Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Effect of Cobalt Doping on the Growth, Structural, Optical, Thermal and Mechanical Properties of Ammonium Dihydrogen Phosphate Single Crystals

Paras H. Trivedi*[1], Haresh K. Patel[2] and K.G.Raval[2]

[*1]Shree Jayendrapuri Arts& Science College, Bharuch, Gujarat, India,
[2]Narmada College of Science & Commerce, Zadeshwar, Gujarat, India,
E-mail: parry.trivedi@gmail.com, Mobile: 09825728763

ABSTRACT:

Non linear optical single crystals of pure and Cobalt doped ADP were grown by slow evaporation solution growth technique at ambient temperature. The objective of the study is to find out the influence of cobalt on the growth morphology, optical and thermal characteristics of the ADP single crystals. The unit cell dimensions and crystalline nature of the grown crystals were verified by X-ray diffraction technique. The hardness of the crystals was determined by Vicker's Micro hardness test. The optical nature of the grown crystals was analyzed using the UV-Vis spectra. Thermo gravimetric analysis shows the thermal stability of the grown crystals. The addition of Cobalt impurity improves the quality, yield and growth rate of the ADP crystals. The optical quality, thermal and mechanical stability showed the suitability of the cobalt doped ADP crystals for optical applications.

KEY WORDS: ADP, Doping, Cobalt, XRD, TGA

***Corresponding Author:**

Paras H. Trivedi

Head & Associate Professor, Department of Electronics

Shree Jayendrapuri Arts & Science College, Old Nh. No. 8, Bharuch-392001

E-mail: parry.trivedi@gmail.com

M: 9825728763

INTRODUCTION

Ammonium Dihydrogen Phosphate ($NH_4H_2PO_4$) is a technologically important inorganic crystals and studies on ADP crystals attract interest because of their unique piezoelectric, antiferro electric, electro optic, dielectric, acousto optical, phase matching, optical mixing and non linear optical (NLO) properties. Numerous applications of the NLO property have been discussed in the field of science and technology such as second, third and fourth harmonic generators for Nd:YAG, Nd:YLF lasers and for electro optical applications such as Q-switches, for Ti:Sapphire, Alexandrite lasers, as well as for acousto optical applications[1-7].As a representative of the hydrogen bonded material, ADP matrixes readily accept both organic and inorganic dopants.

Recent work has been done on the growth and characterization of pure and doped ADP crystals with an aim to improve and engineer the performance of various device based on the ADP crystals with series of organic dopants like ammonium malate, thiourea, L-lysine mono hydrochloride dyhydrate, L-alanine, L-arginine, ammonium acetate and bi-metallic impurities (Ni^{3+}, Mg^{2+}, Ba^{2+}, Fe^{3+}, Co^{2+} etc) [8-21] and their effect on various property of ADP crystals were studied and reported that the addition of impurities in ADP crystal has turned various properties of the material. It is also reported that the second and third harmonic generation efficiency of ADP crystals has been found to be higher than the KDP crystals, which shows that ADP is a good alternative to KDP crystals in the inertial confinement of fusion experiments[22].

In this we have attempted to introduce Co as an impurity in the ADP crystal matrix with different concentrations. Pure and doped ADP crystals were grown and characterized chemically, structurally, optically, thermally and mechanically by using the suitable standard methods and reported results are discussed.

EXPERIMENTAL SECTION

Bulk crystal growth

Good quality and reasonable size of single crystal is pivotal for practical applications. In the existent workanalytical reagent grade (AR) samples of ADP and $CoCl_2$ along with triple distilled water as a solvent were used for the growth of single crystals[23-24]. The supersaturated solution of pure ADP and 0.1 mol% and 0.2 mol% $CoCl_2$ as a doping agent with ADP was blended well to attain the homogenous solution. All three supersaturated solutions of 500 ml filtered and seed crystal of ADP was

allowed to grow with slow evaporation technique at room temperature. After a period of three weeks,transparent colorless crystals of size 50 x 10 x 10 mm^3 of pure ADP, 48 x 12 x 10 mm^3 of 0.1 mol% Co doped ADP and 76 x 14 x 12 mm^3 of 0.2 mol% Co doped ADP crystals were harvested. The photograph of all three grown crystals of pure and Co doped ADP is shown in figure 1 below which depicts good transparency, well defined faces and the morphology of the grown crystals and also the growth rate is more along the crystallographic 'a' axis.

