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Synthesis, Growth and Characterization of maleic acid doped ammonium dihydrogen phosphate crystals

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In this paper, single crystals of maleic acid doped Ammonium Dihydrogen Phosphate (ADP-MA) is grown from aqueous solution, employing slow evaporation technique at room temperature. The presence of maleic acid is confirmed by ^{13}C NMR and FTIR analyses. From the single crystal XRD, the crystal belongs to tetragonal system. The UV–Vis–NIR spectral analysis is carried out to confirm the transparency of the ADP-MA crystal. The microhardness of the grown crystals is determined. Thermal stability of the crystals is estimated using thermo gravimetric analysis. The nature of variation of dielectric constant ε′ and dielectric loss D in the frequency range of 50 Hz to 5 MHz is studied and reported. The second harmonic generation (SHG) efficiency of the crystal is found to be 3.44 times than that of ADP. The ADP-MA crystals have negative photoconducting nature.

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1. Introduction

Ammonium dihydrogen orthophosphate (ADP) ($NH_4H_2PO_4$) is an interesting material, and it belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. Studies on Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) crystal still attracts interest because of their unique non–linear optical, dielectric, piezoelectric and antiferroelectric properties and their variety of uses such as electro-optic modulators, harmonic generators and parametric generators. Several research works have been carried out on pure and doped ADP crystals. [1–5] ADP is antiferroelectric below 148.5 K and belongs to P21 21 21 space symmetry group, while above this temperature it becomes paraelectric having I 4/2 d symmetry. ADP belongs to scalenohedral class of tetragonal crystal systems. ADP has unit cell parameters of a = b = 7.510 Å and c = 7.564 Å**.** It is known that, very little amount of additives can strongly suppress the metal ion impurities and promote the crystal quality. Oxalic acid and amino acids as additives in ADP crystals give appreciable change in optical, thermal, dielectric and mechanical behaviors [6-8] 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 semi organic impurities. Inorganic non linear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power. Maleic acid is a dicarboxylic acid, a molecule with two carboxyl groups with chemical formula $HO_2CCHCHCO_2H$. An attempt is made here to find a new useful material by taking maleic acid and ADP in different ratios. In this work, the structural, spectral and optical properties of ADP-MA crystals have been studied and reported.

2. Experimental

2.1 Crystal growth

Analytical reagent grade (AR) samples of ADP $(NH_4)H_2PO_4$ and maleic acid ($C_4H_4O_4$) along with deionized water is used for the growth of single crystals by slow evaporation method. A supersaturated solution is prepared by dissolving 34.5gm of ADP and 11.6gm of maleic acid. The mixture was thoroughly stirred at room temperature and sealed with a porous cover. Nucleation occurs within 3 days and crystals reach a large size in 14 days. The pH of the solution is noted to be 3. The grown crystals were hard, colorless and exhibit well defined faces. The size of the crystal is 16x14x5.29 mm. Photograph of the crystal as grown is given in Fig.1.

F*ig.1.Photograph of the as grown crystal of ADP-MA.*

3. Results and discussion

3.1 NMR analysis

Carbon is the core element in organic chemistry and hence ^{13}C NMR plays an important role in determining the structure of unknown organic molecules and the study of organic reactions and processes. In the present study, ^{13}C NMR spectral analysis is made on the powder form of the ADP-MA crystal dissolved in D_2O solvent and recorded using AMX 400 NMR analyzer at 27°C. The ^{13}C NMR spectrum of ADP-MA is shown in Fig.2 with reference to literature the standard maleic acid ^{13}C NMR spectrum produces characteristics peaks at 166.53 ppm and 129.99 ppm corresponding to HO-C and C=C bond.

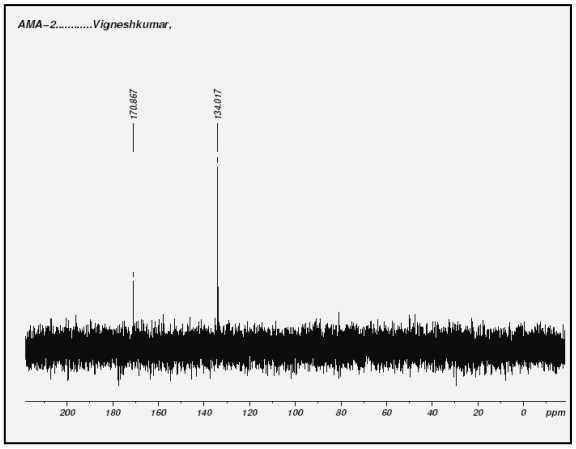

Fig.2. ^{13}C NMR spectrum of ADP-MA.

