GROWTH AND STUDIES OF PURE AND DL-MALIC ACID DOPED POTASSIUM DIHYDROGEN PHOSPHATE SINGLE CRYSTALS

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ABSTRACT

Optically good quality single crystals of pure and Dl-malic acid (DLM) doped Potassium dihydrogen phosphate (KDP) were grown from aqueous solution employing slow evaporation technique. The crystallinity and cell parameters of the grown pure and DLM doped KDP crystals was characterized by powder X-ray diffraction analysis. The mechanical strength of the grown crystals were analyzed by Vickers microhardness test. The enhancement in transmittance of the grown KDP crystal with addition of DLM was determined by UV-Visible spectral analysis. The various investigations indicate changes in structural,mechanical and optical properties of the KDP crystal due to the incorporation of DLM into the KDP crystal lattice.

Keywords: *crystal growth , NLO materials, doping , characterization*

1. INTRODUCTION

The rapid development in the field of science and technology necessitates the search for newer and efficient nonlinear optical materials. KDP crystal is extensively studied from various aspects and widely used NLO crystal. Its excellent qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cut-off wavelength and high laser damage threshold has drawn the attention of several crystal growers [1]. The rapid growth of good quality KDP crystals, the newly developed techniques, and the effect of organic and inorganic impurities and metal ions on the properties of KDP crystals have been reported by several researchers [2-13]. Dl-malic acid (DLM) is an organic material which crystallizes in combination with other materials. DLM combined with ammonium solution gives ammonium malate, L-malic acid with urea produces urea L-malic acid single crystals. Dl-malic acid with boric acid and rubidium carbonate yeilds semiorganic material rubidium bis-dl-malato borate for second order NLO applications [14,16]. In the present work, single crystals of pure KDP and 5 mol% Dl-malic acid doped KDP have been grown and characterized by powder XRD, microhardness and UV-Vis transmission studies to study the effect of Dl-malic acid on the properties of KDP crystal.

2. EXPERIMENTAL METHODS

2.1. CRYSTAL GROWTH

Single crystals of pure and 5 mol% Dl-malic acid doped KDP were grown by solution growth employing slow evaporation technique at room temperature. Using AR grade KDP salt and deionised water, the saturated solution of KDP was prepared in accordance with the solubility data. The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8.The beaker containing the saturated solution (200 ml) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Transparent, good quality KDP crystals were harvested within 20-30 days. For the growth of 5 mol% Dl-malic acid doped KDP crystals, KDP salt was added with AR grade salt of Dl-malic acid in the molar ratio 1: 0.05 to form a saturated solution with deionised water . The solution was thoroughly stirred for homogenization and then filtered into a borosil beaker using Whatmann filter paper. The pH of the solution was noted as 3.8 The beaker containing the saturated solution (200ml) was closed with perforated cover and kept in a dust free atmosphere to allow slow evaporation of the solvent. Single colourless, transparent crystals of 5 mol% DLM doped KDP were harvested within 20-30 days. The photograph of pure and 5 mol% DLM doped KDP crystals are shown in figure1(a) and figure 1(b) respectively.

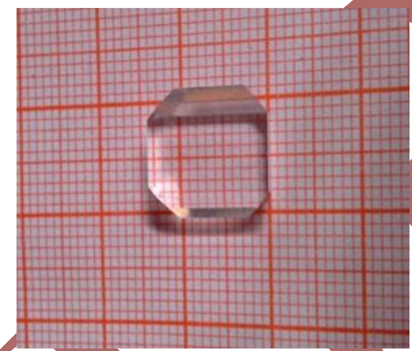


Fig. 1(a)

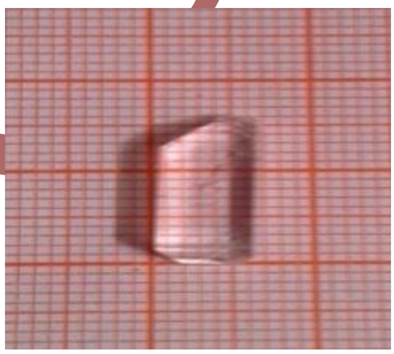


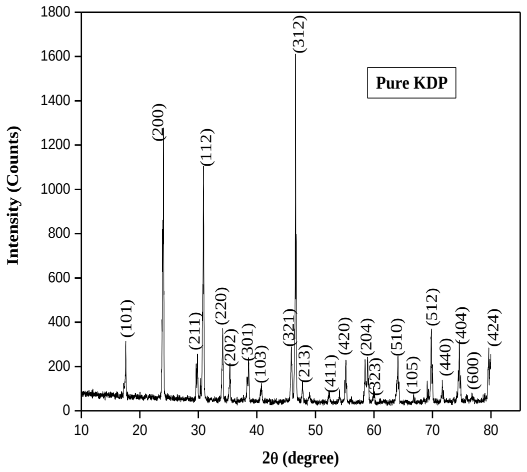
Fig. 1(b)

