ISSN 2229-5518

C NONLINEAR OPTICAL MATERIAL: CRYSTAL GROWTH RIZATION

Optical, Thermal and NLO actions of Pure and Neem Leaves Extract Doped Ammonium Dihydrogen Phosphate Crystal

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Abstract: Ammonium dihydrogen phosphate (ADP) (NH4H2PO4) is an excellent inorganic non linear optical material with different device applications. In this present work, ADP crystal and neem leaves extract doped ADP (NADP) crystal has been grown by slow evaporation solution growth technique. The grown crystals were characterized by powder X-ray diffractometion (XRD) method. The XRD pattern confirms the crystalline nature and the purity of the grown crystals. UV-Vis spectrum showed that good optical quality of ADP & NADP crystals. The functional group frequencies were identified and assigned from FTIR spectra.The emission spectra of the crystals were recorded using spectrofluorometer. The emission peaks of pure ADP and NADP were absorbed at 452 nm & 530 nm respectively.The optical band gap energy were estimated as 2.7468 eV & 2.3425 eV. Nonlinear optic measurement has been used to find the SHG efficiency. Thermal stability increases in ADP crystal by an organic additive of neem leaves extract has been determined by Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). Some novel results of a combined sequential study of growth spirals on the basal surface of the ADP and NADP crystals by Scanning Electron Microscopy (SEM) is presented and discussed. Using Energy Dispersive X-ray Spectroscopy (EDAX), presence of element with weight percentage has been calculated.

Index Terms: Fluorescence, FTIR, ADP, NADP, NLO, UV-Vis, XRD, TG-DTA, SEM- EDAX

1 INTRODUCTION

Ammonium Dihydrogen Phosphate (ADP) is a well known inorganic material. It has aroused considerable interest amongst several research workers because of its wide frequency conversion, good UV transmission, high damage threshold against high power laser and high birefringence, though its NLO coefficients are relatively fashionable [1],[2]. Neem is a natural antibiotic, which kill or stop the growth of microorganisms including both bacteria and fungi. In medical chemistry, antibacterial is chemically semi synthetic modifications of various natural compounds[3],[4].Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) is a technologically important inorganic crystal and studies on ADP crystal attract interest because of their unique piezo-electric, antiferro-eletric, electro-optic, di- electric and nonlinear optical properties [5],[6]. From this motivation we select ADP and Neem extract as additive have been selected to this work. The grown pure ADP and neem leaves extract doped ADP (NADP) crystal has been subjected Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis Spectroscopy, X-ray Diffraction (XRD) Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), Nonlinear optic measurement (NLO), Fluorescence Spectroscopy, Thermo gravimetric and differential thermal analysis (TGA-DTA).

2 MATERIALS AND METHODS

2.1 GROWTH TECHNIQUE

In the present study Ammonium Dihydrogen Phosphate of AR (Merck) grade powder was selected as source material. This Powder was initially added with double distilled water and stirred well using magnetic stirrer. Then the prepared solution was filtered with micro filter paper with 0.1 μm porosity and transferred into two clean Petri dishes. One Petridis have pure ADP solution (100 ml) was allowed to evaporate at room temperature and another Petridis have pure ADP solution and neem leaves extract (100ml Pure ADP solution along with 10 ml Neem extract were added) i.e.10:1 ratio. Both ADP and NADP crystals were grown by slow evaporation aqueous solution growth technique at room temperature. Within four days the nucleation takes place and a seed crystal in Petri dishes has been obtained. The good quality seed crystals were harvested and again placed in the respective

ISSN 2229-5518

solutions for the even growth of considerable sizes of the crystal. After completion of growth run, the crystals were harvested in 3 weeks as shown in Fig.1.with an average size of 7x4x3mm ADP and 8x7x5mm NADP crystals.

