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EFFECT OF L-PROLINE ON OPTICAL AND MECHANICAL PROPERTIES OF AMMONIUM DIHYDROGEN PHOSPHATE (ADP) SINGLE CRYSTALS

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ABSTRACT

L-Proline (1 mol%) doped Ammonium Dihydrogen Phosphate (ADP) single crystals were grown by slow evaporation solution growth technique. The grown crystals were characterized by Powder XRD, Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis Spectroscopy, Microhardness Test and Nonlinear Optical Studies. The powder XRD reveals that crystallinity and perfection of the crystal. FTIR shows that functional groups and UV-Vis spectroscopy is used to say about the optical property of the crystal. The mechanical property of the crystal was determined by Vicker's microhardness test and the NLO property was studied by nonlinear optical studies.

KEYWORDS : Optical Properties, Mechanical Properties, Meyer's Index, Stiffness Constant

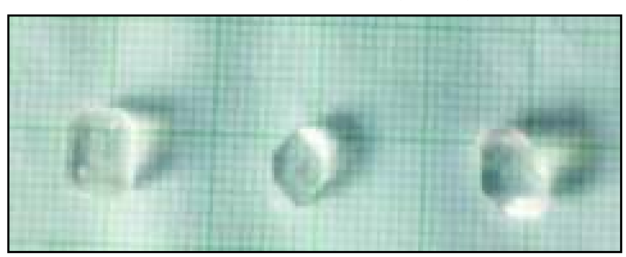
Ammonium Dihydrogen Phosphate (ADP) is a nonlinear optical material having application in photonics for frequency mixing, parametric amplification and electro optical modulation (P.Rajesh and P.Ramasamy, 2009). ADP is a representative of hydrogen bonded materials that possess excellent dielectric, piezoelectric, 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 (Rajesh and Ramasamy, 2009). In recent years, efforts have been taken to improve the quality, growth rate and properties of ADP, by the addition of organic, inorganic and semiorganic impurities (Rajesh and Ramasamy, 2009; Claude et al., 2006; Joseph John and Mahadevan, 2008; Rajesh et al., 2001; Rajesh and Ramasamy, 2009; Rajesh et al., 2009; Dhanaraj et al., 2008; Yokotani et al., 1986). Materials with large optical nonlinearities are needed to realize applications in optoelectronics, telecommunication industries, laser technology and optical storage devices (Tukubo and Makita, 1989; Xu and Xue, 2008; X. Ren, D. Xu and D. Xue, 2008; D. Xu and D. Xue, 2008; Xu and Xue, 2006; Zhang and Xue, 2009). In present work, L-Proline was used as the dopant to improve the optical and mechanical properties of ADP single crystals. NLO single crystal with high conversion efficiencies for second harmonic generation is desirable in various applications. With the aim of discovering new useful materials for academic and industrial use an attempt has been made of modify ADP crystals by adding some amino acids (Xue and Ratajczak, 2005; Latajka et al., 2009; Meena and Mahadevan, 2008). Since most of the amino acids exhibit NLO property, it is expected that the addition of some amino acids, such as L-Aginine, in ADP could also improve the various properties (P.Selvarajan et al., 2009). Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH_2) group in them (Li and Xue, 2010).

MATERIALS AND METHODS

Experimental Method

L-Proline of 1 mol% was saturated with the 100ml of de-ionized water by stirring with the magnetic stirrer. Ammonium Dihydrogen Phosphate salt was added with that of L-Proline added solution until the saturation attain and stirred for 6hrs to get the homogenous solution. The solution was filtered with whatmann filter paper. The filtered solution was kept in a Petridis with the covered top by holes. After one week duration, the seed crystals were found at the bottom of the Petridis. The good quality seed crystals were taken to grow the bulk crystals. The transparent good quality single crystals were harvested after 20days duration.

L-Proline Doped ADP Single Crystals



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RESULTS AND DISCUSSION

Powder XRD

The crystallinity and the crystal perfection were determined using by Powder XRD which was carried out using XPERT PRO diffractometer with CuKα radiation. The reflection mode was maintained with the scanning rate at 1.6 per min. The powder XRD pattern was shown in fig.2.

