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Growth Structural and Spectral Studies on L-Proline Added Ammonium Dihydrogen Phosphate Single Crystals

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Abstract

Single crystals of pure and L-proline added Ammonium Dihydrogen Phosphate (ADP) were grown from aqueous solutions, employing slow evaporation technique at room temperature. The grown crystals were subjected to single crystal X- ray diffraction studies and powder X-ray diffraction studies to study their structural characteristics. Fourier transform infrared (FTIR) spectral analysis was performed to identify the presence of various functional groups in the crystals. The UV-Visible-NIR spectral analysis was carried out to confirm the improvement in the transparency of the ADP crystal on the addition of L-proline. The second harmonic generation (SHG) efficiency was investigated to explore the enhancement in the nonlinear optical characteristics of the crystals. The studies performed have revealed the incorporation of L-proline into the lattice of ADP crystal.

Key Words: ADP; L-proline; Crystal growth; X-ray diffraction; SHG; Single crystal

Introduction

Ammonium Dihydrogen Phosphate (ADP) is a representative of hydrogen bonded materials that possesses excellent dielectric, piezoelectric, antiferroelectric, electro-optic and nonlinear optical properties. Growth and studies of ammonium dihydrogen phosphate is a centre of attention to researchers because of its unique properties and wide applications. Single crystals of ADP are used for frequency doubling and frequency tripling of laser systems, optical switches in inertial confinement fusion and acousto-optical devices[1]. ADP crystallises in a body centred tetragonal structure with the space group $I\bar{4}2d$ and has tetramolecular unit cell[2] with unit cell parameters a = b = 7.510 Å and c = 7.564 Å. ADP has been the subject of a wide variety of investigations over the past decades. Reasonable studies have been done on the growth and properties of pure ADP[3-10]. In recent years, efforts have been taken to improve the quality, growth rate and properties of ADP, by employing new growth techniques, and also by the addition of organic, inorganic and semiorganic impurities[11-18]. Organic nonlinear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power as compared with inorganic materials. Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH2) group in them[19]. Amino acids, when added as impurities, have improved material properties[20]. Amino acid, L-proline has formed several complexes, which are promising materials for second harmonic generation [21-22]. In the light of research work being done on ADP crystals, to improve the properties, it was thought interesting and worthwhile to investigate the effect of L-proline on ADP. In this work, the structural spectral and nonlinear optical behaviour of single crystals of L-proline added ADP against pure ADP has been studied and reported.

Experimental Methods

Crystal growth

Ammonium dihydrogen phosphate and L-proline (Merck-Germany) along with de-ionised water were used for the growth of single crystals. ADP was mixed with L-proline in the ratio 1:0.01 to prepare 200 ml of saturated solution at 30°C. The pH of the solution was noted as 3.8. The solution was stirred for two hours using magnetic stirrer and filtered using Whatman filter paper. The filtered solution was transferred to borosil glass beaker. It was porously sealed and placed in a dust free atmosphere for slow evaporation. 200 ml of saturated solution of pure ADP was also prepared with de-ionised water at 30°C. The pH of the solution was noted as 3.8. The solution was stirred for two hours using magnetic stirrer. It was then filtered using Whatmann filter paper, transferred to borosil glass beaker, porously sealed and kept in a dust free atmosphere for slow evaporation. The grown crystals were harvested after a period of 30 days. Pure and 1 mol% L-proline added ADP crystals grown are shown in figure 1(a) and figure 1(b) respectively.

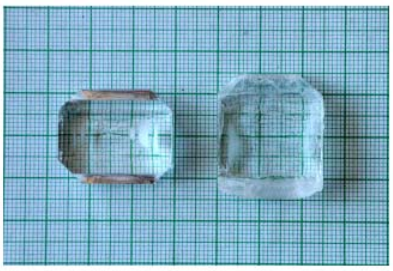

Fig. 1: Photograph of (a) pure ADP (b) 1 mol% L-proline added ADP

Characterization

Single crystal X-ray diffraction (XRD) studies

Single crystal X-ray diffraction studies was carried out for the pure and L-proline added ADP crystal using Bruker AXS Kappa APEXII CCD Diffractometer using ω and 2θ scan modes. Initially the reflections were collected for 36 frames in three different crystallographic zones or orientations with 12 frames each and the cell parameters were determined by indexing the reflections by the method of difference vectors. The unit cell parameters of pure ADP are a=b=7.486(2) Å, c=7.547(3) Å, $\alpha=\beta=\gamma=90°$ unit cell volume=422.9(2) $(Å)^3$ and it belongs to the tetragonal system. The reported values of unit cell parameters for pure ADP[23] are a=b=7.4997(4) Å, c=7.5494(12) Å, $\alpha=\beta=\gamma=90°$ in good agreement with the obtained values. The unit cell parameters of L-proline added ADP are a=b=7.510 Å, c=7.550 Å, $\alpha=\beta=\gamma=90°$ unit cell volume=426 $(Å)^3$. The Single crystal XRD result shows that there is slight variation in the unit cell parameters of the L-proline added ADP crystal when compared to ADP. The changes in the lattice parameters are due to the incorporation of L-proline into the lattice of ADP crystal.

