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Dielectric Study of KCl Doped ADP Crystal

***Shaikh Kalim s/o Shaikh Hanif[1] A.B Lad[1], B.H.Pawar[2]**

[1]Department of Physics, Amolakchand Mahavidyalaya, Yavatmal, Maharashtra, India.

[2]Ex, Head of Physics department, Sant Gadge Baba Amravati University, Amravati, India.

*Corres.author: shaikhkalim70@yahoo.in

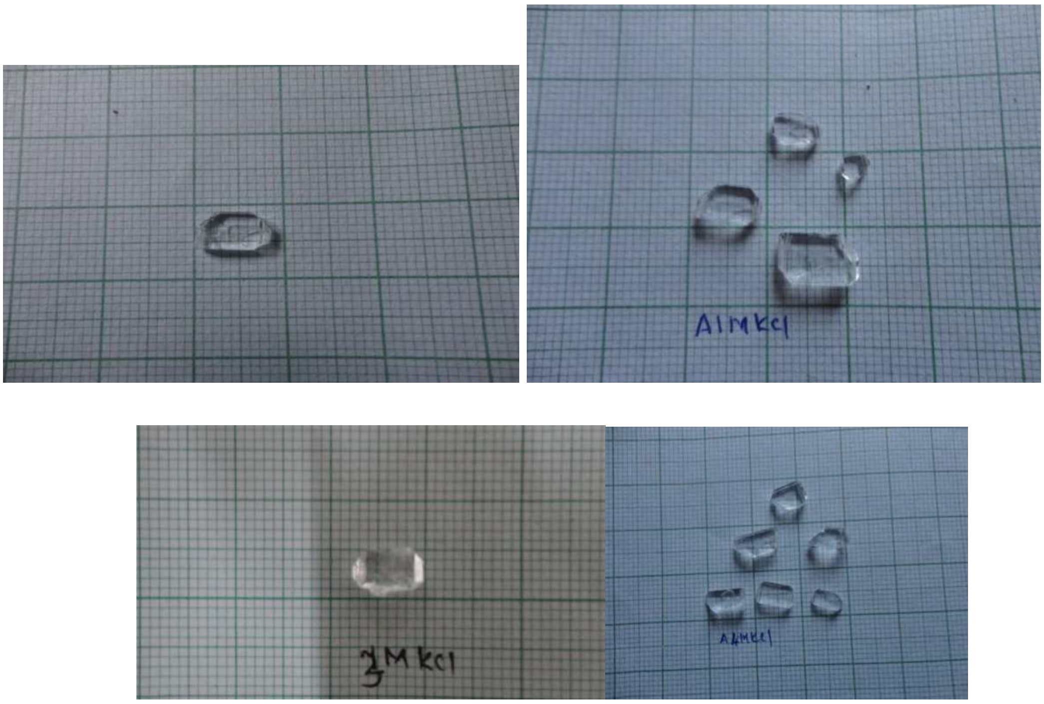
Abstract: The experimental results of the influence of low and high concentration of potassium chloride dopant on ADP crystals are presented. The dopant results to an enhance crystal growth rate. Further high concentration of dopant improves the quality of the crystal with better transparency in UV- visible region of electromagnetic spectrum. FTIR spectra confirmed the presence of dopant in pure ADP crystal. UV-Visible spectroscopic studies reveal that on increasing the dopant concentration in ADP, the lower cut of wavelength increases, it is 250nm and crystal shows good transparency in UV- Visible region. The dielectric constant measured indicates that the crystal is less defective and has high value of damage threshold. The dielectric constant decreased with increase in frequency and temperature of crystal. The crystal developed has low value of dielectric constant proves to be a good in NLO property. The powder SHG measurement showed that the efficiency increased with increase in concentration of KCl in ADP crystal than the pure ADP crystal and efficiency high at the high concentration of KCl in ADP crystal.
Key Words: ADP, inorganic dopants, UV-Visible, FTIR and Dielectric constant, NLO efficiency.

