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EFFECT OF COMPLEXING AGENT (1,10-PHENANTHROLINE) ON ADP AND KDP CRYSTALS

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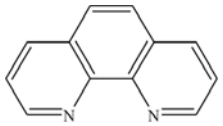
1,10-Phenanthroline (Phen) as a new additive was added into the solutions of KH_2PO_4 (KDP) and $NH_4H_2PO_4$ (ADP) in a small amount (~$2.5\cdot10^{-3}$ M L^{-1}). The crystals were grown from the aqueous solutions of pH ~4.5 at constant temperature by solvent evaporation technique. It leads to an increase in metastable zone width and assists the bulk growth process. The growth rate of crystals in the presence of Phen decreases considerably with an increase in impurity concentration (~$2.5\cdot10^{-2}$ M L^{-1}). Not much variation is observed in FTIR and XRD of pure and doped ADP/KDP. It appears that the growth promoting effect (GPE) of Phen is caused by the adsorption of the organic additive on the prism faces of ADP/KDP crystals. Higher optical transmittance is observed in the presence of the dopant. Detailed microhardness studies of ADP crystals reveal the anisotropy in the hardness behaviour. Scanning electron microscope (SEM) photographs exhibit the effectiveness of the impurity in changing the surface morphology of ADP/KDP crystals. Contrary to expectations, Phen depresses the NLO efficiency of ADP/KDP, suggesting that the molecular alignments in the presence of Phen results in cancellation effects disturbing the non-linearity.

Keywords: *characterisation, non-linear optical, 1,10-phenanthroline, thermal analysis, XRD*

Introduction

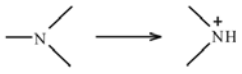
Potassium dihydrophosphate, KH_2PO_4 (KDP) and $NH_4H_2PO_4$ (ADP) are widely used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. The crystals are widely used for electro-optical applications as Q-switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers, as well as for acousto-optical applications. In the present paper, we are reporting a systematic investigation of the effect of complexing agent, a new additive 1,10-phenanthroline on ADP/KDP crystals.

Generally for the crystallisation to occur the homogeneous phase must be metastable (i.e., supersaturated). A small quantity of an impurity leads to an increase in the metastable zone width of the solution when the complex adsorption on the growing surface is not very stable [1]. This very much assists the bulk growth process. Ethylenediaminetetraacetic acid (EDTA), a surfactant is a good additive and the main reason for the rapid growth process in the presence of EDTA is its ability to form complex with impurities, particularly the trace metal ions in solution. These positive aspects of the complexing agents lead us to investigate the crystal growth of ADP/KDP crystals in the presence of a complexing agent, a new additive 1,10-phenanthroline.

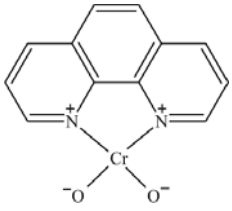


1,10-Phenanthroline

It can easily undergo protonation.



It can easily form complexes with metal ions in solution. For instance, it can form a complex with chromium [2].



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Many authors have investigated the interactions and influences of organics and inorganics and their chemical, thermal, spectral, physical, biological and many other properties [3–22]. We have grown the ADP/KDP crystals in the presence of a small quantity of Phen. A systematic comparison is made between crystals grown from pure solution and Phen added solution.

Experimental

Crystal growth

ADP and KDP crystals were grown by solvent evaporation technique in the presence of a small quantity of Phen (~$2.5 \cdot 10^{-3}$ M L^{-1}) (Figs 1a–d). The crystal growth and the quality of the crystals are much better, when the solution is slightly acidic and the pH of the growth medium is ~4.5. A considerable GPE of Phen on ADP/KDP crystals is observed.