Powder X-ray diffraction (XRD) studies

Powder X-ray diffraction studies was carried out for the pure and 1 mol% L-proline added ADP crystals using XRERT PRO Diffractometer with copper (K- Alpha 1) radiation

(λ= 1.54056 Å) operating at a voltage of 40 kV and a current of 20 mA. The scanning rate was maintained at 1.6° / min over a 2θ range of 10 - 70° employing the reflection mode for scanning. All the reflections of powder XRD pattern have been indexed using the TREOR software package following the procedure of Lipson and Steeple[24] . The indexed X-ray powder diffraction patterns of pure and

1 mol% L-proline added ADP crystals are shown in figure 2 and figure 3 respectively.

The sharp peaks indicate the crystallinity of the grown crystals. There is slight shift in the diffracted peaks in the XRD pattern of L- proline added ADP crystals when compared to that of ADP. The observed prominent peaks are (101), (200), (112), (220), (301) and (312). The intensity of the diffracted peak (112) is found to vary in the XRD pattern of L-proline added ADP crystal. The above mentioned changes are due to the presence of the additive L-proline into the lattice of ADP crystal. However, there are no other phases emerging besides the tetragonal system. The observed results are in good agreement with the reported values[25]. The unit cell parameters of pure and L-proline added ADP crystals were calculated using "UNIT CELL" software package as a=b=7.4972 Å, c= 7.5438 Å, volume=424.0246 $(Å)^3$ for pure ADP and a=b=7.4917 Å, c= 7.5429 Å, volume=423.3511 $(Å)^3$ for L-proline added ADP respectively.

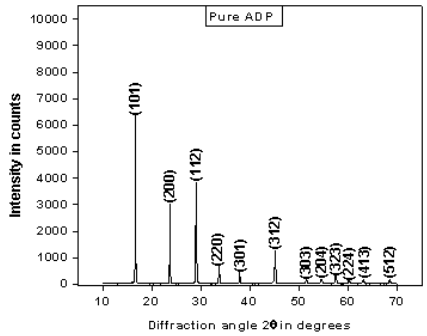

Fig. 2: Powder XRD pattern of pure ADP

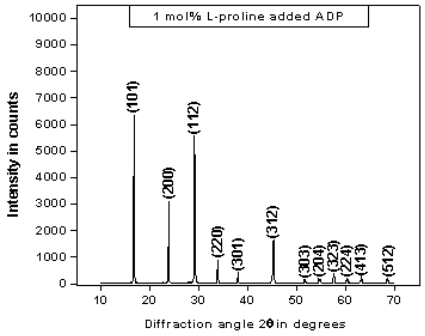

Fig.3: Powder XRD pattern of L-proline added ADP

The Single and Powder XRD results show that the L-proline added ADP crystal retains its original tetragonal structure and that L-proline has entered into the lattice of ADP crystal. The lattice parameters obtained by powder XRD studies are found to be in comparable with the results obtained from single crystal XRD studies.

Fourier transform infrared (FTIR) spectral studies

The Fourier Transform infrared spectrum was recorded for powdered samples of pure and L-proline added ADP crystals using Perkin- Elmer FTIR spectrometer by KBr pellet technique in the range 400-4000 cm^{-1}. The FTIR spectra of pure and L-proline added ADP crystals are shown in figure 4 and figure 5 respectively.

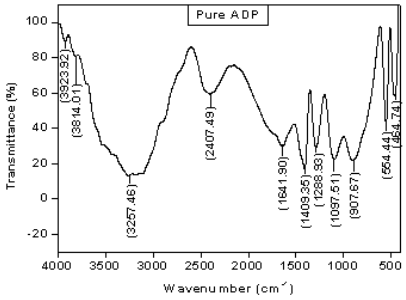

Fig. 4: FTIR spectrum of pure ADP crystal

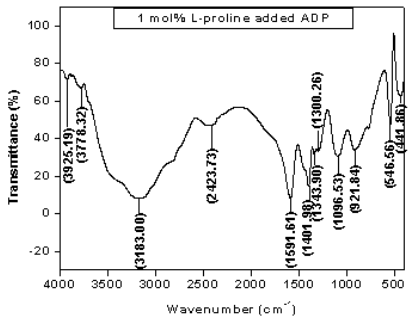

Fig. 5: FTIR spectrum of L-proline added ADP crystal

The effect of L-proline on the vibrational frequencies of the functional groups of pure ADP crystal has been identified in the spectra. In the spectrum of ADP, the broad band around 3257 cm^{-1} is due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium. The band at 2407 cm^{-1} is assigned to hydrogen bond[8] . The broadness is due to the hydrogen bonding interaction with adjacent molecules. The bending vibrations of water give the peak at 1642 cm^{-1}. The peak at 1409 cm^{-1} is due to the bending vibrations of ammonium. The peak at 1289 cm^{-1} is due to the combination of the asymmetric stretching vibration of PO_4 with lattice. The peaks at 1098 cm^{-1} and 908 cm^{-1} represent

P-O-H vibrations. The peaks at 554 cm^{-1} and 465 cm^{-1} are due to the PO_4 vibrations.

