Structural, Optical and Mechanical properties of pure and EDTA doped ADP crystals

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Abstract

Pure ammonium dihydrogen phosphate (ADP) and Ethylene diamine tetra acetic acid (EDTA) doped ammonium dihydrogen phosphate crystals were grown from aqueous solution by natural evaporation process. The concentration of dopants in the mother solution varied from 2.5 to 20 M%. The grown crystals were characterized by UV-visible spectroscopy and microhardness analysis. Crystal structure has been studied by powder X-ray diffraction. Pure and doped crystals both possessed tetragonal structure. Some crystals were undertaken for radiation studies. The UV-visible spectroscopy studies reveal that the doped ADP crystals have high transmittance as compared to pure ADP crystals. Microhardness studies indicate the mechanical strength of the doped and irradiated crystals are not good.

Keywords: ADP, EDTA, Slow evaporation, Microhardness

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1. INTRODUCTION

In the last decade the numerous applications of the nonlinear optical (NLO) crystals have been discussed in the field of science and technology [1,2].But recent interest is focused on the development of the properties of the new NLO materials. Ammonium Dihydrogen Phosphate (ADP) is a well known NLO material which also has many interesting ferroelectric and antiferroelectric properties. ADP was one among the earliest materials which were exploited for their NLO properties. They are still widely used as nonlinear optic devices and are the choicest electro-optic materials having wide practical applications [3]. Several researchers have carried out a lot of studies on pure and doped ADP crystals [4]. In the crystal growth, the growth promoting effect is observed in the presence of organic additives [5-7] as well as inorganic additives [8,9]. In addition, the minute amounts of additives such as KCl and EDTA can effectively suppress the metal ions and promote the crystal quality [9,10]. With the aim of discovering new useful NLO material, in our work, the crystals of ADP were grown by solution growth technique by slow evaporation method at room temperature. Presence of EDTA as dopant in different molar concentration plays a vital role in altering the various properties of the parent crystal.

2. EXPERIMENTAL

2.1 Crystal Growth

The pure ADP and EDTA (AR grade) doped ADP crystals were grown by slow evaporation method. ADP was added with EDTA separately each in six different ADP: impurity molar ratios, viz 1:0.000 (pure ADP), 1:0.025, 1:0.05, 1:0.075, 1:0.100 and 1:0.200. The impurity was dissolved in 3.6M solution of ADP. Supersaturated aqueous solution of the mixture was prepared in a 50 ml beaker and allowed to equilibrate at the desired temperature. The crystals were grown in unstirred condition and the whole set up is kept at room temperature.. The grown crystals are under taken for different studies and some of the crystals were irradiated with THERATRON 780C providing γ radiation of energy 1.25 MeV with dose irradiate 19.5 Gy/hr.

2.2 RESULTS AND DISCUSSION

2.2.1 Powder X-ray diffraction analysis

Fig 2 shows the powder XRD patterns of pure and EDTA doped ADP crystals. PXRD studies were carried out using Rich Seifert X-ray diffractometer employing CuKα (1.54056Å) radiation. The powder sample was scanned over the range 10-60^o at a scan rate of 1^o/min to study the crystallinity of the grown crystal. From the diffraction pattern it was observed that the diffracted peaks are same in pure and EDTA doped ADP crystals in different molar ratios. The observed prominent peaks of pure and doped ADP are (1 0 1),(2 0 0), (1 1 2), (2 0 2), (3 0 1) and (3 1 2) but the intensities of the diffracted peaks are found to be varied. It reveals that the structure of ADP is not distorted when EDTA of different molar ratios is added with ADP. X-ray diffraction studies confirmed the tetragonal structure with the unit cell parameters a, b and c values are agree well with the JCPDS (89-7401) values as shown in the table 1.

System	a(Å)	b(Å)	c(Å)	VOL (Å)^3
JCPDS	7.479	7.479	7.516	420.41
Previous reported Values [11]	7.510	7.510	7.564	426.61
1:0.000 (Pure ADP)	7.552	7.552	7.52	427.21
1:0.025	7.541	7.541	7.511	427.15
1:0.05	7.537	7.537	7.517	427.01
1:0.075	7.494	7.494	7.528	422.77
1:0.1	7.531	7.531	7.519	426.45
1:0.2	7.505	7.505	7.522	423.68

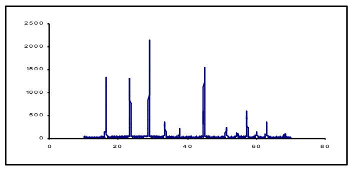
Table 1 Comparison of lattice constants with the JCPDS values and early reported values

2.2.2. UV-Vis study

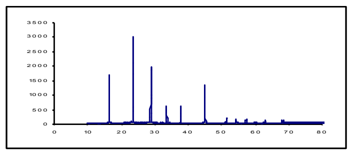
The UV-Vis optical transmission spectra of pure and EDTA doped ADP crystals are shown in fig 3.The spectra were recorded in the wavelength region from 190 to 1100 nm using a Lambda 35 spectrophotometer. It is observed from the figure that the grown crystals have good transmission in the entire visible region. Also it is observed that the pure ADP has 55% transmittance and the similar result was observed by Claude etal [12]. Also, EDTA doped ADP crystals have 61% transmittance in the visible region. The above results indicate that the addition of EDTA has increased the transmittance. The large transmission in the entire visible region enables it to be a good candidate for electro-optic applications.