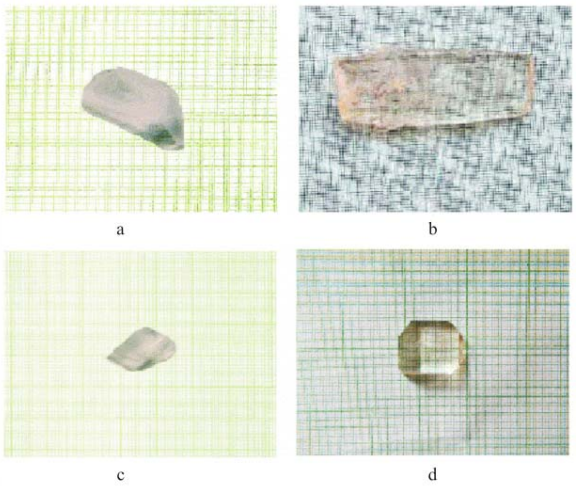

Fig. 1 Photographs of as grown crystals of ADP, ADP in the presence of Phen, KDP and KDP in the presence of Phen a – pure ADP, b – Phen added ADP, c – pure KDP and d – Phen added KDP

Studies follow the general trend that the growth rate of crystals in the presence of impurities always decreases with an increase in the impurity concentration (~$2.5 \cdot 10^{-2}$ M L^{-1}). At high concentration of Phen, the solution becomes reddish and the red colour shades are visible inside the crystal too. At high concentrations of the dopant, the adsorption film blocks the growth surface and inhibits the growth process [23]. Bulk crystals are grown using the optimized growth parameters.

Metastable zone width

Since a very small quantity of additive is added and the additive Phen is nonionic, there is not much of variation in the solubility of ADP/KDP. Metastable zone width was measured by conventional polythermal method [24, 25]. Metastable zone width is an essential parameter for the growth of large size crystals from solution, since it is a direct measure of the stability of the solution in its supersaturated region [26]. Metastable zone width is determined for Phen added ADP/KDP solutions and the comparison shows that it is greatly wider than the case of pure ADP/KDP solutions. Widening of metastable zone width results in GPE.

Results and discussion

X-ray diffraction study

The powder X-ray diffractometry (XRD) analysis was performed with a graphite monochromated CuK_α radiation. The XRD data is analysed with Rietveld method with RIETAN-2000. XRD patterns of ADP crystals grown rapidly in $2.5 \cdot 10^{-3}$ M L^{-1} Phen added solution is compared with that of pure ADP crystal (Figs 2a and b). No change in basic structure is observed in XRD patterns except for the slight reduction in intensities for both ADP and KDP. It belongs to tetragonal system and the lattice parameters are in good agreement with the reported values, JCPDS data card No. 00-037-1479. XRD analysis shows that additive has not entered into the crystal and it has not changed the crystallinity of the material.

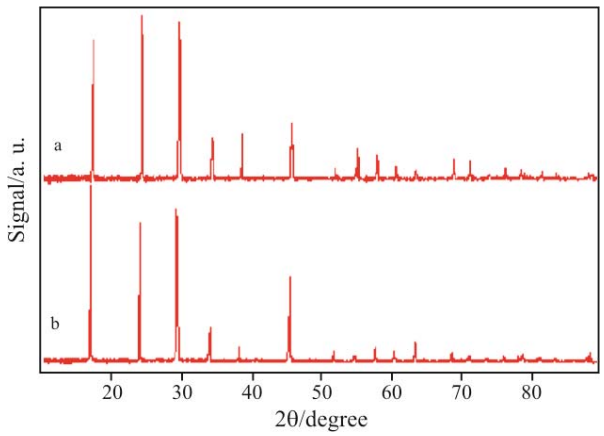

Fig. 2 XRD patterns of crystals grown from aqueous solutions of a – pure ADP and b – Phen added ADP

FTIR spectra

The FTIR spectra was recorded for all four samples including pure ADP/KDP using AVATAR 330 FT-IR using KBr pellet technique in the range 500–4000 cm^{-1}. The characteristic vibrational frequencies of pure ADP/KDP and organic dopant Phen added ADP/KDP is very similar (Figs 3a and b).

