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Studies on the effect of Sodium Chloride on Ammonium Dihydrogen Phosphate Single Crystals

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Abstract - *Single crystals of pure and 0.5 mol% sodium chloride (NaCl) doped ammonium dihydrogen phosphate (ADP) were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystals were characterized by powder X-ray diffraction (PXRD) and the lattice parameters were calculated. The functional groups present in the grown crystals were confirmed by FTIR studies. The optical transparency of the grown crystals was determined using UV-vis-NIR spectroscopic studies. The mechanical property of the crystals was found out by microhardness measurement.*

Key Words: **ADP crystal, slow evaporation technique, PXRD, FTIR, UV-vis-NIR.**

1.INTRODUCTION

Ammonium dihydrogen phosphate with chemical formula $NH_4H_2PO_4$, is a commercially available inorganic dielectric material. ADP has unique nonlinear optical, electro optical, piezo electric and antiferroelectric properties. ADP is widely used as the second, third and fourth harmonic generator for Nd: YAG and Nd: YLF lasers. ADP crystals are used for electro optical applications such as Q-switches for Nd: YAG, Nd: YLF, Ti: Sapphire and Alexandrite lasers as well as for acousto optical applications. Due to its interesting electrical and optical properties, structural phase transitions and ease of crystallization, it has been the subject of a wide variety of investigations for several decades. ADP crystallizes from aqueous solution in anhydrous form in the $I\bar{4}2d$ space group [1,2]. The molecular weight and density of ADP at room temperature are 115.03 g and 1.803 g/cc. ADP crystal has tetramolecular unit cell having unitcell parameters a = b = 7.510 Å and c = 7.564 Å [3]. Determination of the permittivity ε at a frequency of 36 Gc/s is described, the values obtained are $\varepsilon_{||}$ = 14.0 at 21 °C and $\varepsilon_{\perp}$ = 57.1 at 21.5 °C, where $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the values of permittivity when the applied electric field is parallel with or perpendicular to the optical axis [4]. ADP crystal decomposes at 210 °C to orthophosphoric acid with the evolution of ammonia [5]. ADP is a widely used crystal in the field of optics due to its birefringence properties. ADP crystals are piezoelectric which is a property required in some active sonar transducers. Sodium chloride (NaCl) is an inorganic material soluble in water. NaCl exists as ions in solution. NaCl has molar mass 58.44 g. It appears as a clear crystal with little or no odor. NaCl is chosen as the impurity in this work. With the aim of modifying ADP, in the present work, ADP is doped with sodium chloride (NaCl) and pure and 0.5 mol% NaCl doped ADP crystal have been grown and studied.

2. Experimental procedure

2.1 Crystal growth

Single crystals of pure and NaCl doped ADP crystals have been grown by slow evaporation process at room temperature. Ammonium dihydrogen phosphate salt and NaCl salt (GR grade) from Merck and double distilled water were used throughout the work. ADP was doped with NaCl in ratio 1:0.05. The solution was stirred continuously for 2 hours using magnetic stirrer for homogenization. It was then filtered using Whatmann filter paper, and transferred to a 250 ml beaker. The beaker was porously sealed and kept in an undisturbed place for slow evaporation. The supersaturated solution for the formation of NaCl doped ADP crystal was prepared by dissolving required amount of NaCl along with ADP and the saturated solution transferred to another beaker and kept in an undisturbed place. Crystals of considerable size were harvested within 12- 13 days. All the harvested crystals were washed with distilled water and dried using filter paper. The grown crystals were found to be stable, colourless and transparent. The photographs of the grown crystals are shown in fig. 1a and1b.