2.2.3 Microhardness

Vicker's hardness measurement of pure ADP and EDTA doped ADP crystals was taken by varying loads 25g, 50g and 100g.



(a)



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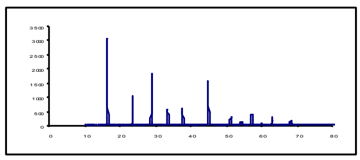

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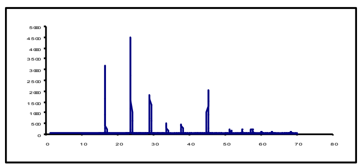

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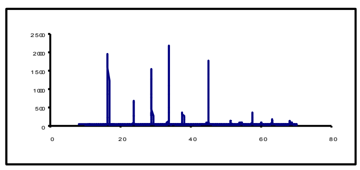


(e)

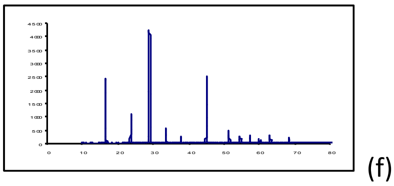
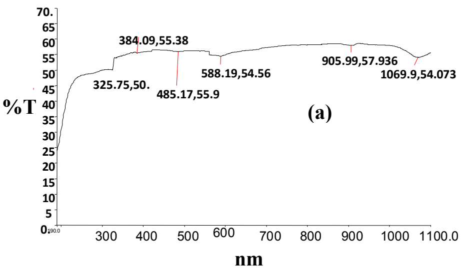


Fig 2: PXRD patterns for the ADP samples grown from different EDTA doped conditions (a) pure ADP (b) 1:0.025 (c) 1:0.05 (d) 1:0.075 (e) 1:0.1 (f) 1:0.2

Vicker's micro hardness number was determined using $H_v=1.8544p/d^2$ where p is the indentation load in Kg and d is the diagonal length of the impression in mm. The variation of hardness with indenter load for the pure,irradiated and EDTA doped ADP crystals are shown in fig 4. The hardness number was increasing with increasing the load in all the cases up to 100gm. Similar result was observed by Rajesh etal [11]. It is observed from the graph that the hardness number was decreased for doped ADP crystal as compared to pure ADP. It was observed that EDTA doped ADP and irradiated ADP crystals have low hardness value as compared to the pure ADP crystals, which indicates that the mechanical strength of the doped crystals are not good. This may be the result of a loosely packed lattice, with reduced bond energy due to the introduction of EDTA into the crystal.



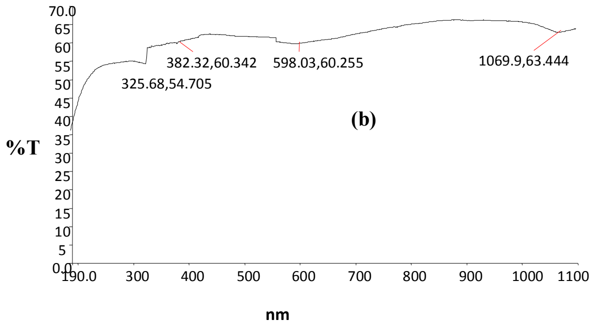


Fig 3: UV Vis spectra of the grown crystals (a) pure ADP (b) EDTA doped ADP

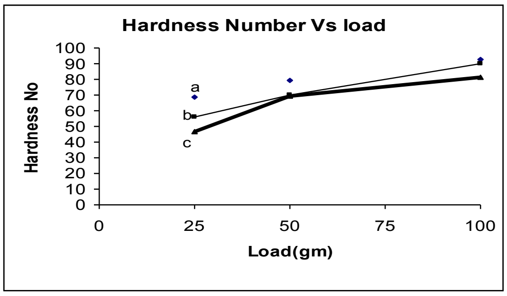


Fig 4: Variation of Microhardness with indenter load for a) Pure ADP b) EDTA doped ADP c) irradiated ADP

3.0 CONCLUSIONS

Pure ADP and EDTA doped ADP crystals were grown by solution growth technique by slow evaporation method at room temperature. The change in structural, optical and mechanical properties of doped crystals were analysed in comparison with the pure ADP crystals. The optical transmission studies reveal that the doped ADP crystals have high transmittance as compared to pure ADP crystals. This indicates that the doped crystals are good for electro optic applications. Micro hardness studies show that the hardness value was low in the case of doped and irradiated ADP crystal.

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5