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FTIR studies of L-arginine doped with ADP and KDP: A Hybrid NLO crystal

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Abstract
The present research paper oversees the FTIR analysis of the crystals of Potassium dihydrogen phosphate (KDP) and Ammonium dihydrogen phosphate (ADP) doped with L-arginine (amino acid). The AR grade samples of Potassium dihydrogen phosphate (KDP) and Ammonium dihydrogen phosphate (ADP) doped with L-arginine in two different stoichiometric ratios of 2:1:1 and 3:1:1 has been grown. The aqueous solutions of these ratios of the sample are kept for slow evaporation at room temperature. The FTIR analysis confirms the presence of functional groups and modes of vibration of the grown crystals.
Keywords: crystal growth, non-linear optic materials, bond-length, FTIR analysis

Introduction

Academically as well as Industrially, potassium dihydrogen orthophosphate (KDP), KH2PO4, and ammonium dihydrogen orthophosphate (ADP), NH4H2PO4, are known to be interesting materials. KDP and ADP are examples of hydrogen bound crystals with excellent electro-optic and nonlinear optical properties, as well as intriguing electrical features [1-3]. Because of the difference in the amount of hydrogen bonds, KDP is ferroelectric and ADP is antiferroelectric. For almost 50 years, they have been the topic of a wide range of investigations due to their intriguing electrical and optical properties, structural phase changes, and ease of crystallisation. The use of huge KDP and ADP single crystals as frequency converter crystals in inertial confinement fusion is increasing demand for high quality large KDP and ADP single crystals [2,3]. Both KDP and ADP are isomorphous to each other and belong to scalenohedral (twelve faced) class of tetragonal crystal system [4]. Hybrid crystals are a new class of materials recently investigated for their interesting properties and stable physiochemical properties, which are important for device fabrication and applied research [5,6]. The main advantage of increasingly demanding new types of crystals in technological applications is that bulk growth of hybrid crystals in all three dimensions makes the growth process easy, which in turn makes it easy to cut and polish the samples for device fabrication [7]. The high nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness of hybrid crystal combines in the strong NLO properties and chemical flexibility of organic materials with the physical sturdiness and excellent transmittance of inorganic materials [8-11]. Hence, the ability to enhance NLO properties of hybrid crystals is presently under thorough investigation due to the incorporated advantages of both organic and inorganic crystals. To increase the quality and properties of semi-organic crystals, several researchers focus on developing families of semi-organic crystals that combine amino acids with inorganic or metal complexes [12]. Amino acid-based complexes have piqued the interest of crystal researchers due to their ability to combine with diverse inorganics and their proclivity to form in crystal systems that are suitable for nonlinear optical applications. In addition, in the last two decades, combining high NLO efficiency organic molecules with favourable physical features of inorganic materials has been a hot topic of research.

Amino acids based on several hybrid crystals have recently been crystallized, and their various properties have been analysed [13-16]. Organic material with high nonlinear optical coefficients combines with inorganic material exhibiting excellent physical properties, giving hybrid material. Hydrogen bonding of acid-based interaction between organic cation and inorganic anion of hybrid material give mechanical strong and thermally stable NLO crystals [17]. According to Srineevasan et al. (2013) [18] and Rajasekaran et al. (2000) [19], NLO features are caused by highly polarizable acid-base interactions of organic and inorganic molecules, as joining through a hydrogen bond network creates non-centrosymmetric structural systems. Rich demand for hybrid complexes in optical storage devices, colour displays and optical communication systems is observable in literature [20]. In semi-organic complexes, movement of π electrons between donor and acceptor groups has also been reported [21]. The amino acid family of crystals has been the topic of intense research by numerous research scientists due to its excellent physiochemical characteristics. Organic amino acid crystals are interesting in terms of NLO applications because they contain a zwitterion, which is a paired donor carboxylic (COOH) and proton acceptor (NH2) group that forms hydrogen bonds. Amino acids with this kind of dipolar character provide excellent candidates for NLO applications. Amino acid-inorganic (metal) salt complexes are potential NLO materials for optical applications such as optical communication, optical computing, optical information processing, optical disc data storage, laser fusion processes, and laser remote sensing, according to the literature [22-24]. Additionally, considerable effort is being made to find new materials that have the optimal characteristics needed for use as nonlinear optical elements [25-29]. Numerous studies have been conducted in recent years to improve molecular engineering, chemical stability, laser damage thresholds, and optical properties of amino acid crystals combined with inorganic complexes (linear and nonlinear). Several hybrid non-linear optical materials incorporating L-Arginine have recently been crystallized, and their structural, optical, thermal and electrical properties have been investigated [30-35]. The present investigation deals with the growth and FTIR characterization of an L-Arginine doped with KDP and ADP.

