

Dielectric Study of LiCl Doped ADP Crystal

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Abstract

The experimental results of the influence of low (3M%LiCl) and high concentration (9M %) LiCl lithium chloride dopant on the ADP crystals is presented. The dopant results an increase in the Meta stable zone width leading to an enhanced crystal growth rate. High concentration of dopant improves the crystalline quality with better transparency. Diffraction pattern reveals that there is no change in basic structure except for variation in intensity of doping, well defined peaks indicate good quality crystal. FTIR spectra show some extra peaks indicate the presence of dopant in ADP crystals. SHGMeasurement reveals that the second harmonic efficiency has been improved with low concentration of LiCl dopant in ADP crystals. The efficiency of A2M%LiCl is found to 1.9 times the efficiency of ADP and 3.3 times efficiency of KDP crystal. It seems that the molecular alignment of the crystal facilitates the nonlinearity in the presence of the dopant. Dielectric constant measured for 3M% and A9M%LiCl crystals found decreases with increase in the frequency.

Key words: FTIR spectra, XRD diffraction patterns, SHG efficiency, Metastable zone width, Transparency and molecular alignment etc.

Introduction

Studies of ADP crystal still attracts interest because of their unique nonlinear optical and dielectric, piezoelectric and antiferroelectric properties and their varieties of uses such as electro-optic modulators, harmonic generators and parametric generators. Several research works have been carried out on pure and doped ADP crystals [1-5]. In recent years the efforts have been taken to improve the quality, growth rate and the

properties of ADP crystal by employing new growth techniques and also by addition of organic, inorganic and semi organic impurities [6-8]. Inorganic nonlinear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power, [9-10]. With an aim of finding new useful materials for academic and industrial use, an attempt has been made to modify ADP crystals by adding 1M%, 3M%, 4M% and 9M% lithium chloride in ADP crystal. In this work the structural, spectral and optical properties of the lithium chloride doped ADP crystals against pure ADP have been reported.

ADP ($\text{NH}_4\text{H}_2\text{PO}_4$) is widely used as the second harmonic generator for Nd: YAG and Nd: YLF lasers. The crystals are widely used for electro-optical applications as Q- switches for Nd: YAG and Nd: YLF lasers as well as for acousto-optical applications. It belongs to the tetragonal system with space group I-42d [9]. The systematic investigation of effect of low and high concentration of LiCl dopant on the properties of ADP crystals has not been reported.

Thermal analysis, XRD, microhardness testing, SEM, FTIR and UV-visible spectra are very useful technique to study the material properties. In this work we grow the pure and lithium chloride doped crystals by slow evaporation technique at 32°C . The grown crystals are characterized by FTIR spectroscopy, UV – visible spectroscopy, powder XRD and dielectric studies.

Crystal Growth

Single crystals of pure and doped ADP were grown from supersaturated solution at 32°C by natural evaporation process using AR grade samples of ADP and lithium chloride. Dopants were added separately with pure ADP solution, each in definite molecular ratio, namely ADP: X (X- is being dopant). solutions with 3M% and 9M% LiCl doped ADP were prepared. Each solution was stirred using magnetic stirrer for 2hours at 33°C and the solutions were filtered using Whitman filter papers and the filtered solutions were kept in constant temperature bath which was set at 32°C , after two weeks good colourless, stable and transparent single crystals were obtained by slow evaporation technique. The grown crystals were characterized using FTIR, UV-visible spectroscopy technique and powder XRD technique.

Characterization

The FTIR spectra of pure, lithium chloride doped ADP crystals were recorded by KBr pellet technique using Shimadzu FTIR spectrometer in the range $4000\text{-}500\text{ cm}^{-1}$ at Government Pharmacy College, Amravati. The dielectric constant studies were carried out at Department Of Physics SantGadge Baba, Amaravati University, and Amravati. The optical properties of the grown crystals were studied using Shimadzu (UV-1700nm visible spectrometer in wavelength range 200nm- 800nm at Government Pharmacy College, Amravati.