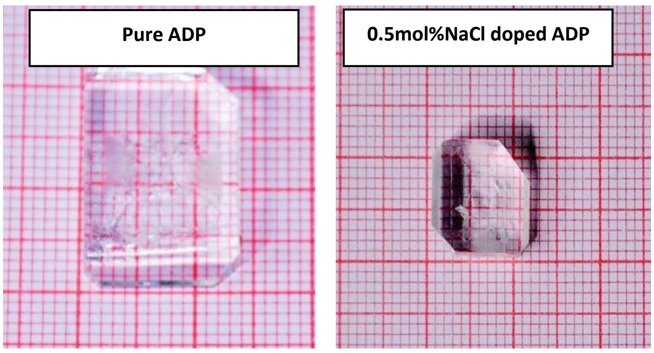

Fig. 1a **Fig. 1b**

Fig. 1 Photographs of pure and 0.5 mol% NaCl doped ADP

3. Results and discussion

3.1 Powder X-ray diffraction analysis

X-ray diffraction (XRD) is one of the most important non destructive tools to analyze all kinds of matter ranging from fluids, to powders and crystals. The structural characterization of the grown pure and sodium chloride doped ammonium dihydrogen phosphate crystals was carried out by powder X-ray diffraction (PXRD) analysis with XPERT-PRO X-ray diffractometer using copper (K- Alpha 1) radiation of wavelength 1.5406 Å operating at a voltage of 40 kV and a current of 20 mA. The scanning rate was maintained at 1.6 °/min over a 2θ range of 10-80° employing the continuous mode for scanning. The reflection positions and intensities of the resultant diffracted peaks of radiation produce a pattern, which is characteristic of the sample. Indexing of a powder pattern consists of the assignment of the three numbers h, k, l (the miller indices) to each reflection. The reflections in the PXRD patterns have been indexed using the JCPDS card number 89-7401. The sharp peaks in the PXRD pattern indicate good crystalline nature of the grown crystals. The diffraction positions in the PXRD pattern of pure ADP crystal coincides well with the powder diffraction standard card. The material of the grown crystal of pure ADP is thus confirmed. The PXRD pattern patterns obtained for NaCl doped ADP crystals are similar to that of pure ADP crystal with variations in the intensities of diffracted peaks and slight shifts in the 2θ values. The changes observed indicate the doping of NaCl into the lattice of ADP crystal. Similar literature has been reported in literature [6]. The indexed PXRD patterns of pure and 0.5 mol% NaCl doped ADP crystals are shown in fig. 2

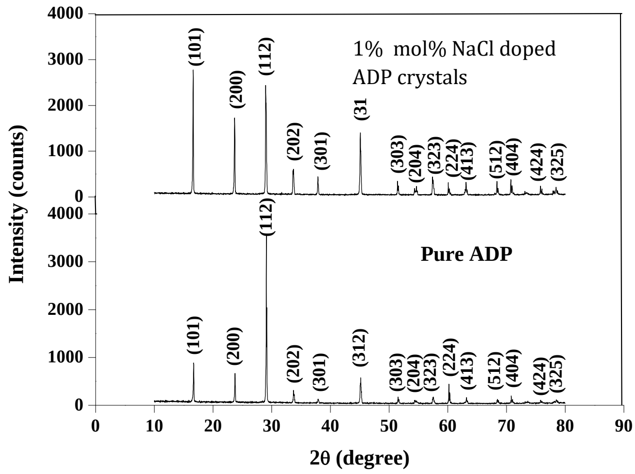

Fig. 2 PXRD pattern of pure and 0.5 mol% NaCl doped ADP crystals

The unitcell parameters of pure and NaCl doped ADP crystal is a=b= 7.4987 and c=7.5348 and the volume is 423.6908 (Å)^3 and the results are found to be in good agreement with the reported values [7]. For NaCl doped ADP a=b=7.5157 and c=7.5479 and volume is 425. 8971 (Å)^3. However, the PXRD pattern reveals the absence of additional phase due to NaCl doping, thus retaining the tetragonal structure and cinfirming that the NaCl molecules have entered into the ADP crystal lattice.

3.2 Fourier transform infrared spectroscopy

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. The FTIR spectra of the grown crystals were recorded by KBr pellet technique using Perkin Elmer FTIR spectrometer in the range 4000-400 cm^{-1}. The FTIR spectra of pure and NaCl doped ADP crystals are presented in fig. 3. The observed FTIR wavenumbers of pure ADP is compared with the reported values and the vibrational band assignment of pure and NaCl doped ADP crystals.