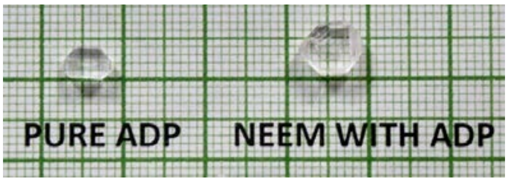

Fig.1. Pure ADP and NADP crystals

2.2 CHARACTERIZATION

The harvested single crystals have been analyzed by different instrumentation methods in order to check its suitability for device fabrication. The Powder X-ray diffraction (XRD) analysis has been carried out for the as grown crystals of ADP and NADP using SHIMADZU Model XRD 6000 made in Japan.The powdered samples were scanned in the range 10-90° at a scan rate of 2°/min. The Fourier transform infrared spectrums were recorded by SHIMADZU Model IR Perstege 21 made in Japan. The presences of functional groups were identified from this spectral analysis in the range 4000-750 cm^{-1}. The UV-Vis spectrums were recorded in the range 200-800 nm using JASCO - Vis NIR Model V-670 spectrometer. The emission spectra of ADP and NADP crystals were recorded in the range 250-700 nm using PERKIN ELMER Model LS-45 Spectrofluorometer. Non linear optic measurements were carried out by using Kurtz powder technique. A Q-switched Nd:YAG laser beam of 1064nm wavelength with 1.9 mJ/pulse input power, 8ns pulse width and repetition rate 10Hz was used to estimate SHG efficiency of the as grown crystals.The Thermal stability of the samples were tested using thermo gravimetric analysis (TGA) and Differential thermo gram analysis (DTA) using SIINT Model TG/DTA 6200 made in Japan. The analyses were carried out between 30°C and 800°C in the nitrogen atmosphere at a heating rate of 20°C min^{-1}. The Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDAX) were performed using the JEOL Model JSM – 6390 made in Japan.

3 RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

Fig. 2. Shows the X-ray powder diffraction pattern of the grown crystal of ADP & NADP. The sharp and well defined Bragg's peaks at specific 2θ angles confirm the crystalline nature and purity of the crystal. The lattice parameter values were calculated and compared with JCPDS values(Table1).The obtained lattice parameter values confirmed that the addition of neem did not change the tetragonal structure of ADP, having space group $I42dd$.The lattice parameters are in good agreement with the reported values [7].

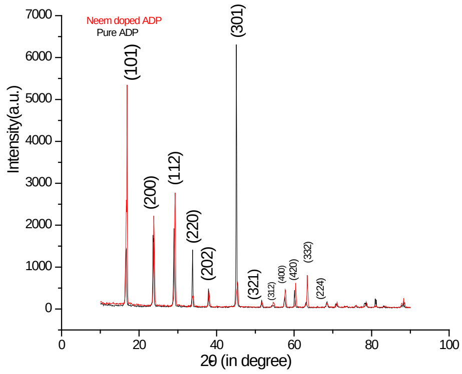

Fig.2. Powder X-Ray diffraction pattern of pure ADP and NADP.

TABLE 1
LATTICE PARAMETERS OF PURE AND DOPED ADP CRYSTALS.

S.No	Lattice parameter In Å units	Pure ADP calculated value	NADP calculated Value	JCPDS values for pure ADP
1	A	7.5006	7.5031	7.499
2	B	7.5006	7.5031	7.499
3	C	7.5490	7.5498	7.549
4	Volume ($Å^3$)	424.6991	425.0273	424.5180

3.2 UV-Vis ANALYSIS

The large transmission in the entire visible region enables ADP and NADP to be a good material for electro – optic and NLO applications [8]. Fig.3. shows the absorbance spectra of the grown crystals. The lower cut-off wavelength is found to be nearly 250 nm. The high transmission in the entire visible region suggests its suitability for second harmonic generation. Good transparency in UV-visible region is due to the delocalization of electrons of bonded oxygen long P=O which is expected to largely destroy the double bond character. The presence of low cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity [9].

ISSN 2229-5518

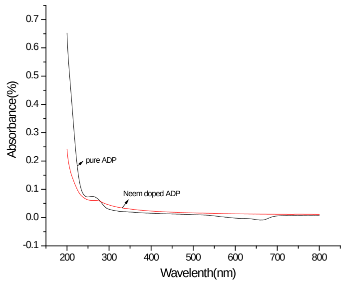

Fig. 3.UV- Vis spectrum of Pure and Doped ADP crystals.

