# Thermal and Mechanical Properties of KDP-ADPMixed Crystals Added with Glycine

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***Abstract*** **- Pure and glycine added (in two different concentrations, viz. 0.005 and 0.010 M) $K_{1-x}(NH_4)_xH_2PO_4$ (with x = 0.0, 0.25. 0.5, 0.75 and 1.0) single crystals (a total of 15) have been grown and characterized thermally and mechanically. The crystals were grown by the free evaporation of solvent at room temperature. Thermogravimetric (TGA) measurement was carried out in the temperature range 30-700 $^oC$ for the five pure mixed crystals only expecting that small amount of glycine addition may not affect the thermal stability much. Vicker's microhardness measurements were carried out on the {100} face of all the 15 crystals grown and various mechanical parameters were evaluated to understand the mechanical strength of the crystals. Results obtained indicate that the crystal with the middle mixed composition exhibits more thermal stability. Further, it is found that the pure and glycine added mixed crystals grown in the present study belong to hard materials category.**

***Keywords: Crystal growth from solution, KDP–ADP mixed crystals, Glycine doped crystals, Thermal properties, Mechanical properties.***

## 1. INTRODUCTION

KDP ($KH_2PO_4$, potassium dihydrogen phosphate) and ADP ($NH_4H_2PO_4$, ammonium dihydrogen phosphate) single crystals have drawn special attention of research workers due to their importance and interesting properties for more than six decades in the past. Both are isomorphous to each other and belong to the tetragonal crystal system at room temperature.

For many emerging technologies, it is necessary to form hybrid materials (by doping or forming mixed crystals) with improved physical properties. The mixed composition/impurity concentration dependence, on forming hybrid materials, may vary significantly from system to system and from property to property. In some cases, these dependences may be highly nonlinear and the magnitude of the physical property may vary significantly from those of the pure (end member) ones.

Several researchers have grown and characterized pure, impurity added and mixed crystals of KDP and ADP and reported several interesting results [1-15]. In principle, the system KDP-ADP forms a series of solid solutions over the whole range of compositions. However, earlier authors have found it difficult to grow bulk single crystals from all compositions [14]. It was ascribed to the development of internal stress due to the strong chemical bonding interaction between $K^+$ and $H_2PO_4^-$ ions and the competitive growth of $NH_4^+$ and $K^+$ ions affects the quality and morphology of the crystal.

Aiming at discovering new materials, Mahadevan and his co-workers have planned and executed a research program on the growth and characterization of hybrid single crystals based on KDP and ADP. Several useful results have already been reported [16-26]. As a part of the above program, we have grown by the free evaporation of solvent method at room temperature and characterized glycine (a simple but important organic nonlinear optical material) added (0.005 and 0.010 M are the concentrations considered) mixed crystals of KDP and ADP [$K_{1-x}(NH_4)_xH_2PO_4$ with x = 0.0, 0.25. 0.5, 0.75 and 1.0]. The structural and optical properties have already been reported [27]. Herein, we report the thermal and mechanical properties.

## 2. MATERIALS AND METHODS

Analytical reagent (AR) grade samples of KDP, ADP and glycine were used as the precursors. Double distilled water was used as the solvent. The single crystals were grown as we have reported earlier [27].

It was expected that the small amount of glycine addition might not have modified significantly the thermal properties of $K_{1-x}(NH_4)_xH_2PO_4$. So, the five undoped crystals grown were subjected to thermogravimetric(TGA) measurement. A thermal analyzer (model SDT – Q600) was used for the purpose and the measurements were carried out in nitrogen atmosphere in the temperature range 30 – 700 ℃ at a heating rate of 10 ℃/min. In order to characterize mechanically, all the fifteen crystals grown were subjected to Vicker's microhardness measurement on the {100} face using a SHIMADZU HMV – 2T microhardness tester with a diamond indenter. The diagonals of the indentations made (d) along with the crack length (c) were measured for three different loads (25, 50 and 100 g) in each case. The measurement was repeated at different places on the same surface of the crystal and the average values were considered. Various mechanical parameters were also evaluated.