Experimental Procedure

The AR grade of L-arginine, KDP, and ADP were selected for the present paper. The pure materials KDP, ADP, and L-Arginine were taken in two different ratios which are 2:1:1 and 3:1:1.

For 3:1:1 - KDP:ADP: L-Arginine and for 2:1:1 - KDP:ADP: L-Arginine. All the materials were dissolved in double-distilled water in a glass beaker and were mixed homogeneously using a magnetic stirrer for 3 hrs. pH measurements of both the ratios were calculated using pH meter, pH for the 3:1:1 sample is 5.93 and that for the 2:1:1 sample is 6.09. The homogeneously mixed solutions were poured in a clean glass beaker for 2 weeks. The grown crystals of 2:1:1 and 3:1:1 ratio are shown in fig (1, a & b) respectively.

Figure 1 (a) Grown crystal of stoichiometric ratio 2:1:1 – KDP:ADP:L-Arginine

Figure 1(b) Grown crystal of stoichiometric ratio 2:1:1 – KDP:ADP:L-Arginine

Results and Discussions

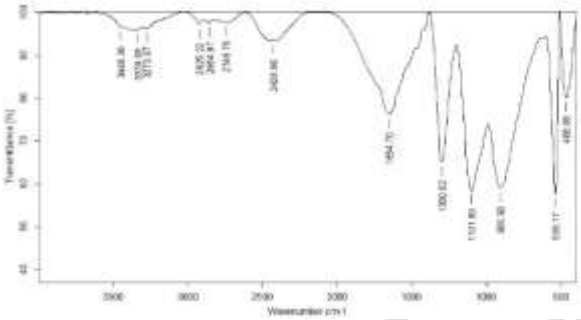

Figure 2 FTIR Spectrum of 3:1:1 crystal

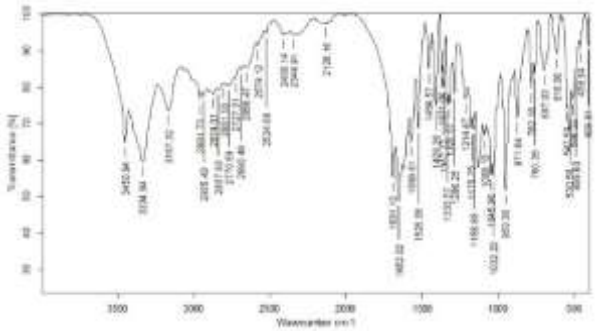

Figure 3 FTIR Spectrum of 2:1:1 crystal

The FT–IR spectrum of L-arginine doped ADP and KDP crystals in the stoichiometric ratio of 3:1:1 and 2:1:1 is shown in figure 2 &3 respectively. The broad envelopes observed between 2428.86 and 3448.36 in the case of 3:1:1 while for 2:1:1 2344.91 and 3450.94 cm–1 are mainly due to P–OH stretching of H2PO4, O–H stretching of COOH and water of crystallization, N–H stretching of NH+ 3, C–H stretching of CH2 and CH. The broadness is generally considered to be due to hydrogen bonding interaction of H2PO– 4, COOH– and NH+ 3 with adjacent molecules. The C=O stretching and –C=NH4 stretching are revealed by minor absorption peak within 1654.70 in case of 3:1:1 and 1652.02 cm–1 in 2:1:1 crystal. The CH2 bending attributes the absorption at 1300.82 in 3:1;1 and 1320.57cm–1in case of 2:1:1. The absorption occurring at 1101.89 and 906.90 cm–1 in 3:1:1 and 1088.10 and 950.36 in case of 2:1:1 crystal are due to P–OH stretching. Intense absorption observed at 538.17 and 468.88 cm–1 in 3:1:1 and in case of 2:1:1 absorption observed at 530.58 and 459.54 are due to P–OH deformation. By comparing the spectra of doped and undoped crystals, one can easily find missing absorptions for N–H stretching of NH+ 3, C–H stretching of CH2 and CH and conclude that L-arginine doping was successfully achieved.

