INTERNATIONAL JOURNAL OF SCIENCE AND NATURE

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EFFECT OF LOW AND HIGH CONCENTRATIONS OF NaCl ON PROPERTIES OF ADP CRYSTAL

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ABSTRACT
Optically good quality single crystals of pure and NaCl doped ADP have been grown by slow evaporation technique at 35^{0}C. The effect of alkali salt NaCl of different concentrations as a dopant on growth and characterization of ADP crystals has been studied. The grown crystals are characterized. The presence of functional groups of crystals are qualitatively analysed from FTIR spectra. The transparency of grown crystals has been confirmed using UV- visible spectra. It has been found that the SHG efficiency of ADP containing NaCl is higher than pure ADP crystals. The SHG efficiency of A3M% NaCl crystal is 1.15 times the efficiency of ADP crystal. The efficiency was found to decrease with increase in concentration of dopant in ADP crystal. Well defined peaks in XRD spectrum suggest good quality single crystals.

KEY WORDS: UV-Visible spectra, transparency, SHG efficiency, FT-IR spectra, XRD spectra and functional groups etc.

INTRODUCTION
Since the discovery of second harmonic generation of ruby laser radiation in a quartz crystal by Franken[1] in 1961, the search for new crystals with good frequency conversion properties continues even today. The very first material to be used and exploited for their nonlinear optical (NLO) and electro-optic properties was potassium dihydrogen phosphate (KDP) and ADP, with the aim of improving the SHG efficiency of ADP crystals, researchers have attempted to modify ADP crystals by doping different types of impurities. There are few reports available on the effect of different concentrations of NaCl as a dopant on the properties of ADP crystals. Since conductivity in this material is due to entirely to ionic motion, as it is in alkali halides. When alkali halides are doped in ADP and KDP crystals implying that anions and cat-ions make comparable contributions to the conductivity. Such crystals could have large heat capacity than that can be explained by lattice and molecular harmonic motions and thermal expansion coefficient is very high that make these crystals with large damage threshold value and good optical nonlinear crystals with less defects. It is shown that by using initial high purity salts and fine filtration of solution followed by after growth annealing, it is possible to increase the optical break down threshold of profiled rapidly grown crystals to values corresponding the requirement of modern laser design.

Crystal Growth
Analytical reagent grade samples of ADP and NaCl along with double distilled water were used for the growth of single crystals. Supersaturated solutions of ADP with (1M%, 6M% and 9M %) concentrations of NaCl have been crystallized by slow evaporation technique. The solution of ADP and NaCl was stirred using magnetic stirrer for one and half hour at temperature 40^0 C. The solution was filtered using Whitman filtered paper and kept in constant temperature bath at 35^{0}C. The good quality single crystals were obtained in about two weeks.

Characterization
The ADP crystals modified with different concentrations of NaCl were characterized by XRD, FTIR, optical transmission spectra and dielectric measurements. The SHG intensity of samples were tested by the modified version of powder technique developed by Kurtz and Perry[3] using quanta ray spectra physics model; Prolab 170 Nd; YAG 10ns laser with a pulse repetition rate of 10Hz working at 1064nm.

RESULTS & DISCUSSION
X-ray diffraction analysis
The crystals grown in present study are found to be stable, colourless, and transparent.
Powder X-ray diffraction study was conducted to verify the single phase nature of the samples. Well defined Bragg's peaks are obtained at specific 2Θ angles indicating that crystals are ordered. The 'd' spacing hkl values for prominent peaks in the spectrum were identified and compared with ICDD (international centre for diffraction data). Using tetragonal crystallographic equation, lattice parameter values are calculated. This suggest that the crystals retain almost the single phase structure and exhibit very slight variation in the unit cell parameters on doping NaCl. The variation in the intensities of various diffraction patterns on changing the concentration of doping was observed. The low value of FWHM shows the crystalline perfection. The effect of low angle boundaries may not be significant in many applications, but for the phase matching applications, it is better to know these minute details regarding crystalline perfection. The UV –Visible optical absorption spectrum of pure and doped ADP