1. Introduction:

Ammonium di-hydrogen phosphate (ADP) is a well known NLO material which also has many interesting Ferroelectric and Ant ferroelectric 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 one choicest electro- optic materials having wide practical applications [1-5]. The nuclear fusion experiment require a NLO crystal of large second harmonic generation (SHG) efficiency, thermal and mechanical stability, high laser damage [6]. Lot of research work has been devoted to improve the properties of ADP by adding different impurities or altering growth conditions like change of pH and lowering temperature with different rates etc [7-8]. Presence of small amount of impurities in the form of anionic dopant K^+ and Na^+ plays a vital role in the growth rate, habit of the crystal and its properties of crystals. ADP and KCl doped ADP crystals were grown by solution growth technique by slow evaporation technique at 32 ^{0}C, KCl doped as 1,2,3, and 4 M% in ADP crystals. The grown crystals were subjected to different types of characterizations.

2 .Synthesis of KCl doped ADP crystal

Analytical reagent grade samples of ADP and KCl with double distilled water were used for the growth of single crystals. 10 gm ADP is dissolved in 30 ml double distilled water 0.0222 gm of KCl is dissolved in 10ml doubled distilled water. Both solutions are mixed to get ADP doped with 1M% KCl solution. The solution is stirred using magnetic stirrer at 33 ^{0}C for two hours to get homogenous solution and filtered it using whatman filter paper kept beaker of solution in a constant temperature bath at 32 ^{0} C. Similarly ADP doped with 2M%, 3M% and 4M% KCl have been crystallized by slow evaporation technique at 32 ^{0} C in about two weeks. The grown crystals are as under.



(a) A1M% KCl (b) A3M%KCl (C) A4M% KCl

3. Characterization

3.1 UV-Visible spectroscopy

The UV- Visible spectrum of KCl doped ADP crystals was recorded using UV-Visible spectrometer (Model: SHIMADZU UV-160). The transparent behaviour of KCl doped ADP in the entire UV-Visible spectrum shown in fig. d. 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. This behaviour may enhance three dimensional bonding interaction of phosphate with neighbouring units in the crystal. The less electronegativity of potassium is also important in strengthening such interactions [11]. On increasing the dopant concentration the low cut of wavelength decreses. Dopant increased the transparency of the crystal in UV-visible region. The recorded optical absorption spectrum of the grown crystals in wavelength range (200-400nm) is shown in figures 5 and 6. It is inferred from the spectrum that the grown crystals have low absorbance in entire UV-Visible region considered and the cut off wavelength is around 230nm for 1M% KCl doped ADP and 250nm for 4M%KCl doped ADP crystal, thus the high concentration of KCl in ADP increases the low cut off wavelength, means decreased the transparency of the crystals. The presence of low cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity [14].

