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# EFFECT OF LOW AND HIGH CONCENTRATIONS OF KCl DOPANT ON ADP CRYSTAL PROPERTIES

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The experimental results of the influence of low (1 M%) and high (10 M%) concentrations of potassium chloride (KCl) dopant on ADP crystals are presented. The dopant results in an increase in the metastable zone width leading to an enhanced crystal growth rate, at its low concentrations. In the presence of high concentrations of the dopant in the medium, the growth rate decreases appreciably. Further, low concentrations of dopant improve the crystalline quality with better transparency. The diffraction patterns reveal that there is no change in basic structure except for variation in intensity by doping. Slight broadening is observed in FTIR of ADP in the 3500–3000 $cm^{-1}$ range in the presence of high [KCl]. It appears that the dopant has not altered much the optical transparency of the crystal. SEM studies of pure and doped samples reveal that structure defect centers are formed in ADP crystals by the dopant. Second harmonic generation (SHG) efficiency measurements indicate that nonlinear optical (NLO) property is enhanced appreciably by [KCl] dopant and the SHG is more pronounced at high concentrations. It seems that the molecular alignment of the crystal facilitates non-linearity in the presence of the dopant.

***Keywords:*** *ADP, inorganic dopant, non-linear optical material, scanning electron microscope, thermal analysis, XRD*

## Introduction

ADP ($NH_4H_2PO_4$) is widely used as the second, third and fourth harmonic generator for Nd:YAG and Nd:YLF lasers. The crystals are widely used for electro-optical applications as Q-switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers, as well as for acousto-optical applications. It belongs to the tetragonal system with the space group 1-42d [1]. A systematic investigation of the effect of low and high concentrations of KCl on ADP single crystals has not been reported.

The growth promoting effect (GPE) is observed with inorganic dopants like potassium chloride (KCl) and ammonium chloride ($NH_4Cl$) [2] due to the complexation of trace metal ion impurities in solution. Entry of the resulting complex into the crystal is ruled out and the GPE in the presence of the complexing agent is appreciable. Also, in the presence of dopants in the growth medium, the secondary nucleation is effectively controlled. Further, it was observed that organic additives like EDTA, urea and thiourea lead to an increase in the growth rate and improvement in quality of different crystals [3]. Thermal analysis, XRD, microhardness testing, SEM, FTIR and UV-Vis spectra are very useful techniques to study the materials properties. Therefore, many authors have used these techniques to characterize various materials [4–36]. We have systematically analyzed the effects of various structurally different organic dopants on tristhioureazinc(II)sulphate crystals. The GPE in the presence of very low concentrations of organic dopant is caused by adsorption of dopants on the flat surface or the step edges of the crystal. In this paper, we focus on the concentration effects i.e., effects of low and high concentrations of the dopant KCl on the growth of ADP crystals and their properties.

## Experimental

### *Crystal growth*

The crystal growth rate and quality of the crystals were much better when solution is slightly acidic and the studies were carried out at pH~4.5. The crystals were grown by solvent evaporation technique. Different concentrations of dopant 1 and 10 M% of KCl were used in the growth medium. As reported earlier [2] in the case of KDP crystals, the addition of KCl enhances the metastable zone width of ADP solution.

The growth rate of crystals is much better with low concentration of dopant and decreased with an increase in dopant concentration. At high concentra-

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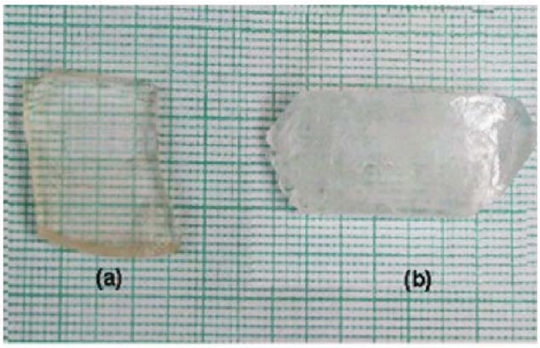

**Fig. 1** Photographs of low and high concentrations of KCl doped ADP a – 1 M% KCl doped ADP and b – 10 M% KCl doped ADP

tions of the dopant, the adsorption film blocks the growth surface and inhibits the growth process [37]. Bulk crystals are grown using optimized growth parameters. The quality of the crystal is much better with better transparency in the presence of low concentrations of dopant in the growth medium. Less transparency and occlusions are observed with 10 M% KCl. Photograph of the as-grown KCl doped ADP crystals are shown in Fig. 1.

*Measurements*

The powder X-ray diffractometry analysis was performed with a graphite monochromated CuK$_\alpha$ radiation.

The FTIR was recorded for all the samples including pure ADP using AVATAR 330 FT-IR by KBr pellet technique in the range 500–4000 cm$^{-1}$.

The UV-Vis absorption spectra were recorded using a Hitachi UV-Vis spectrophotometer in the spectral range 250–800 nm for all the samples.

Vickers microhardness was evaluated for the well-polished grown crystal and dominant (100) plane using Reichert 400E ultra microhardness tester.