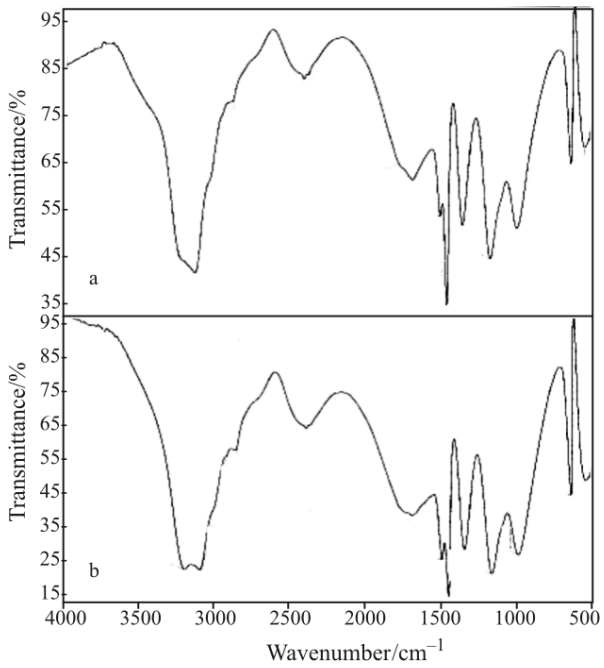

Fig. 3 FTIR spectra of a – pure ADP and b – Phen added ADP

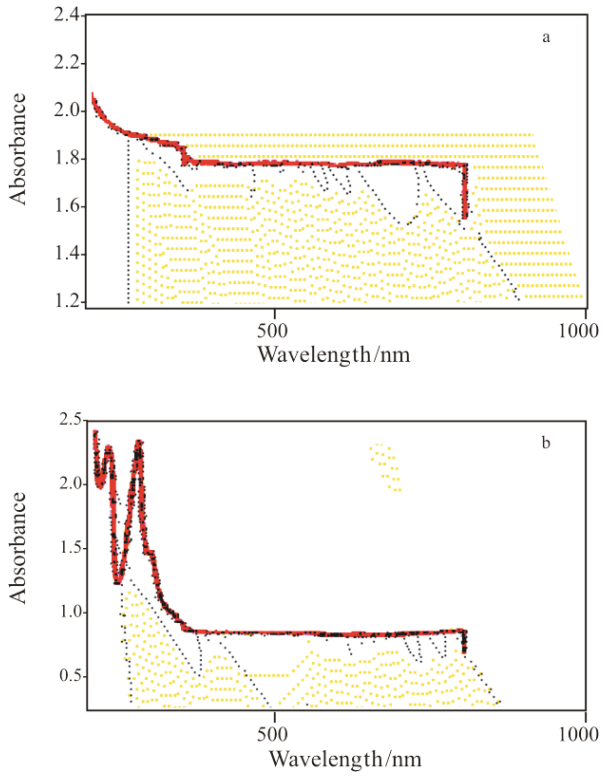

Fig. 4 Optical transmission spectra of crystals grown from pure and doped solutions a – pure ADP and b – Phen added ADP

XRD and FTIR spectral studies clearly reveal that the GPE of organic dopant is not connected with the additive entering into the crystal. When the impurity distribution coefficient is very low, the impurities are practically not incorporated into the crystal [27]. The rapid growth process is caused by the adsorption of the impurity at the flat surface or at the step edge [28]. It has been reported that at low dopant concentrations, adsorption can take place at kink sites (Bliznakov mechanism) or at the surface terrace (Cabrera Vemilyea mechanism) [29].

Optical transmission spectra

Comparison of spectra reveals that percentage transmittance in UV-Vis region is much better in the case of crystals grown in the presence of Phen. There is no appreciable change in the lower cut off wavelength region. Hence, addition of Phen in small quantities is effective for the growth of bulk ADP crystals with higher transmittance.

Microhardness measurements

Microhardness studies were carried out for the well polished ADP crystal faces free from any microstructures or defects to understand the mechanical behaviour. Vickers hardness test method is employed. The hardness H_v was computed using the relation,

$$H_v=1.8544\ p/d^2$$

where p is the load in kg and d is the mean diagonal length in mm.

