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Research Article

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A study of L-Asparagine Doped ADP single crystals

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ABSTRACT

This study proposed to discuss a novel nonlinear optical material Ammonium Dihydrogen Orthophosphate (ADP) doped with L-Asparagine (LAADP) which was grown by slow evaporation technique from the mixture of aqueous solutions of L- Asparagine and ADP at an ambient temperature. Studies on structural, optical properties of the crystal were carried out. Formation of the new crystal has been confirmed by Powder XRD and FTIR spectra. LAADP belongs to orthorhombic system. Optical transmission spectra revealed the optical properties of the grown crystal. The thermal stability of the crystal was investigated using thermo-gravimetric analysis. Vicker's Hardness number (Hv) increases with increase in load. The NLO property of the crystal was confirmed by powder SHG test.

Keywords: Growth from solution; LAADP; FTIR; XRD; TGA; NLO.

INTRODUCTION

The search for new advanced materials is an important area of contemporary research in numerous disciplines of science and development of many new technologies. The Nonlinear optical (NLO) crystals have become of great research interest and importance in the recent years for the fabrication of devices used in the field of telecommunication, optical signal processing, optical switching and Photonics [1]. Now a days, various growth methods and apparatus have been continuously developed to improve the quality and growth rate. Compared to the other techniques, the slow evaporation technique is mostly used in several types of crystals. Organic crystals in terms of NLO properties posses advantages when compared with inorganic counterparts [2-4]. Organic materials allow their fine tuning of their chemical structure and properties for the desired NLO properties [5]. The adaptable nonlinear optical frequency conversion materials are vital importance of optical modulation, optical switching, optical logic, optical storage, computing and optical information process [6]. Organic materials draw more interest because of their superior performances involving fairly high NLO coefficient and fast response than their inorganic counterparts.[7] Nonlinear optical crystals are very important for laser frequency conversion. Potassium dihydrogen phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard. Ammonium dihydrogen phosphate (ADP) is a well known nonlinear optical material for various optoelectronic applications. ADP continues to be an interesting material both for academically and industrially [8-10]. Several researches have been carried out in pure and doped ADP crystals [11-14].Amino acid based crystals exhibit excellent NLO application and electro optic properties. In addition several researcher have investigated various organic materials and characterized them

various thermal, optical, XRD and spectral analysis.[15-18] Asparagine is one of the 20 most common natural amino acids in the living organisms. It has carboxamide as the side-chain's functional group. It is not an essential amino acid. This work focused on the spectral, optical, thermal, dielectric and mechanical properties of LAADP. It has centrosymmetry in Second harmonic conversion efficiency.

EXPERIMENTAL SECTION

2.1. Crystal Growth

LAADP was synthesized with high purity Ammonium Dihydrogen phosphate (Sigma – Aldrich, CAS Number 7722-76-1, 99.99%) and L-Asparagine (Sigma – Aldrich, CAS Number- 70-47-3, 98%) in the ratio 1:1. The stoichiometric amounts of reactance were dissolved in 100 ml deionized water (resistivity 18.2 MΩ cm) and the mixture were stirred well using a magnetic stirrer for about 10 hrs. This was then filtered using high quality Whatmann filter paper (Cat no. 1001124). Optically good transparency defect free seed crystals were selected and it was suspended in the mother solution which was allowed to evaporate at the temperature of 30° C in a constant temperature bath. Bulk crystals with excellent external morphology are harvested with in the period of 45 days and seed crystals are shown in fig 1.

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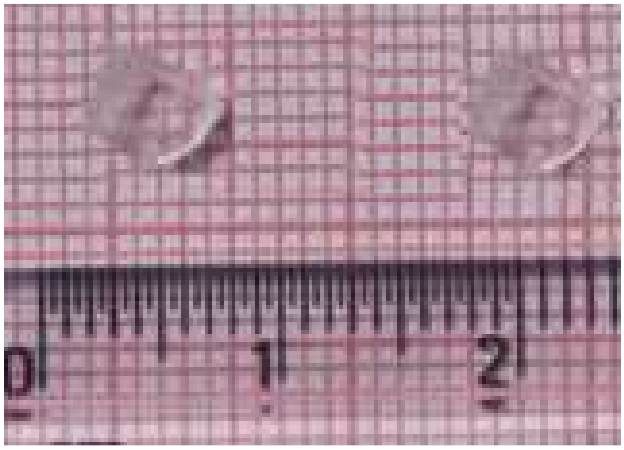

