Optical, microhardness, thermal and NLO behaviour of L-histidine doped ADP crystals

Z Delci*, D Shyamala, S Karuna, A Senthil & A Thayumanavan

Department of Physics, D G Vaishnav College, Chennai 600 106, India
*Department of Physics, S R M University, Chennai 600 089, India
Department of Physics, A V V M Sri Pushpam College, Thanjavur 613 503, India
*E-mail: delcidgvc@gmail.com

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Pure ammonium dihydrogen phosphate (ADP) and L-histidine doped ammonium dihydrogen phosphate have been grown by slow solvent evaporation method at room temperature. The grown crystals are characterized by Fourier transform, Energy dispersive X-ray, UV-Vis, hardness, thermal property and SHG efficiency. The crystal structure has been studied by single crystal and powder X-ray diffraction. FTIR spectral analyses were performed to identify the presence of various functional groups in the crystals. UV-Vis studies show improvement in the transparency of the doped crystal. SHG efficiency of doped ADP is greater than the pure ADP. Vicker’s microhardness study reveals the increase in the hardness of the doped crystal. Thermal analysis has been performed on the grown crystals.

Keywords: Optical properties, Microhardness, Thermal proprieties, NLO, Crystal structure, FTIR

1 Introduction

Ammonium dihydrogen phosphate (ADP) is a well established inorganic, piezoelectric and nonlinear optical material with a wide range of applications. It is used as a piezoelectric material in transducer devices, has found applications also in nonlinear optics (NLO), electro-optics and as monochromators for X-ray fluorescence analysis. Below 148.5K, ADP is antiferroelectric and belongs to P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} space symmetry group while above this temperature it becomes paraelectric having I4/2d symmetry. ADP is a nonlinear optical material and has been used as optical modulation Q-switch, quantum electronics and frequency converters. Particularly, optical crystals with lower impurity and higher damage threshold are required for inertial confinement fusion. But recent interest is focused on the development of the new semi-organic (NLO) materials with improved properties. Semi-organic materials possess the advantage of both organic and inorganic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher SHG (second harmonic generation) and high damage threshold. Amino acid family crystals are playing an important role in the field of non-linear optics. Recently, several new complexes incorporating the amino acid L-alanine have been crystallized and their structural, optical and thermal properties have been investigated. Many reasonable studies have been carried out on pure ADP crystals. The effect of additives such as amino acids on growth, habit modification and different structures of ADP crystals has been studied. It is also reported that the addition of amino acid as dopant enhances the nonlinear optical and piezoelectric properties of inorganic material. So L-histidine doped inorganic material like ADP will be of special interest as a fundamental building block to develop many complex crystals with improved NLO properties.

In the present paper, the effect of L-histidine as impurity on the growth of ADP by slow evaporation method at room temperature has been studied. The grown crystals were characterized by FT-IR, EDAX, single crystal XRD, powder XRD, optical, TGA analysis, NLO behaviour and Vicker’s microhardness. A comparative study on the results obtained for pure and doped ADP crystals is detailed below.

2 Crystal Growth

Analytical reagent grade (AR) samples of pure ADP and L-histidine along with triple distilled water were used for the growth of single crystals. In the present study, ADP, with an L-histidine content of 0.1 mole % was prepared by adding 1.55 g of L-histidine with 11.5 g of ADP. The pH of the reaction mixture was monitored to be 5. The solution...
was stirred for 6 h and then filtered. It was porously sealed and placed in a dust free atmosphere for slow evaporation. Optically transparent crystals of size 10.45 mm×6.39 mm×3.93 mm and 7.23 mm×6.45 mm×2.50 mm were harvested in 15 days. The photograph of pure and L-histidine doped ADP crystals are shown in Figs 1 and 2.

3 Experimental Details

3.1 Energy Dispersive X-ray diffraction (EDAX)

The sample of grown crystals was subjected to EDAX analysis using the QUANTA 200 FEG Scanning Electron microscope. The EDAX spectra for pure ADP and doped ADP crystal recorded are shown Figs 3 and 4. The elements were identified and presented as atomic %.

3.2 X-Ray diffraction study

The single crystal X-ray diffraction analysis of L-histidine doped ADP crystal and pure ADP crystal were performed using Bruker Kappa APEX II single crystal X-ray diffractometer to determine the unit cell dimensions. The cell parameters obtained for the pure ADP are \( a=b=7.491 \) Å, \( c=7.546 \) Å, \( \alpha=\beta=\gamma=90^\circ \) and it belongs to tetragonal system. The unit cell parameters for the doped ADP crystal are \( a=b=7.480 \) Å, \( c=7.532 \) Å, \( \alpha=\beta=\gamma=90^\circ \). It is seen that only a marginal variation in the values of the lattice parameters is observed and the grown crystals retain their original structure.

The powder X-ray diffraction has also been recorded for pure and doped ADP using Bruker-35 kV copper K-alpha radiation and the results are shown in Fig. 5. The observed prominent peaks of both crystals are (101), (200), (112),(202),(301) and (312) but the intensities of the diffracted peaks are

![Fig. 1 — Photograph of as-grown pure ADP crystal](image1)

![Fig. 2 — Photograph of as-grown L-histidine doped ADP crystals](image2)

![Fig. 3 — EDAX of pure ADP crystal](image3)

![Fig. 4 — EDAX of L-histidine doped ADP crystal](image4)
found to be varied. The sharp peaks confirm that the crystallinity of the grown crystals is good.

