

Effects of Dopants on the Growth of Ammonium DI-Hydrogen Phosphate Crystals

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Abstract: Single crystals of Ammonium Di-hydrogen Phosphate were doped with anionic Cobalt, Magnesium, Nickel and Lithium and grown by constant temperature solution growth technique. The grown crystals were verified for their structural characteristics using powder XRD technique. FTIR analysis were done on the grown samples. High resolution XRD confirmed that the crystallinity of the material was found to decrease with the addition of impurity dopants in KDP.

Keywords: ADP, solution growth, crystal, XRD, FTIR.

1. Introduction

Presence of small amount of impurities in the form of anionic dopants Co^{3+} , Mg^{2+} , Li^{2+} , and Ni^{3+} plays a vital role in the growth rate, habit of the crystal and its properties[1,2,3,4]. Some impurities enhance the properties of the crystal, but some tend to suppress. The inclusion of some dopants can possibly play a significant part in changing the properties of the parent crystal. Crystals of ADP were grown by solution growth technique by slow evaporation technique at room temperature. The solubility studies were done for pure and the doped ADP.

2. Solubility Studies

The solubility of a chemical species in a solvent refers to the amount of solute that can be dissolved at constant temperature, pressure, and solvent composition. In other words, it is the concentration of the solute in the solvent at equilibrium[5,6]. The solubility of ADP in the pure state and that of ADP with dopants were studied. The various dopants were taken in 1 mol % by weight of ADP and their solubility were studied independently (Fig.1). Solubility of ADP

in its undoped state was found to be 32 grams per 100ml of the solvent (double distilled water). By adding every dopant it was observed that additional solute was required for saturation of the solution at the same temperatures. This can be attributed to the increase in the density of the dopants in the solution which increases the ionic nature of the solution.

3. Metastable zonewidth

The metastable zone width is the measure of stability of a solution in its supersaturated region where the largest width implies the substance having higher stability during crystal growth [7]. 100 ml of the saturated solution was kept in the cryostat and the temperature reduced at 5°C per hour while the solution was stirred continuously. The temperature of formation of the first speck was found which corresponds to the width of the metastable zone. The metastable zone width of ADP was found to be the maximum in the lower temperature gradients than the higher gradients (Fig. 2).