FTIR Spectroscopic Study

In the present work, FTIR spectra of pure and lithium chloride doped ADP crystals

were compared and complete vibration band assignments were carried out. The comparative FTIR spectral studies confirmed the presence of lithium ion and chloride ion in the respective doped crystals.

In spectrum of pure ADP, the broad band around 3250cm^{-1} is due to the O-H vibrations of water, P-OH group and N-H vibrations of the ammonium. The band at 2387cm^{-1} was assigned to hydrogen bond [11].

The broadening was due to the hydrogen bonding interaction with the adjacent molecules. The O-H bending vibrations gave the peaks at $1706, 1642\text{cm}^{-1}$. The peaks at 1409cm^{-1} was due to the bending vibrations of ammonium. The very strong band at 1292cm^{-1} was due to the combination of the asymmetric stretching vibrations of PO_4 with lattice.

The peaks at 1098 and 910cm^{-1} represented P-OH vibrations. The medium bands at $560, 405\text{cm}^{-1}$. In FTIR spectra of A2M%LiCl 3202cm^{-1} is due to the Li-OH stretching. Strong peaks at 1404cm^{-1} band vibrations of the NH_2 in ADP crystal, in this crystal 1279.12cm^{-1} due to O-H deformation and P=O stretching is shifted to 1271cm^{-1} due to the presence of dopant.

Strong peaks at 542.01 and 455cm^{-1} . Are due to the HO-P-OH bending and torsional oscillations.

In region between 1300 and 650cm^{-1} there are single bond stretching frequencies and bending vibrations of polyatomic systems involving motions of bonds linking a substituent group to molecule. Strong absorption bands for lattice water (antisymmetric and symmetric OH stretchings) at 3231 were also observed.

This can be attributed to the fact that when certain solute crystallize from aqueous solutions, they are the hydrated salts, which contain water and solute in a specific stoichiometric ratio. The water in such instances is referred to as water of hydration, and no. of water molecules associated with each solute molecule may vary with the crystallization temperature. Frequency range $545-439\text{cm}^{-1}$ strong PO_4 vibrations in ADP crystal. 533cm^{-1} is attributed to metal oxygen band. In FTIR, spectrum, the absorption bands in the region $3568-2600\text{cm}^{-1}$ are due to OH stretching mode, water and C-H stretch. The peak at 2242cm^{-1} in ADP is shifted to 2043cm^{-1} and 2142cm^{-1} this can be attributed due to the dopant introduced. There is absorption between 1500cm^{-1} to 2500cm^{-1} it is due to doping of LiCl. In FTIR spectra of A9M%LiCl the peaks at 2242cm^{-1} in ADP is shifted to 2234 and 2132 this is attributed to dopant introduced. Strong 1434cm^{-1} is due to bond vibration of NH_2 in ADP crystal, strong peaks appear at 495 is P-OH deformation. Strong peaks at $455-433\text{cm}^{-1}$ is due to torsional oscillations. The peaks from Li-OH bending and Li-O stretching all occur in $700-1000\text{cm}^{-1}$ region.

UV-Visible Study

The UV-visible spectrum of pure and doped ADP crystals was recorded by using UV-visible spectrometer. The transparent behaviour of lithium chloride doped ADP crystals in the entire UV-visible region is clearly illustrated by above figures. The UV-visible spectra clearly reveal that the lithium chloride doped ADP crystals better transparency than the pure ADP crystals. All the crystals grown show good transparency in UV-visible region, it also reveal that the lower cut of wavelength

decreases with the concentration of lithium chloride in pure ADP crystals. Hence the dopant increases the transparency of the crystal and makes it a good candidate for nonlinear crystal. The recorded optical absorption spectrum of grown A3M%LiCl and A6M LiCl crystals in the wavelength range 200-800nm is shown in figure 1 and 2. It is inferred from the spectrum that the grown crystals have low absorbance in the entire UV-Vis-NIR region considered and the cut off wavelength is around 240nm, closer to UV range. The spectrum further indicates that the crystals have wide optical transmission window range from 200-800nm. The presence of low cut off wavelength and the wide optical transmission window range are the most desirable properties of materials possessing NLO activity[18].