3.3 FTIR STUDIES

The FTIR analysis is a technique that provides information about the chemical bonding or molecular structure of materials. The functional groups of pure ADP and NADP crystals involved in vibration frequency have been identified using FTIR spectroscopy. The grown ADP and NADP FTIR spectrum were taken between wave number 750 to 4000 cm^{-1} shown in Fig.4. The absorption peaks correspond to the molecular group vibrations are tabulated in table 2. The relations of molecular group vibrations and the characteristics absorption bands were assigned according to the theories of infrared spectra [10]. In the spectrum of pure ADP and NADP, the broad band around 3116 and 3122 cm^{-1} was due to the O-H vibrations of water. The band at 2880 cm^{-1} was assigned to combination band of stretching of vibration [11]. The broadness was due to the hydrogen bonding interaction with adjacent molecules. The NH_2 bending vibration gave the peaks at 1440, 1448 cm^{-1}. The peak at 1404 cm^{-1} was due to the bending vibration of ammonium. The very strong band at 1288 cm^{-1} was due to the combination of the asymmetric stretching vibration of PO_4 with lattice. The peaks at 1095 and 918cm^{-1} represented P-O-H vibrations. A strong absorbption peak in 2360 cm^{-1} could be the evidence for neem leave extract doped into the crystal site.

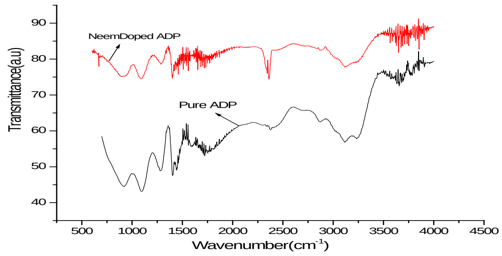

Fig. 4. FTIR Spectrum of ADP and NADP.

TABLE 2

VIBRATIONAL BAND ASSIGNMENTS OF PURE ADP & NADP CRYSTALS.

S. No	Observed FTIR Frequencies (cm^{-1}) for pure ADP	Observed FTIR Frequencies (cm^{-1}) for NADP	Vibrational Assignments
1	3116	3122	O-H Stretching and Water Bending (O-H stretching)
2	2880	2875	Combination bond of Vibration
3	2376	2360	Combination band of stretching
4	1440	1448	Bond vibration of NH2
5	1404	1404	Bending Vibration of Ammonia
6	1284	1288	P-O Stretching Vibration
7	1095	1091	P-O-H Stretching(Vibration)
8	918	896	P-O-H Vibration

3.4 FLUORESCENCE STUDIES

The spectrum recorded by the emission of photo generated minority carriers is a direct way to measure the band gap energy [12]. Fig.5. shows the emission spectrum of ADP and NADP. The peaks at 452 nm and 530 nm were observed in the emission spectrum as shown in Fig.5. Band gap energy of ADP and NADP crystals were calculated using the formula Eg= hc/λe. Where h, c and e are constant λ is the wavelength of fluorescence. The calculated band gap energy of pure ADP crystal is 2.7468 eV and NADP is 2.3425 eV.

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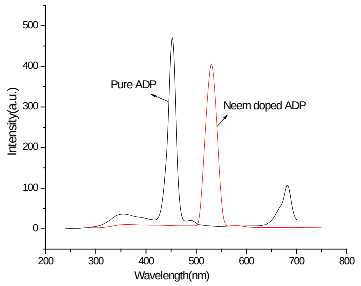

Fig.5.Emission spectrum of ADP and NADP

3.5 KURTZ AND PERRY POWDER SHG TEST

The grown crystals of pure ADP and NADP were grounded into a fine powder and then packed in a micro-capillary of uniform bore and exposed to laser radiation. The fundamental input radiation (1064nm) was separated or filtered by a monochromator and the output was measured. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R5 109). SHG was confirmed by the emission of green light. Using the Potassium dihydrogen phosphate (KDP) crystalline powder as reference material, the output of SHG signal were compared and found that the SHG conversion efficiency of pure ADP is 1.23 times that of KDP and NADP is 1.06 times that of KDP.