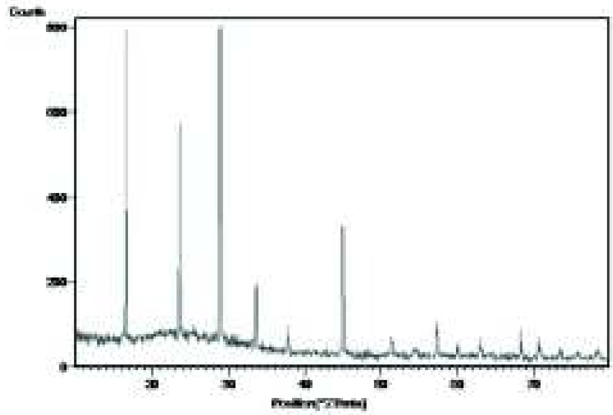


Figure 2 : Powder XRD Pattern of L-Proline Doped ADP

The planes were indexed with the reference of JCPDS standard card value (441593). The predominant peaks were found to be (1 1 1), (2 0 2), (1 1 2),etc. The grain size was calculate using Scherrer's equation

$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

The lattice parameters were determined using the following relation

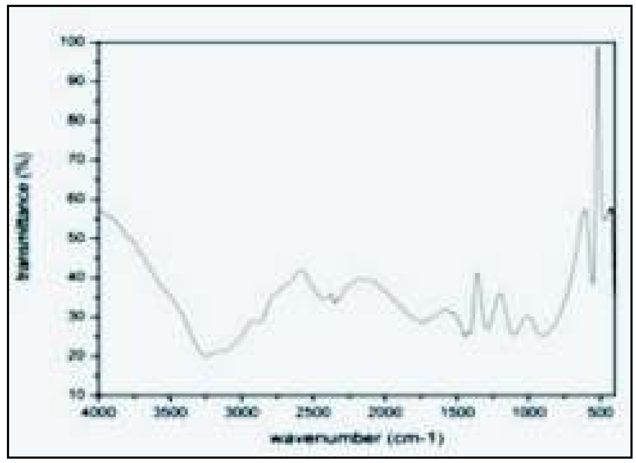
1/d2={(h2+k2)/a2}+1/c2

The lattice parameters were calculated and verified with the standard values as a=b=7.494, c= 7.562 and unit cell volume is v=424.682 $Å^3$. There were slight shifts were observed when compared with the pure ADP a=b=7.510 A˚, c=7.564 A˚[8].

Fourier Transform Infrared Spectroscopy

The functional groups of the L-Proline doped ADP single crystal was carried out using Perkin Elmer spectrometer. The KBr pellet technique was used in the range 400-4000cm^{-1}. The FTIR spectrum was shown in figure 3. The functional groups were assigned at 3169cm^{-1} was due to the N-H vibration of the dopant L-Proline. The band at 3246cm^{-1} was for O-H vibration of water and P-O-H group. 2436cm^{-1} band was due to the hydrogen bonding interaction. The bending vibration of ammonium was at 1403cm^{-1}. 1291cm^{-1} was due to the asymmetric stretching of PO_4. The CH_4 wagging was at 1351cm^{-1}. The broadness is generally considered to be due to hydrogen bonding interaction of H_2PO_4, $COOH^-$ and NH^{3+} with adjacent molecules(Rajesh et al., 2009).

FTIR Spectrum of L-Proline Doped ADP



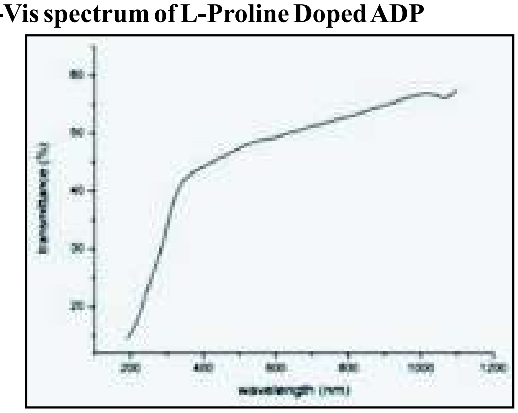
Optical Studies

The UV-Vis NIR spectrum was carried out using Perkin Elmer Lambda 35 UV-Vis spectrometer in the range 190-1100nm. The spectrum for the grown L-Proline doped ADP single crystal exhibits the good transmittance in the entire visible region with the transmittance around 60% and it was shown in figure 4. The optical band gap was calculated by the relation

$$Eg = hC/\lambda$$

The optical band gap was found to be 3.36eV.