In our recorded spectrum peaks are observed at 170.86 ppm and 134.01 ppm similar to that of the standard spectrum. Hence the presence of maleic acid in the grown crystal is confirmed from the recorded NMR spectrum.

3.2 Single crystal and powder X-Ray diffraction

Single crystal X-ray diffraction studies of ADP-MA crystals were carried out using Bruker Kappa APEX II single X-ray diffractometer to determine the cell parameters. The ADP-MA crystals crystallize in tetragonal crystal system with space group I-42d. The unit cell parameters for the ADP-MA crystal are a=b=7.553Å, c=7.594 Å α=β=γ= 90°. It is seen from comparison with values reported in literature for ADP there is only a slight variation in the lattice parameters. This implies that the grown crystal retains its original structure and the slight variations may be due to the influence of maleic acid in the ADP crystal lattice.

The powder X-ray diffraction pattern is recorded on a Bruker-35kV Copper K-alpha radiation and Fig.3 shows the results obtained for all molar concentrations. The ground fine powder is scanned in steps of 0.001 °/min over a 2θ range of 10 – 80° [9]. The preferred orientation peaks of ADP-MA crystals are (1 0 1), (2 0 0), (1 1 2) and (2 0 2). From the XRD spectrum of ADP-MA, it is seen that there are no additional peaks, but only a strong increase in the intensity of the peaks.

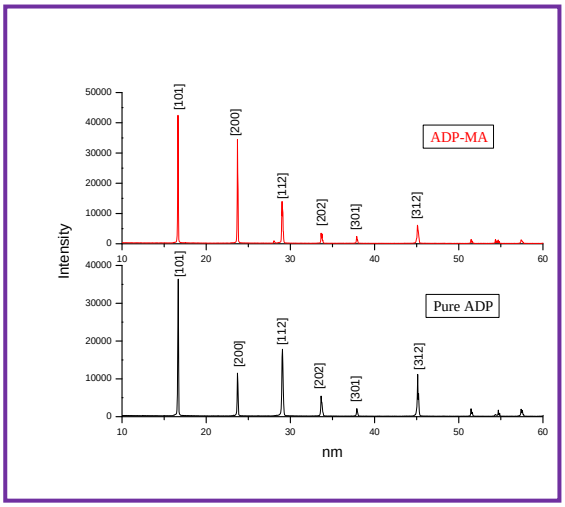

Fig.3. Powder XRD of ADP-MA Crystals.

3.3 FTIR analysis

The FTIR spectra of pure ADP and ADP-MA are recorded using Perkin Elmer model RXI Spectrometer in the range 400-4000cm^{-1} by KBr pellet technique. The spectrum is shown in Fig.4. The broad band is due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium [10]. The broadness is generally considered to be due to hydrogen bonding interaction of H_2PO^{-4}, $COOH^-$ and NH^{3+} with adjacent molecules. It is seen that usually in the region 4000cm^{-1} peak occurs due to NH^{3+} vibrations. In our case these vibrations seen to have smoothened out probably due to the influence of maleic acid in the lattice. The peak at 2370cm^{-1} is due to the combination of band of vibrations occurring at 1281 and 1199 cm^{-1}. Also the peak at 1636cm^{-1} assigned to C=O stretching is shifted to 1716cm^{-1}, a higher frequency region. This shifting establishes the presence of additive in the lattice sites of ADP. The peak at 1402cm^{-1} is due to bending vibrations of ammonium. The peaks at 1094 and 916cm^{-1} represent P-O-H vibrations. The PO_4 vibrations give their peaks at 544 and 470cm^{-1} In the structure of ADP strong bonding is there between P and O. The presence of maleic acid makes a small change in the hydrogen bonds leading to some variations in the values of stretching vibrations and in the intensity of the peaks. So from the observation of the FTIR spectra it is concluded that maleic acid has influenced the nature of ADP.