## 3. RESULTS AND DISCUSSION

### *3.1 Crystals Grown*

All the fifteen crystals grown are found to be stable in atmospheric air, colorless and transparent. The single crystals grown in the present study can be represented as

KA1 → K $_{(1-x)}$ $(NH_4)_xH_2PO_4$ with x = 0.0 (Pure KDP)
KA2 → K $_{(1-x)}$ $(NH_4)_xH_2PO_4$ with x = 0.25
KA3 → K $_{(1-x)}$ $(NH_4)_xH_2PO_4$ with x = 0.50
KA4 → K $_{(1-x)}$ $(NH_4)_xH_2PO_4$ with x = 0.75
KA5 → K $_{(1-x)}$ $(NH_4)_xH_2PO_4$ with x = 1.0 (Pure ADP)
KA6 → KA1added with 0.005M glycine
KA7 → KA2added with 0.005M glycine
KA8 → KA3added with 0.005M glycine
KA9 → KA4added with0.005M glycine
KA10 → KA5added with 0.005M glycine
KA11 → KA1 added with 0.010M glycine
KA12 → KA2 added with 0.010M glycine
KA13 → KA3 added with 0.010M glycine
KA14 → KA4 added with 0.010M glycine
KA15 → KA5 added with 0.010M glycine

The chemical compositions observed through density measurement for the mixed crystals, viz. KA2, KA3 and KA4 are $K_{0.84}(NH_4)_{0.16}H_2PO_4$, $K_{0.66}(NH_4)_{0.34}H_2PO_4$ and $K_{0.54}(NH_4)_{0.46}H_2PO_4$ respectively and all these fifteen crystals are found to be nonlinear optically active and significantly exhibit second harmonic generation [27].

### *3.2. Thermal properties*

Figure 1 shows the TGA patterns observed for the undoped crystals grown in the present study. Absence of weight loss observed around 100$^{o}$C indicates the absence of water of crystallization in the molecular structure. The major weight loss occurs (see the TGA patterns in Figure 1) due to decomposition before melting for all the five crystals considered in the present study. The temperatures of this decomposition observed for KA1, KA2, KA3, KA4 and KA5 are 281.32, 282.6, 201.72, 252.5 and 207$^{o}$C respectively. It should be noted that the decomposition rate with temperature decreases with the increase in ammonium content in the crystal. Further, KA3 [$K_{0.5}(NH_4)_{0.5}H_2PO_4$ in the solution used for crystallization] is found to be thermally less stable. The thermal stability observed for pure KDP and ADP crystals is in agreement with that reported in the literature [14, 25, 26 ].

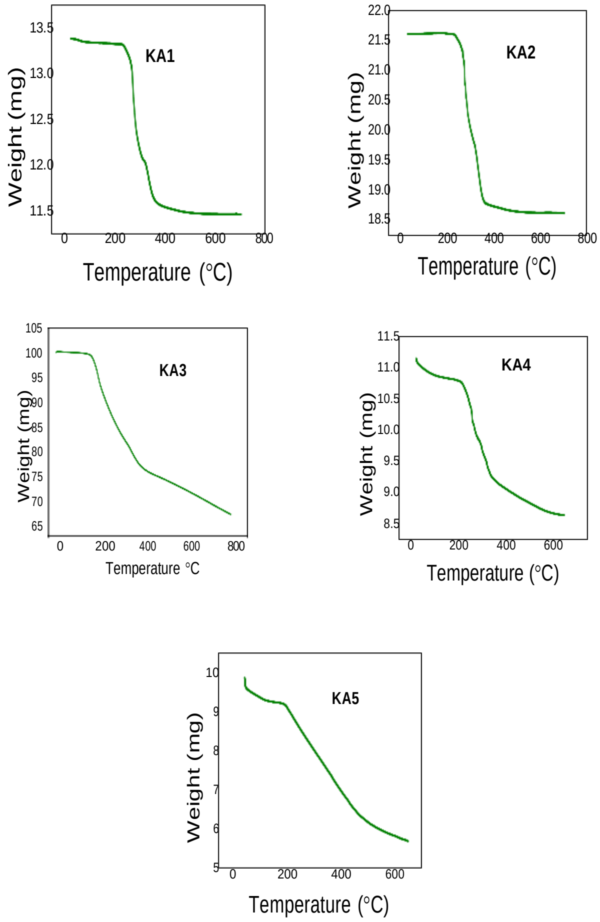


Fig -1: The TGA patterns observed for the KA1, KA2, KA3, KA4 and KA5 crystals

The weight losses observed in the present study for KDP and ADP crystals are almost similar to those reported earlier[14]. So, the decompositions can be considered in a similar way in accordance with the following relations (s and g represent solid and gas respectively):

