

# Mechanical Studies on Pure and Fe<sup>3+</sup> Doped Potassium Hydrogen Phthalate Single Crystals for Device Fabrications

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## Abstract

**Background/Objectives:** Mechanical properties of the selected materials play an important role in device fabrications. Thus the perfect cleavage (010) plane of doped and un-doped Potassium Hydrogen Phthalate (KHP) crystal is subjected to Vicker's micro hardness study. **Methods/Statistical Analysis:** Slow evaporation solution growth method is employed for the growth of Fe<sup>3+</sup> doped and un-doped Potassium Hydrogen Phthalate (KHP) crystals. Here, 0.1 mol% of FeCl<sub>3</sub> used as dopant. Saturated solution of both doped and un-doped KHP solutions are prepared according to the solubility data (12.5g/100ml at 30°C). **Findings:** A well developed (010) plane of pure and un-doped crystals have been subjected to hardness studies with various loads. It is found that Vickers Hardness numbers ( $H_v$ ) for un-doped and doped KHP crystals varied for different loads. Meyer's index or work hardening co-efficient ( $n$ ) values are found to be greater than 1.6 which reveals that the grown crystals are belongs to soft material's category. i.e., for pure KHP the value of 'n' is 3.68 and for Fe doped KHP, it is 3.46. The minimum load indentation ( $W$ ) to initiate the plastic deformation on the surface of the crystals are calculated based on Hays and Kendall's theory. The value of  $W$  for KHP and doped KHP are found to be 1.965 and 4.368 respectively. The hardness related constants like materials constant ( $k_i$ ) and load dependent constant ( $A_i$ ) for the pure and un-doped KHP crystals have been estimated. The Elastic stiffness constant ( $C_{11}$ ) are also calculated from Vickers micro hardness values. **Applications/Improvements:** Potassium Hydrogen Phthalate (KHP) is an efficient crystal analyzer material and is used in X-ray spectrometer. The improvement in hardness by dopant provides the use of materials for efficient optical device applications.

**Keywords:** Elastic stiffness constant, Load dependent constant, Material constant, Meyer's index; Minimum load indentation, Vickers Hardness number

## 1. Introduction

Semi organic crystals are generally believed to satisfy the materials demands in an electronic industry. Hence in

the recent years the developments of new semi organic crystals are in progress for the device construction. Single crystals of potassium hydrogen phthalate  $K(C_6H_4COOH.CO_2O)$  is believed to be an excellent material in the crys-

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tal analyzer for X-ray spectrometer<sup>1,2</sup>. KHP crystallizes in orthorhombic structure with the space group of Pca<sub>2</sub><sub>1</sub> and the lattice parameters are  $a = 9.605 \text{ \AA}$ ,  $b = 13.331 \text{ \AA}$ ,  $c = 6.473 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ <sup>3,4</sup>. Potassium Hydrogen Phthalate crystals are having a perfect cleavage (010) plane. Hence it is a suitable material for surface morphological studies<sup>5</sup>. Non linear optical Potassium Hydrogen Phthalate (KHP) crystals are having pyro-electric, piezo-electric, elastic and mechanical properties<sup>6-8</sup>. Hence in the recent years many of the crystal growth studies are going on this material.

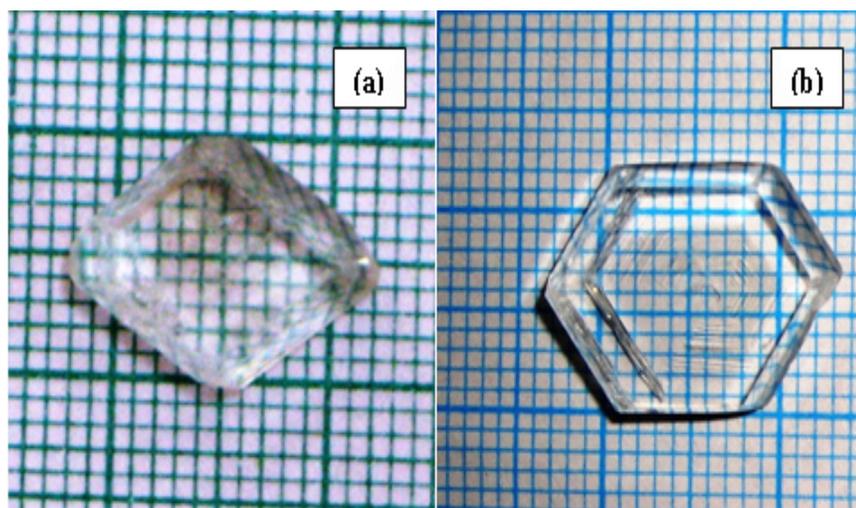
Vickers micro hardness study provides the mechanical properties of the materials which are very essential for the device fabrications<sup>9</sup>. Vickers micro hardness study is a suitable measure of the plastic properties and mechanical strength of a material<sup>10</sup>. The micro hardness studies on pure and deuterated KHP crystals have been reported<sup>11</sup>. The chemical forces in a crystal resist the dislocation motions as it involves the atomic displacement. This resistance reveals an intrinsic hardness of the crystal. The hardness properties are basically related to the crystal structure and molecular composition of the material. Hence, in order to understand the plasticity of the crystal, hardness studies were carried out on the crystalline materials.