3.3 FTIR analysis

The Fourier transform infrared spectrum of pure ADP and L-histidine doped ammonium dihydrogen phosphate (ADP) crystals were recorded using Perkin-Elmer model RXI Spectrometer in the range 400-4000 cm\(^{-1}\) by KBr pellet technique. The recorded spectrum is shown in Fig. 6. Bands in the region from 3700 to 3100 cm\(^{-1}\) are usually due to various O-H and N-H stretching vibration. The bonded O-H groups usually give rise to a broader band than N-H groups. All these bands shift to higher wave numbers and much become narrower and weaker in intensity when the hydrogen bond is broken\(^{25}\). So, in the pure ADP a broad band is observed in the range 3800-3200 cm\(^{-1}\) which is assigned to O-H stretching. The same band in doped ADP, has narrowed down which is probably due to the addition of L-histidine and the elimination of water molecule in the crystal. So, in the higher wave number region the pure N-H stretch of histidine appears as a sharp peak at 3223 cm\(^{-1}\). The P-O-H vibrations give rise to peaks at 1098 and 910 cm\(^{-1}\). The PO\(_4\) vibrations occur at 544 and 470 cm\(^{-1}\) in pure ADP and these peaks in the case of doped ADP seem to have suffered an intensity diminution suggesting that the dominant COO\(^{-}\) vibrations of L-histidine must have caused this change. So from the FTIR spectrum of pure and doped ADP 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-histidine in ADP has brought about this shift.

3.4 UV-VIS spectral studies

The UV-VIS spectrum of the crystal was recorded in the region 190-1200 nm using Perkin Elmer Mode-Lambda 35 spectrometer. Pure ADP crystals have more absorbance in the entire spectral range in comparison with the doped specimen as shown in Fig. 7. For doped ADP, better lower cut-off wavelength is noted. The transparency of the doped crystal is better thereby enabling it to be a good candidate for electro-optic applications and also SHG efficient.

3.5 Microhardness test

Microhardness tests are useful to find the mechanical hardness of the crystal grown. To estimate the threshold mechanical stress that the crystal can withstand samples of pure ADP and L-histidine doped ADP were indented with Vickers pyramidal indenter having an optical angle of 136° between the opposite pyramidal. Observations of the various indentation tests were done using the Metallux-II Metallurgical Microscope. An indentation time of 10 s was applied...
uniformly for loads 20 to 100 g. The hardness values of the cut and polished crystal samples were found to increase slowly with the applied loads. Further application of higher loads showed that the hardness value sharply increased and developed mild cracks due to the attainment of the threshold mechanical stress. The hardness values were calculated using the formula:

\[ H_v = \frac{1.8544P}{D^2} \text{ kg mm}^2 \]

where \( H_v \) is the Vickers hardness number, \( P \) is the indenter load in g and \( D \) is the diagonal length of the impression in mm. The microhardness value was taken as the average of the several impressions made with both diagonals being measured. A plot drawn between the hardness value and corresponding load is shown in Fig. 8. From Fig. 8, it is observed that the hardness of the pure ADP is lesser than that of the doped ADP crystals. Higher hardness value for doped ADP grown crystal indicates that greater stress is required to form dislocation.

3.6 Kurtz and Perry powder SHG test

Kurtz second harmonic efficiency test (SHG) is performed for the comprehensive analysis of second order nonlinearity. The non-linear optical property of the grown samples of ADP and L-histidine doped ADP is determined. In the present work, a single shot mode of 8 ns laser with a spot radius of 1 mm was used. The experimental set-up used a mirror and 50/50 beam splitter, to generate a beam with pulse energy of 0.68 J. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The second harmonic output was generated from the irradiated powder sample of doped ADP by a pulsed laser beam. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. The relative conversion efficiency was calculated from the output power of L-histidine doped ADP crystals with reference to pure ADP crystal output power. When a laser input of 0.68 J was passed through pure and doped ADP, it is found that the output power is 3.6 mJ and 6.8 mJ, respectively. Thus, the SHG efficiency of the L-histidine doped ADP crystal is nearly 1.88 times greater than that of pure ADP.

3.7 Thermal analysis

Thermal analysis of the pure and 0.1 mol% L-histidine doped ADP crystals was done by
recording the TGA curve using Perkin Elmer TGA7 at a heating rate of 20° C/min under nitrogen atmosphere to determine the thermal stability of the crystal. The TGA curves of pure and doped ADP samples are shown in Fig. 9. The recorded TGA curve of pure ADP shows maximum 18% weight loss in the temperature range 41-325°C, which is due to the decomposition of ADP, liberation of ammonium and water molecules. The above study reveals that pure ADP is thermally stable up to 230°C, after which the sample undergoes an appreciable weight loss. For L-histidine doped ADP crystals, the weight loss is about 15.74% in the temperature range 41-350°C and this corresponds to loss of water molecules. So in case of L-histidine doped ADP crystals, decomposition temperature is increased to 250°C. This marginal increase in the decomposition temperature for the doped ADP crystal, suggests that the substitution of amino acid namely L-histidine has increased the thermal stability of the grown crystal.

4 Conclusions

Optical quality, colourless and transparent single crystals of pure and L-histidine doped ADP were grown employing slow evaporation solution growth technique. Single crystal X-ray diffraction studies reveal that the tetragonal structure of ADP is preserved and that the lattice parameter of doped ADP crystal is slightly changed. The FT-IR spectral studies confirm the presence of all the functional groups in the grown crystal. The optical transmission spectrum shows good transmission in the entire visible region for both the crystals. TGA analysis reveals the different stages of decomposition. The thermal stability of the doped crystals is found to be improved. The microhardness values of doped ADP crystals are found to be increased by the presence of the dopant. The SHG conversion efficiency of doped crystal is 1.88 times higher than that of pure ADP. This result indicates that the grown crystals are useful for device application. It is observed that the addition of L-histidine has enhanced the transparency, thermal stability, microhardness and NLO efficiency of pure ADP crystals.

References