGA curve, it can also be recognized that the crystal does not decompose before 200 °C. The DTA curve reaches the maximum around 357 °C and decreases sharply. Both the traces indicate that the sample starts decomposing around 300-360 °C with an appreciable weight loss of 78% as shown by TGA. Further

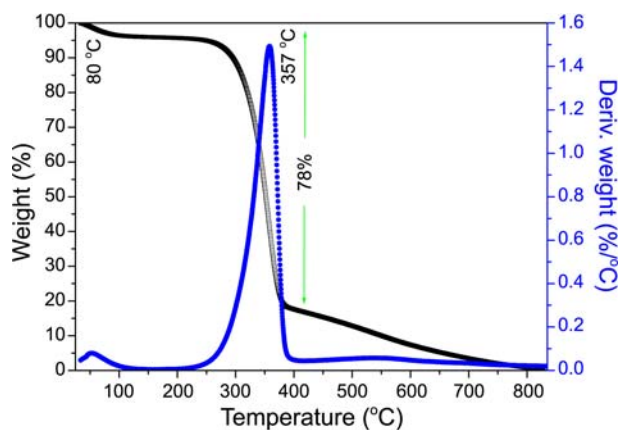


Figure 6. TG and DTA curve of LiKP single crystal.

heating induces decomposition of the residue and results in the release of volatizable compounds of  $CO_2$  and  $CO$ .

The transmission spectrum was recorded for LiKP crystals shown supplementary Figure 1. From the measurements, it has been found that the crystal shows a good transparency in the wave length region 220-1500 nm with a  $\lambda$  cutoff of 203 nm. After the  $\lambda_{max}$  region of the spectrum, the absorption decreases rapidly around 220 nm and leads to the efficient transmission. Since, there is little optical absorption in the visible region and in the near IR region; the crystals of LiKP may be useful for both high frequency and as well as lower frequency third order nonlinear optical device applications.

Fluorescence may be expected generally in the molecules that are aromatic or molecular that contains multiple conjugated bonds with a high degree of resonance stability.<sup>21</sup> The sample was excited at 200 nm and the emission spectrum as shown in supplementary Figure 2 was measured in the range 200-400 nm. A peak at 397 nm was observed in the emission spectrum. The results indicate that LiKP crystal shows UV fluorescence emission at  $\lambda = 397$ nm.

The third-order nonlinearity of LiKP single crystals samples were investigated from the Z-scan technique, a simple and accurate method to determine both the nonlinear index or refraction,  $n_2$ , and the nonlinear absorption coefficient,  $\alpha_2$ .<sup>26,27</sup> The Z-scan experimental setup details have been reported elsewhere<sup>24,25</sup> and therefore, only a brief description is presented here. The Z-scan experiments were performed using a 632.8 nm He-Ne laser beam, which was focused by 20 cm focal length lens. The schematic diagram of the experimental set-up is shown in Figure 7. The typical laser source and sample parameters used for the experiment are tabulated in supplementary Table 10. Basically, the method consists in translating the nonlinear sample through the focal plane of a tightly focused Gaussian beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and as a consequence of the transverse Gaussian intensity profile, the sample presents lens-like behaviour. The induced self-phase modulation has the tendency of defocusing or recollimating the incident beam, depending on its z position with respect to the focal plane. By monitoring the transmittance change through a small circular aperture placed at the far-field position, one is able to determine the nonlinear refractive index. Any nonlinear absorption present at the sample can be found from this measurement by removing the aperture (open aperture Z scan).<sup>10</sup> In this case, once the sample is scanned through the laser beam focal plane the sample transmittance is measured as function of the intensity. With this procedure we generate z scan signatures and the transmittance change between the peak and the valley  $\Delta T_{p-v}$  can be extracted from them.<sup>11</sup> Using the relation;

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25}/\Delta\Phi_0$$

Where  $S = 1 - \exp(-I_a^2/\omega_a^2)$  is the aperture linear transmittance (0.01),  $\Delta\Phi_0$  is the on-axis phase shift. The on-axis phase shift is related to the third-order nonlinear refractive