crystals are shown it is clear that from the figure 1, 2 & 3 that the percentage of transmission decreases with increase in the concentration of NaCl in ADP crystals. All of them have sufficient transmission in entire visible and near IR region. The UV transparency cut-off limits increases with the doping concentration. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Using formula E=hc/λ, the band gap energies were found to be 3.3 to 4.13 eV where 'h' is Plank's constant, c, is velocity of light. Hence it could be concluded that the NaCl doping plays an important role in improving the crystal and optical quality of ADP crystals. This is the most desirable property of materials possessing NLO activity.

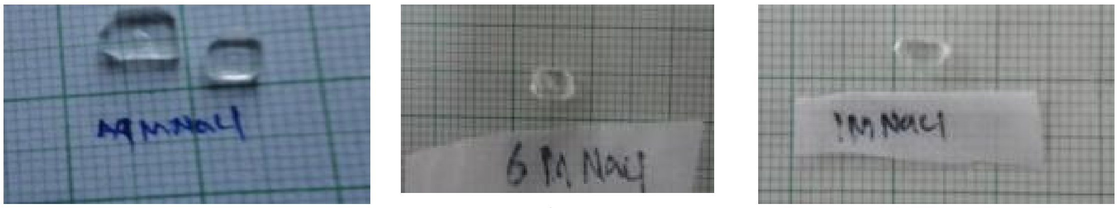


FIGURE 1: grown single crystals of Sodium chloride doped ADP crystals

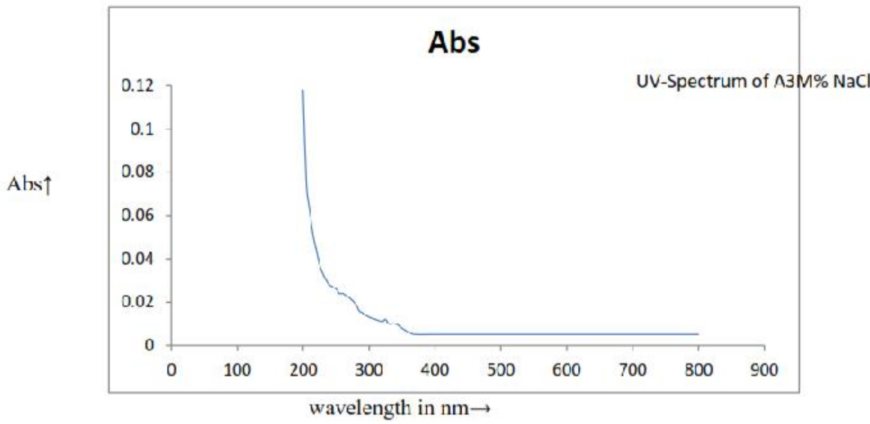


FIGURE 2: UV-Visible spectrum of A3M% NaCl Crystal

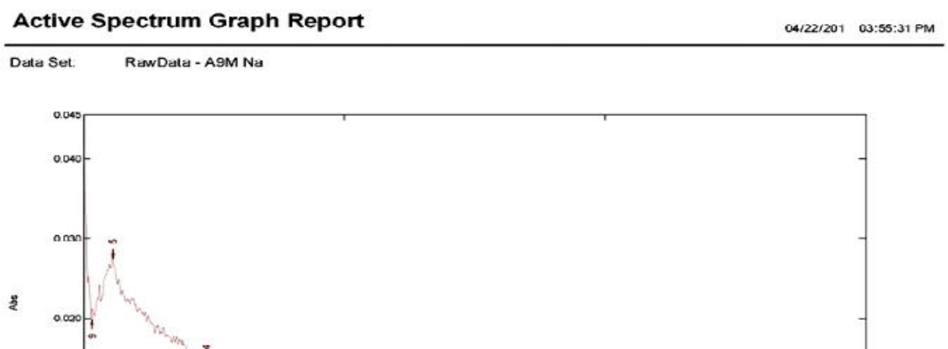


FIGURE 3: UV-Visible spectra of A9M%NaCl crystal

FTIR Spectroscopy study

FT-IR study of NaCl doped ADP crystal

The powdered specimen of ADP doped NaCl crystal has been subjected to FTIR analysis by using Shamzadu Fourier transforms infra-red spectrophotometer. Using KBr pellet technique in wavelength range between 