Characterization of Organic Compound Doped Inorganic Ammonium Phosphate: Crystal Formation and Opto-Electrical Properties

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Abstract. The opto-electrical properties of mixing organic compound with inorganic material is the subject matter of electronic industry. Nonlinear active single crystals of amino acid doped ammonium phosphate was characterised using various experimental techniques. Specifically alanine was doped with inorganic material and characterised in terms of carbon role in structure formation and related properties. The structural and electrical properties are studied by analysing absorption, transmission, hardness and conductivity of the doped one. The structure and electrical framework are well suited with expected values of pure inorganic one. Otherwise the organic one mixed with inorganic one does changes these properties remarkably which are essential for application in modern livelihood of human nature. The single crystal obtained from doping of organic one with the properties of inorganic material proves to be suitable for robo one to walk away with newer developments. It promises a newer way of developing crystals with good mechanical strength, flexible and all kinds of opto-electrical properties. Interestingly the modern electronic appliances will greatly benefit from this development of organic one to the inorganic one.

Keywords: Ammonium phosphate; Alanine doped; Nonlinear optical; Doping; Piezo-electric;

1. Introduction

The ammonium orthophosphate (AP) and potassium orthophosphate (KP) are the crystals grown in bulky size for several applications three decades ago. The isomorphous ammonium phosphate crystal is an analogous inorganic material having nonlinear optical (NLO), dielectric, piezoelectric and anti-ferroelectric properties with a widespread possibility of distinct applications [1]. The researchers focusing their attentiveness more on AP NLO crystals because of their distinctive piezoelectric properties.

Over the past decades, there have been extensive research carried out to grow organic, inorganic, and semi organic NLO single crystals [2]. The crucial aspect for material selection provoke interest on not only on laser conditions but also on the physical and chemical nature of the crystal like transparency, damage threshold, phase matching, conversion efficiency and temperature solidity. The microelectronic industries are always in requirement of crystals having low dielectric constant at higher frequency. By keeping this in mind, strenuous efforts have been allotted to grow and analysis the optical, electrical and mechanical properties of NLO crystals. The room temperature solution growth method is a flexible procedure which can be used to grow new NLO materials and so it excites substantial interest amongst the crystallographers. Henceforth, it is useful to prepare semi...
organic crystals which combine the positive aspects of organic and inorganic materials for various optoelectronic applications [3].

The literature survey signifying that there is improved physicochemical properties of AP by doping amino acids or carboxylic acids on optical, electrical, structural, thermal, properties have been reported [4-7]. There is no systematic data on optical, optical band gap and dielectric studies of amino acid doped AP. In this scenario, we have found that carbon role in bio-molecular structure is crucial on function [8, 9]. Based on the principle evolved from there, the present investigation is of its kind to report the amino acid doped AP crystal characterized.

2. Experimental Analyses

A good quality single crystals of doped alanine ammonium phosphate (AAP) have been prepared from the mother solution. All the grown crystals were found to be very stable, colourless and transparent (shown in figure 1). This is further characterised by the following experiments.

![Figure 1. Single crystal of AAP](image)

X-ray Crystallography
The crystal structure of the sample compound was studied by powder XRD. The diffraction pattern of the crystals shown here in result section.

IR Spectroscopy
The IR spectrum over the regions 400 to 4000 cm\(^{-1}\) is recorded dividing into two groups such as frequency and fingerprint.

Transmission Spectroscopy
The transmission spectra were recorded for the grown crystals using UV-vis spectrophotometer. The recorded transmittance spectra are in the wavelength range 190-1100 nm as shown results section.

Absorption Spectroscopy
The absorption spectra were recorded at room temperature in the UV region 200-400nm and visible region 400-800nm. The plot between absorbance and wavelength is shown in the result section.

Hardness Analysis
Sample of pure AAP crystals indented using a micro hardness tester fitted with a pyramidal indenter having an optical angle of 136°.
Conductivity Analysis
The conductivity analysis of AAP crystal was studied in the frequency region 50Hz-200KHz at room temperature. The variation of conductivity frequencies of applied AC field is given in results section of this work.

Second Harmonic Generation Studies
The second harmonic generation (SHG) was measured by the powder technique using 1064nm with pulse width of 8ns and a repetition rate of 10Hz. The crystal was grounded to grain size 125-150nm.

3. Results and Discussion
3.1. X-Ray Diffraction
The preferential orientation observed from the X-ray diffraction data along [112], indicates maximum growth of the crystal along that direction. The crystal orientations along different h, k and l values are present. The main peaks appeared at various diffraction angles 2θ. The powder X-ray diffraction studies of grown crystals confirmed the tetragonal structure. The prominent peaks are at [101], [200], [112], [202], [301] and [312].