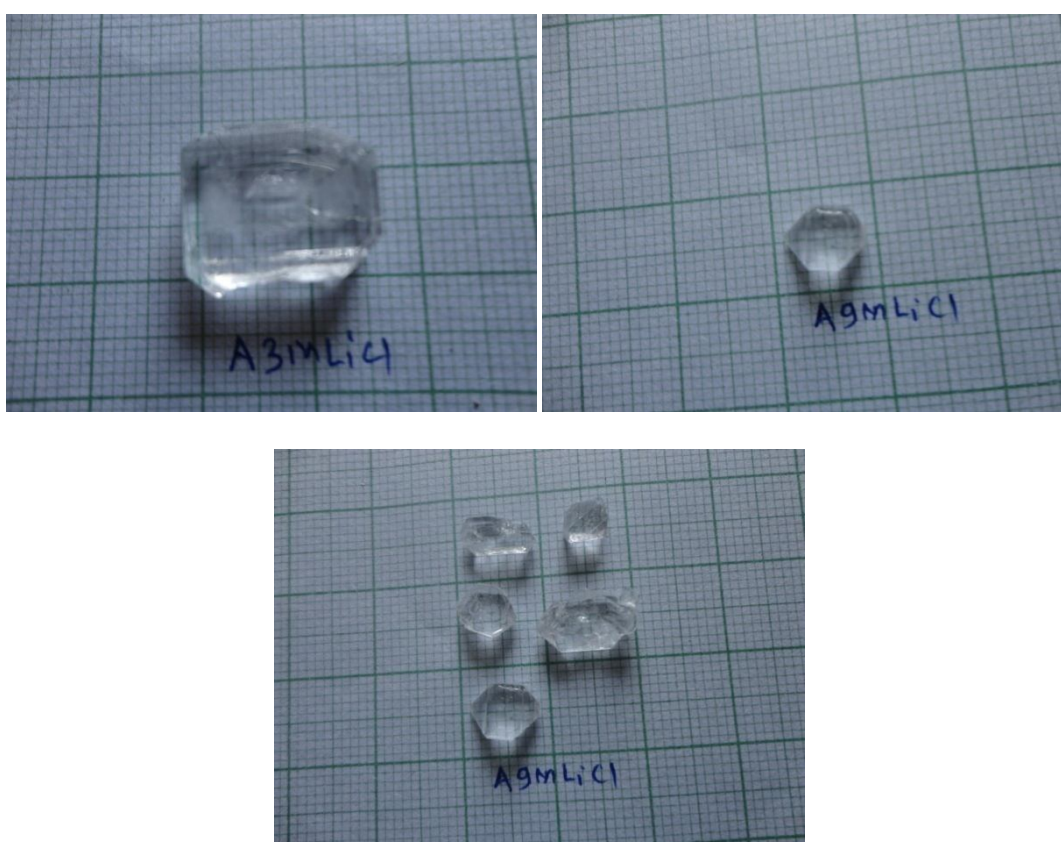


Figure 1 lithium doped ADP crystals

Powder XRD Analysis

The powder XRD diffraction study was conducted to verify the single phase nature of the samples. Well defined Bragg's peaks were obtained at specific 2θ angles indicating that the crystals grown are ordered. There is a slight shift in the diffracted peaks in XRD pattern of lithium chloride doped ADP crystals than the pure ADP crystal. The X radiation used was copper radiation $\lambda = 1.54056 \text{ \AA}$ operating at a voltage of 40 KV and a current of 20mA. The scanning rate was maintained at $1.6^\circ/\text{min}$ over a 2θ

range of 10-70° employing the reflection mode of scanning. When compared to that of pure ADP, the intensity of the diffracted peaks was found to vary in both the XRD patterns of doped ADP crystals. However, there were no other phases emerging besides the tetragonal system. The powder XRD showed that the original tetragonal structure is maintained and the lithium chloride entered into the lattice of ADP crystals.