400 and 4000cm^{-1}carried out the FTIR analysis of A3M%NaCl, A6M%NaCl and A9M%NaCl are shown in figure3 and 4.In the spectrum of pure ADP crystal the broad band around 3250cm^{-1}was due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium. The band at 2387cm^{-1}was assigned to hydrogen bond. The broadness was due the hydrogen bonding interaction with the adjacent molecules. The O-H bending vibrations gave peaks at 1706, 1642cm$^{-1.}$ The peaks at 1409 were due to the bending vibrations of ammonium. The medium bands at 560, 405 are due to PO_4 vibrations.

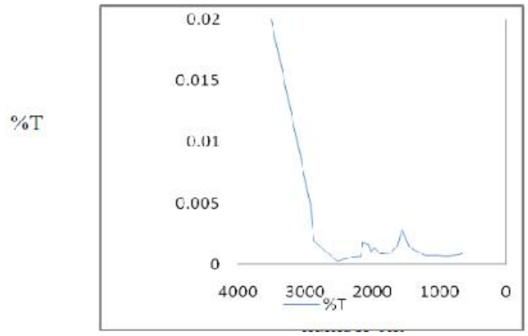


FIGURE 4: FTIR spectra of A6M% NaCl

TABLE 1. Vibrations frequencies for pure ADP and NaCl doped ADP crystals.

Pure ADP cm^{-1}	A6M%NaCl cm^{-1}	A9M%NaCl cm^{-1}	Assignment
3100	3099	3203.76	O-H stretching
2850	-	3024.38	N-H stretching
2300	-	2397.52	Combination band of stretching
1695	1627.92	1658	N-H bending of NH_4
1400	1448	1404.18	Bending stretching of NH_4
1295	1265	1315	Combination band of stretching
1100	-	1118.71	P-O-H stretching
800	877.61	-	P-O-H stretching
545	-	584	PO_4 stretching
405	-		PO_4 stretching

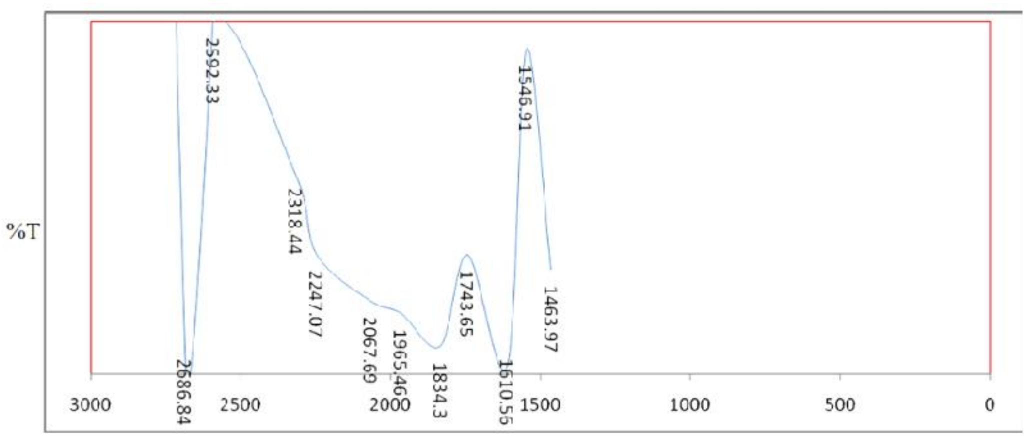
For A6M%NaCl Crystal, 3805.65, 3556.74, 3528.73cm^{-1} indicate the presence of NaCl in pure ADP crystal.