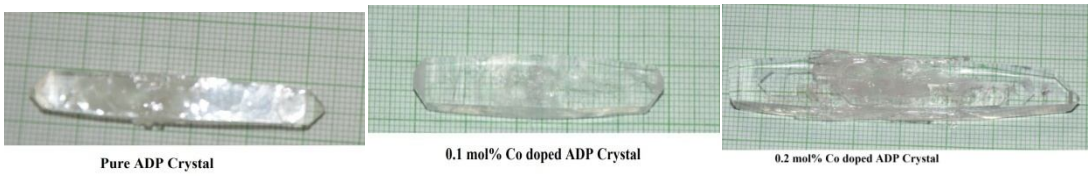

Figure 1: Photographs of the Pure and Co doped ADP crystals

Characterization

XRD patterns were recorded by Philips Xpert MPD system. The data was analyzed using the powder X software. EDAX analysis of the grown crystals was done using Nova NanoSEM 450 to verify the functional groups present in the sample. Transparency of the crystals in the wavelength range 400-1100 nm was studied by using Perkin Elmer Lambda 19. The thermal analysis was carried out using the LINSEIC STA-PT 1600 TGA, DTA set up. Micro hardness of the grown crystals was measured using Vickers Micro Hardness tester with constant indentation period.

RESULTS AND DISCUSSION

EDAX analysis

In order to confirm the presence of functional group, the samples of grown crystals were subjected to EDAX analysis using theNova NanoSEM 450. The EDAX spectra for pure and 0.1mol% and 0.2mol% of Cobalt doped ADP crystals were recorded and analyzed. The figures 2 and 3 below confirm the presence of C, O, P and Co in 0.1 mol% and 0.2 mol% Cobalt doped ADP crystalline lattice. The observed weight percentage of elements in the 0.1 mol% and 0.2 mol% Cobalt doped ADP crystals are given in the table 1 below, where the presence of cobalt is 0.29 wt% and 1.47 wt% respectively which is quite low compared to oxygen , carbon and phosphorous in both the samples.