Photographs of pure and 5 mol% DLM doped KDP crystals

3. RESULT AND DISCUSSION

3.1 POWDER X-RAY DIFFRACTION STUDIES

The powder X-ray diffraction studies have been carried out to confirm the crystallinity and to determine the lattice parameters of the grown crystals. Powder X-ray diffraction (PXRD) analysis was carried out using XPERT-PRO diffractometer with CuKα radiation of wavelength 1.5406Å .The 2θ range was analysed from 10^0 to 80^0 and the prominent peaks have been indexed. PXRD studies for pure and 5 mol% DLM doped KDP grown crystal reveal the appearance of sharp and strong peaks which confirms the good crystallinity of the grown crystals, there are no other phases emerging besides the tetragonal system. It is found that the reflection lines of the doped KDP crystal correlate well with those observed in the individual parent compound with a slight shift in Bragg angle. PXRD pattern for pure and 5 mol% DLM doped KDP crystals are shown in fig. 2(a) & 2(b) respectively.



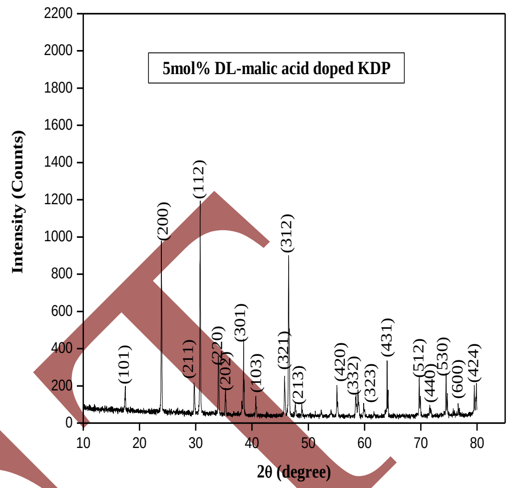


Fig 2(a) **Fig 2(b)**

Powder XRD pattern of pure and 5 mol% DLM doped KDP crystals

The lattice parameters and cell volume are calculated using 'UNIT CELL' software package. The unit cell parameters of pure KDP are a=b=7.431 Å, c= 6.979 Å, $\alpha=\beta=\gamma=90^0$ the unitcell volume is 385.41 $(\text{Å})^3$ and it belongs to tetragonal system. The unit cell parameters of 5 mol% DLM doped KDP crystals are a=b=7.450 Å, c= 6.972 Å, $\alpha=\beta=\gamma=90^0$ the unitcell volume is 386.98 $(\text{Å})^3$. There is a slightly variation found in the lattice parameter values, compared to pure KDP crystal confirming the incorporation of Dl-malic acid into KDP crystal. The compound retains almost single phase structure and exhibits very slight variations on doping. The comparison of unit cell parameters of the doped KDP crystals with pure KDP suggests that both pure and doped KDP crystals crystallize in the body centered tetragonal structure with the space group $I\bar{4}2d$ and have tetramolecular unit cell. The results of the present work are in good agreement with the reported values [18, 19].

3.2 MICROHARDNESS MEASUREMENTS

Microhardness characterization is a measure of the resistance a material offers to local deformation. The micro-indentation test is a useful method for studying the nature of plastic flow and its influence on the deformation of the materials, higher hardness value of a crystal indicates that greater stress is required to create dislocation. To find surface hardness of the grown pure KDP crystal and KDP crystal doped with 5 mol% DLM microhardness was measured for 25g, 50g and 100g load using Shimadzu HMV-2 microhardness tester. The transparent crystal free from cracks was selected for hardness measurement. The Vickers hardness number (H_v) calculated from the relation $H_v = 1.8544\ P/d^2\ kg/mm^2$ where P is the applied load in kg and d is the diagonal length of the indentation mark in mm. Figure 3 shows the variation of Vickers hardness number with load for pure and DLM doped KDP crystals

