Effect of l-lysine on Growth and Characterization of Ammonium dihydrogen phosphate, a Novel Semi-Organic Crystal

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Abstract

Single crystals of ADP doped with 1% of l-lysine, a semi-organic nonlinear optical (NLO) material, have been grown by slow evaporation method. Good optical quality single crystals with dimensions up to 20 x 5 x 15 mm^3 are obtained. It is observed that growth rate of doped ADP is higher than pure ADP. The grown crystals were characterized by FTIR, UV absorption and microhardness studies. The thermal stability of the crystal was studied by thermo-gravimetric analysis (TGA).

Keywords: ADP–L-lysine doped crystal; FTIR, TGA, microhardness, UV analysis etc.

1. Introduction

Introduction Ammonium dihydrogen phosphate (ADP), a hydrogen bonded compound, belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. These molecular crystals exhibit low-temperature order–disorder phase transitions. Below148.5K, ADP is antiferroelectric and belongs to P_{212121} space symmetry group while above this temperature it becomes paraelectric having a I42d symmetry [1–3]. Ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) are nonlinear optical materials and have 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 [4, 5]. In recent years, various growth methods and apparatus have been continuously developed to improve the crystal quality and the growth rate [6–8]. One of the obvious requirements for an on-linear optical crystal is that it should have excellent optical quality. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage in applications. It is difficult to grow large optical quality crystals of these materials for device application.

Semiorganic nonlinear optical crystals formed by amino acids with inorganic materials possess the combined advantages of high optical nonlinearity of the organic amino acids and the favorable mechanical and thermal properties of inorganic solids. The importance of amino acids in NLO applications is due to the fact that all the amino acids except glycine contain chiral carbon atom and crystallize in noncentrosymmetric space groups. In solid-state, amino acid contains a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH_3^+).

This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO applications. L-lysine, l-valine, l-arginine, l-arginine phosphate, l-threonine, l-threonine acetate, l-histidine, l-hisditine hydrochloride, are some of the examples of the amino acids.

In the present studies, our aim is to investigate the thermal, mechanical and other properties of the single crystals of l-lysine doped ADP crystal. ADP doped with l-lysine crystals of dimension up to 20 x 5 x 15 mm^3 have been grown by slow evaporation method at room temperature, and the Fourier transform infrared (FTIR) analyses, Thermal behavior of crystal, microhardness and UV measurements have been studied and discussed.

2. Experiment

2.1. Material synthesis

Crystal growth the commercially available ADP was used for growth, after repeated recrystallization. Single crystals of pure and l-lysine added ADP were grown using deionized water as a solvent by slow evaporation technique. According to the solubility data [9], 400 ml saturated solution of ADP was prepared and filtered at room temperature and the solution was divided equally into two beakers and it was named as A and B. The beaker A was kept closed with porously sealed cover, then1 mol% of l-lysine was added into the beaker B and it was closed with the same type of covers. Solutions in all the beakers were allowed to evaporate in an identical condition. After seven days, tiny crystals were seen in the beaker B, where as in A, it was observed one day later only. All crystals reached maximum size in 30days. The colourless transparent pure ADP crystals harvested were of size up to 15 x 5 x15 mm^3 and doped crystals of size upto 20 x 5 x15mm^3. It was observed that the growth rate of l-lysine added ADP is faster than the pure ADP and comparably big crystals were obtained in L-lysine added solution. The L-lysine doped ADP is shown in Fig. 1(a). Ammonium dihydrogen phosphate and L-lysine and L-histidine used in the present study were from Merck, India.

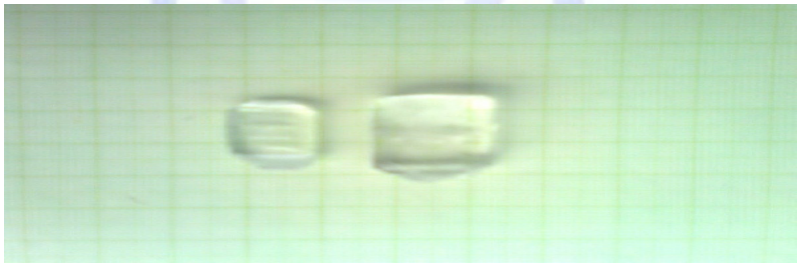

Fig.1. Grown crystals of L-lysine doped ADP

3. Characterization studies

3.1. FTIR analyses

The FT-IR spectrum was recorded for L-lysine doped ADP crystals using JASCOFT-IR410 spectrometer by KBr pellet technique in the range 400–4000 cm^{-1} and is shown in Fig. 2. The effect of AM on the functional groups of the pure ADP crystal has been identified by the spectrum. The broad band in the high-energy region is