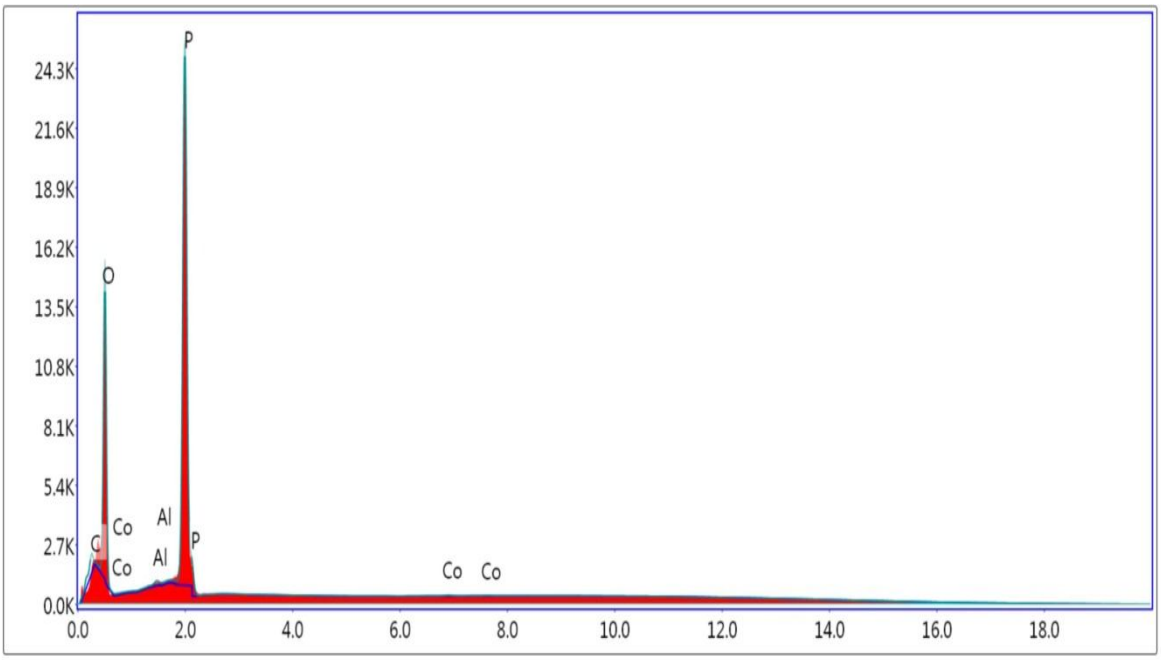

Figure 2: 0.1 mol% Co doped ADP crystal

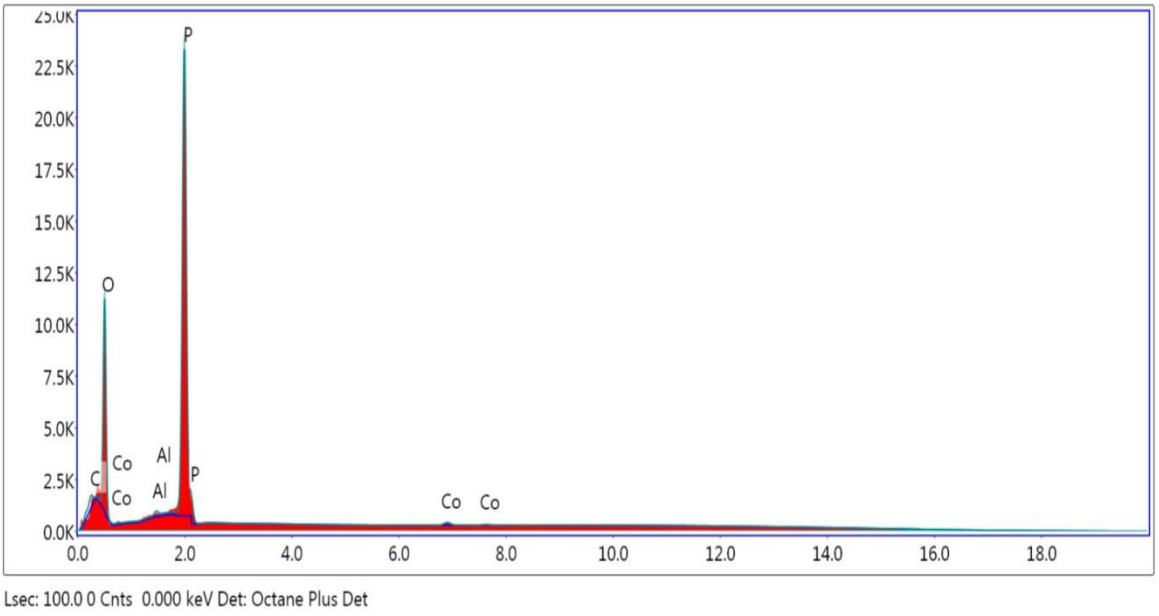

Figure 3: 0.2 mol% Co doped ADP crystal

Table 1: "EDAX data"

Sr. No.	Element	0.1 mol% Co doped ADP		0.2 mol% Co doped ADP	
		Weight %	Atomic %	Weight %	Atomic %
1	C K	7.24	11.42	3.23	5.43
2	O K	55.70	65.98	52.28	66.00
3	P K	36.62	22.41	42.75	27.87
4	Co K	0.29	0.09	1.47	0.50

X ray diffraction analysis

X- ray diffraction analysis of 0.1 mol% and 0.2 mol% Co doped was carried out by Philips Xpert MPD system which confirms the single phase nature of the samples and Bragg's peaks were obtained at 2 θ angles indicating that crystals are in order.