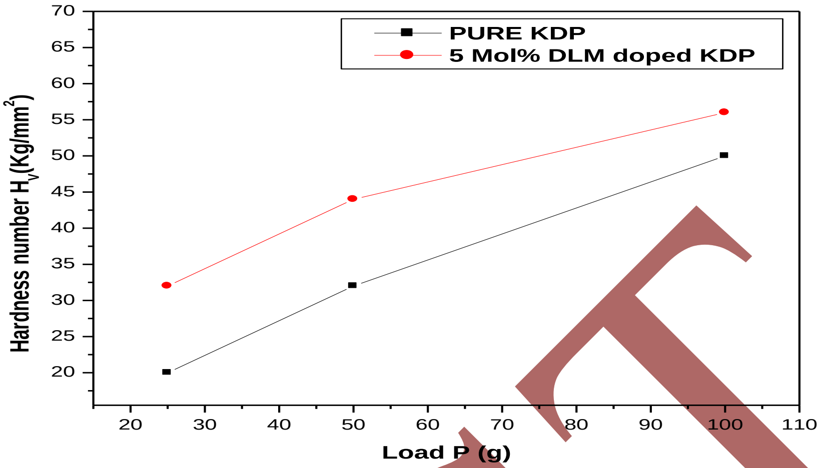
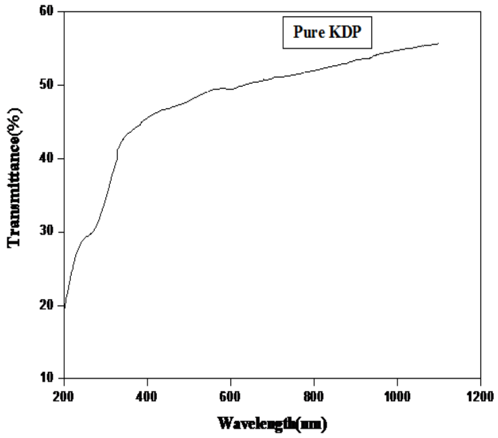


Fig 3: Variation of Vickers hardness number with load for pure and 5mol% DLM doped KDP crystals

Microhardness studies show that hardness number H_v increases with load for all the grown pure and doped KDP crystals. The Dl-malic acid doped KDP crystal has the hardness number greater than the pure KDP crystal. Thus the mechanical strength of Dl-malic acid doped KDP crystal is better compared to pure KDP crystal. Higher hardness value of the doped crystals indicates that greater stress is required to form dislocations, thus confirming greater crystalline perfection. Similar results have been reported for KDP crystal [20,21].

3.3 OPTICAL TRANSMISSION STUDIES

The UV-Vis spectrum of pure and 5 mol% DLM doped KDP crystals were recorded using Perkin Elmer UV-Vis-NIR spectrometer (Model:Lambda35) in the wavelength range 190-1100 nm. Optically polished single crystals of thickness 2mm were used for this study. Optical transmission spectra of pure and 5 mol% DLM doped KDP crystals are shown in figure 4(a) and 4(b) respectively. The UV-Vis transmittance study reveals that the grown pure KDP crystal has a transmittance of 58% . KDP crystals doped with 5 mol% Dl-malic acid has a transmittance of 68%. Thus the addition of Dl-malic acid has increased the transmittance of pure KDP. Hence it is a good candidate for optical devices. From the spectra, it is also observed that both the pure and 5 mol% DLM doped KDP crystals show good transmittance in the entire visible and NIR region.



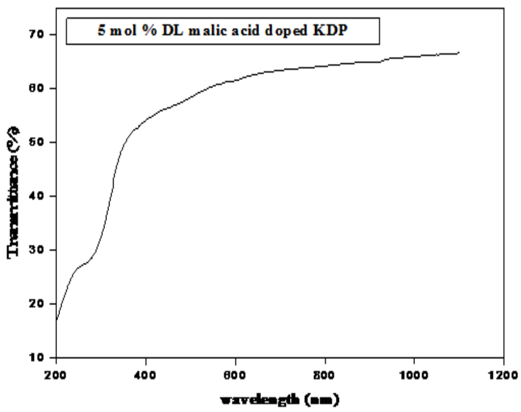


Fig. 4(a) **Fig. 4(b)**

UV-Vis transmission spectra of pure and 5 mol % DLM doped KDP crystals

Observation also show that the cut-off wavelength for the pure KDP crystal and KDP crystals doped with Dl-malic acid are almost the same. The transmission window in the UV region and visible region enables good optical transmission of the second harmonic frequencies of ND:YAG laser [22].

4. SUMMARY AND CONCLUSION

High quality stable and transparent Potassium dihydrogen phosphate (KDP) single crystals and KDP crystals doped with 5 mol% Dl-malic acid have been grown from aqueous solutions by slow evaporation technique at room temperature. The structural, mechanical and optical properties of pure KDP single crystalsand KDP crystals doped with 5 mol% Dl-malic acid have been studied. Powder XRD studies shows that the grown crystals are crystalline in nature and tetragonal in structure and slight changes in lattice parameters of the grown crystals have been noticed when KDP crystal is doped with Dl-malic acid. The Dl-malic acid doped KDP crystals have the hardness number greater than the pure KDP crystal. Thus the mechanical strength of Dl-malic acid doped KDP crystals are better compared to pure KDP crystal. The cut-off wavelength for the pure and doped KDP crystals is almost the same. The transmittance of pure KDP crystal 58%. KDP crystal doped with 5 mol% Dl-malic acid has a transmittance of 68%. Hence these crystals are good candidates for optical devices. Also UV-Visible transmission spectra shows that both the pure KDP crystal and KDP crystals doped with Dl-malic acid show good transmittance in the entire visible and NIR regions which enables them to be potential candidates for optoelectronic application.

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