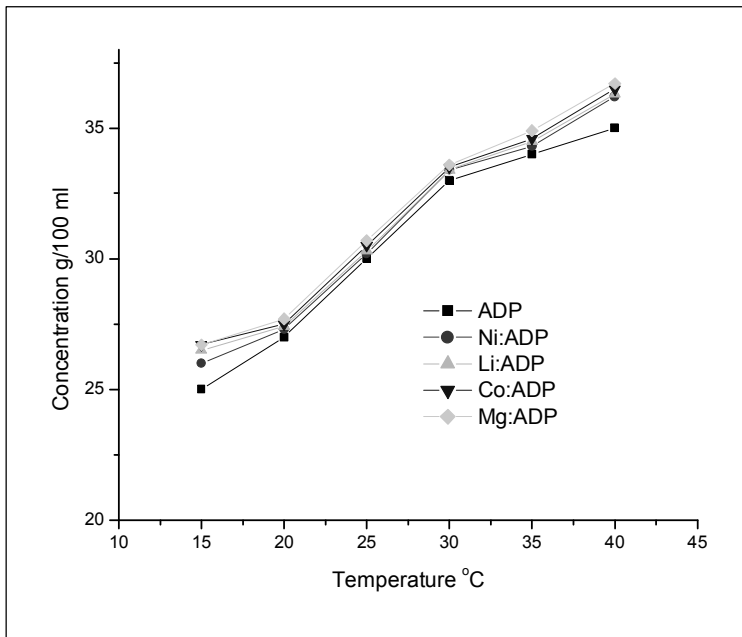


Fig 1. Solubility studies of pure and doped ADP crystals

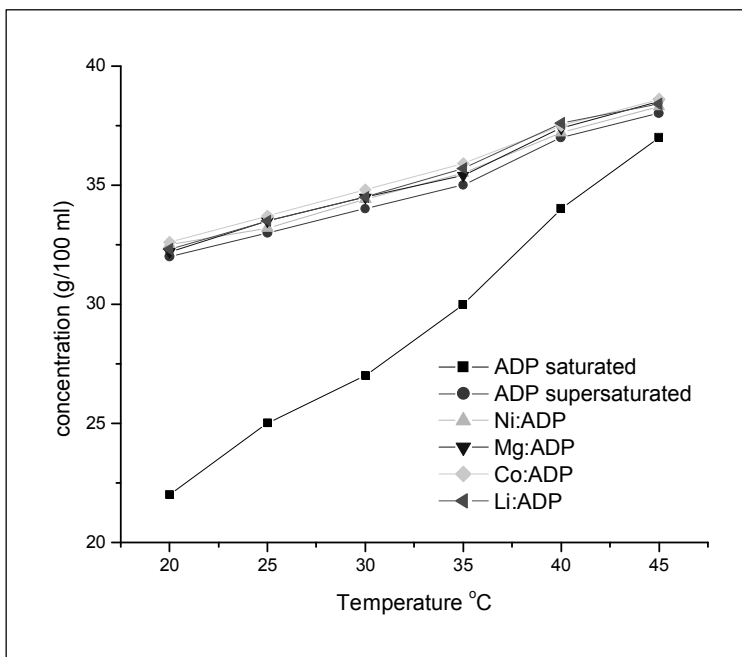


Fig 2. Metastable zone width of ADP and doped ADP

4. Induction period

Nucleation and growth occurs simultaneously in a supersaturated environment. The relative rates at which these occur are primary determinants of the characteristics of the final crystal size. One way of influencing product size distributions is through the control of variables such as supersaturation, temperature, and mixing characteristics. Obviously, those factors that increase nucleation rates relative to growth rates lead to only smaller crystals. Thus the exact moment of the formation of the first speck or

nuclei (induction period) is carefully analysed and studied in every solution growth process. The induction period was observed for pure and doped crystals of ADP. It was found that the maximum induction period of 325 seconds was observed for concentration 1.5 and a minimal period of 60 seconds was noted for a concentration of 1.1. When ADP was doped with Magnesium the formation of the initial nuclei was observed to be the fastest where Lithium doping resulted in the slowest formation period (Fig.3).