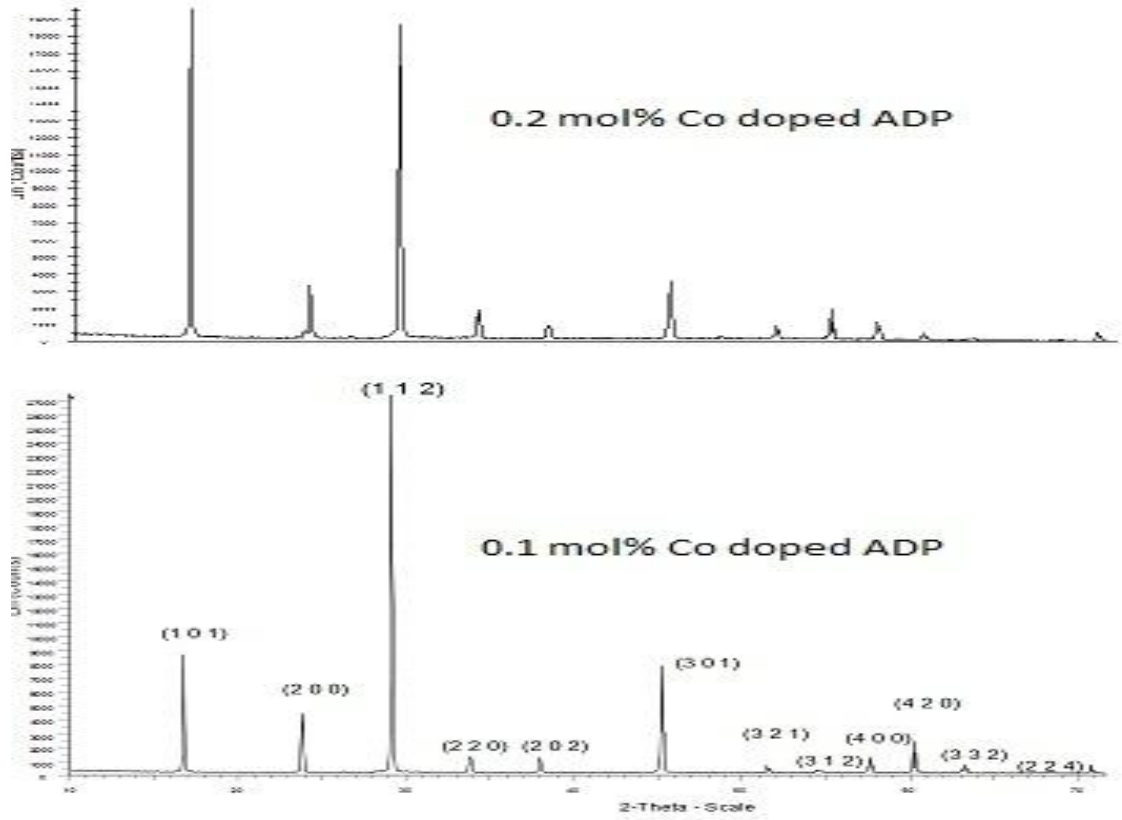

Figure 4: XRD patterns for 0.1 mol% and 0.2 mol% Co doped ADP crystals

The‘d’ spacing hkl values for prominent peaks in the spectrum were identified and compared with ICDD as shown in Figure 4above. The XRD patterns of doped ADP had three prominent peaks at (101), (112), (301). The cell parameters were found as shown in table 2 below which shows good agreement with the reported value. There is slight increase in cell parameter values due to doping and both samples belong to tetragonal system with I-42d space group.

Table 2: “Unit cell parameters”

Sample	Lattice Parameter (Å)		Cell Volume (Å^3)	α = β = γ
	a = b	c		
Pure ADP	7.502	7.554	421.0	90°
0.1 mol%doped ADP	7.515	7.559	427.3	90°
0.2 mol%doped ADP	7.532	7.655	434.2	90°

UV-Vis-NIR spectroscopy

The UV-Vis-NIR spectra observed using Perkin Elmer Lambda 19 for all samples grown are shown in figure 5 below. 5 mm thick crystal wafers are used for the transmission study. The observed optical transmission intensity and cut-off wavelengths indicate that both samples exhibit good transmittance towards the visible and infra-red region and low cut-off wavelengths. This transparent nature of the grown samples is the desirable property to have NLO applications.