due to the O–H vibrations of water, P–O–H group and N–H vibrations of ammonium. The peaks at 1092 and 932 cm^{-1} represent P–O–H vibrations. The PO_4 vibrations give their peaks at 544 and 470 cm^{-1}. The peak at 2370 cm^{-1} is due to the combination of band of vibrations occurring at 1293 and 1290 cm^{-1}. The broadness is generally considered to be due to hydrogen bonding interaction of $H_2PO_4^-$, $COOH^-$ and $NH3^+$ with adjacent molecules. The bending vibrations of water give its peak at 1646 cm^{-1}. The peak at 1402cm^{-1} is due to the bending vibrations of ammonium. In the structure of ADP strong bonding is there between P and O. The addition of l-lysine can make a small change in the hydrogen bonding of the crystals. The changes in the hydrogen bonds make some variations in the stretching vibrations and in the peak positions. Although this spectrum also carries similar features of that of ADP, there is a distinct evidence for the presence of l-lysine in the lattice of ADP. The peaks appearing at 1567 and about 1415 cm^{-1} are due to asymmetric mode of —COO and CQC stretching and symmetric mode of —COO and C–N stretching of l-lysine. In addition, shift in the peak positions of P–O–H and PO_4 vibrations compared to ADP established the presence of the additive in the lattice sites

of ADP.

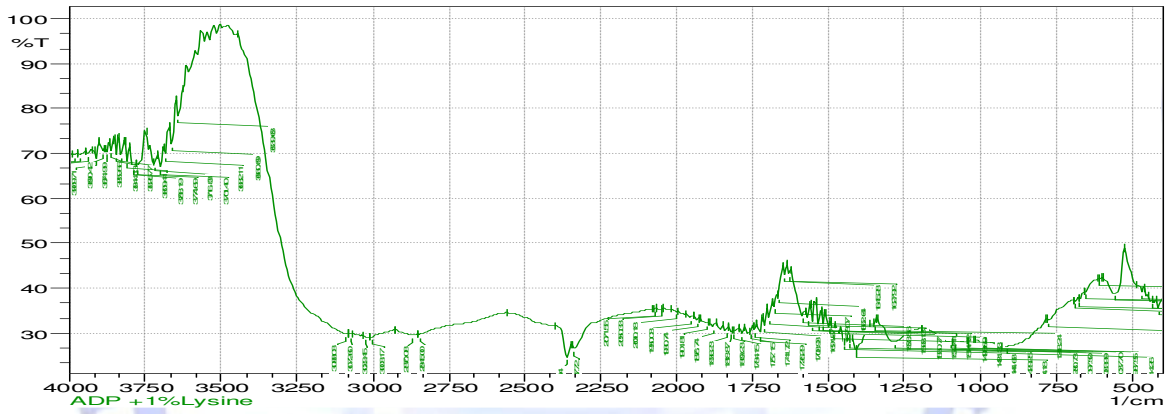

Fig.2. FTIR spectra of L-lysine doped ADP

3.2. Thermal Analysis

TGA of ADP mixed with 10 mole% of BGSN was carried out between room temperature (28℃) and 600℃ at a heating rate of 10 K min^{-1} as shown Fig. 3. The experiment was performed in nitrogen atmosphere. Although the TG trace representing the decomposition temperature of the crystals. It is seen from the TG that the weight loss started for the pure ADP at 195 ℃, a careful examination of DTA thermogram revealed a endothermic peak around 207.5 ℃. After 195 ℃ weight loss started and a steady decrease in weight observed (63.4%) up to 533℃, which may be due to the decomposition of the sample. At temperatures above 595℃, the final stage of decomposition occurs, giving a total loss equal to 90%. The DTA of L-lysine doped ADP was carried out between 28 and 600 ℃ in nitrogen atmosphere using NETZSCH STA 409 PC at a heating rate of 10 K min^{-1}. The DTA trace indicates a strong endothermic starting at 207.5 ℃ due to its melting of the crystal. Hence, from these thermal studies, it is concluded that the crystal can retain texture up to 207.5 ℃. Its application is restricted up to 207.5 ℃ only, which is less

than pure ADP (215℃) but greater than other semi-organic materials like L-alanine cadmium chloride (LACC) (110℃), triallyl thiourea cadmium chloride (ATCC) (101℃), triallyl thiourea cadmium bromide (ATCB) (97 ℃), triallyl thiourea mercury chloride (ATMC) (133 ℃) and allyl thiourea mercury bromide (ATMB) (125 ℃) [10 –14].