For ADP,

$$2NH_4H_2PO_4\ (s) \longrightarrow 2NH_3\ (g) + 3H_2O\ (g) + P_2O_5\ (s)$$

For KDP,

$$KH_2PO_4\ (s) \longrightarrow KPO_3\ (s) + H_2O\ (g)$$

For the mixed crystals, the decomposition takes place as evaporation of water and then ammonia. The ammonia evaporation is found to increase with the increase in ammonium content of the crystal.

### *3.3. Mechanical properties*

The hardness of a material is a measure of its resistance it offers to local deformations [26].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 [26]. The values of d (average diagonal of the indentation made) and c (crack length) observed in the present study are provided in Table 1.

Table -1: The measured d and c values

| Crystal | d (μm) for | | | c (μm) |
|---|---|---|---|---|
| | 25g | 50g | 100g | |
| KA1 | 36.29 | 45.69 | 53.84 | 34.44 |
| KA2 | 34.60 | 41.35 | 53.49 | 41.63 |
| KA3 | 43.80 | 48.89 | 54.43 | 18.45 |
| KA4 | 42.97 | 54.00 | 66.28 | 20.67 |
| KA5 | 34.99 | 40.73 | 48.51 | 24.74 |
| KA6 | 33.29 | 41.15 | 47.53 | 34.70 |
| KA7 | 52.83 | 67.96 | 74.48 | 26.14 |
| KA8 | 26.47 | 36.63 | 43.55 | 19.69 |
| KA9 | 33.89 | 37.77 | 46.42 | 35.08 |
| KA10 | 30.16 | 36.49 | 44.38 | 35.26 |
| KA11 | 28.59 | 32.59 | 43.15 | 34.38 |
| KA12 | 37.53 | 41.46 | 49.62 | 31.33 |
| KA13 | 34.27 | 35.93 | 42.53 | 35.53 |
| KA14 | 35.54 | 45.91 | 57.57 | 19.09 |
| KA15 | 37.24 | 51.39 | 64.65 | 57.25 |

The Vicker's hardness number ($H_v$) is defined as [26]

$$H_v = 1.8544(P/d^2)\ \text{kg/mm}^2, \qquad (1)$$

where P is the load applied and the Meyer's law [26] is expressed as

$$P = K_1 d^n \qquad (2)$$

where $K_1$ is the material constant and n is the Meyer index (work hardening coefficient).

The $H_v$ values estimated using equation (1) are shown in Figure 2. The $H_v$ value is found to increase with the increasing load for all the fifteen crystals grown. However, there is no systematic variation observed with the mixed composition/glycine concentration. Figure 3 shows the plots between log P and log d. As these plots are found to be nearly linear, the Meyer index (n) could be evaluated from the slope of the best fitted line. The n values obtained are provided in Table 2. According to Onitsch and Hanneman, n should lie between 1.0 and 1.6 for hard materials and above 1.6 for soft ones [26]. The n values obtained in the present study lie between 1.0 and 1.6 for all the crystals. This indicates that the crystals grown in the present study belong to the hard material category.