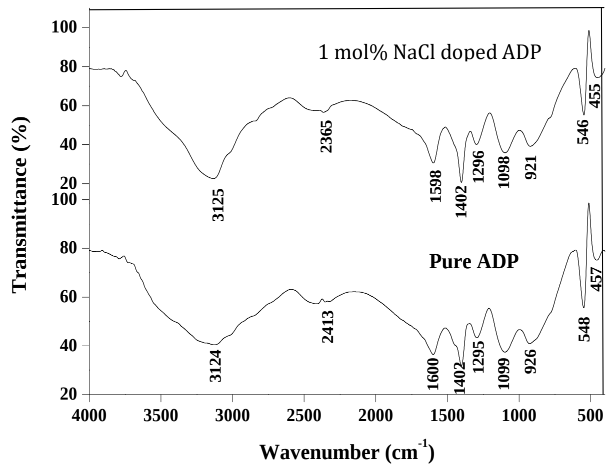

Fig. 3 FTIR spectrum of pure and 0.5 mol% NaCl doped ADP crystals

In the FTIR spectrum of pure ADP, the broad band appearing at 3124 cm^{-1} corresponds to O-H vibrations of water, P-O-H group and N-H vibrations of ammonium [8]. The band at 2413 cm^{-1} is assigned to hydrogen band [5]. The bending vibration of water gives the peak at 1600 cm^{-1}. The peak at 1402 cm^{-1} is due to the bending vibration of ammonium. The bands at 1099 cm^{-1} and 926 cm^{-1} represent the P-O-H vibrations. The bands at 548 cm^{-1} and 457 cm^{-1} are due to the PO_4 vibrations.

In the FTIR spectra of 0.5 mol% sodium chloride doped ADP the broad band centered at 3124 cm^{-1} in pure ADP, is shifted to 3135 cm^{-1}. This band is found to become narrower as the NaCl concentration increases. The hydrogen band assigned in pure ADP is shifted to 2365 cm^{-1}. The band at 1600 cm^{-1} in pure ADP gets shifted to 1598 cm^{-1}. The peak 1402 cm^{-1} is due to bending vibrations of ammonium. The band assigned as P-O-H vibrations at 1099 cm^{-1} and 921 cm^{-1} in pure ADP are shifted to 1098 cm^{-1} and to 921 cm^{-1}. The bands at 548 cm^{-1} and 457 cm^{-1} in pure ADP assigned as the PO_4 vibrations appear at 546 cm^{-1} and at 455 cm^{-1}.

The slight shift in the peak positions of NaCl doped ADP when compared to that of pure ADP and also the increase in the narrowing of the band in the high energy region as the NaCl concentration increases are clear evidences for the incorporation of NaCl into the ADP crystal lattice.

3.3 UV-vis-NIR spectral studies

The Ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy is one of the most important analytical and characterization techniques which is useful in characterizing the absorption, transmission, and reflectivity of a variety of technologically important materials. The UV-vis-NIR spectra were recorded for the pure and NaCl doped ADP single crystals using a Perkin Elmer Lambda 35 UV-visible spectrometer in the range 190-1100 nm. Crystal plates of thickness 2 mm, cut and polished without any antireflection coating were used for optical measurements. The UV-vis transmission spectra obtained for the pure and NaCl doped ADP crystals are shown in fig. 4. It is observed from the figure that the transmittance is good in the entire visible and near infrared regions for all the grown crystals. The pure ADP crystal has approximately 58% transmittance. This result is in good agreement with the reported value of 55% of transmittance for conventional method grown ADP crystal [9].