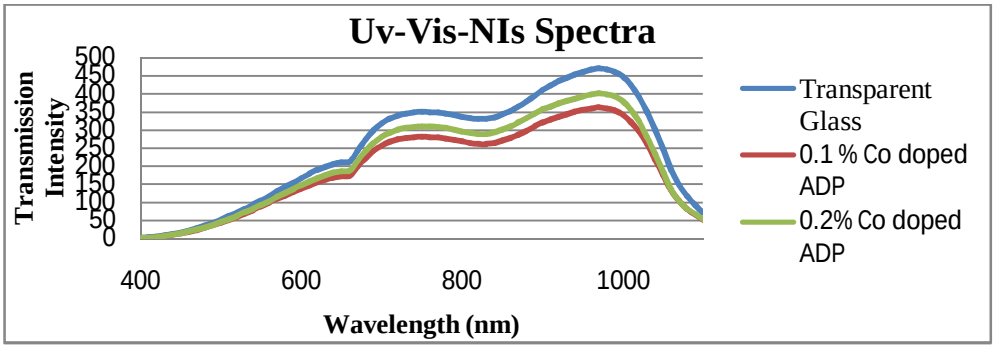

Figure 5: UV-Vis-NIS spectra for 0.1 mol% and 0.2 mol% Co doped ADP crystals

Thermal analysis

Thermal analysis of the 0.1 % and 0.2 % Co doped ADP crystals were recorded using the LINSEIC STA-PT 1600 TGA, DTA set up at a heating rate of 20 °C/min to determine the thermal stability of the crystals. The recorded curves shown in figure 6 and figure 7 below shows that there is no weight loss ~ 155 °C in both the samples, indicating no inclusion of water in the crystal lattice which is used as a solvent for crystallization.The decomposition of ADP and Co starts at 155 °C and terminates at 300 °C and 160 °C and 300 °C respectively. It is observed that 0.2 % Co doped crystals show slow weight loss percentage. The results confirm the increase in thermal stability of Co doped ADP crystals as compared to pure ADP crystals.