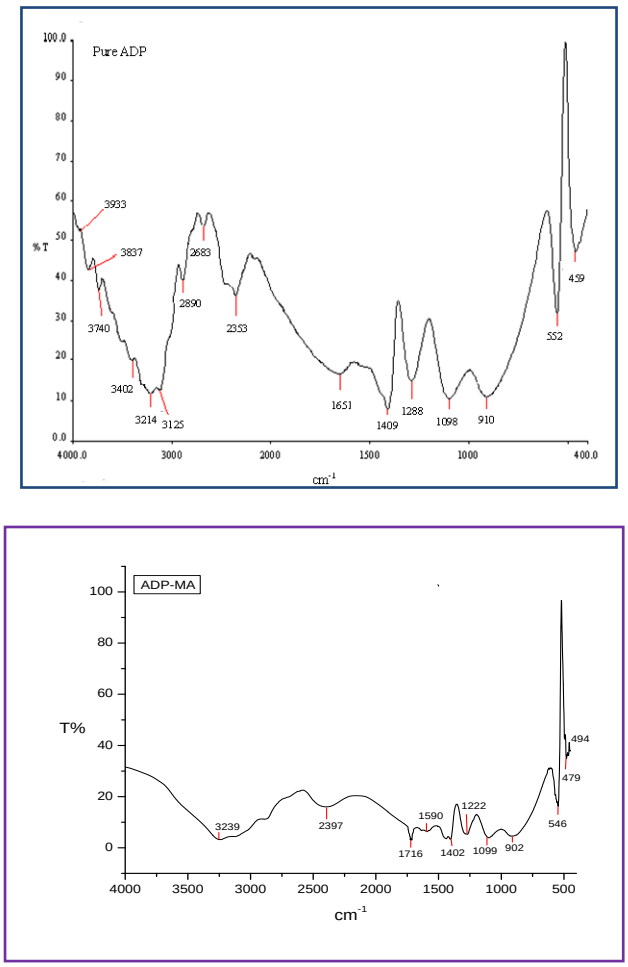

Fig. 4. FT-IR Spectrum of ADP-MA crystals.

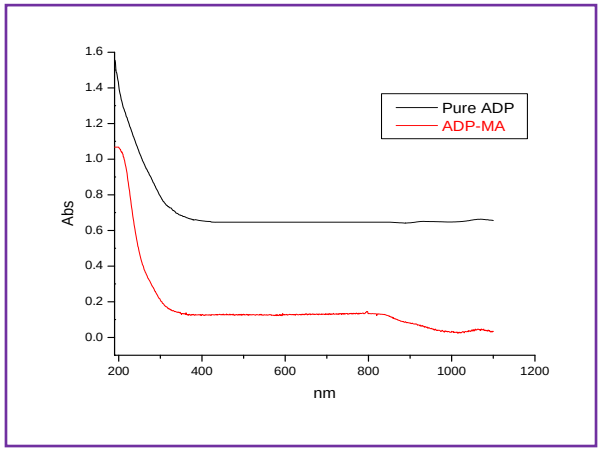

Fig.5. UV-VIS Spectra of ADP-MA crystals.

3.4 UV-VIS spectral studies

The UV-VIS spectrum of the crystal is recorded in the region 190 to 1200 nm using Perkin Elmer Model-Lambda 35 spectrometer. As seen from the spectrum shown in Fig.5. ADP-MA crystals have minimum absorbance in the entire spectral range compared to pure ADP crystals. Since the absorbance is less it suggests an enhanced transmittance than pure ADP. The addition of the dopant therefore has improved the optical quality of the crystal.

3.5 Microhardness test

The fastest and simplest method to evaluate the mechanical properties of the crystals is the hardness measurement. ADP-MA crystals which are free from cracks and transparent were selected for microhardness measurements [11]. Micro hardness studies were carried out for the ADP-MA crystals using Leitz Wetzlar Vickers micro hardness tester by varying the applied load from 25 g to 100 g. The indentation time was kept as 5sec for all the loads. Fig.6 shows the variation of Vickers hardness number with load being applied with respect to (001) plane of the ADP-MA crystals. The hardness of the crystals in general is found to increase with increasing load. This is probably due to strengthening of ADP by the influence of maleic acid in the lattice.