Fig. 1. Photograph of as grown LAADP crystals

2.2. Characterization Technique

The grown crystals of LAADP were confirmed by powder X ray diffraction analysis, using RIGAKU ULTIMA III X-Ray diffractometer. The Functional groups were identified by Fourier transform infrared studies using PERKIN – ELMER 783 spectrometer in the range of 400-4000 cm^{-1}. The optical properties of the crystals were examined between 200 – 1100 nm using PERKIN-ELMER LAMBDA 35 spectrometer. Thermal behaviour of the grown up crystal was tested by TA Instruments Q 600 V20.9 Simultaneous Thermal Analyzer. The micro hardness of the grown crystal was studied by using SHIMADZU (HMV-2T) micro hardness tester. The NLO property of the crystal was confirmed by Nd:YAG laser. The detailed discussions of the obtained results are presented herewith.

RESULTS AND DISCUSSION

3.1. X – ray diffraction studies

The crystallinity and the structure of the grown LAADP single crystal have been confirmed by power diffraction analysis using RIGAKU ULTIMA III X-Ray diffractometer. The crushed powder sample was subjected to intense X ray wavelength 1.5418A° at a scan speed of 1°/min. The lattice parameters have been calculated using TEROR software. The LAADP crystal retained its Orthorhombic structure with lattice parameters a =14.847A°, b = 9.447A° , c =7.102A°, α=β=γ= 90° and volume (V) = 996.151 A^3 and space group $P_{212121.}$ The indexed powder X ray diffraction pattern of LAADP crystal are shown in Fig. 2.