The probable error of the mean value of H_v based on a number of trials of indentation for a given load was always within 4% of the mean value. It is interesting to note that anisotropy in the hardness behaviour has been observed. Figure 5b like type hardness plots has been reported in literature [30, 31]. Figures 5a and b clearly establish the anisotropy in the hardness behaviour. In Fig. 5b peak is observed at 150 g. Major contribution to the increase in hardness with load is attributed to the high stress required for homogeneous nucleation of dislocations in the small dislocation-free region indented. The anisotropy owing to plastic deformation has been exhibited. Many crystals deform plastically by means of a translational slip, in which one part of the crystal slides as a unit across a neighbouring part. Slip is anisotropic, and it occurs more readily along certain crystal planes and directions than along others. The variation of hardness with load indicates that there is a possibility for the crystal to undergo crystallographic phase transformation with increasing pressure.

In the Knoop microhardness studies of urinary calculi initial increase in hardness with load is explained due to work hardening and subsequent decrease with increase in load was due to work softening processes (Fig. 6).

$$p=ad^n$$

where n is the work-hardening exponent and a is the constant for a given material. The value of n, determined by least square fit method is 0.418 in the load region 50–150 g (Table 1).

Hence, small quantity of organic impurity increases the microhardness value significantly.

Table 1 Comparison of H_v values at a particular load

	p (load)/g	H_v/kg mm^{-2}
Pure ADP	200	89.4
ADP+Phen	200	108.5

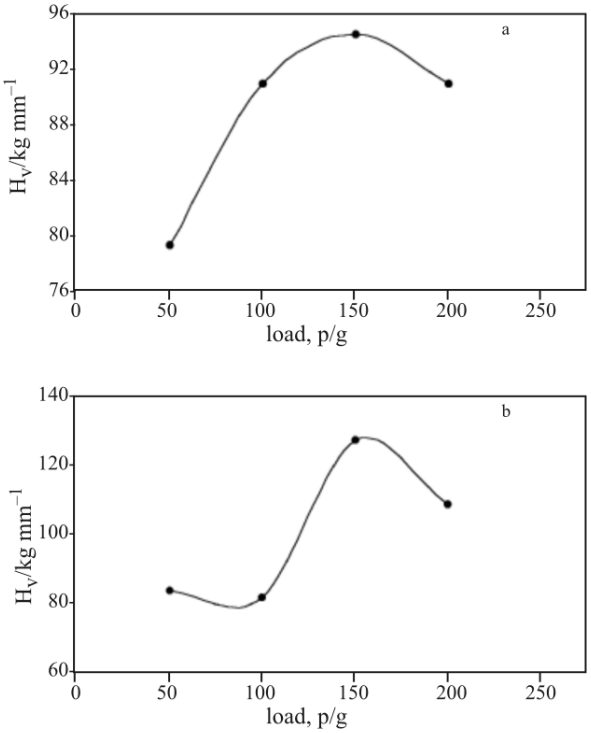

Fig. 5 Hardness anisotropy behaviour on (001) and (100) orientations a – (001) and b – (100) orientation

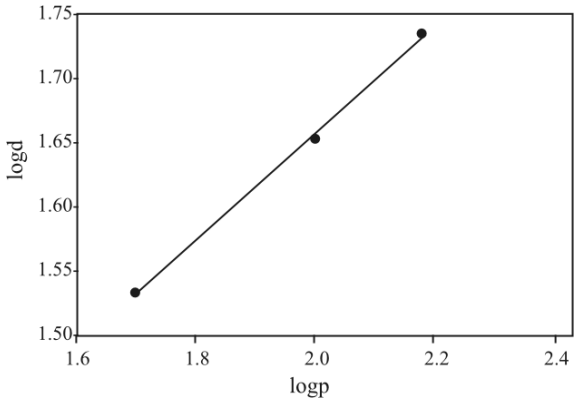

Fig. 6 Meyer plot

Thermal studies

The simultaneous obtained TG-DTA curves in air at a heating rate of 20°C min^{-1} reveal that there is no physically adsorbed water in the molecular structure of crystals grown from Phen added ADP solution. TG curve also show a gradual mass loss and residual mass obtained at 650°C is only 36.13% (Fig. 7a).

The TG-DTA analysis of crystals grown from Phen added KDP solution was carried out between 50 and 600°C in the nitrogen atmosphere. TG curves shows that there is a mass loss of about 15% due to volatile substances in the compound. Further, the mass loss is negligible after 340°C. In DTA curve there is a broadened peak without much resolution endotherm lying in between 220 and 300°C (Figs 7b and c).