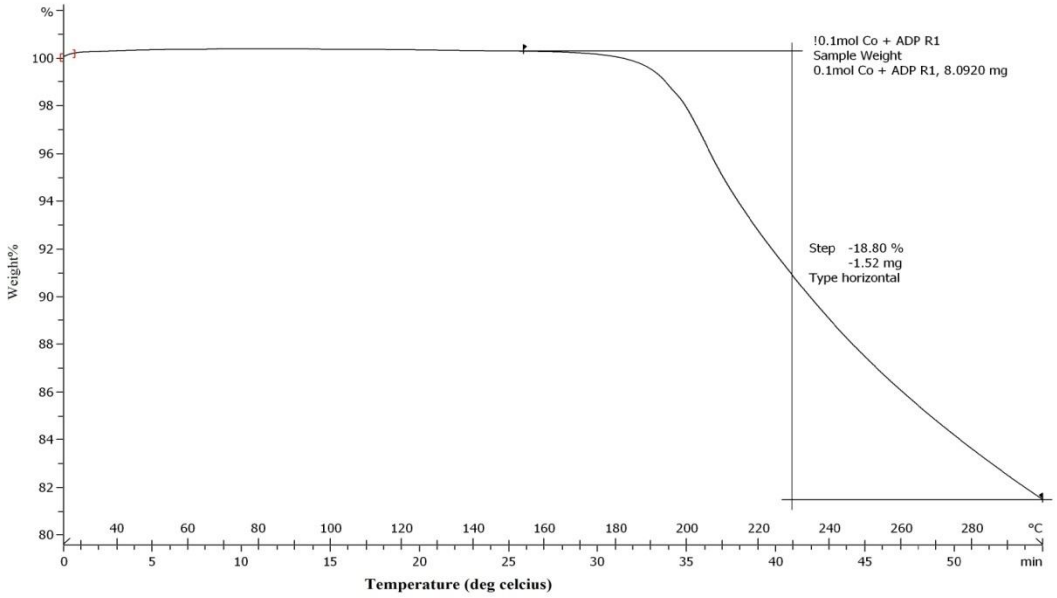

Figure 6: TGA curve of 0.1 % Co doped ADP

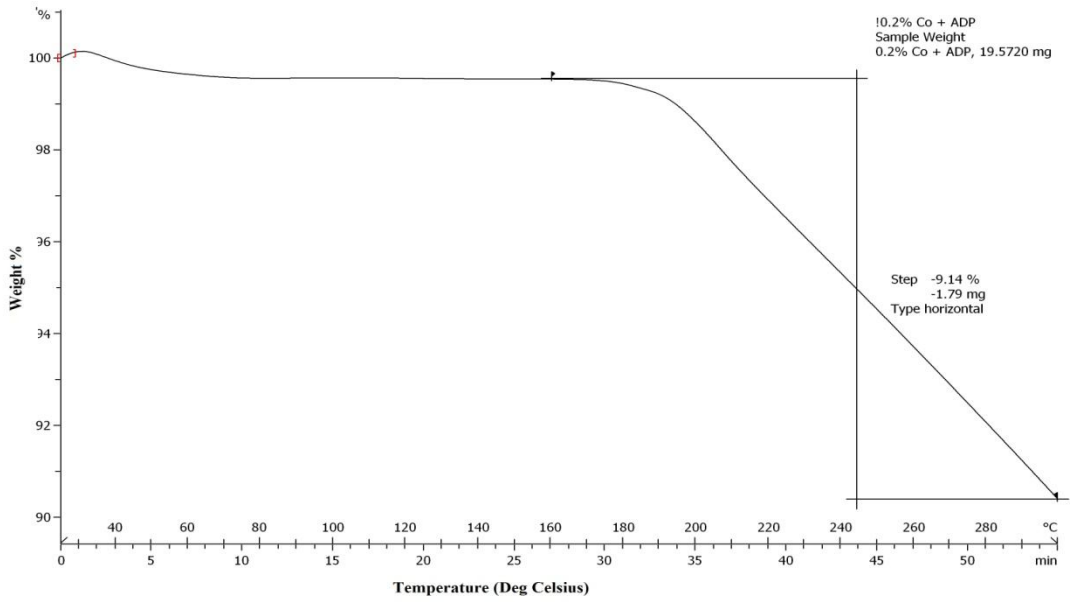

Figure 7: TGA curve of 0.2 % Co doped ADP

Micro hardness study

The good quality crystals are needed for various applications not only with good optical performance but with also good mechanical behavior. Hardness test is useful to find the mechanical hardness of the crystals and to estimate the threshold mechanical stress. Hardness of crystal is due to the resistance offered by a solid to the movement of dislocation, practically which is caused by scratching or indentation. Vicker's hardness measurement of pure ADP and 0.1 % and 0.2 % Co doped ADP crystals were noted by applying various load for an indentation time of 10 sec for each trial. The collected data is presented in table 3 below.

Table 3: Microhardness value of doped ADP

Load P	**0.1 mol% Co doped ADP**			**0.2 mol% Co doped ADP**		
(gf)	**X (microns)**	**Y (microns)**	**Hardness H_V**	**X (microns)**	**Y (microns)**	**Hardness H_V**
10	12.9	12.3	116	12.3	11.8	127
25	20.2	19.9	115	19.4	19.1	125
50	26.8	26.1	132	26.5	26.0	134
100	38.6	37.2	129	38.0	36.5	134
200	56.2	54.3	121	54.1	52.9	130

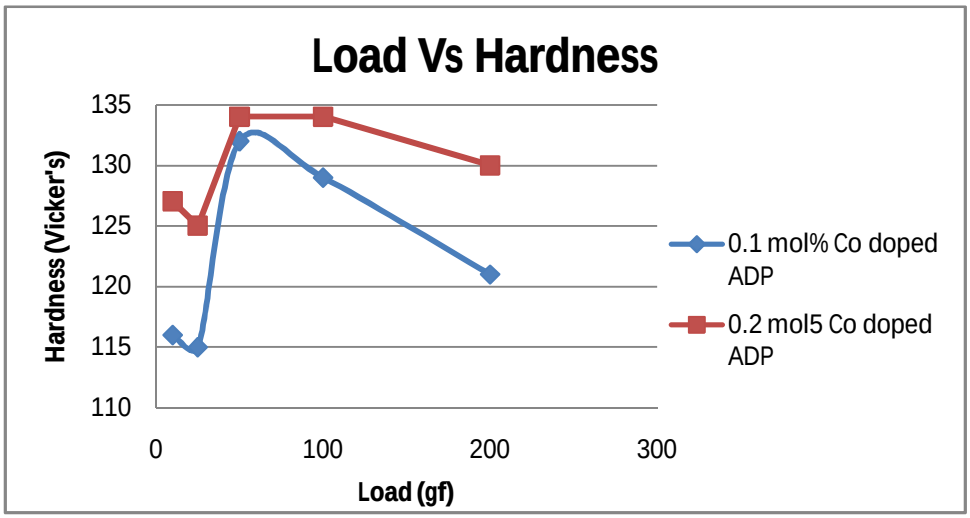

Figure 8: Microhardness Results

Results show that between 50 to 100 gm load hardness value increases in both the samples. It also shows that the hardness value of 0.2 mol% Co doped ADP crystals are higher than that of 0.1 mol% Co doped ADP crystals for constant indentation time which can been seen from Figure 8 above. This is because of the addition of Cobalt ions into superficial crystal lattice and removing defect centers reduce the weak lattice stresses on the surface. Vicker's micro hardness number was determined using relation $H_v = 1.854P/d^2$.