UV-Vis spectrum of L-Proline Doped ADP



Vicker's Hardness Test

The hardness of the material is a measure of its resistance to plastic deformation (Li and Xue, 2010; Li et al., 2008). The different loads were applied with different magnitudes. With different applied loads the indentation time was maintained as 10s. The hardness value was determined using the relation

$$H_v = 1.8544 P / d^2$$

Where P is the applied load (kg), d is the diagonal length of the impression (mm). The graph was drawn between the applied load (P) and the hardness value (Hv). The graph depicts as the applied load increased the hardness value also increased which says the mechanical stability of the grown crystal.

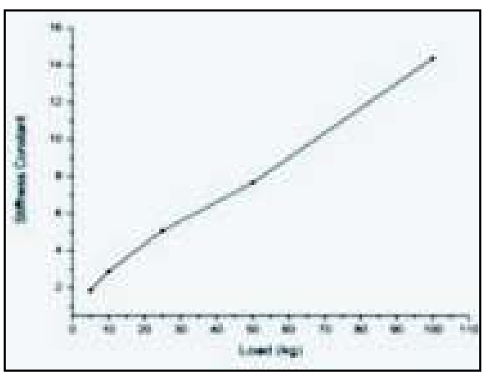
Determination of Stiffness Constant and Meyer's Index

The stiffness constant was calculated using the equation

$$C_v = (H_v)^{7/4}$$

The graph was drawn between the hardness values (Hv) and the stiffness constant (Cv). As the hardness value increased, the stiffness constant also increased. It shows the elastic nature of the grown crystal was good.

Stiffness constant vs. Load for L-Proline doped ADP

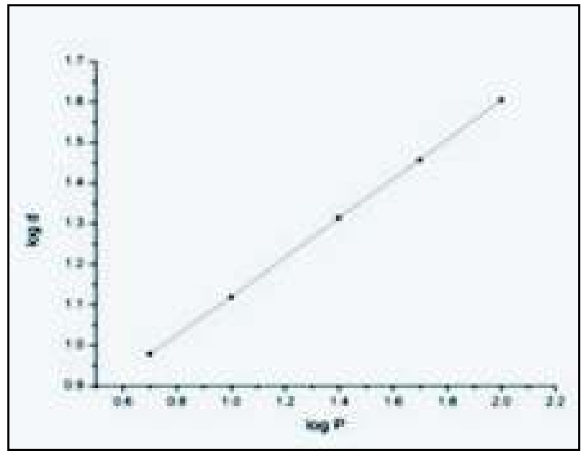


Meyer's index was determined using the relation

$$P = kdn$$

Where P is the applied load (kg), k is the material constant, d is the indentation length and n is the Meyer's index. From the above equation, the n can be calculated by plotting the graph between log P and log d. The n has been calculated as 2.06 which say that the grown L-Proline doped ADP single crystal belongs to the soft material category.

Log P Vs Log d for L-Proline Doped ADP



Second Harmonic Generation Studies

The test to study the second harmonic generation was carried out using Kurtz and Perry powder technique. The beam of wavelength is at 1064nm. Q-switched Nd:YAG laser was used to examine the efficiency of second harmonic generation. The input of 0.68mJ/pulse. The green light was emitted which confirms the SHG. The emission wavelength was found to be at 532nm. The efficiency was determined at 8.02 which is more efficient than compared to pure ADP SHG efficiency of (3.82) (Josephine Rani et al., 2011).

CONCLUSION

The single crystals of L-Proline doped Ammonium Dihydrogen Phosphate were grown by slow evaporation solution growth technique. The grown crystals were characterized to determine the nature and properties of the crystals. The good crystallinity and crystal perfection was determined using powder XRD pattern. The functional groups were identified using Fourier Transform Infrared Spectroscopy. The optical property was determined using UV-Vis spectroscopy studies and the optical band gap was calculated as 3.36eV. From this we can say this crystal can be used for device fabrication in optoelectronic applications. The mechanical stability was analyzed using Vicker's hardness test. From the microhardness test, the stiffness constant and the Meyer's index have been calculated. The stiffness constant graph says that the grown crystal has the elastic property and the Meyer's index says that the crystal belongs to the soft material category and can be used for the mechanical applications.

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