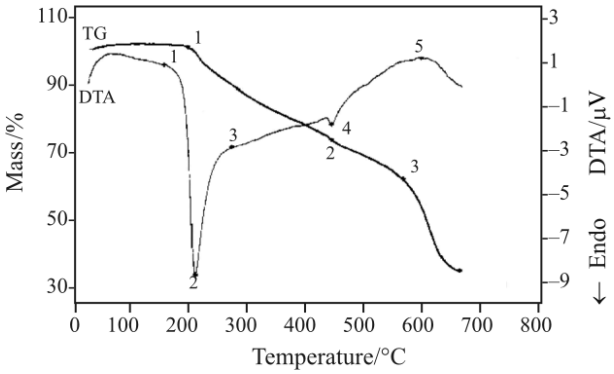

Fig. 7a TG-DTA curve of Phen added ADP

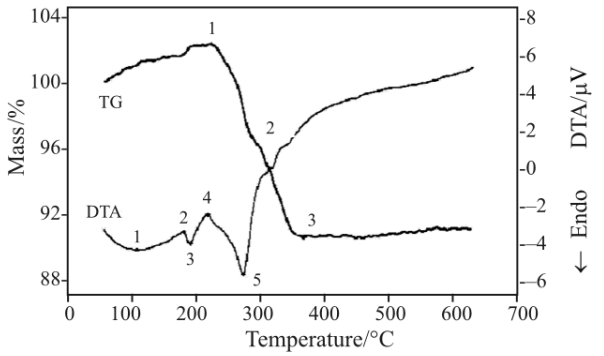

Fig. 7b TG-DTA curve of pure KDP

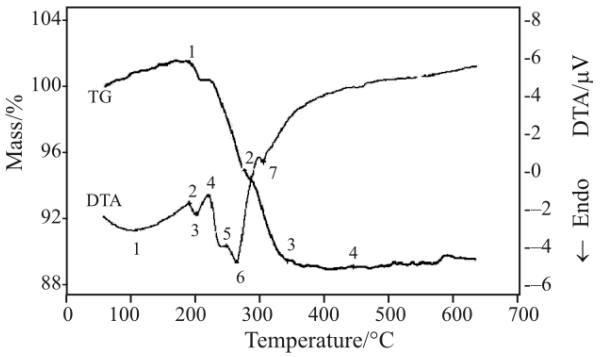

Fig. 7c TG-DTA curve of Phen added KDP

Scanning electron microscope (SEM)

SEM study gives information about the surface nature and its suitability for device fabrication. It is also used to check the presence of imperfections. It has been reported that the effectiveness of different impurities in changing the surface morphology is different [29]. At low concentrations of dopants the effects are reflected by changes in configuration of grown structures [29]. The SEM photographs are given in Figs 8a–d.

SEM photograph of ADP (Fig. 8a) shows a layered structure, mostly defect-free. In Fig. 8b, dentritic growth is observed. The scattered center can be understood as a kind of liquid inclusion, mainly mother solution during the crystal growth. SEM photograph of KDP (Fig. 8c) exhibits a layered structure with crack developments and etch pits. KDP crystal grown from Phen added solution (Fig. 8d) shows lot of crystalline imperfection with bubble voids and deep crack developments during the growth.

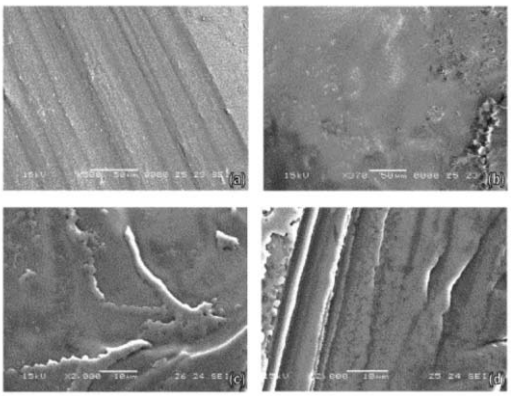

Fig. 8 SEM photographs of crystals grown from ADP, Phen added ADP, KDP and Phen added KDP solutions
a – pure ADP, b – Phen added ADP, c – pure KDP and d – Phen added KDP

Particle size analysis

Particle sizes are measured for ADP using HORIBA LA-910 laser scattering particle size distribution analyzer. Average particle size of ADP becomes much smaller in the presence of the organic dopant (Figs 9a and b).