In this connection we have made hardness measurements on (010) cleavage plane of pure and Fe<sup>3+</sup> doped KHP single crystals.

## 2. Experimental

Pure and Fe<sup>3+</sup> doped Potassium Hydrogen Phthalate (KHP) crystals were grown by slow evaporation technique. KHP salt (E-merck) was purified by successive recrystallization process in order to eliminate impurities in the KHP salt. By the use of reported solubility data (12.5g/100ml at 30°C), the saturated aqueous solution of Potassium Hydrogen Phthalate was prepared<sup>12,13</sup>. The deionized water of resistivity 18.2 MΩ.cm was used as a solvent for the preparation of saturated KHP solution. Ferric ions (Fe<sup>3+</sup>) in the form of FeCl<sub>3</sub> at 0.1 mol% is used as dopant.

In order to get a clear homogeneous solution, the saturated aqueous solutions of pure and Fe<sup>3+</sup> doped KHP were stirred for about 10 hours. The pH of the solution was maintained as 3.98 at room temperature. The transparent bulk sized crystals of pure and doped KHP were harvested after 25 days from the petri dish solution. As grown pure and Fe<sup>3+</sup> doped KHP (FKHP) crystals are shown in Figure 1.



**Figure 1.** As grown crystal of (a) pure KHP, (b) 0.1 mol% FeCl<sub>3</sub> doped KHP crystals.

### 3. Results and Discussion

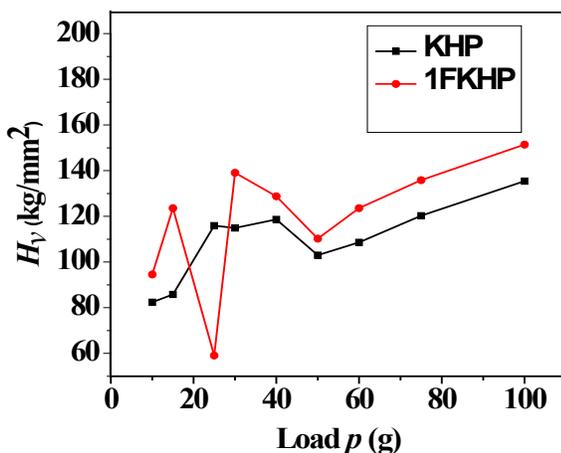
#### 3.1 Vickers Microhardness Test

Micro hardness test is one of the best methods for understanding the mechanical properties of the materials. microhardness analysis of defect free cut and polished crystals pure and transitional element  $\text{Fe}^{3+}$  ion doped KHP single crystals have been studied by using Leitz-Wetzlar Vickers micro hardness tester with diamond square indenter at room temperature. The loads ranging from 10 to 100g were used for hardness studies and the loads were applied slowly by pressing the indenter on the surface of the sample being tested. The average value of indentation impression for every load was used to calculate the Vickers microhardness value ( $H_V$ ). These trials

are very important in order to avoid the surface effects.

Vickers microhardness value was calculated for the crystals by the following equation,

$$H_V = \frac{1.8544p}{d^2} \text{kg/mm}^2 \quad (1)$$



**Figure 2.** Variation of Vickers hardness with Load for pure and  $\text{Fe}^{3+}$  doped KHP crystals.

Where  $p$  is the applied load in  $\text{kg}$  and  $d$  is the diagonal length of the indentation in  $m$

A plot of Vickers hardness number ( $H_V$ ) as a function of load ( $p$ ) is shown in Figure 2.