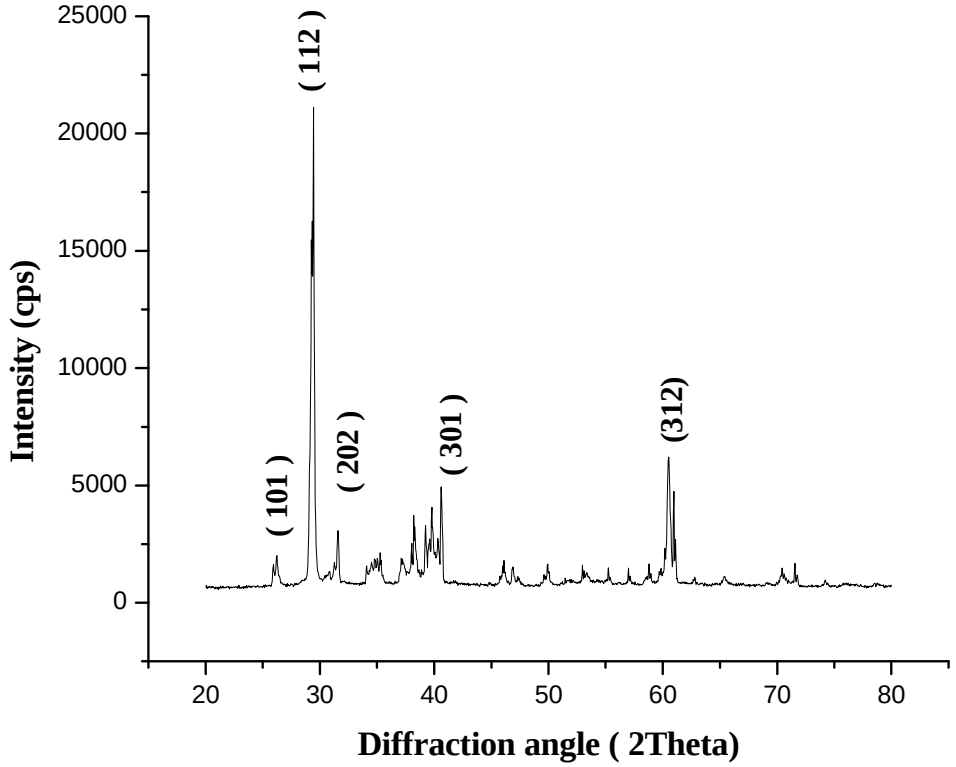

Figure.2. Powder X ray diffraction pattern of LAADP crystal

3.2. FTIR analysis

The Fourier transform intra-red analysis is a technique in which almost all the functional groups in a molecule absorb characteristic frequencies. The FTIR spectrum of LAADP crystal has been recorded in the KBr phase in the frequency region of 400 – 4000 cm^{-1} using Perkin – Elmer 783 spectrometer and shown in Fig.3. The recorded spectrum has been compared with available review literature [19-20]. The broad intense band in the higher energy region around 3447-3178 cm^{-1} is assigned to NH stretch of NH_2 vibration and O-H stretching respectively of LAADP molecule. The CH_2 vibration of the amino acid shows its peak at 2380 cm^{-1} and the C=O vibration of COO group vibration at 1621 cm^{-1}. The CH_2 bends of amino acid are seen at 1392 cm^{-1} [21]. The spectrum shows strong absorptions bands at 1282.42 cm^{-1} and 1092.59 cm^{-1} which could be assigned to P-O-H stretching vibration mode of vibration. The O-H stretching modes have intense broad absorption band between 3500 and 2400 $cm^{-1.}$ The $(PO4)^{3-}$ symmetric bending was observed at 534.73 cm^{-1} and 464 cm^{-1}. A strong peak of P-O plane bending was identified at 912 cm^{-1}.

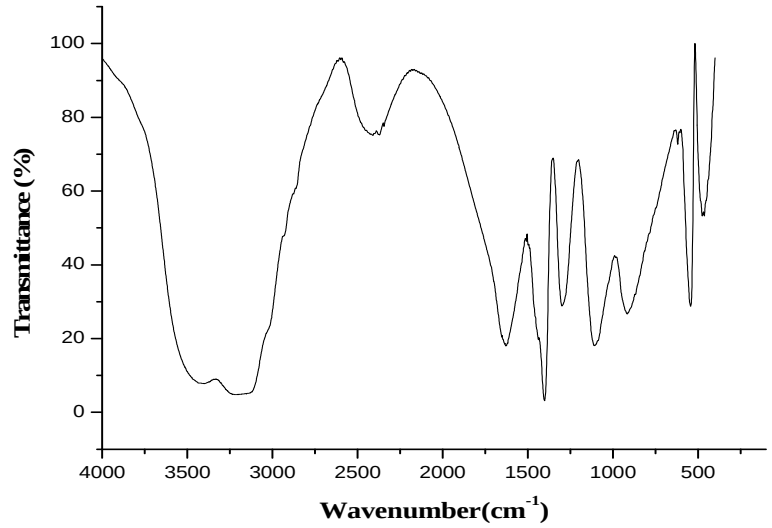

Fig. 3. FTIR spectrum of grown LAADP crystals

3.3. Optical Transmittance studies

Optical transmittance range and transparency cut off of the grown crystal are the important factors of the optical and laser applications. It was observed that the LAADP crystal was conveniently transparent in the entire optical window region well below 200 nm to 1200 nm. The optical transmittance spectrum is shown in Fig.4a. The lower cut off wavelength of the crystal is found to be 261 nm. The absorption was almost zero in the UV and the visible region. It clearly indicates that LAADP crystal can be used as window material in optical instruments. The Higher percentage of transmittance in the visible region obviously depicts the intrinsic property of amino acid and the crystal is free from any defects.