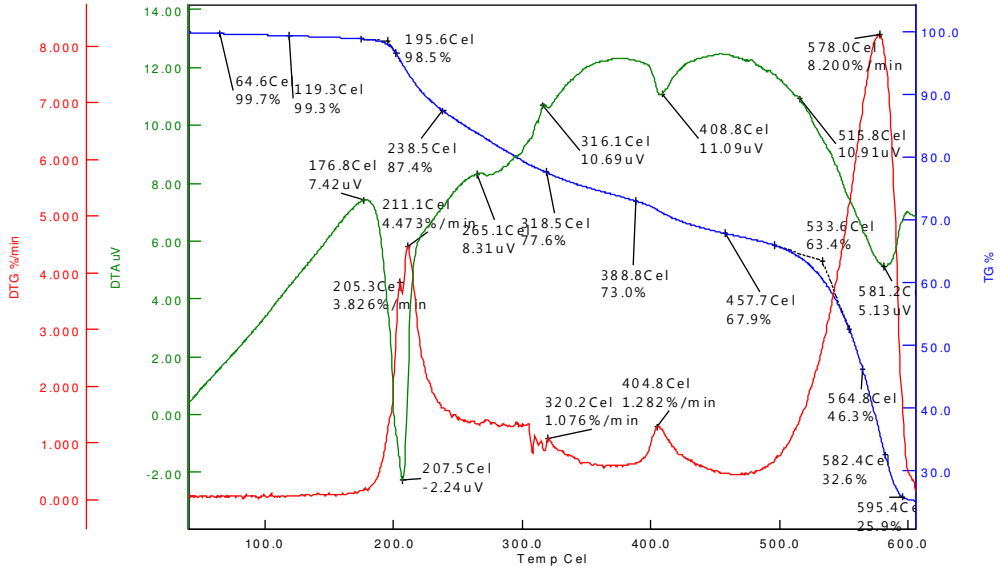

Fig.3. TGA/DTA of ADP doped with 1% L-lysine.

3.3. UV-visible spectral study

Since single crystals are mainly used in optical applications, the optical transmission range and the transparency cutoff are important. Therefore UV-Vis. transmission spectroscopy was carried out using a Shimadzu spectrophotometer. The absorption spectrum of ADP doped with L-lysine is shown in figure 5. A strong absorption peak corresponding to the fundamental absorption appears at 230 nm and the crystal shows the transmittance of 83 % which prove the good optical quality.

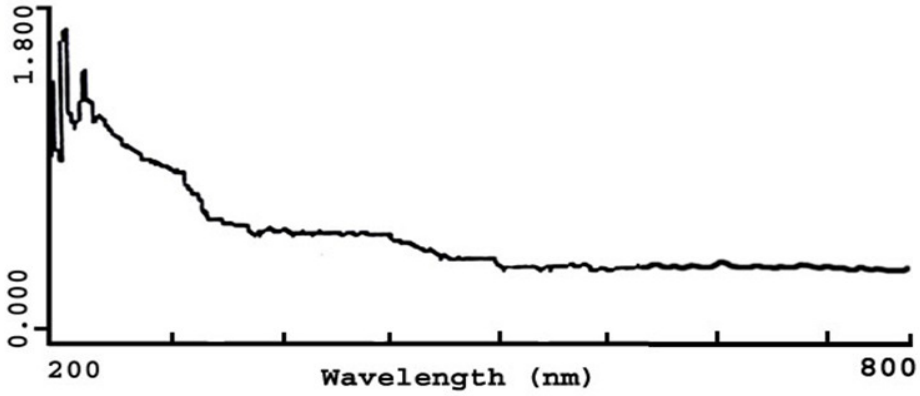

Fig.4. UV–visible absorption spectrum of ADP doped with 1% L-lysine

3.4. Microhardness

The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behavior. A hardness study of

the doped and undoped ADP crystal has been carried out and is reported. It is well known that microhardness is not only a mechanical characteristics but also it has been developed as micro structural investigations method due to fact that microhardness is sensitive to structural parameters as well as to mechanical characterization parameters (Yield stress, modulas of elasticity, some secondary transitions, etc.) The hardness of the material is defined as the resistance it offers to the motion of dislocations, deformation or damage under an applied stress. The general definition of indentation hardness, which relates to the various forms of indentaters, is the ratio of the applied load to the surface area of the indentation. The suitable size of the grown crystal was selected for microhardness studies. Indentations were carried out using Vicker's indenter for varying loads. For each load (p), several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness of the crystals. Vicker's microhardness number was determined using $Hv=1.8544p/d^2$. A plot drawn between the hardness value and corresponding loads is shown in Figure