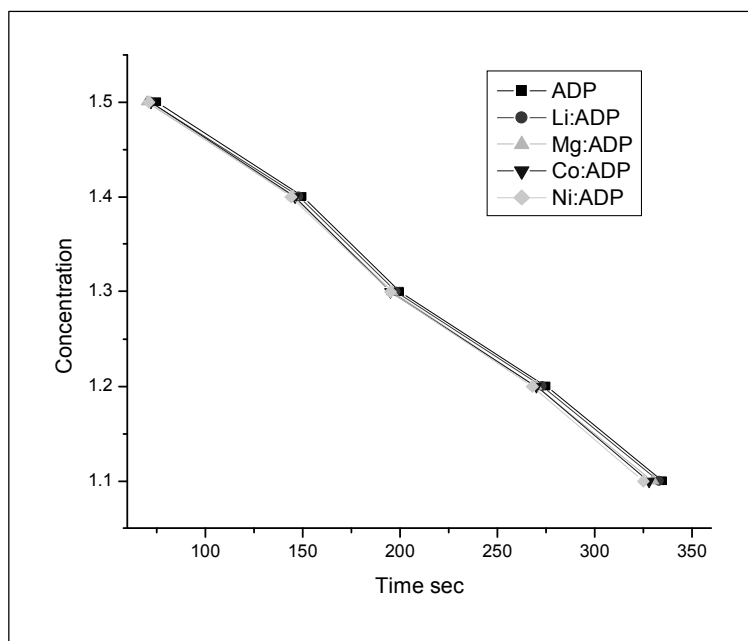


Fig 3. Induction period of pure and doped ADP

5. Structural Investigations

XRD studies were carried out with the grown crystals in powdered form. The powder samples were loaded into a Rigaku X-Ray diffraction apparatus using $\text{CuK}\alpha$ radiation having $\lambda = 1.5405$ and analysed. Results were compared with the JCPDS database file number 37-1479 where the prominent peaks of the reported values coincided with the investigated patterns. The powder XRD pattern of ADP as well as doped ADP had three prominent peaks at (202), (201), (204) respectively (Fig 4). The cell parameters were found to be $a = 7.502 \text{ \AA}$, $c = 7.554 \text{ \AA}$ where the unit cell volume was 425.139 respectively which is in good agreement with the reported values [8].

6. FTIR spectroscopy

Infrared spectrometry involves examination of the twisting, bending, rotating and vibrational modes of atoms in a molecule. Upon interaction with infrared radiation, portions of the incident radiation are absorbed at specific wavelengths. The multiplicity of vibrations occurring simultaneously produces a highly complex absorption spectrum that is uniquely characteristic of the functional groups that make up the molecule and of the overall configuration of the molecule as well. The Fourier Transform Infra Red (FTIR) investigations were also carried out on the powdered samples of ADP and doped ADP. The spectrum was observed from a Perkin-Elmer 781 spectrophotometer in the regions $400\text{-}4000\text{cm}^{-1}$ using a

KBr pellet. Many useful observations were observed. The group frequency region was located between ($4000\text{-}1300\text{cm}^{-1}$) and the fingerprint region ($1300\text{-}650\text{cm}^{-1}$). The intermediate frequency range, $2500\text{-}1540 \text{ cm}^{-1}$ (*unsaturated* region) contains triple bond frequencies which appear from 2500 to 2000 cm^{-1} and double bond frequencies from 2000 to 1540 cm^{-1} . In the region between 1300 and 650 cm^{-1} there are single bond stretching frequencies and bending vibrations (skeletal frequencies) of polyatomic systems involving motions of bonds linking a substituent group to the molecule. The lower regions $667\text{-}10 \text{ cm}^{-1}$ contains the bending vibrations of carbon, nitrogen, oxygen and fluorine with atoms heavier than mass 19. The observed frequencies for the diatomic molecule O_2 was at 1582cm^{-1} . Dopants like Mg had absorption peaks at 544 cm^{-1} , Ni^{3+} at 540cm^{-1} and strong absorption bands for lattice water (antisymmetric and symmetric OH stretchings) at 3231 cm^{-1} were also observed. This can be attributed to the fact, that when certain solutes 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 the number of water molecules associated with each solute molecule may vary with the crystallization temperature. It was observed (Fig.5) in Ni^{3+} doped KDP an additional absorbance was detected at 3237 cm^{-1} which implies that the inclusion of Nickel modifies the transparency of the crystal at that region. This was very much prominent in the Nickel Magnesium

bimetallic crystal which had an increased absorbance at 3293 cm^{-1} . The rest of the dopants were not seen to appreciably modify the FTIR spectrum. Cobalt doping on ADP had a functional peak at 535 cm^{-1} and a wide oxygen double bond stretching at 1720 cm^{-1} . Lithium peak was at 543 cm^{-1} , and OH bond interaction in

Lithium doped ADP at 2857 cm^{-1} . In Nickel Magnesium ADP, the peak at 2424 cm^{-1} is found to be missing and the peak at 3293 cm^{-1} seems to broaden up. This can be attributed to the double dopant introduced.