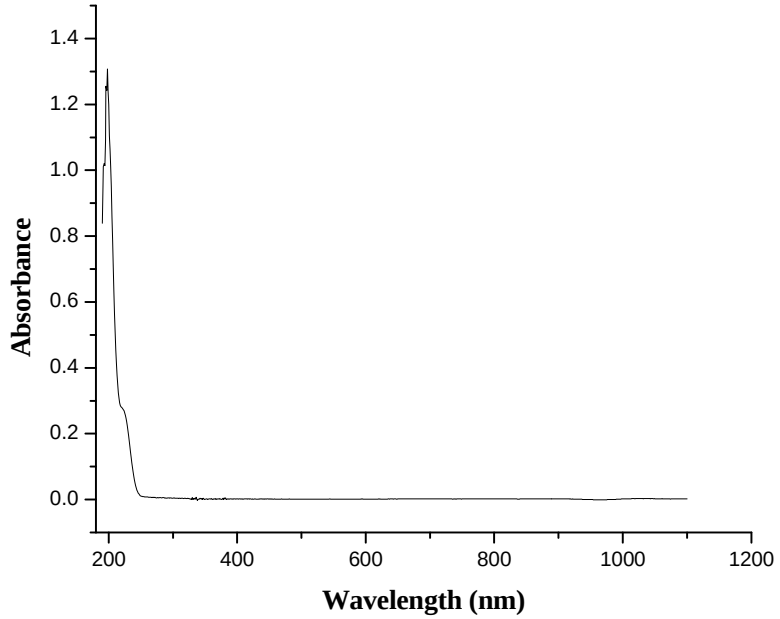

Fig. 4. UV-Visible-NIR transmission spectra of grown LAADP crystal

3.4. TGA-DSC analysis

The thermal stability of LAADP single crystal was examined by TGA and DSC analysis. The analysis was preformed between 25 and 1000°C at a heating rate of 10°C min^{-1} in the nitrogen atmosphere. The TGA thermogram of the LAADP crystal is shown in Fig.7. The TGA curve indicates that there is a major weight loss (61.45%) of the sample starts from the region 178°C and ending at 250°C. It illustrates that the absence of physically adsorbed or lattice water in the crystals and the elimination of volatile compounds like carbon monoxide, ammonia molecules. This accounts for 56.60% mass loss observed in TGA curve. From DSC curve, it is observed that LAADP undergoes the single stage irreversible endothermic transition at 213°C which indicates the melting point of the material. When the sample was heated above 213°C the volatile compounds were eliminated from the material. Extended heating upto 1000°C did not produce any significant endothermic or exothermic peaks in the DSC curve because it becomes inactive due to the improper contact with the molten substances, whereas TGA shows the complete weight loss. Hence we conclude that the LAADP crystal is suitable for the NLO applications up to 213°C.

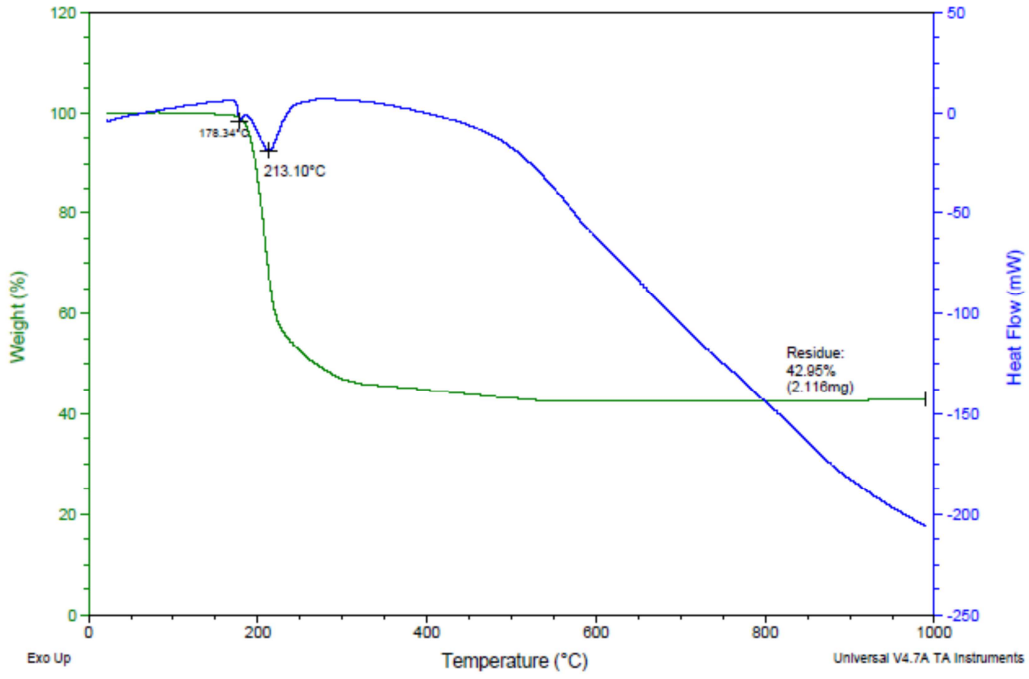

Fig. 5. TGA –DSC Curve of LAADP crystal

3.5. Micro Hardness Analysis

Hardness is a measure of a material's resistance to localized plastic deformation and it is commonly used to determine the strength of the material which relates the bond strength and defect structure. The LAADP crystals were indented using a SHIMADZU (HMV-2T) micro hardness tester fitted with a Vickers pyramidal indenter having an optical angle of 136˚ between the opposite pyramidal. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. Indentations were carried out using Vickers indenter for varying loads. The loads applied were 25 to 300 grams and were applied for a time period of 10 seconds at room temperature. Vickers micro hardness number was determined using the relation