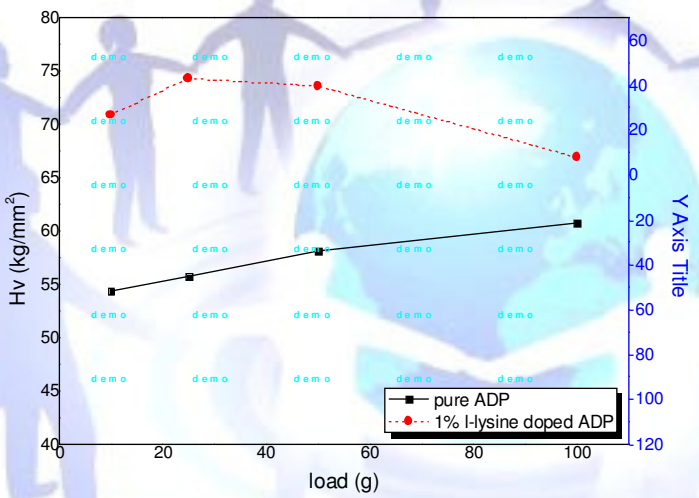

Fig.5. Microhardness of ADP doped with 1% L-lysine.

It is observed from the figure that hardness of L-lysine doped ADP crystal is higher than the pure ADP crystal. Hence the addition of L-lysine in ADP has enhanced the hardness of the crystal. It is also observed that up to 100g no cracks have been observed in doped crystal.

Conclusion:

The L-lysine doped ADP single crystal is synthesized by slow evaporation method. The optically good quality of single crystal of maximum size up to 20 x 5 x 15 mm^3 is obtained. It is observed that the growth rate of doped ADP is greater than pure ADP. FTIR analysis confirms the presence of all functional group. From TGA/DTA analysis it is found that the crystal is thermally stable up to 207.5 ^{0} C. The UV absorption analysis shows a strong absorption peak at 230nm and crystal shows transmittance of 83% which proves a good optical quality.

References

[1] R. Ueda, J. Phys. Soc. Jpn. 3 (1948) 328.

[2] R.O. Keeling and R. Pepinsky, Z. Krist. 106 (1955) 236.

[3] A.A. Khan and W.H. Baur, Acta Cryst. B 29 (1973) 2721.

[4] L. Tenzer, B.C. Frazer and R. Pepinsky, Acta Cryst. 11 (1958) 505.

[5] P. Bennema, Z. Krist. 121 (1965) 312.

[6] B. Dam, P. Bermema and W.J.P. van Enckevort, in: Extended Abstracts 6th Int. Conf. on Crystal Growth, Vol. 4, Moscow, September (1980) p. 18.

[7] H.J. Kolb and J.J. Comer, J. Am. Chem. Soc. 67 (1945) 894.

[8] B. Dam, P. Bennema and W.J.P. van Enckevort, J. Crystal Growth 74 (1986) 118.

[9] D. Eimert, S. Velsko, L. Davis, F. Wang, G. Loiaccono, G. Kennady,IEEE J. Quantum Electron. 25 (1989) 179.

[10] D.R. Yuan, N. Zhang, W.T. Yu, D. Xu, X.T. Tao, M.H. Jiang, Chin. J. Lasers 17 (1990) 332.

[11] D.R. Yuan, N. Zhang, X.T. Tao, D. Xu, X.T. Tao, M.H. Jiang,Chin. Phys. Lett. 7 (1990) 334.

[12] W.B. Hou, D.R. Yuan, D. Xu, N. Zhang, W.T. Yu, M.G. Liu, X.T. Tao, S.Y. Suo, M.H. Jiang, J. Crystal Growth 133 (1993) 71.

[13] Y.P. Tian, C.Y. Duan, C.Y. Zhao, X.Z. You, T.C.W. Mak, Z.Y. Zhang, Inorg. Chem. 36 (1997) 1247.

[14] T. Pal, T. Kar, W. Xin Qiang, Z. Guang Ying, W. Dong, C. Xiu Feng, Y. Zhao He, J. Crystal Growth 235 (2002) 523.