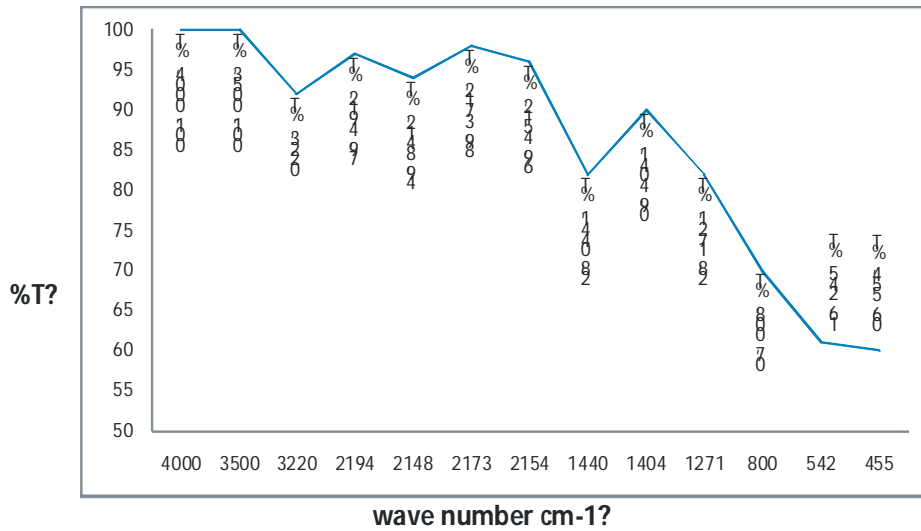


Figure 2 - FTIR A2M%LiC

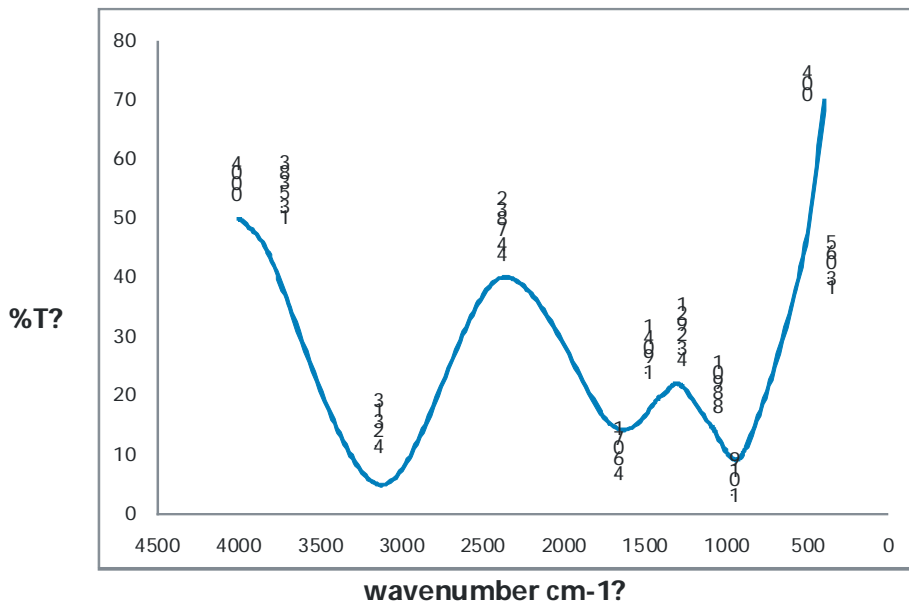


Figure 3 - FTIR spectrum of pure ADP crystal

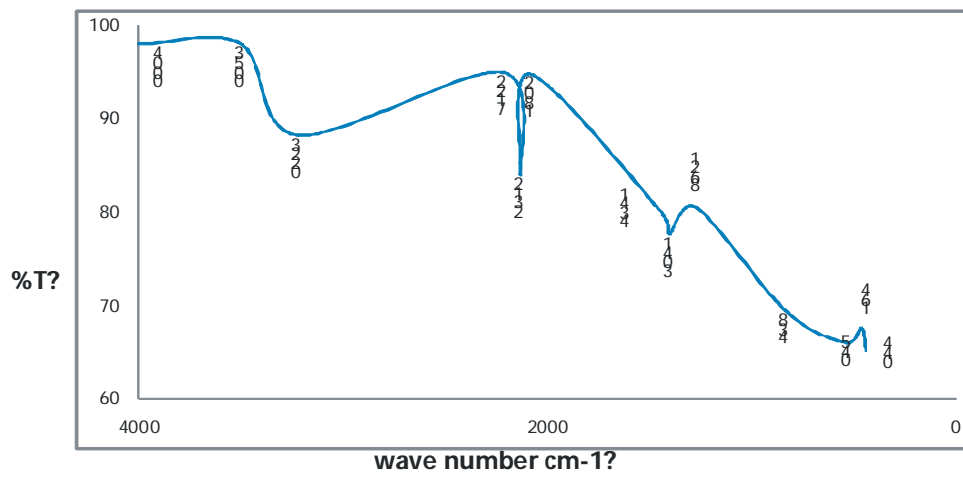


Figure 4 FTIR spectra of A6M%LiCl

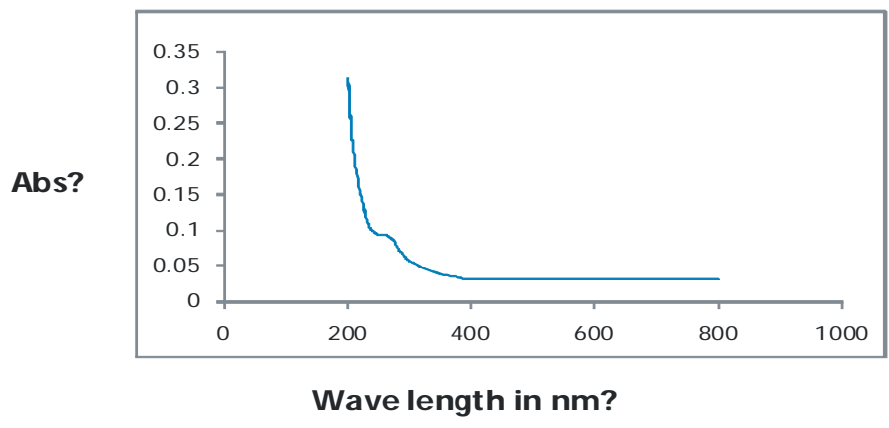


Figure 5 UV-Visible spectra of pure ADP crystal

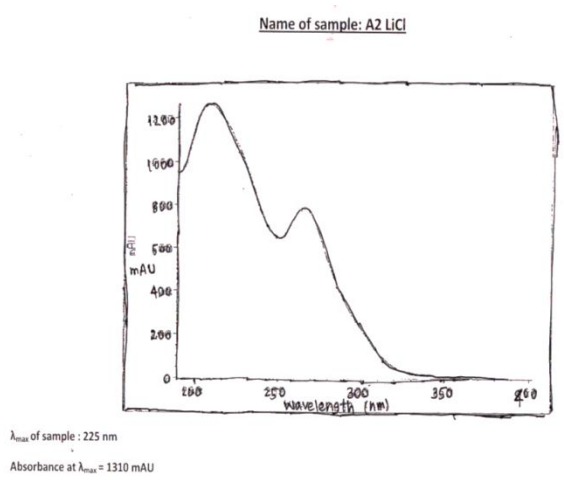


Figure 6 UV-Visible spectra of A2M%LiCl single crystal

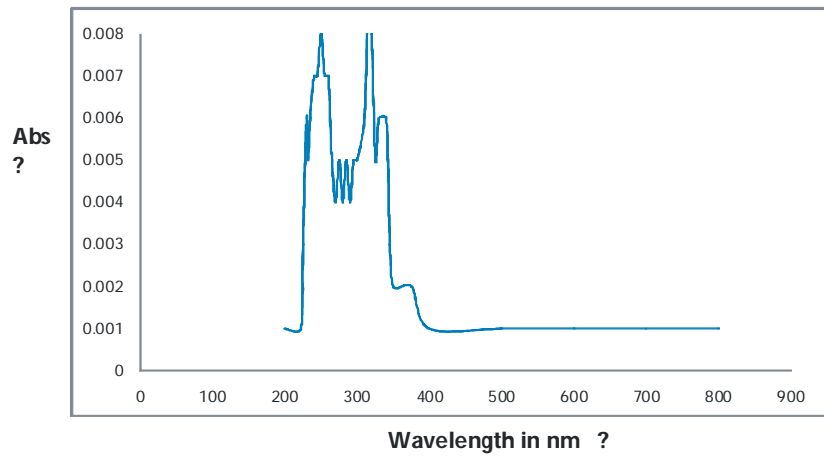


Figure 7 UV- visible spectrum of A3M% LiCl

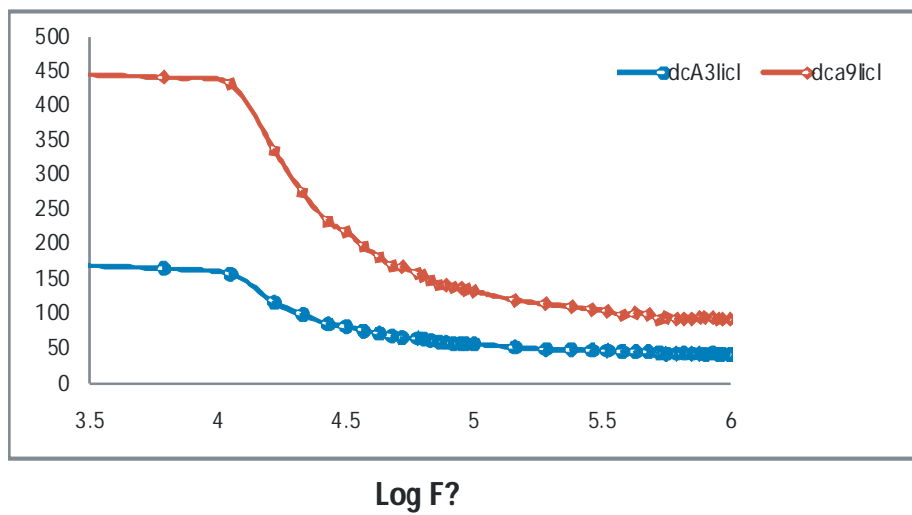


Figure 8 dielectric constant v/s the logf

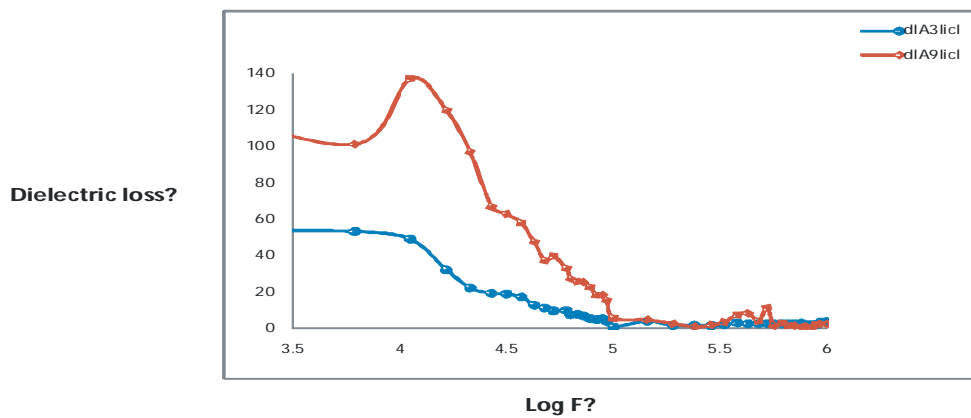


Figure 9 dielectric loss v/s the logf

Conversion Efficiency

The conversion efficiency of the crystal was checked using powder SHG technique developed by Kurtz and Perry [12]. The crystal was ground into powder and density packed in a glass capillary tube. An Nd:YAG laser beam of wavelength 1064nm of 4.4mJ energy was made to fall normally on the sample cell. The emission of green light confirms the second harmonic generation on ADP as well as lithium chloride doped ADP crystals. A sample of powdered