The hardness and strength of the materials depends on dislocation movement of the material. From the graph it is clear that as the load increases, the hardness of the material will increase initially for both pure and doped KHP crystals. The initial increase of micro hardness for the applied load may be due to continued increase in frequency of dislocation interaction resulting in dislocation line (Meyer's index). When the applied load is at around 30g the hardness value decreases for the pure and doped KHP crystals.

Further decrease in material hardness with increase in applied load is due to work softening process, which results from an activation of cross slip and the movement of piled-up dislocations<sup>14</sup>. But for the applied load of above 60g the depth of penetration of indenter impression increases. Hence, the effect of both very inner and outer layers contributes the hardness of the materials which varies linearly with the applied loads for all the pure and doped KHP crystals. Until to reach the load of 100g there has been no cracks were observed. But these crystals may get cracked above the load of 100g. This may be due to an internal stresses released by the application of applied load. The main contribution to materials hardness is attributed to the high stress required for homogeneous nucleation of dislocation in the small region of indentation<sup>15</sup>. Hence higher value of hardness for the pure and doped KHP crystal confirms that a greater stress is required to form dislocations, which confirms higher crystalline perfection<sup>16</sup>.

The calculated values of Vickers hardness number ( $H_V$ ) for pure and doped KHP crystals are shown in Table

1.

**Table 1.** Calculated Vickers hardness and Elastic stiffness constant values of pure and doped KHP crystals.

Load ( <i>p</i> ) ×10 <sup>-3</sup> kg	KHP		FKHP	
	<i>Hv</i> ×kg/mm <sup>2</sup>	<i>C<sub>11</sub></i> ×10 <sup>14</sup> Pa	<i>Hv</i> ×kg/mm <sup>2</sup>	<i>C<sub>11</sub></i> ×10 <sup>14</sup> Pa
10	82.417	6.9863	94.612	8.8945
15	85.851	7.5037	123.626	14.2040
25	115.900	12.6870	59.132	3.9076
30	114.942	12.5041	139.080	17.4553
40	118.681	13.2246	128.777	15.2558
50	103.022	10.3238	110.249	11.6245
60	108.656	11.3321	123.626	14.2040
75	120.311	13.5441	135.820	16.7456
100	135.456	16.6672	151.379	20.2456

From the Table 1, it was observed that hardness have been increased comparatively to the doped KHP crystal. This may be due to strong bond formation of Fe<sup>3+</sup> ions with the phthalate group. The improvement of hardness by dopant increases the possibilities of these crystals towards optical device applications<sup>17</sup>.

### 3.2 Work Hardening Co-Efficient (*n*) and Minimum Load Indentation (*W*)

The load variation with an indentation impression can be interpreted by using Meyer's law,

$$p = k_1 d^n \quad (2)$$

Where *p* and *d* are the usual meanings.

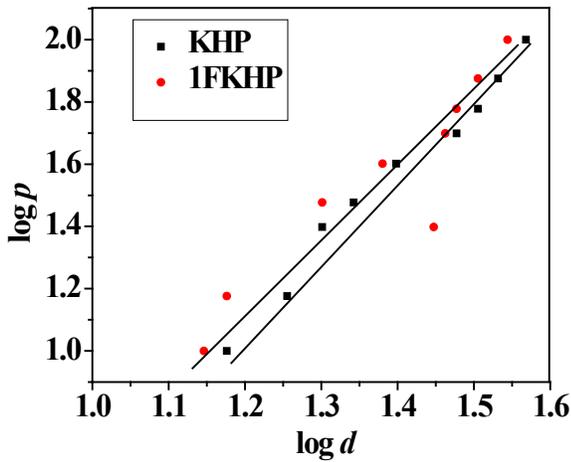
The plot of log *d* against log *p* for pure and Fe<sup>3+</sup> doped KHP crystals are results in straight lines and are shown in Figure 3.