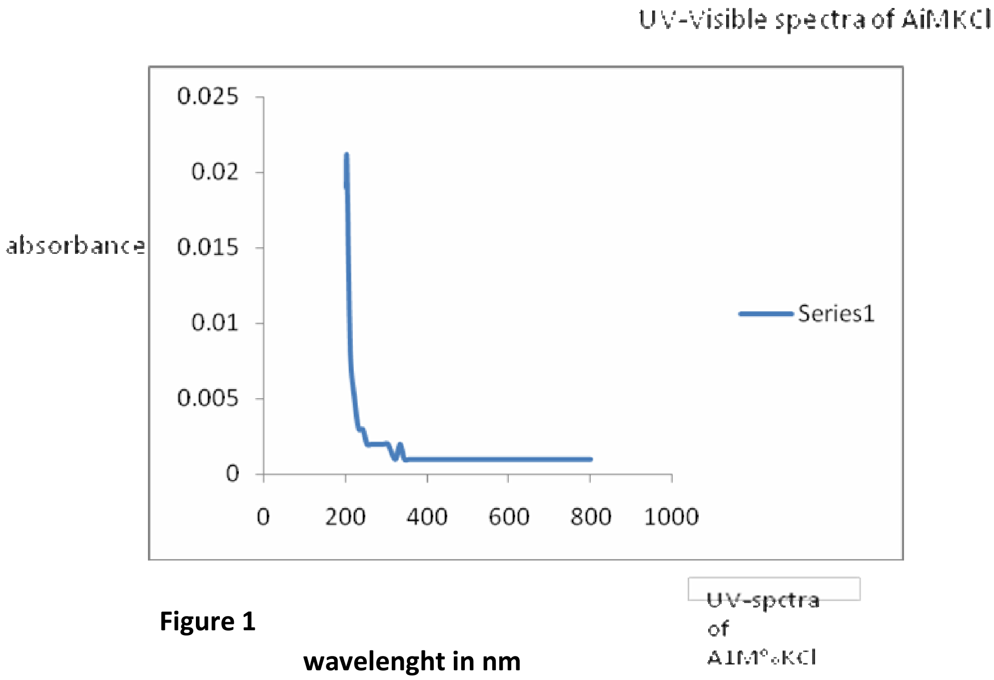


Figure 1

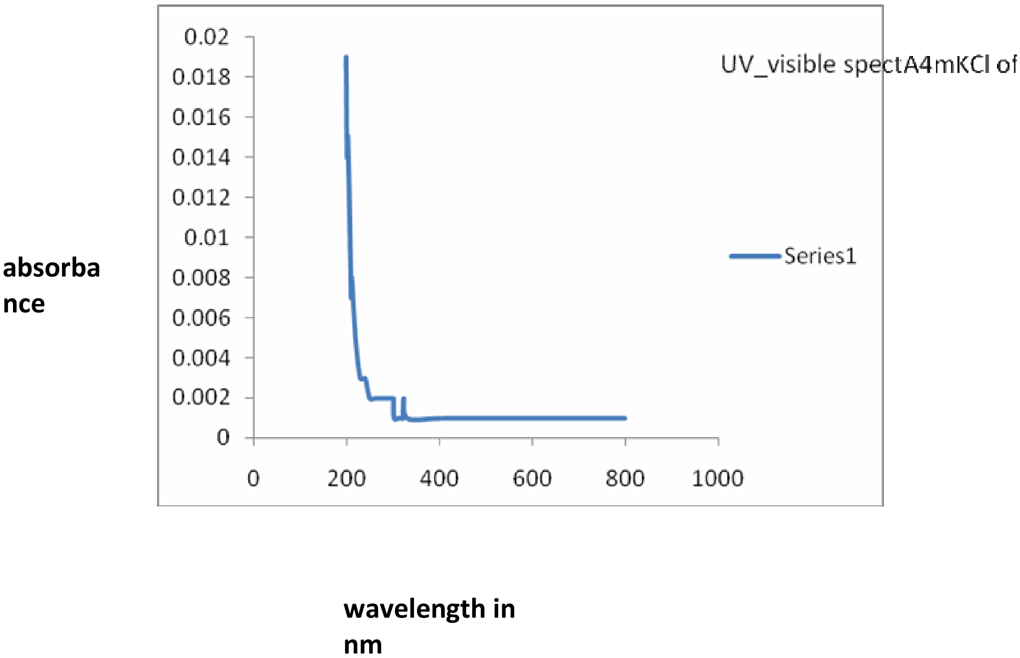


Figure 2 UV-Visible spectrum of A4M%KCl

3.2 Powder SHG measurement

The SHG intensity of the samples were tested by the modified version of the powder technique developed by Kurtz and Perry in 1968 using Quanta Ray Spectra Physics model: Prolab 170 Nd:YAG 10ns laser with a pulse repetition rate of 10HZ working at 1064nm at the department of Inorganic Physical Chemistry, Indian Institute of Science Bangalore. The energy per pulse is 4.4mj. The SHG was confirmed by the emission green radiation (λ = 532nm) which was finally detected by a photomultiplier tube and displayed on the oscilloscope. Measured powder SHG efficiency of pure ADP is 123mV and the for 2M% KCl doped and 3M% KCl doped ADP crystals are 98mV and 133mV respectively. The NLO property increases with the concentration of KCl in ADP crystals. Hence, the concentration of dopant increases in ADP crystal increased the SHG efficiency.