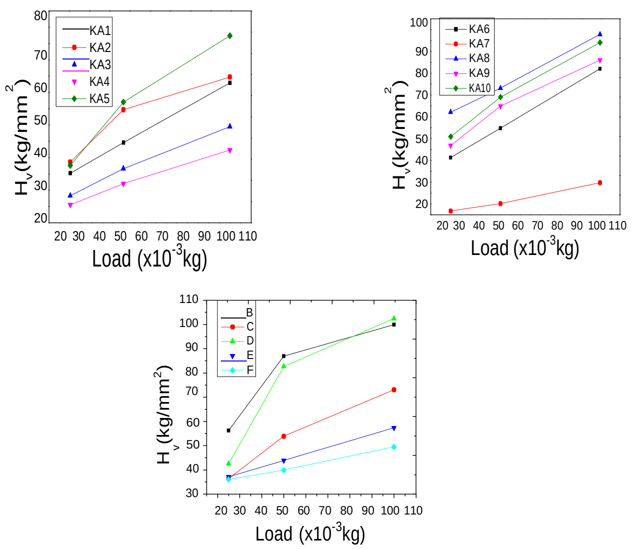


Fig -2: The estimated $H_v$ values

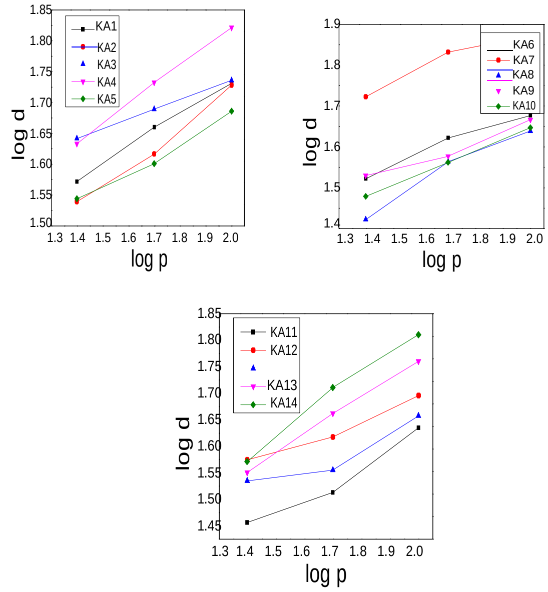


Fig -3:The log P versus log d plots

Table -2: The estimated work hardening coefficients

| Crystal | Work hardening coefficient | Crystal | Work hardening coefficient | Crystal | Work hardening coefficient |
|---|---|---|---|---|---|
| KA1 | 1.303 | KA6 | 1.293 | KA11 | 1.345 |
| KA2 | 1.369 | KA7 | 1.281 | KA12 | 1.223 |
| KA3 | 1.169 | KA8 | 1.432 | KA13 | 1.225 |
| KA4 | 1.266 | KA9 | 1.255 | KA14 | 1.416 |
| KA5 | 1.488 | KA10 | 1.321 | KA15 | 1.489 |

Measurement of c along with d leads to the estimation of various mechanical parameters like fracture toughness ($K_c$), brittleness (B), yield strength ($\sigma_v$) and elastic stiffness constant ($C_{11}$).The mechanical contact between the indenter and the crystal surface produces radial cracks which can be determined from the crack length (distance between the center of indentation mark and crack tip). Fracture toughness ($K_c$) is the ability of a material containing a crack to resist fracture. It determines how much fracture stress is applied under uniform bending and it is an important parameter for the selection of materials in practical applications where the load exceeds the limit. The variation of crack length and fracture toughness on load can be attributed to the depth of penetration of indenter into surface. The fracture toughness is given by [28]:

$$K_c = \frac{P}{\beta c^{3/2}} \qquad (3)$$

Here, β is the indenter constant (value is 7).

Brittleness (B) determines the fracture without any appreciable deformation. This property helps to understand the laser damage tolerance and it is resolved by the relation [28]:

$$B = \frac{H_v}{K_c} \qquad (4)$$

The yield strength ($\sigma_v$) is the stress at which the material begins to deform plastically and it can be computed from the hardness value using the relation [28]:

$$\sigma_v = \frac{H_v}{2.9}\{1-(2-n)\}\left[\frac{12.5(2-n)}{1-(2-n)}\right]^{2-n} \qquad (5)$$

The elastic stiffness constant is the tightness of bonding between neighboring atoms. It is a property of the material by virtue of which can absorb energy before fracture occurs and it is calculated by the Wooster's empirical formula [28]

$$C_{11}=H_v^{7/4} \qquad (6)$$

The estimated mechanical parameters are provided in Table 3. It is found that the $K_c$, $\sigma_v$ and $C_{11}$ values increase whereas the B value decreases with the increase in load. This shows the normal mechanical behavior.