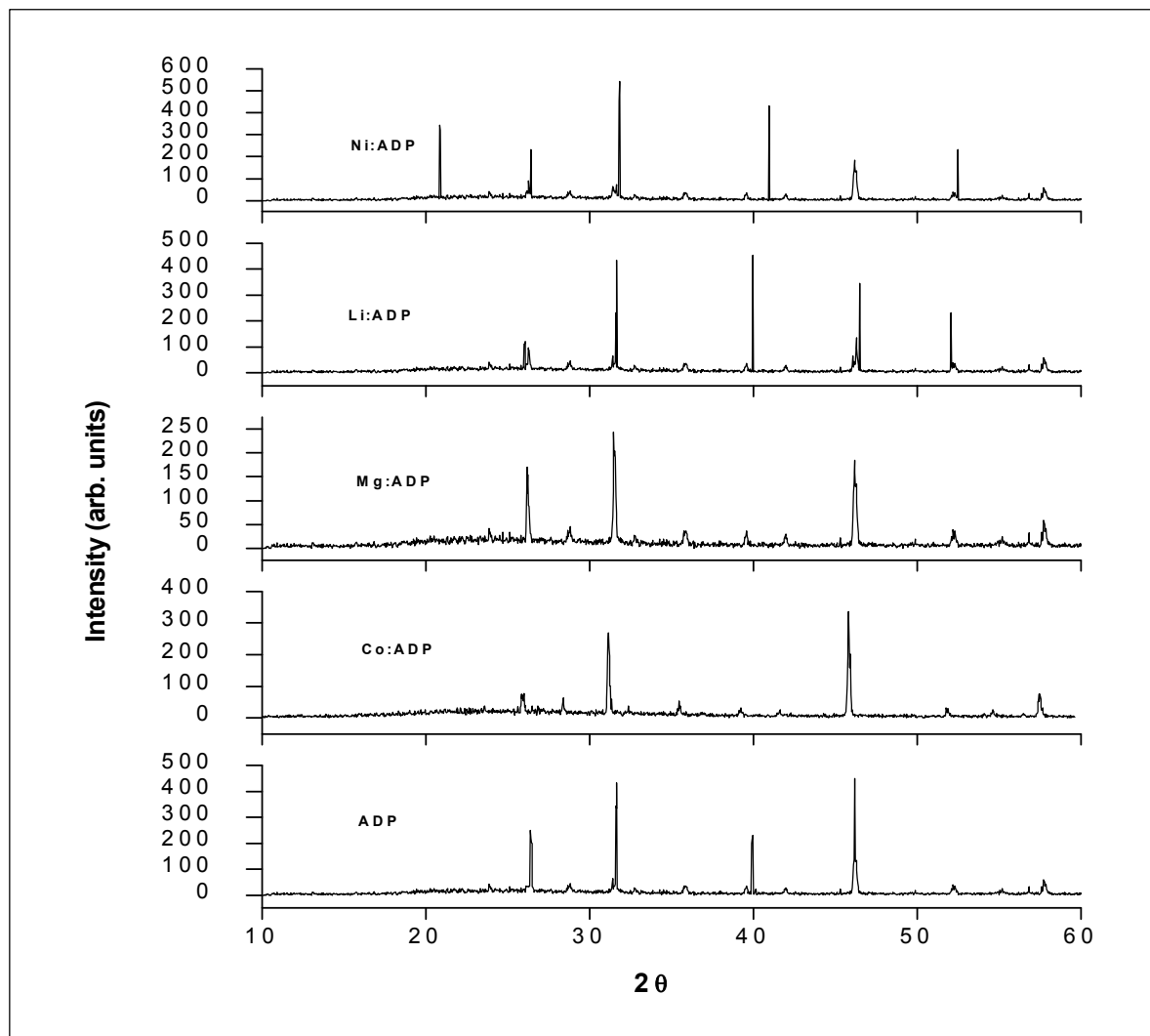


Fig. 4 XRD pattern of pure and doped ADP

7. High Resolution XRD studies

The high-resolution diffraction curves recorded for specific diffracting planes which are mentioned in the curved brackets with the multicrystal X-ray diffractometer (10) in symmetrical Bragg geometry. A well-collimated and monochromated $\text{MoK}\alpha_1$ beam obtained from a set of three plane (111) Si monochromator crystals set in dispersive $(+,-,-)$ configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the $(+,-,-,+)$ configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s)

and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant.