Table 1. The SHG efficiency measurement of pure and KCl doped crystals

Name of crystal	signal in mV	SHG efficiency
1. ADP	123mV	1
2. A2M% KCl	98mV	0.79
3. A3M% KCL	133mV	1.081

3.3 FTIR spectroscopy studies

The FTIR analysis is a technique that provides information about the chemical bonding or molecular structure of materials. The FTIR spectrum of the grown crystal is shown in fig. 4 the absorption peaks correspond to the molecular group vibrations. The relations of molecular group vibrations and the characteristics absorption bands were assigned according to the theories of infrared spectra [12].

The FTIR spectrum of ADP crystal doped with 1M%, 2M%, 3M% and 4M% KCl was recorded using FTIR spectrometer Shimadzu in the region 4000 cm^{-1} to 500cm^{-1} , slight broadening is observed in observed in FTIR of ADP in the 3500-3000cm^{-1} range in presence of high KCl concentration. 3820cm^{-1}coresspons to free OH stretching hydrogen bonded of ADP. 2740cm^{-1}P-OH asymmetric stretching of ADP. 2407cm^{-1} is due to the P-OH bending of ADP and 900 is due P-OH stretching. 503cm^{-1} is due to HO-P-OH bending for 1M% KCl 3446, 3367, 3290 3155 and 2924 extra peaks were observed which proved the presence of dopand in ADP. For 3M%KCl 3365.78, 3170,2924,2856,5826.77,2549, 2279 and 2237cm^{-1}extra peaks were observed. For 4M%KCl extra peaks were 3367, 2924, and 2853cm^{-1}.