3.6THERMO-GRAVIMETRIC & DIFFERENTIAL THERMAL ANALYSIS

Fig.6. and Fig.7.Shows Thermo gravimetric and differential thermal analyses give information regarding phase transition and different stages of decomposition of crystals. In TGA, there is no weight loss up to nearly 200°C for both ADP and NADP crystals. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. However, above this temperature, weight loss has been observed. In the DTA curve for NADP crystals weight loss is lower than ADP crystal.

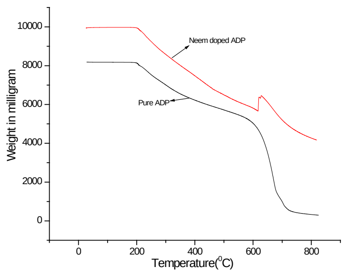

Fig.6.TGA curves of pure ADP and NADP Crystals.

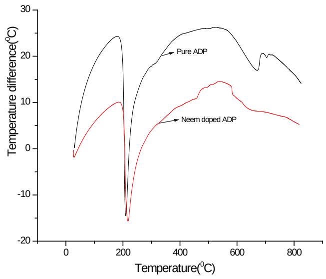

Fig.7. DTA curves of pure ADP and NADP crystals.

3.7 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

SEM images were shown in the Fig.8.and Fig.9. for ADP and NADP crystals. The surfaces of the crystals at a higher magnification, showing that the surfaces of both crystals are rough. The slight change in NADP SEM structure prove that the presence of dopant.

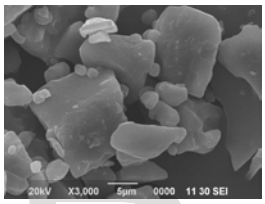

Fig.8.SEM image of pure ADP crystal.

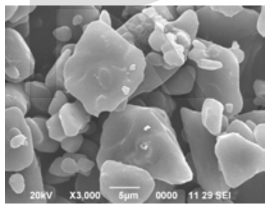

Fig.9. SEM image of NADP crystal.

3.8 ENERGY DISPERSIVE X-RAY DIFFRACTION (EDAX) ANALYSIS

Fig.10. and Fig.11 shows the Energy Dispersive X-ray spectrum analysis of pure ADP and NADP crystals. From EDAX spectrum the chemical composition weight has been calculated. The estimated percentage of P and O in pure ADP and NADP crystals are shown in table 3.

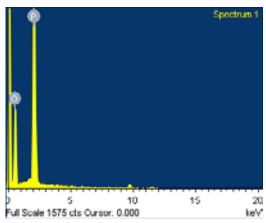

Fig.10 .EDAX spectrum of pure ADP crystal.

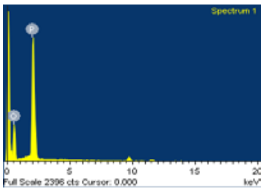

Fig.11. EDAX spectrum of NADP crystal.

TABLE 3
ESTIMATED WEIGHT PERCENTAGE OF PURE ADP & NADP CRYSTAL

S. No	Element	Pure ADP		NADP	
		Weight %	Atomic %	Weight %	Atomic %
1	O K	55.62	70.81	57.28	72.19
2	P K	44.38	29.19	42.72	27.81
3	Total	100	100	100	100

4 CONCLUSION

Pure ADP and organic impurity neem leaves extract doped ADP (NADP) crystals were grown using slow evaporation technique in room temperature. The X-ray diffraction analysis determines the incorporation of neem leaves extract into ADP crystal lattice and the sharp well defined Bragg's peaks confirm the crystalline nature of the materials. FTIR analysis confirms the presence of organic additive neem leaves extract in Ammonium dihydrogen phosphate (ADP). The Fluorescence behavior of the crystals was determined and the SHG efficiency also calculated. The decomposition of these crystals has been studied by Thermal Analysis. The addition of organic impurity increased the thermal stability of ADP crystal. SEM reveals that the external surface of pure ADP and NADP crystals. The presence of chemical composition has been identified by Energy Dispersive X-ray Spectroscopy and its weight percentage has been calculated. From the results, it can be considered that the ADP and NADP crystals were candidate for fluorescence and NLO applications with limited level.

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