$$Hv = 1.8544p/d^2 (Kg/mm^2)$$

The variation of Hv with the applied load P is shown in Fig. 8. The prominent (112) face, which reveals that the hardness increases with the increase in load without any crack [22-25] above which cracks start developing. The RISE phenomenon essentially takes place in the crystals which readily undergoes plastic deformation [26]. It is observed that that the LAADP crystals have the good mechanical strength.

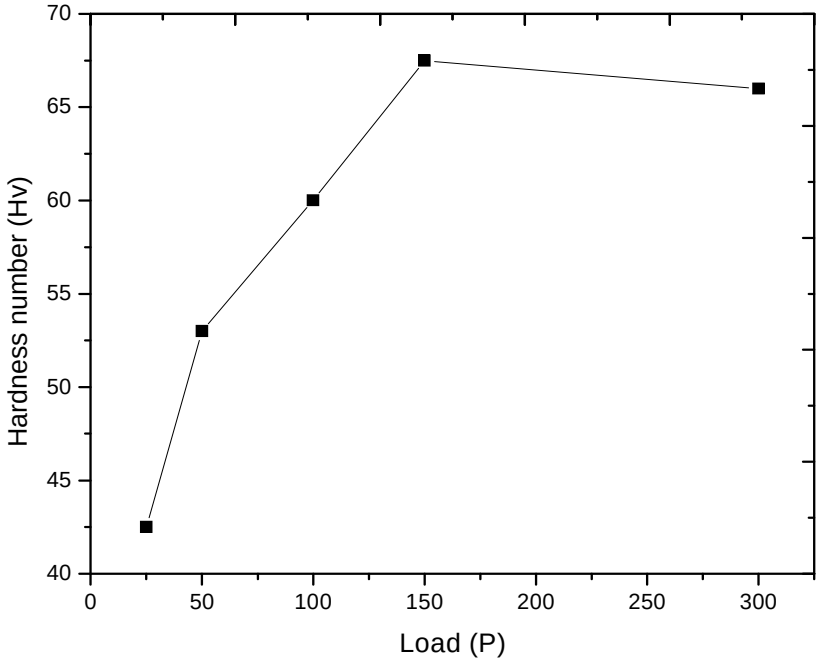

Fig. 6 . Microhardness curve of grown LAADP crystals

3.6. Second Harmonic conversion efficiency

The SHG conversion of LAADP was determined by modified version of the powder techniques by Kurtz and Perry [27]. In order to confirm the NLO property of the grown crystals, they were characterized with Nd:YAG laser with wavelength of about 1064 nm with pulse width of 8 ns ad repetition rate 10 Hz with beam energy 2.149mJ/pulse was allowed to pass through the powdered sample. The second harmonic green signal was generated (λ=532nm) by the material confirmed that the material reveals the NLO property. The results show that SHG efficiency of the grown crystals was 0.8 times that of the standard Potassium dihydrogen orthophosphate (KDP) crystal.

CONCLUSION

Optically transparent NLO crystals of LAADP were profitably grown from an aqueous solution by employing the slow evaporation technique. Powder XRD analysis confirmed that LAADP crystal belongs to orthorhombic system with space groupP_{212121}. The FTIR spectrum reveals that the mode of vibration of different molecular group present in the titled compound. Transparency range of LAADP was found to be from 200 nm to 1200 nm that confirms wider optical transmission range to extend its applications in the entire visible and UV region. The TGA and DSC analysis affirm that the titled compound undergoes the thermal stability up to 213°C due to no phase transition exist in the component. Micro hardness study reveals the mechanical strength of the material and also confirms the grown crystal satisfies the RISE phenomena. The NLO behavior of the LAADP crystal has been found using Kuntz-Perry power techniques and the results show that the observed values is 0.8 times better than that of KDP crystal.

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