All the curves were observed to have single peaks. This diffraction curve shows that though the quality of this crystal is very good, the specimen contains one *very low* angle boundary. The FWHM of the ADP peaks (Fig. 6) were $13''$ and the cobalt doped crystals (Fig. 7) were $27''$. This implies that the undoped crystal of ADP had a good order of crystallinity than the Cobalt doped Crystal of ADP.

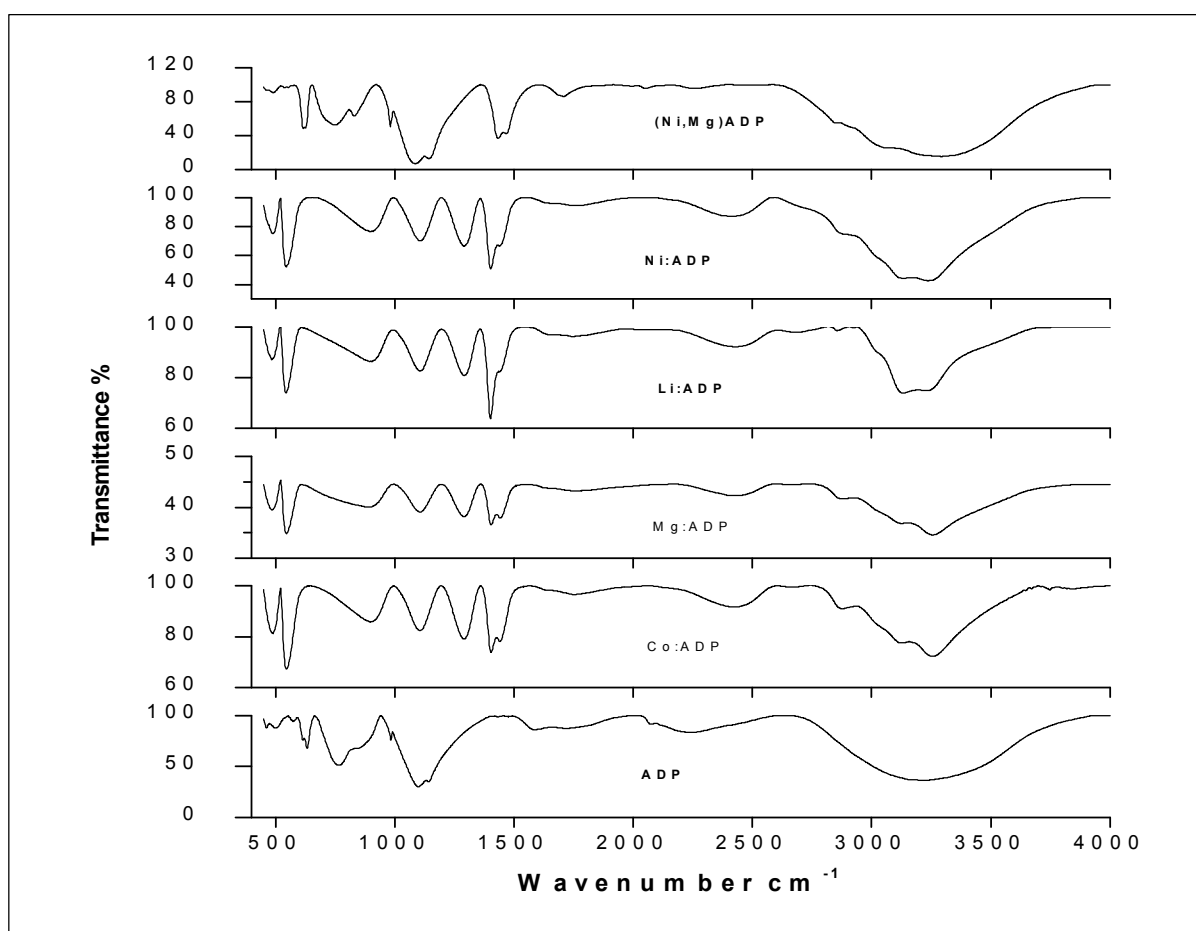


Fig. 5 FTIR pattern of pure and doped ADP