DSC curves were recorded on a DSC-60 Shimadzu analyzer at a heating rate of 20°C min$^{-1}$.

Second harmonic generation test on the crystals was performed by Kurtz powder SHG method [38]. An Nd:YAG laser with a modulated radiation of 1064 nm was used as the optical source and directed on the powder sample through a filter.

## Results and discussion

XRD patterns of ADP crystals grown rapidly in 1 and 10 M% KCl doped ADP crystals are compared with that of pure ADP crystal. No change in basic structure is observed except for the slight variation in intensity with dopant KCl (Fig. 2). The XRD data is analysed with Rietveld method with RIETAN-2000.

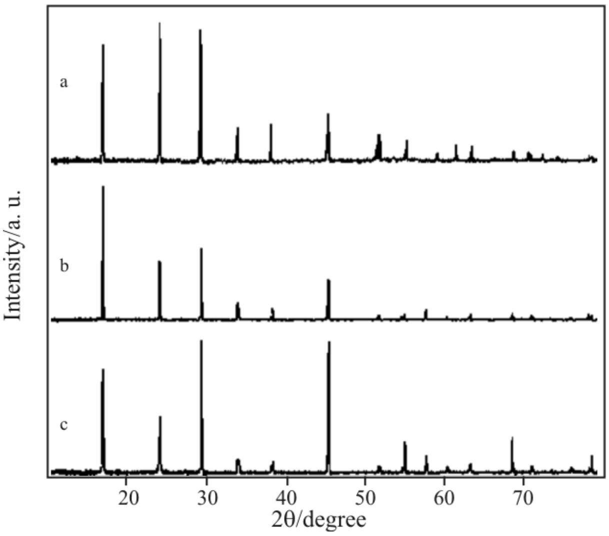

**Fig. 2** XRD patterns of a – pure ADP, b – 1 M% KCl doped ADP and c – 10 M% KCl doped ADP

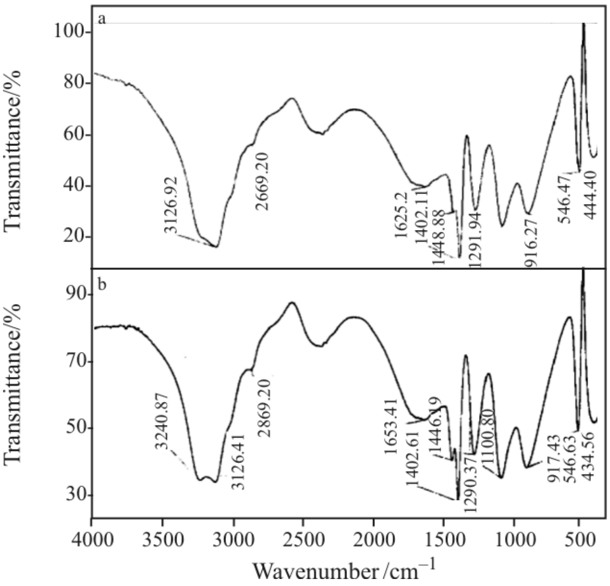

**Fig. 3** FTIR spectra of a – 1 M% KCl doped ADP and b – 10 M% KCl doped ADP

The characteristic vibrational frequencies of pure ADP and KCl doped ADP are very similar. Oxygen stretching and bending frequencies of PO, $\nu_{PO}$ and $\delta_{PO}$ are similar in the pure and doped samples. The –NH group hydrogen stretching frequency at 3500–3000 cm$^{-1}$ is slightly broadened in the presence of high concentrations of KCl indicating some type of interaction between the dopant and –NH group of ADP (Fig. 3).

The dopant has not destroyed the optical transparency of the crystal.

Microhardness number, H$_v$ decreases by doping from 90 to 70–75 kg mm$^{-2}$ for a test load of 150 kg. Low and high concentrations of doping of KCl almost give the same H$_v$ value (70–75 kg mm$^{-2}$).

DSC curves of pure ADP, 1 M% KCl doped ADP and 10 M% KCl doped ADP are presented in Figs 4a–c, respectively. All three DSC curves exhibit an endothermic peak at 213.49, 222.21 and 215.90°C, respectively. The addition of 1 M% KCl has shifted the peak temperature higher (222.21°C) than the pure ADP peak temperature (213.49°C). But the addition of 10 M% KCl has shifted the peak temperature a little bit higher (215.90°C) than the pure ADP peak temperature (213.49°C) but lower than 1 M% KCl doped ADP peak temperature (222.21°C).

SEM study (JEOL JSM 5610 LV) gives information about the surface nature and its suitability for device fabrication. Also, it is used to check the presence of imperfections. The investigation of the influence of the low and high concentrations of dopant KCl on the surface morphology of ADP crystal faces reveal the formation of structure defect centers. In the presence of 10 M% KCl in the growth medium, SEM photograph of ADP crystal shows a fibrous structure (Fig. 5a). Larger scatter centers are observed in 1 M% KCl doped ADP (Fig. 5b).