Second harmonic generation (SHG) efficiency

Second harmonic generation test on the crystals were performed by Kurtz powder SHG method [32]. An Nd:YAG laser with a modulated radiation of wavelength 1064 nm was used as the optical source and directed on the powdered sample through a filter. The doubling of frequency was confirmed by the green radiation of wavelength 532 nm. Non-linear coefficient

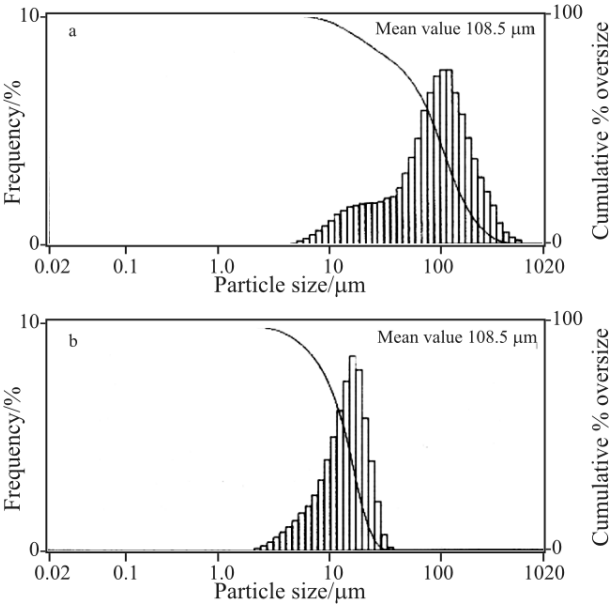

Fig. 9 Particle size analysis of a – ADP and b – Phen added ADP

Table 2 SHG output

System	$I_{2\omega}$/mV
ADP	715–717
ADP+Phen	437–439
KDP	373–375
KDP+Phen	100–102

at 1064 nm for KDP and ADP crystals are d_{36}=0.39 and 0.47, respectively (Table 2).

Although many materials have been identified that have higher molecular non-linearities, the attainment of second-order effects requires favourable alignment of the molecule within the crystal structure [33]. The efficient SHG demands specific molecular alignment of the crystal to be achieved facilitating non-linearity in the presence of dopant. It has been reported that the SHG can be greatly enhanced by altering the molecular alignment through inclusion complexation [34].

Input radiation used is 5 millipoise/pulse. Intensity of second harmonic generation gives an indication of NLO efficiency of the material. Depressed SHG output in the case of Phen dopant is quite likely due to the disturbance of charge transfer. It appears that because of the orientational cancellation, the second-order susceptibility for SHG vanishes.

We believe that by changing the growth conditions and the method, Phen can be an effective dopant in enhancing the NLO properties. Our belief is based on the fact that the presence of delocalized aromatic organic molecule resulting in a proper molecular

alignment can result in much higher second-order NLO efficiencies. Crystal growth and characterization studies at higher concentrations of Phen and particularly the influence on SHG efficiency are the works in progress.

Conclusions

The metastable zone width of ADP/KDP solutions in their supersaturated region is found to be enhanced by the incorporation of small quantities of 1,10-phenanthroline, a new additive. Phen well promotes the crystal growth process of ADP/KDP in slightly acidic solutions (pH ~4.5). XRD and FTIR studies reveal that the growth promoting effect of organic dopant is caused by the adsorption of dopant on the flat surface or the step edges of the crystal. High concentrations of Phen inhibit the growth process by blocking the active sites. Optical transmission studies reveal that the percentage of transmittance is much better with the presence of Phen in the growth medium. Anisotropy in the hardness behaviour has been observed. Depressed SHG efficiency with Phen dopant is rationalised by envisaging an unfavourable molecular alignment affecting the non-linearity.

Acknowledgements

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