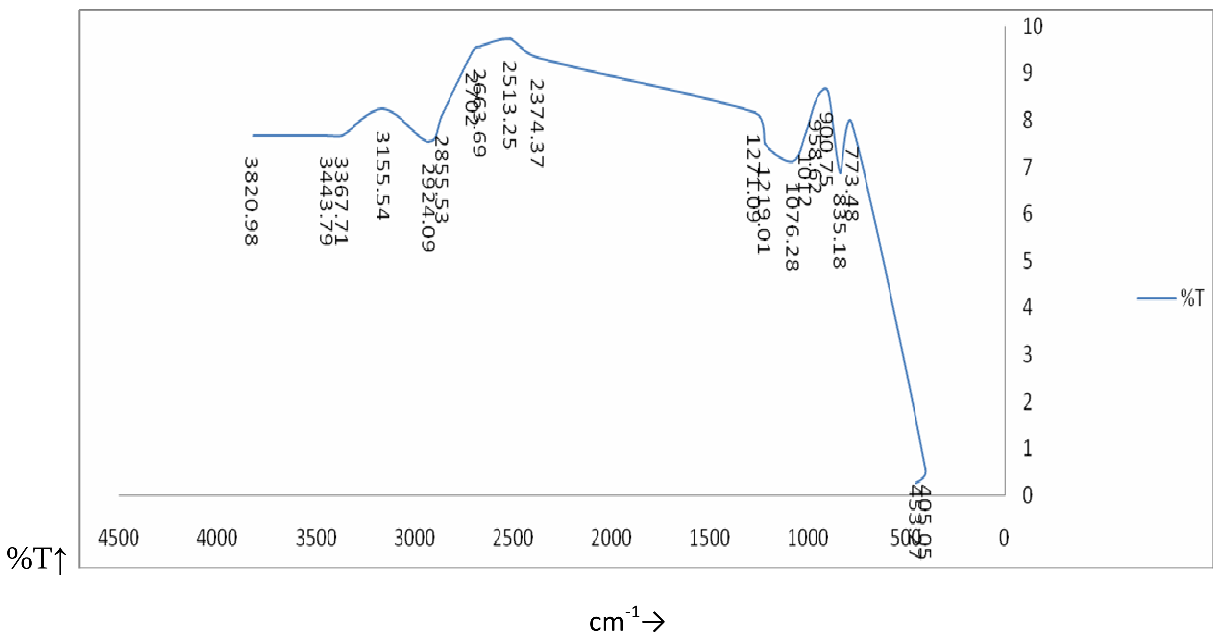
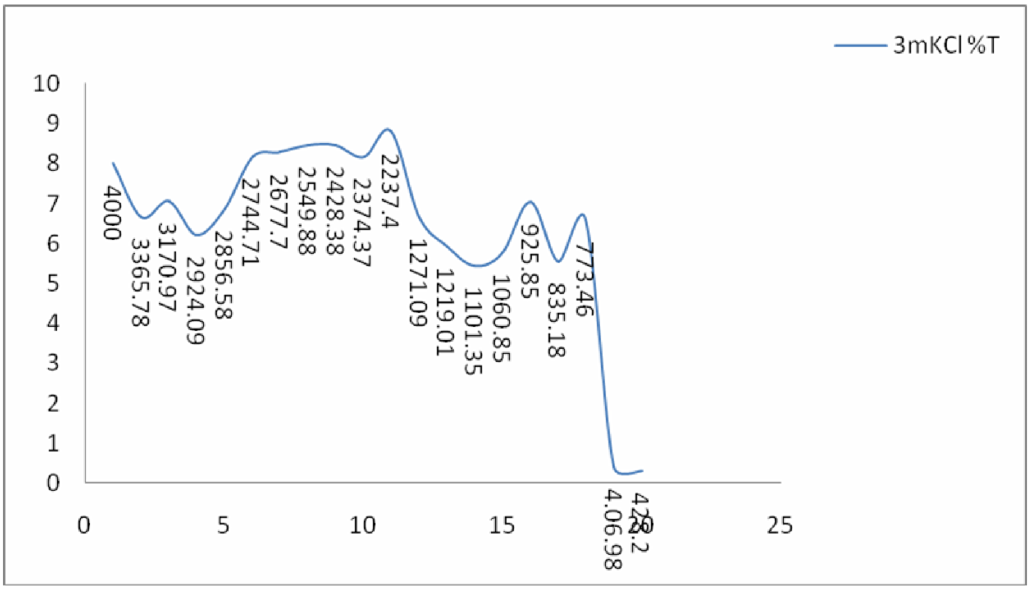


Figure 3 FTIR Spectra of 2M%KCl

%T↑



cm^{-1} →

Figure 4 FTIR Spectra of 3M%KCl Doped ADP Crystal

3.3 Dielectric Studies:

Comparative study of dielectric constant v/s log of frequency for A1m%KCl and A3M% KCl.