Table -3: The estimated mechanical parameters

| Crystal | $K_c$ ($kg^{-3/2}$) X $10^4$ for | | | B ($m^{-1/2}$) for | | | $\sigma_v$ (MPa) for | | | $C_{11}$ ($10^{14}$ Pa) for | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 25g | 50g | 100g | 25g | 50g | 100g | 25g | 50g | 100g | 25g | 50g | 100g |
| KA1 | 1.77 | 3.53 | 7.07 | 19.9 | 12.6 | 8.90 | 38.2 | 48.4 | 68.2 | 5.08 | 7.69 | 14.1 |
| KA2 | 1.32 | 2.64 | 5.28 | 29.2 | 20.7 | 12.3 | 33.9 | 48.1 | 56.8 | 5.97 | 11.0 | 14.8 |
| KA3 | 4.51 | 9.01 | 18.0 | 6.27 | 4.06 | 2.75 | 50.5 | 65.3 | 88.3 | 3.47 | 5.44 | 9.26 |
| KA4 | 3.80 | 7.60 | 15.2 | 6.71 | 4.21 | 2.78 | 31.4 | 39.4 | 52.1 | 2.89 | 4.30 | 7.02 |
| KA5 | 2.90 | 5.81 | 11.6 | 12.9 | 9.81 | 6.67 | 23.6 | 35.8 | 48.6 | 5.71 | 11.8 | 20.2 |
| KA6 | 1.75 | 3.49 | 6.99 | 23.5 | 15.7 | 11.7 | 46.2 | 61.4 | 92.1 | 6.69 | 11.0 | 22.3 |
| KA7 | 2.67 | 5.35 | 10.7 | 6.25 | 3.76 | 2.78 | 19.5 | 24.2 | 34.7 | 1.38 | 1.91 | 37.8 |
| KA8 | 4.09 | 8.18 | 16.4 | 15.2 | 8.94 | 5.96 | 45.3 | 53.4 | 71.4 | 13.7 | 18.3 | 30.4 |
| KA9 | 1.72 | 3.44 | 6.88 | 27.2 | 18.9 | 12.5 | 60.0 | 83.2 | 110 | 8.37 | 14.8 | 24.3 |
| KA10 | 1.71 | 3.41 | 6.82 | 29.8 | 20.2 | 13.8 | 52.1 | 70.5 | 96.2 | 9.69 | 16.5 | 28.4 |
| KA11 | 1.77 | 3.54 | 7.09 | 31.8 | 24.6 | 14.1 | 53.3 | 82.3 | 94.9 | 11.6 | 24.8 | 31.8 |
| KA12 | 2.04 | 4.07 | 8.15 | 17.8 | 13.2 | 8.97 | 52.5 | 77.8 | 105 | 5.39 | 10.7 | 18.3 |
| KA13 | 1.69 | 3.37 | 6.75 | 25.2 | 24.5 | 15.2 | 61.0 | 118.4 | 146 | 7.10 | 22.7 | 33.0 |
| KA14 | 4.28 | 8.56 | 17.1 | 8.69 | 5.13 | 3.36 | 28.4 | 33.5 | 43.8 | 5.60 | 7.50 | 11.9 |
| KA15 | 0.82 | 1.65 | 3.30 | 44.0 | 24.2 | 15.0 | 22.6 | 25.0 | 31.1 | 5.31 | 6.35 | 9.25 |

## 4. CONCLUSIONS

Pure and glycine added single crystals (a total of 15) have been grown by the free evaporation of solvent method and characterized thermally and mechanically. Thermal measurements indicate that the crystal with the middle mixed composition [$K_{0.5}(NH_4)_{0.5}H_2PO_4$ in the solution used for crystallization] exhibits less thermal stability and the decomposition rate with temperature decreases with the increase in ammonium content in the crystal. The microhardness measurements indicate that the pure and glycine added mixed crystals grown in the present study belong to hard materials category. The determined mechanical parameters, viz. $H_v$, $K_c$, $\sigma_v$, B and $C_{11}$indicate that all the fifteen crystals grown in the present study exhibit the normal mechanical behavior.

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