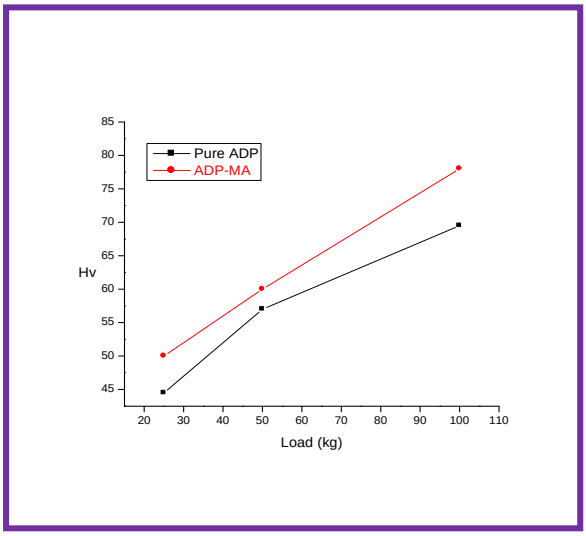

Fig.6. Plot for Vickers Hardness of ADP-MA crystals.

3.6 Thermal studies

Single crystals ADP-MA crystals were subjected to thermo gravimetric analysis (TGA) using Perkin Elmer TGA7 instrument, in the nitrogen atmosphere at a heating rate of 20° C/min. Fig.7 shows the resulting TGA traces of the ADP-MA crystals. The decomposition of the material starts at 220º C. The material is found to be thermally stable up to 220º C which agrees with the reported values in literature [12].

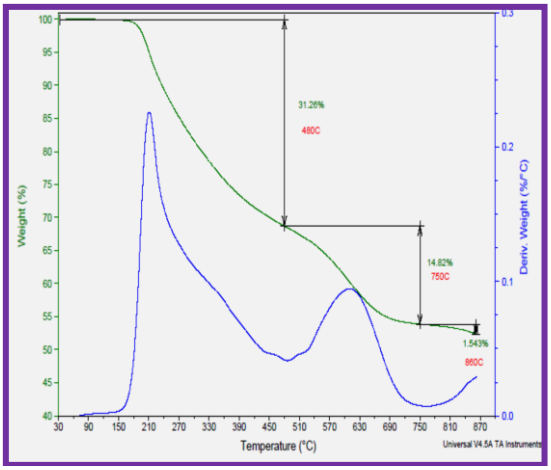

Fig.7.Thermo-gravimetric curve of ADP-MA crystals.

3.7 Dielectric studies

The dielectric study of ADP-MA single crystals were carried out using the instrument Multi-frequency LCR meter (LCR-800 SERIES). The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at room temperature. The dielectric constant is high at low frequencies and decreases with the applied frequency.

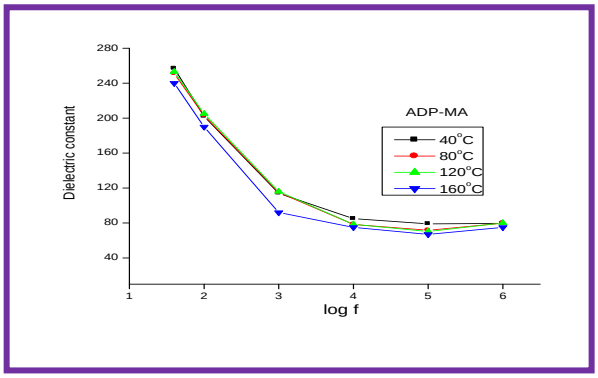

Fig.8. Variation of dielectric constant with frequency at different temperature.