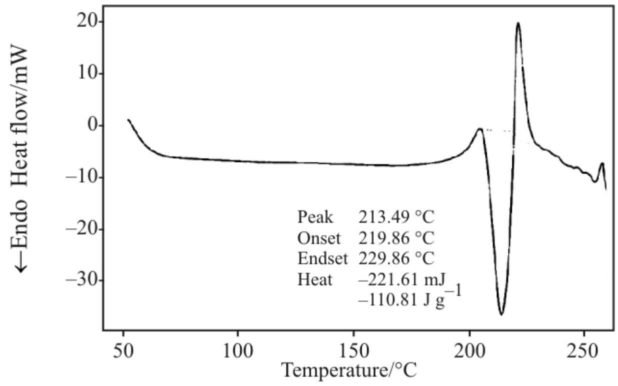

**Fig. 4a** DSC curve of pure ADP

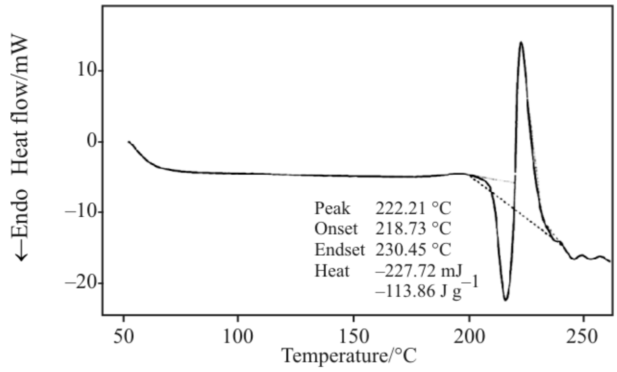

**Fig. 4b** DSC curve of 1 M% KCl doped ADP

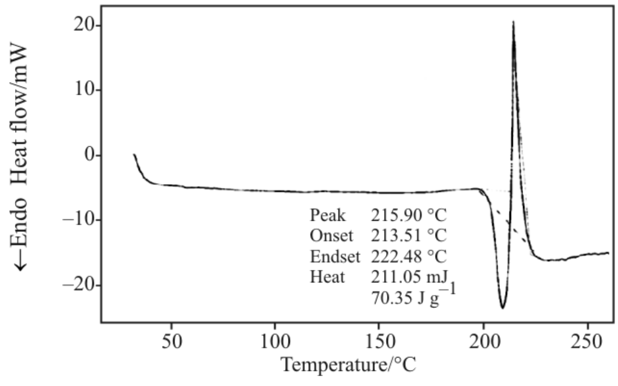

**Fig. 4c** DSC curve of 10 M% KCl doped ADP

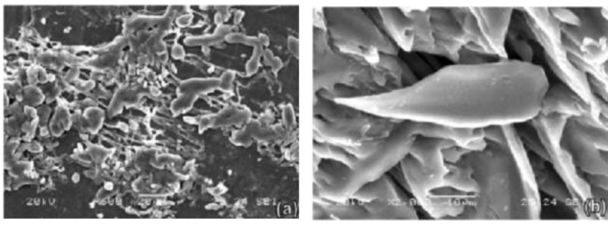

**Fig. 5** SEM photographs of a – 10 M% KCl doped ADP and b – 1 M% KCl doped ADP

**Table 1** SHG output

| System | $I_{2\omega}$/mV |
|---|---|
| ADP | 500–600 |
| ADP/1 M% KCl | 800–900 |
| ADP/10 M% KCl | 900–1100 |

An Nd:YAG laser with a modulated radiation of 1064 nm was used as the optical source and directed on the powder sample through a filter. The doubling of frequency was confirmed by the green radiation of 532 nm (Table 1).

Input radiation is 5.4 mJ pulse$^{-1}$. Intensity of second harmonic generation gives an indication of NLO efficiency of the material. Non-linearity is facilitated in the presence of the dopant. The dopant has a catalytic effect on the NLO properties of ADP crystals. It is interesting to observe that the SHG efficiency is more pronounced in the presence of high concentration of the KCl dopant in the growth medium. It appears that the attainment of second-order effects requiring favourable alignment of the molecule within the crystal structure [39] is well facilitated in the presence of the inorganic dopant KCl. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation [40].

## Conclusions

The following conclusions can be drawn from the present study:

- Potassium chloride (KCl) as dopant influences the thermal properties of ADP
- KCl enhances the metastable zone width of ADP solutions and well promotes the crystal growth process at its low concentrations

- High [KCl] inhibits the growth process
- Crystalline quality of ADP is much better with better transparency in the presence of 1 M% KCl
- XRD and FTIR studies reveal that the GPE of dopant is quite likely caused by adsorption of dopant; the dopant is not entering into the ADP crystal
- FTIR studies in the presence of high concentration of the dopant reveal some weak interaction between the dopant and ADP
- Optical transparency is not destroyed by doping
- SEM studies reveal that external morphology of ADP changes by doping
- Dopant appreciably improves the SHG efficiency because of a favourable molecular alignment improving the non-linearity; higher the concentration of dopant, KCl, better the SHG efficiency of ADP crystals.

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