In the spectrum of L-proline added ADP crystal, the broad band appearing at 3183 cm^{-1} includes O-H vibrations of water and N-H vibrations of ammonium and L-proline. The sharp peak at 1289 cm^{-1} in the spectrum of ADP is missing. The peaks at 1300 cm^{-1} and 1344 cm^{-1} are due to CH_2 wagging vibrations of L-proline[26,27]. In addition, shift in the peak positions of P-O-H and PO_4 vibrations compared to ADP established the presence of the additive L-proline in the lattice of ADP.

Optical Transmission spectral studies

Single crystals of ADP are mainly used for optical applications. The study of the optical transmission range of the grown crystals is thus very important. Pure and L-proline added ADP crystal plates with a thickness of 2 mm without any antireflection coating were cut and used for optical measurements. The UV-Visible-NIR transmission spectrum was recorded using Perkin-Elmer Lambda 35 UV-Visible Spectrometer in the range 190 nm to 1100 nm. From the spectra, it is observed that both the pure and L-proline added ADP crystals show good transmittance in the entire visible and NIR regions. The pure ADP crystal has 52 % and L-proline added ADP crystal has 63 % transmittance at 1100 nm. Thus the addition of L-proline has increased the transmittance of pure ADP. The higher percentage of transmittance for L-proline added ADP when compared to pure ADP suggests the enhancement of optical quality.The UV-Visible-NIR transmission spectra of pure ADP and L-proline added ADP are shown in figure 6.

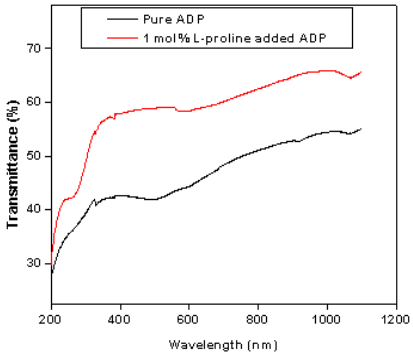

Fig. 6: UV-Visible-NIR transmission spectra of pure ADP and L-proline added ADP

Second harmonic generation (SHG) test

Kurtz and Perry powder technique is extremely useful for the initial testing of materials for second harmonic generation (SHG). The fundamental beam of wavelength 1064 nm, from a Q-switched Nd:YAG laser was used to test the second harmonic generation property of the grown crystals. The pure and L-proline added ADP crystals were ground into fine powder and packed in micro capillary tubes mounted in the path of laser pulses with pulse width 6 ns and repetition rate 10 Hz, having an input energy of 0.68 mJ/pulse. The second harmonic generation was confirmed by the green emission of wavelength 532 nm from the samples. The output energy for pure and 1 mol% L-proline added ADP samples was measured to be 2.6 mJ/pulse and 5.5 mJ/pulse respectively. The values of SHG efficiency for pure ADP, L-proline added ADP and KDP samples are provided in the table 1. This increase in SHG of ADP with the addition of L-proline is due to the fact that L-proline has NH_3^+ and COO^- groups. The optically active amino group may get added in the ADP structure and increase its non centro symmetry thereby increasing its SHG efficiency.

Table 1: Values of SHG efficiency for pure ADP, L-proline added ADP and KDP samples

Sample	Input energy (mJ)	Output energy (mJ)	SHG Efficiency
Pure ADP	0.68	2.6	3.82
ADP+1 mol% of L- proline	0.68	5.5	8.09
KDP	0.68	8.8	12.94

Conclusion

Optical quality, colourless and transparent single crystals of pure and 1 mol% L-proline added ADP were grown employing slow evaporation solution growth technique. The single crystal and powder XRD studies reveal that the tetragonal structure of ADP is preserved and that the lattice of ADP crystal is slightly distorted due to the addition of L-proline. The FTIR spectra confirm the presence of all the functional groups and the presence of L-proline in the grown crystals. The optical transmission spectrum shows good transmission in the entire visible and NIR region for both the crystals with higher transmission for the L-proline added crystal. The SHG efficiency of pure ADP has been enhanced by the addition of L-proline in the ADP crystal. Thus the grown L-proline added ADP crystal is better than pure ADP for optoelectronic and laser applications.

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