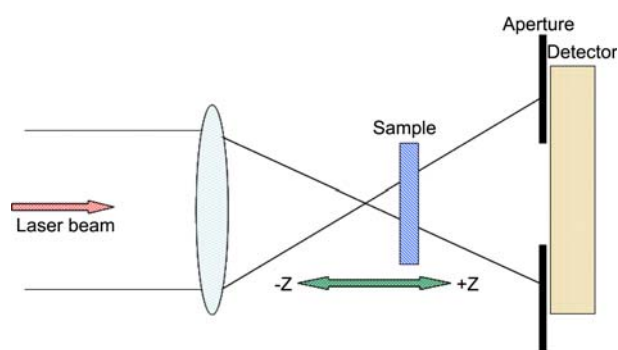


Figure 7. Schematic diagram of the Z-scan technique.

index by

$$|\Delta \Phi_0| = k n_2 L_{\text{eff}} I_0$$

Where  $k = 2\pi/\lambda$ ,  $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$  is the effective thickness of the sample,  $\alpha$  is the linear absorption coefficient,  $L$  the thickness of the sample,  $I_0$  is the on-axis irradiance at focus and  $n_2$  is the third-order nonlinear refractive index.

The nonlinear absorption and refractive index of LiKP crystals (thickness  $\approx 2.7$  mm) were estimated using the above formalism for the laser beam of intensity 60 mW and of wavelength of 632.8 nm. Depending on whether nonlinear refraction is positive or negative the sample causes an additional focusing or defocusing. In the most reported experiments,  $0.1 < S$  (transmittance)  $< 0.5$  has been used for determining nonlinear refraction. Obviously, the  $S = 1$  corresponds to the collection of all transmitted light and therefore is insensitive to any nonlinear beam distortion due to nonlinear refraction.<sup>22-24</sup> Since the source used to probe the nonlinear material is a low power continuous wave laser, the origin of optical nonlinearity of LiKP is attributed to the thermal variation of local refractive index in the medium. The response time of the material as recorded by an oscilloscope is found to be millisecond regime, which is to be expected in the case of such thermal nonlinearity. Nonlinear absorption property of the  $D - \pi - A$  type  $\pi$ -electron system can be related closely to the  $\pi$ -electron conjugate degree and delocalization capacity of the molecule. The three dimensional X-ray crystal structure solution of LiKP crystal showed that the torsional angles  $C(15)-O(5)-K(1)-O(9) = 41.94(2)$ ,  $O(8)-Li(2)-O(10)-K(1) = 43.12(3)$ ,  $K(1)-C(9)-C(15)-O(5) = 40.1(1)$ ,  $K(1)-C(7)-O(2)-Li(1) = 44.1(3)$ ,  $O(3)-Li(1)-O(2)-K(1) = 43.1(5)$  and  $K(1)-C(7)-O(2)-Li(1) = 44.1(3)$  seem to have conjugated chains with coplanar planes. These may be some of the features that are favorable to nonlinear optical absorption, particularly to saturated absorption. Nonlinear refractive index ( $n_2$ ) of LiKP was calculated as  $15.8770 \times 10^7$  cm<sup>2</sup>/W and the value of nonlinear absorption coefficient has been measured from the open Z-scan as  $\beta \sim 4.0128 \times 10^{-3}$  cm/W. The results have been compared with other known compounds and presented in the supplementary table 11.

## Conclusions

Single crystals of lithium potassium phthalate single crystals

have been synthesized by the slow evaporation technique and bulk crystals were grown from slow cooling technique. Single crystal XRD measurement reveals that the grown crystal belongs to the Triclinic system with a space group of  $P\bar{1}$ . FT-IR spectrum was carried out to investigate the functional groups of the grown crystal. Optical studies confirmed that LiKP crystal is transparent in the wavelength region 210-1200 nm, with the UV transparency cutoff at 200 nm. Fluorescent property of the title compound has been confirmed through emission spectrum. Thermal stability of the grown sample was also studied by TGA and DTA analyses and it was found that the crystal is thermally stable upto 150 °C. The successive fragmentations of the crystal were studied through mass spectrum. The third order nonlinear measurement using Z-scan techniques reveals the negative nonlinear property (self defocusing) of the samples is due to the localized variation of refractive index occurs from laser assisted thermal heating. The nonlinear refractive index ( $n_2$ ) and nonlinear absorption coefficient ( $\beta$ ) of the crystal at 632.8 nm has been found to be  $n_2 = 15.8770 \times 10^7$  cm<sup>2</sup>/W and be  $\beta \sim 4.0128 \times 10^{-3}$  cm/W respectively.

**Crystal Structure Deposition.** Full crystallographic data (cif file) relating to the crystal structure of LiKP have been deposited with the Cambridge Crystallographic Data Centre in CCDC 843912. Copies of this information can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; <http://www.ccdc.cam.ac.uk>). [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)

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