The slope of each straight line gives the work hardening co-efficient value (*n*). The value of materials constant

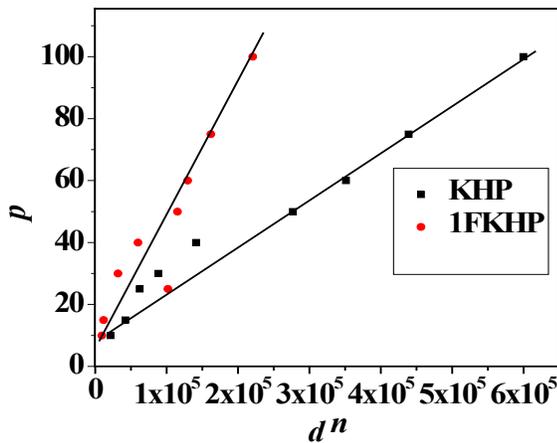
(*k<sub>1</sub>*) can be found out from the plot of *d<sup>n</sup>* versus *p*. The

graph will result in straight lines and are shown in Figure 4. The slope of each straight line gives the value of materials constant (*k<sub>1</sub>*).

From the deep observations on several materials, Onitsch<sup>18</sup> suggested that the value of *n* lies between 1 –



**Figure 3.** Plots of  $\log d^n$  vs.  $\log p$  for pure and  $\text{Fe}^{3+}$  doped KHP crystals.



**Figure 4.** Plots of  $d^n$  vs.  $p$  for pure and  $\text{Fe}^{3+}$  doped KHP crystals.

1.6 for moderately hard materials and is greater than 1.6 for the soft materials. Thus the value of work hardening co-efficient ( $n$ ) for all the pure and doped KHP crystals

reveals that they are under soft materials category. The resistance pressure of the crystalline material is a mini-

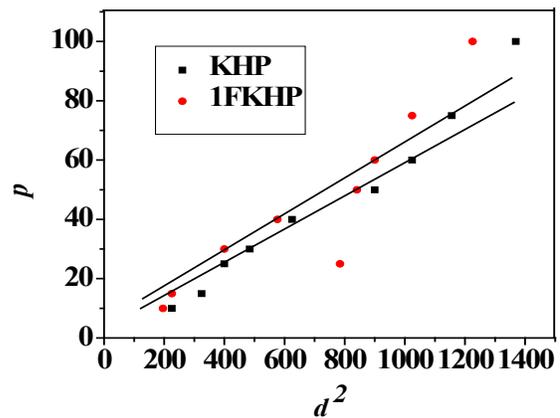
mum load indentation ( $W$ ) below which there is no plastic deformation<sup>19</sup>.

Load dependence of hardness can be explained by Hays-Kendall law<sup>20</sup> and is given by,

$$p = W + A_1 d^2 \tag{3}$$

Here  $W$  is the minimum applied load required to initiate plastic deformation and  $A_1$  is the load dependent constant.

The values of  $W$  and  $A_1$  can be found from the plots drawn between  $d^2$  versus  $p$  results in straight line and are shown in Figure 5.



**Figure 5.** Plots of  $d^2$  vs.  $p$  for pure and  $\text{Fe}^{3+}$  doped KHP crystals.

The intercept of each straight line along load axis gives the value of  $W$  and slope of each straight line gives the value of  $A_1$ .

### 3.3 Elastic Stiffness Constant ( $C_{11}$ )

The elastic stiffness constant ( $C_{11}$ ) for the pure and Fe<sup>3+</sup> doped KHP crystals were calculated by Wooster's empirical relation<sup>21</sup>,

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

The stiffness constant values for different loads have been calculated for pure and doped KHP crystals. The parameters related to hardness such as  $n$ ,  $k_1$ ,  $W$  and  $A_1$

are shown in the Table 2.

**Table 2.** Vickers hardness related constants for pure and doped KHP crystals

Sample	$n$	$k_1$ (kg/mm)	$W$ (g)	$A_1$ (kg/mm <sup>2</sup> )
KHP	3.68	18.7057	1.965	70.9
FKHP	3.46	11.1112	4.368	56.8

## 4. Conclusion

The pure and Fe<sup>3+</sup> doped KHP crystals were grown by slow evaporation technique. The Vickers microhardness ( $H_v$ ) was carried out on (010) plane of pure and doped

KHP crystals by applying various loads. It was observed that, the hardness mainly depends on applied loads. This behaviour of hardness of the materials has been explained on the basis of dislocation motion. The Meyer's index ( $n$ ) suggests that all the pure and doped KHP crystals are

under soft materials category. The value of elastic stiffness constant ( $C_{11}$ ) tells the strength of the bonds between the

neighbouring ions. The Value of  $C_{11}$  are very high for the

doped KHP crystals. It is clear that when compared to the pure KHP crystal, the binding forces between the ions are very strong in the doped KHP crystals. Hence, the

improvement of hardness by dopant in the KHP crystal provides high possibilities towards the optical device applications.

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