potassium dihydrogen phosphate (KDP) was used as the reference material in SHG measurement. From the data obtained, the efficiency of A2M%LiCl crystal is 1.9 times the efficiency of the ADP crystal and 3.3 times the efficiency of KDP crystal. Anomalous behaviour of lithium is due to extremely small size of lithium its cation on account of small size and high nuclear charge lithium exerts the greatest polarizing effect out of all alkali metals on negative ion. Consequently lithium ion possesses remarkable tendency towards salvation develops covalent character in its compounds lithium differ from other alkali metals its dipole moment, it has more dipole moment than other alkali helides. It is hard and hygroscopic, it is not affected by the air. Its dipole moment is the main cause to increase the SHG efficiency of LiCl doped ADP crystals.

Dielectric Studies

The capacitance of the crystal was measured using the conventional parallel plate capacitor method with frequency range 20HZ to 1MHZ using Precision 4284 LCR meter at 50 °C and 80 °C temperature. Dielectric properties are correlated to the optical properties of the crystals. The magnitude of the dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar and space charge polarization which depends on the frequency [15]. At low frequency all polarizations are active. The space charge polarization is generally active at lower frequencies [16]. In KDP and ADP crystals, many reports are available about its dielectric behaviour and in our present work the measured dielectric constant values are in good agreement with the reported results [16-17]. The study clearly ensures the crystalline perfection of the crystals. The dielectric constant for 3M% LiCl doped ADP crystal and A9M%LiCl are measured at 50C and 80 °C. The dielectric constant goes on decreasing on increasing the frequency of the applied field. This low value of dielectric constant indicates that the grown crystals are reasonably good quality. The magnitude of dielectric constant depends on the degree of polarization and the charge displacement in the crystal. The decrease in dielectric constant at higher frequencies is attributed to the absence of charge polarization near the grain boundary interface[19]. For a material to be potential candidate for NLO applications, dielectric loss must be kept as low as possible. From the graph 9 it is clear that above crystals exhibits very low dielectric loss at high frequencies and can be used for NLO applications[20].

Conclusion

The pure and doped ADP crystals with different concentration of lithium chloride of best quality were grown from the solution within 2-3 weeks. The doping in the crystals was qualitatively confirmed by the FTIR spectroscopy. The SHG efficiency

study shows that the improvement in the efficiency of the doped crystals. Increasing transparency with concentration of the dopant in the host crystal has been confirmed by UV-visible spectroscopy. The lattice parameters have been determined from powder XRD study. Doping in the ADP crystals leads to negligible change in the lattice parameters, and crystal system and space group of the ADP retained. Low value of dielectric constant reveals that the grown crystals are of good quality. The SHG efficiency of A2M%LiCl is found to be 1.9 times the efficiency of ADP crystal and 3 times the efficiency of KDP crystal.

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