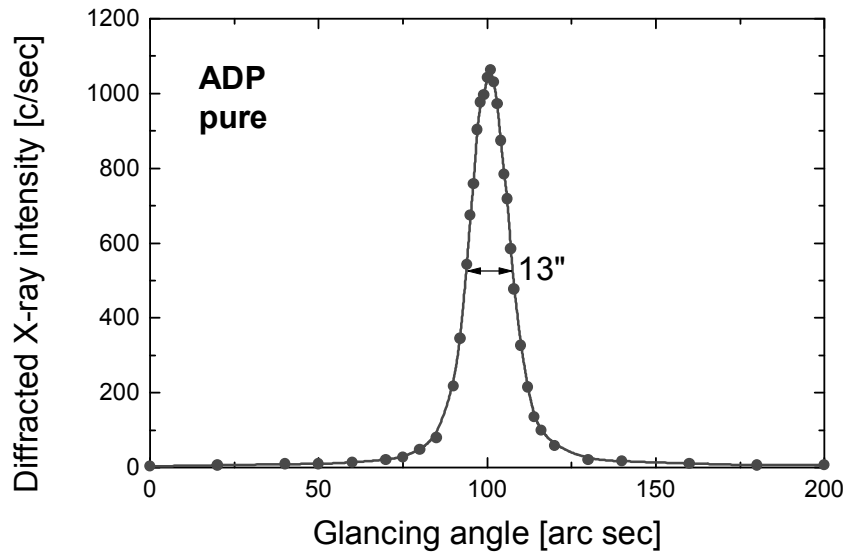


Fig. 6 HXRD of pure ADP crystal

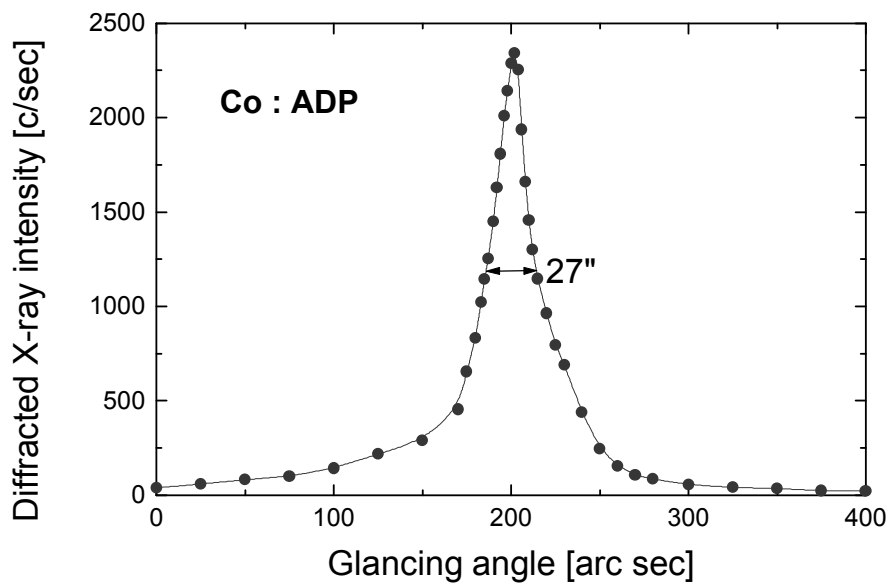


Fig. 7 HXRD of cobalt doped ADP crystal

8. Conclusion

The crystals grown doped with impurities in the form of dopants were found to have faster nucleation rates and quicker induction periods. The crystallinity was found to be comparatively good in undoped ADP crystal than the Cobalt doped crystal

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