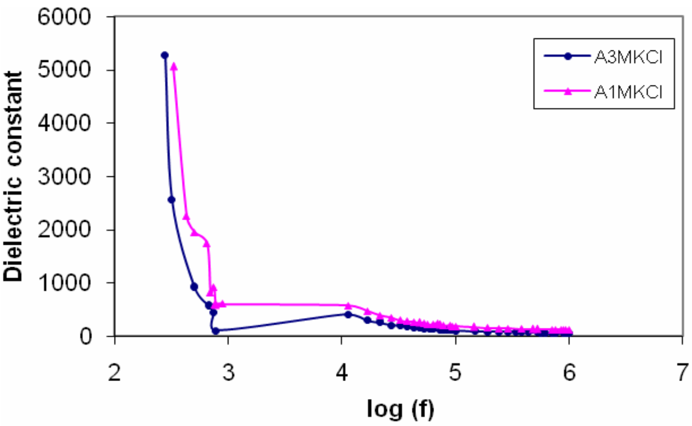


Fig. 5- Variation of dielectric constant with frequency at 35°C

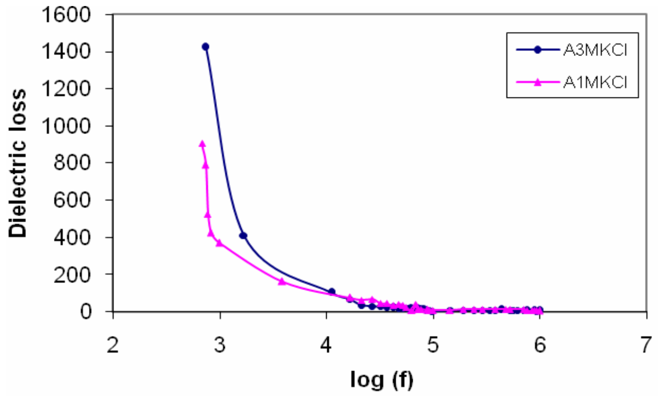


Fig. 6 - Variation of dielectric loss with frequency at 35°C

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence the grown crystals KCl doped ADP crystals with different concentration A1M% KCl and A3M% KCl single crystals were subjected to dielectric studies using 4284 A LCR meter (20- 1MHz) at different temperatures. The cut and polished crystals were used for the dielectric studies. The surface of the sample was electrode with silver paste for the electrical contact. The experiment was carried out for the frequency from 1KHZ to IMHZ with temperature 30, 35, 40 and 45 ^{0}C. The dielectric constant Єr=Cd/AЄ0 where A, C, d and Є0 are the area, capacitance of the crystal and Є0 is the dielectric constant. The study of dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material.

From the analysis of dielectric constant as function of frequency and temperature, the different polarization mechanism in solids can be understood. The defect free and transparent crystal was selected and for the dielectric measurement and opposite faces of the sample crystal was coated with good quality silver paste to promote good conduction[13].

Figure 5 shows the comparative study of dielectric constant at 35 ^{0}C with varying the frequecncy for crystal 1M% KCl and the crystal 3M% KCl. The graph shows that the dielectric constant is the function of frequency of the applied field, it goes on decreasing with increasing in frequency of the applied field for both the cases. But the dielectric constant of the crystal with more concentration of dopant showed lower value than 1M% KCl doped ADP crystal. Thus high concentration of the dopant lowers the value of dielectric constant. The lower value of dielectric constant is a suitable parameter for the enhancement of the SHG signal. A graph between dielectric constant and frequency at different temperature for a crystal 1M% KCl doped ADP crystal indicates that the on increasing the temperature of the sample the dielectric constant decreases. Figure 6 shows that the dielectric loss decreases with increasing frequency means lesser defect in crystal A1M%KCl and A3M%KCl hence are good candidate for NLO applications.

4.Conclusion

Transparent, colourless crystals of pure and potassium chloride doped with 1,3, and 4M% KCl doped ADP single crystals were grown by slow evaporation technique at 32 ^{0}C. The FTIR study confirms the presence of KCl in the doped crystals. The absorption spectra reveals that potassium chloride have not destroyed the optical transparency of the crystals and have sufficient transmission in the entire UV-visible and IR regions. High concentration of dopant increase the value of low cut off wavelength. The dielectric study reveals that the dielectric constant decreased with increase in the frequency and temperature of the sample. The doped crystal with high concentration of dopant KCl showed low value of dielectric constant. The lower value of dielectric constant is a suitable parameter for the enhancement of SHG signal and sign of good quality less defective single crystal. Thus KCl reduces the dielectric constant of ADP. SHG efficiency of the KCl doped crystal increases with increased in the concentration of dopant, at lower concentration the efficiency is less than the pure ADP crystal.

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