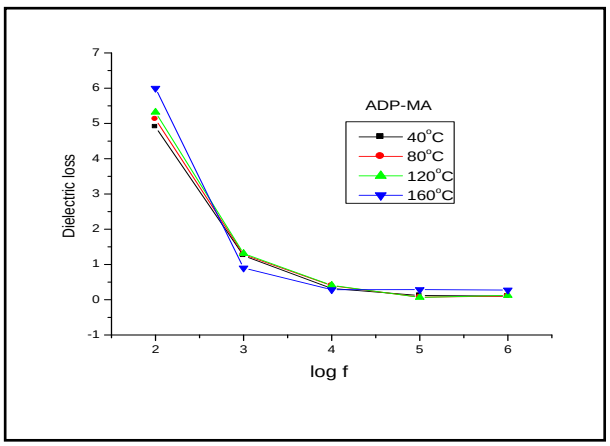

Fig. 9. Variation of dielectric loss with frequency at different temperature.

The plot of dielectric constant (ε_r) versus log frequency and the variation of dielectric loss with frequency for ADP-MA crystals are shown in Fig.8 and Fig. 9. The low dielectric loss with high frequency of the ADP-MA crystals proves that these materials possess enhanced optical quality with lesser defects [13]. This characteristic is an important parameter for nonlinear optical materials for useful applications.

3.8 Photoconductivity studies

Photoconductivity studies were carried out at room temperature for the pure and doped ADP crystals, using Keithley 485 picoammeter. The dark current was recorded for the samples by keeping them unexposed to any radiation. The light from the halogen lamp (100 W) containing iodine vapour is focused on the respective samples and the photo currents of the samples were measured. The DC inputs were increased in steps and the photo currents were measured. Fig.10 shows the plot of photocurrent and dark current as a function of the applied field for ADP-MA crystals. It is observed from the plot that dark current (I_d) and photo current (I_p) of the sample increase linearly with the applied field and the dark current is always higher than the photocurrent, hence it is concluded that ADP-MA shows negative photoconductivity [14]. This phenomenon can be attributed to reduction of mobile charge carriers by the absorption of photons.

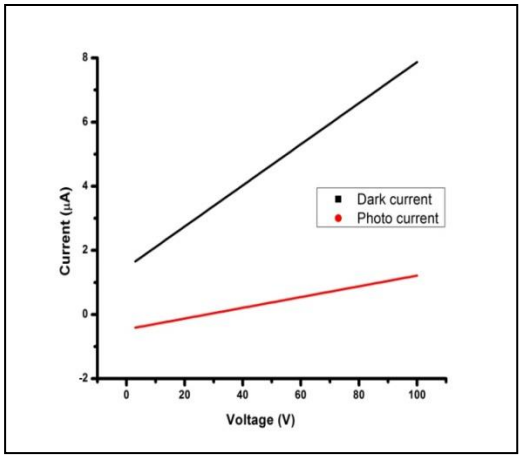

Fig.10. Variation of dark and photo current with applied field for ADP-MA.

3.9 NLO studies

Nonlinear optical (NLO) property of pure and doped ADP were found by subjecting them to Kurtz powder SHG test using the Nd:YAG Q-switched laser beam [15]. The sample of ADP-MA is illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2mJ. The second harmonic signal generation in the crystals was confirmed by the emission of green radiation from the crystals. The second harmonic signal of 12.4 mJ was obtained for ADP-MA crystal with reference to pure ADP (3.6mJ). Thus, the SHG efficiency of ADP-MA crystal is

3.4 times respectively higher that of pure ADP. The ADP-MA crystals are found to have efficiency higher than that of pure ADP. Thus, it is concluded that maleic acid has definitely improved the NLO efficiency of pure ADP crystals.

4. Conclusion

Single crystals of ADP-MA crystal is grown successfully by slow evaporation technique. ^{13}C NMR studies have confirmed the presence of the maleic acid in the crystal lattice. Single crystal X-ray diffraction studies were carried out, and the lattice parameters are determined. Optical absorption studies show that the sample has minimum absorption in the entire visible region. The hardness of ADP-MA crystal is verified. The photoconductivity studies of ADP-MA crystal show that it possess negative photoconductivity. The dielectric loss with frequency of ADP-MA crystal proves that these materials possess enhanced optical quality with lesser defects. Thermal studies reveal that the sample is thermally stable upto 220^{o}C. NLO studies prove that the maleic acid has increased the SHG efficiency of pure ADP. The presence of maleic acid has improved the nonlinear optical (NLO) nature of ADP and hence the ADP-MA crystal can be used as a promising material for academic and industrial use.

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