Bands in the region from 3700 to 3100 cm−1 are usually due to various O-H and N-H stretching vibration. The bound O-H groups produce a wider band than the N-H groups. When the hydrogen bond is broken, all of these bands shift to higher wave numbers and become much narrower and weaker in strength. So, in the pure ADP and KDP a broad band is observed in the range 3800-3200 cm−1 which is assigned to O-H stretching. The same band in doped KDP and ADP, has narrowed down which is probably due to the addition of L-arginine and the elimination of water molecule in the crystal. So, in the higher wave number region the pure N-H stretch of arginine appears as a sharp peak at 3334.94 cm^-1 2:1:1 and 3448.36 in 3:1:1 crystal. The band observed around 2422.86 in 3:1:1 and 2349.91 in 2:1:1 cm−1 is due to the overtones of lower bands occurring around 1300. The band appearing around 1650 cm−1 for pure ADP and KDP is due to O-H bending vibrations and this peak has shifted around 1654.17 in 3:1:1 and 1652.02 cm−1 for 2:1:1 crystal of the L-arginine doped ADP and KDP. The P-O-H vibrations give rise to peaks around 1000 to 900 cm^-1. The PO4 vibrations occurs around 550 to 450 cm−1 in pure ADP and KDP these peaks in the case of doped ADP and KDP seem to have suffered an intensity diminution suggesting that the dominant COO−vibrations of L-arginine must have caused this change. Hence, the doped ADP and KDP it is seen that there are no additional peaks but almost all the major peaks have shifted towards the higher wave number region, implying that the presence of the dopant L-arginine has brought about this shift.

Bond-Length calculation:

The vibrational frequency of different bond can be determined by the equation:

$$\upsilon = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \text{.....(1)}$$

where ν is wave number, c is the velocity of light, k is average force constant of the bond and μ is the effective mass of the bond (for example O-H) given by the relation:

$$\mu = \frac{M_O * M_H}{M_O + M_H} \text{.....(2)}$$

The force constant can be correlated with the average bond length (r) by the relation,

$$k = \frac{17}{r^3} \text{.....(3)}$$

with the use of Eqs. (1)–(3), the values of effective mass, force constant and the bond lengths were calculated from the FTIR spectra data and the calculated values are shown in table below,

TABLE 1

BOND	WAVE-NUMBER 3:1:1 cm^-1	WAVE-NUMBER 2:1:1 cm^-1	BOND-LENGTH 3:1:1Å	BOND-LENGTH 2:1:1Å
O-H	1654.17	1652.02	1.226	1.227
P-OH	538.17 468.86	530.58 459.54	1.692 1.864	1.701 1.889
N-H	2422.86	2349.91	1.396	0.451

Conclusion

Crystals of L-arginine doped with KDP and ADP in two different ratios were grown using slow evaporation technique and comparative analysis of FTIR spectrum has been done. The broadband observed between 2428.86 and 3448.36 in the case of 3:1:1 while for, 2:1:1 2344.91 and 3450.94 cm–1 are mainly due to P–OH stretching of H2PO4, O–H stretching of COOH and water of crystallization, N–H stretching of NH+ 3, C–H stretching of CH2 and CH. In the both 2:1:1 as well as 3:1:1 there are no additional peaks but almost all the major peaks have shifted towards the higher wave number region, confirming the presence of the dopant L-arginine. Hence, FTIR analysis confirms the presence of all functional groups as well as the dopant.

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