3.2. IR Spectrum
The IR spectrum of AAP crystals is given in figure 2. The spectrum identifies all functional groups. The spectrum shows the O-H bending observed at 3638 cm\(^{-1}\), N-H stretching at 3530 cm\(^{-1}\) and O-H stretching at 3423 and 3213 cm\(^{-1}\). The absorption band at 2903 cm\(^{-1}\) indicates the presence of NH\(_4^+\) ion. A peak at 2407 cm\(^{-1}\) is assigned to the O-H-O strong hydrogen bonded system. The infrared peak at 1406 cm\(^{-1}\) is due to the bending vibrations of ammonium. The peak at 1290 cm\(^{-1}\) is due to the combination of the asymmetric stretching vibration of PO\(_4\) with lattice. The band at 1099 cm\(^{-1}\) is due to the P-O-H vibrations and the band at 550 cm\(^{-1}\) is due to PO\(_4\) vibrations. The peaks observed around 911 and 473 cm\(^{-1}\) produces a shift in the peak positions of P-O-H and PO\(_4\) vibrations, respectively. So the IR spectrum proves the presence of N-H bond, P-O-H bond, NH\(_4^+\) ion and PO\(_4^-\) ion.

![Figure 2. FTIR spectrum of AAP.](image)
3.3. Optical Transmission Analysis
Transmission analysis provide information on localised states and electronic band structures of materials. For optical applications, the crystal should be highly transparent in these region of wavelength. Single crystals of AAP are mainly used for such applications. In this regard optical transmission spectra is recorded for the AAP crystals as shown in figure 3. It can be noted that the crystal had sufficient transmission in the entire visible region and cut off wavelength around 328 nm.

![Figure 3. UV-Vis transmission spectra of AAP.](image)

3.4. Optical Absorption Analysis
Regarding NLO characters of single crystal the region 200-400 nm is very important. An electron can be influenced by incident photon where it can interact with adjacent one. In this regard, the band absorbance is found out to be at 328nm. Beyond this cut-off value, the rest of the UV and entire visible regions are poor in absorbance which is sufficient for NLO applications. In fact, the absorption band at 328nm can be better used for all other applications where electron excitation required. All other regions are allowed without damaging the crystal structure. The band gap energy associated with cut-off wave length is3.78eV which is obtained from equation $E = \frac{hc}{\lambda}$.

3.5. Hardness Test
Hardness is a resistance performed by a solid to the movement of dislocation [10]. The hardness were measured for the AAP crystal at various load [11]. The hardness numbers (Hv) were calculated from applied load (p) and diagonal length (d) as $Hv = 1.8544p/d$. Relatively, the addition of carbon compounds to inorganic materials give lesser value than that of pure inorganic materials as in this case the hardness value of 70.87 is observed for load of 100 and the for AP, it was found to be 98.0 for the same load. In general the addition of organic compounds give flexibility.
3.6. Conductivity Analysis

The conductivity measurements are carried out at frequency region 50Hz to 200KHz, keeping sample between two metal electrodes [12]. The variations of conductivity with frequencies of the applied field are shown in figure 4. The conductivity increases with frequency. The electrical conductivity increases with doping of alanine.

![Figure 4](image.png)

Figure 4. Variations in AC conductivity with frequencies of AAP.

3.7. Second Harmonic Generation Studies

Before going through a thorough investigations on nonlinearity of materials, powder SHG test assesses the possibility. Using this test a large number of compounds can be screened by pulsed radiation. More diverse organic materials can be doped with inorganic materials for a variety of optoelectronic applications. The second harmonic score value of powder AAP was generated by irradiating pulsed laser beam of Nd:YAG. KP sample was used as the reference material. The powder SHG efficiency of AAP was found to be 1.2 times that of KP.

4. Conclusion

Characterisation of colourless transparent single crystal of alanine doped AP is carried out here via X-ray, IR, UV-Vis, hardness, and dielectric analyses. X-ray studies identifies a tetragonal structure of the crystal formed. The IR spectrum confirms the presence of all the functional groups. The UV-Vis spectrum infer AAP crystal have sufficient percentage of transmission in the entire visible region, which is needed for NLO applications. Hardness analysis identifies a reduced stiffness of the crystal. The dielectric studies confirms low values of dielectric constant and dielectric loss in the crystal. The SHG of AAP was found to be 1.2 times that of KP, which makes AAP a better material for NLO applications. That is the nonlinearity and good mechanical strength favour the AAP for optoelectronic devices.
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