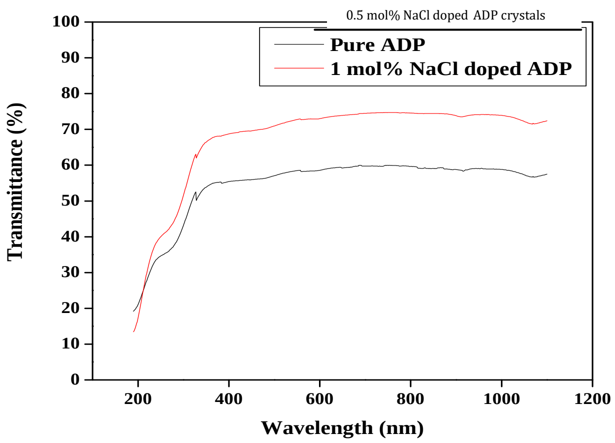

Fig. 4 UV-vis-NIR transmission spectra of pure and NaCl doped ADP crystals

The transmittance of 0.5 mol% NaCl doped ADP crystal is observed to be approximately 74%. The addition of NaCl increases the transparency of ADP crystal and the transmittance increases for 1 mol% NaCl doped ADP crystal.

Thus it is concluded that the dopant NaCl plays a vital role in improving the optical transparency and quality of the ADP crystal.

3.4 Micro hardness studies

Micro hardness tests are useful to find the mechanical hardness of the crystal grown and to estimate the threshold mechanical strength it can withstand [10]. The micro hardness measurement was carried out for the grown crystals using Shimadzu HMV-2T Vickers micro hardness tester fitted with Vickers diamond pyramidal indenter to study their mechanical property. The applied load was varied as 25g, 50g and 100g for constant indentation time of 5s for each trial. The Vickers hardness number was calculated. The variation of Vickers hardness number with the applied load for pure and NaCl doped ADP crystals is shown in fig. 5. In pure ADP crystal, the hardness number increases with increase of load upto 100g. For loads above 100g cracks started to develop around the indentation mark due to the release of internal stress generated locally by indentation.

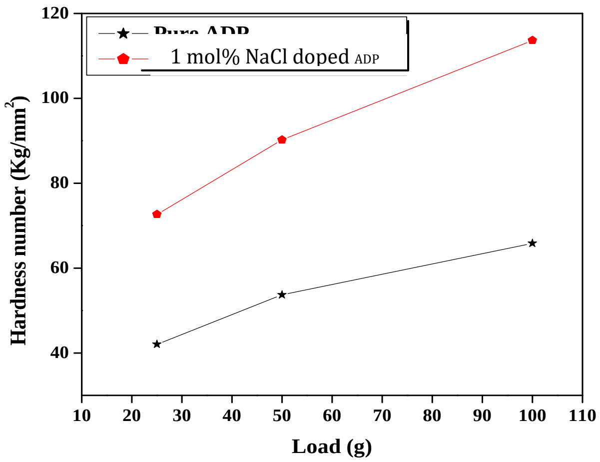

Fig. 5 Variation of Vickers hardness number with the applied load for pure and NaCl doped ADP crystals

The Vickers hardness number for 0.5 mol% NaCl doped ADP crystal is found to increase and it is concluded that the dopant NaCl has enhanced the hardness of pure ADP crystal. Similar observation has been reported in doped ADP crystals [11].

4. CONCLUSION

Single crystals of pure and NaCl doped ADP were grown from aqueous solutions by employing slow solvent evaporation technique at room temperature. The grown crystals were subjected to powder X-ray diffraction analysis and the study revealed that the tetragonal structure of ADP is retained. The FTIR transmission spectra have been recorded in the range 4000-400 cm^{-1} for all the grown crystals. The increase in the narrowing of band in the high energy region, as the NaCl concentration increases and the shift in peak positions observed in the FTIR spectra of NaCl doped ADP provide clear evidence for the presence of the dopant NaCl in the lattice of ADP. The UV-visible-NIR spectral analysis revealed that the pure and NaCl doped ADP crystals were found to have good optical transparency in the visible and NIR regions. The NaCl dopant has thus improved the optical quality of pure ADP with higher transparency. The microhardness measurement was carried out to study the effect of NaCl dopant on the mechanical property of ADP crystal. The hardness number of pure ADP has increased from 65.85 to 113.65 for 0.5 mol% NaCl at 100 g load. The NaCl dopant has thus enhanced the mechanical property of ADP.

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