CONCLUSION

By employing slow evaporation solution growth technique good quality colorless and transparent single crystals of 0.1 mol% Co doped and 0.2 mol% Co doped Ammonium Dihydrogen Phosphate were grown. EDAX confirms the presence of cobalt in the lattice of both the crystals. Single crystal XRD analysis reveals the tetragonal structure of ADP is slightly changed due to the addition of cobalt. The observed optical transmission intensity and cut-off wavelengths in UV-Vis-NIR analysis indicate that both samples exhibit good transmittance towards the visible and infra-red region and low cut-off wavelengths. The TGA analysis confirms the increase in thermal stability of Co doped ADP crystals as compared to pure ADP crystals. The Vicker's micro hardness study shows that addition of Cobalt ions into superficial crystal lattice and removing defect centers reduces the weak lattice stresses on the surface and increases the mechanical stability. This study may prove to be helpful to obtain high quality single crystals for various device applications.

REFERENCES:

1. Marder SR, Tiemann BG, Perry JW et al. Materials for Non-linear optical chemical perspectives. American Chemical Society: Washington. 1991.
2. Muncheryan HM. Lasers and opto-electronics devices. Hemisphere Pub. Co: New York. 1991.
3. Shen YR. Principles of non-linear optics. Wiley: New York. 1984.
4. Meystrey P, Seargent M. Elements of Quantum Optics. Springe-Verlag: Berlin. 1991.
5. Sakai JI. Phase Conjucate optics. Mc GrawHill Inc: New York. 1992.
6. Ramaswamy P, Raghavan PS. Crystal Growth Process and Methods. KRV Pub: Kumbakonam. 1999.
7. Ramaswamy P, Raghavan PS. Recent Trends in Crystal Growth. Pinsa, New Delhi. 2002; 68.
8. Essentia AA, Mahadevan C. Bull of Material Science. 2005; 28: 415.
9. Xu DL, Xue DF. J. of Cryst. Growth. 2006; 286: 108.
10. Rajesh NP, Kannan V, Raghavan PS, Ramaswamy P, Lan CW. Mater. Chem. and Phy. 2002; 76: 181.
11. Mullin JW, Amata AV. App. Chem. 1967; 17: 151.
12. Rajesh P, Ramaswamy P. Mater. Lett. 2009; 63: 2260.
13. Dhanraj PV, Bhagavanarayana G, Rajesh NP. Mat. Chem. Phys. 2008; 112: 490.
14. Rajesh P, Ramaswamy P, Bhagavanarayana G. J. Crystal Growth. 2009; 311: 4069.
15. Jairama A, Dharmaprakash SM. Indian J. of Pure and App. Phys. 2005; 43: 859.
16. Rajesh P, Ramaswamy P, Mahadevan CK. J. Cryst. Growth. 2009; 311: 1156.
17. Ferdousi A, Poddar J. J. Cryst. Process and Tech. 2011; 1: 18.
18. Muley GG, Rode MN, Waghuley SA, Pawar BH. Optoelectronics and Advan. Mater. 2010; 4: 11-14.
19. Rajesh P, Ramaswamy P, Boopathi K. J. of Crystal Growth. 2011; 318: 751.
20. Claude A, Vaithianathan V, Ganesh RB et al. J. App. Sci. 2006; 6: 85.
21. Hudson JA, Mahadevan CK, Padma CM. Intl. J. of Engg. Res. and appl. 2014; 4: 257-266.
22. Feng X, Zhu L, Li F et al. RSC Adv.2016; 6: 33983.
23. Delci Z, Shyamla D, Karuna S et al. Intl. J. of ChemTech Research. 2012: 4; 816-826.
24. Raja R, Saravanan S, Santhanam V, Kurinjinathan P. Intl. J. of Tech. Research and Appl. 2016: 38; 5-8.