3.4 SHG Measurement

TABLE 2: SHG efficiency of NaCl doped ADP crystals

Name of sample	Signal mV	SHG efficiency
ADP	123mV	1
A3M%NaCl	142mV	1.154
A9M%NaCl	116mV	0.94

Reference material is KDP= 71mV



Wave number cm-1

FIGURE 5: FT-IR spectrum of A3M% NaCl

The study of nonlinear optical conversion efficiency was carried out using the experimental set up of Kurtz and Perry[7]. A Q-switched Nd: YAG laser beam of wavelength 1064nm, with an input power of 4.4mJ/pulse. The grown crystals of sodium chloride doped ADP crystals were powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The generation of the second harmonics was confirmed by emission of green light. A sample of potassium di- hydrogen phosphate (KDP) also powdered to the same particle size as an experimental sample, was used as a reference material in the present measurement. The relative SHG efficiency of sodium chloride doped ADP crystals was found to be greater than KDP crystal. At the same time these were compared with the undoped ADP crystal under the same experimental conditions and with the reference material KDP. In this case the efficiency of A3M% NaCl was found to be 1.15 times the efficiency of ADP crystal and two times the efficiency of KDP crystal. However, the efficiency was found to be decrease with increase in the concentration of dopant in ADP crystal[8]. Table 2 shows comparison of SHG signal energy output of NaCl doped ADP crystals with ADP crystal.

CONCLUSION

Transparent, colourless crystals of pure and NaCl doped single crystals were grown by slow evaporation technique at 35^0C. Powder X-ray studies, evaluation of lattice parameters confirmed that the dopant has gone into the lattice of the crystals. This study reveals slight distortion in the unit cell of the crystals. FTIR study confirms the presence of NaCl in doped crystals. The absorption spectra reveals that NaCl additive has not destroyed the optical transparency of the crystal and have sufficient transmission in the entire UV- visible and IR regions. The lower cut-off wavelength increases with increase in the concentration of dopant. NaCl doped crystals have shown an increase in SHG efficiency compared to the pure ADP crystals. It has been observed that addition of sodium chloride enhances the transparency, and NLO efficiency of ADP crystals. Dielectric constant study reveals that the sodium chloride addition reduces the dielectric constant values of ADP crystals.

ACKNOWLEDGEMENT

The authors sincerely thanksn to Dr. PK Das, IPC lab, IISC, Bangalore, Dr. Raghuwanshi, Dr. Wadatkar, Vidyabharti Mahavidyalaya, Amravati, Dr. Charde, Government Pharmacy college, Amravati, Diya lab, Navi Mumbai and Dr. G G Muley, Professor, department of Physics, Sant Gadge Baba Amravati University, Amravati.

REFERENCES

[1]. Gunasekaran, S., Ponnusamy, S. & Rajesekaran, R. Indian J Phy, 78, 7 (2004)553.

[2]. Goma, S., Padma, C.M. & Mahadevan, C.K. Matter Lett 60 (2006) 997.

[3]. Freeda, T.H. & Mahadevan Pramana, J. phy 57, 4(2001) 829.

[4]. Ananda Kumari, R. Indian J, Pure Appl, phy, 47, (2009), pp, 369-371.

[5]. Ferdousi Akhtar & Jiban Poddar, J., Crys, Process, Tech, 2011, 18, 25.

[6]. Muley, G.G. Rode, M.N. and Pawar, B.H. FTIR, thermal and NLO studies on amino acid doped KDP crystals, Acta Physica Polonia A, NO. 6 116(2009).

[7]. Kurtz, S.K., Perry, T.T., J Appl. Phys 1968; 39; 3798.

[8]. Bhagavannarayana, G., Ananthamurthy, R.V., Budakoti, G.C., kumar, B., Bartwal, K.S. J. Appl. Cryst 2005; 38; 768.