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Hardness and Its Related Constants of Pure and Fe^{3+} Doped Potassium Hydrogen Phthalate Single Crystals for Optical Device Fabrications

N. Sivakumar[1], J. Venkatamuthukumar[2,*], A. Jagadesan[3], V. Yogaraj[4] and E. Murugan[4]

[1] *Functional Materials Research Laboratory (FMRL), Department of Physics, Sri Sai Ram Engineering College, West Tambaram, Chennai-600044, India*

[2,*] *Department of Physics, Rajalakshmi Engineering College, Thandalam, Chennai-602105, India*

[3] *Department of Physics, R.M.K. Engineering College, Kavaraipettai-601206, India*

[4] *Department of Physical Chemistry, School of Chemical Science, University of Madras, Guindy Campus, Chennai-600025, India*

Abstract

Single crystals of pure and Fe^{3+} doped Potassium Hydrogen Phthalate (KHP) single crystals were grown by slow evaporation technique. Variations of hardness on the (010) plane of pure and Fe^{3+} doped KHP crystals with various loads were studied. For both pure and doped KHP crystals, the Vickers Hardness values (Hv) were analyzed for varying loads. However, the dopant Fe^{3+} enhances the hardness of crystalline KHP. Hardness Meyer's index (n) values of the pure and Fe^{3+} doped KHP crystals were found to be greater than 1.6 showing the soft materials category. Based on the Vickers micro hardness data, the Elastic stiffness constant (C_{11}) was determined. The results of hardness and the related parameters of the grown crystals are discussed and compared.

Keywords: *Vickers Hardness number, Meyer's index, Material constant, Elastic stiffness Constant.*

1. Introduction

Single crystals with outstanding optical nonlinearity and adequate mechanical hardness are in high demand. These kinds of crystals are crucial for the manufacturing of devices in the electronic sector. Most people agree that semi-organic crystals can meet the requirements for materials in the electrical industry. As a result, new semi-organic crystal advancements for device assembly have been ongoing recently. Potassium Hydrogen Phthalate K (C_6H_4COOH. COO) single crystals are thought to make suitable materials for X-ray spectrometer crystal analyzers [1, 2]. The KHP crystal has the following lattice parameters: a = 9.605 Å, b = 13.331 Å, c = 6.473 Å, α=β=γ=90° [3, 4]. It also has an orthorhombic structure with the space group Pca_{21}. Crystals of potassium hydrogen phthalate have a perfect (010) plane of cleavage. As a result, it is a good subject for surface morphological research [5]. Potassium Hydrogen Phthalate (KHP) crystals with non-linear optical characteristics have pyroelectric, piezoelectric, elastic, and mechanical capabilities [6–8]. As a result, a lot of studies on crystal growth in recent years have focused on this substance.

Vickers hardness testing can provide a thorough understanding of the mechanical properties of a material, including fracture behavior, brittleness index, mechanical yield strength, and temperature of cracking [9, 10]. Hardness is the amount of resistance offered by the crystal against lattice distortion [11]. Both Ashby [12] and Stillwel [13] defined mechanical hardness as opposition to lattice obliteration and crystal hardness as a crystal's capacity to withstand structural collapse in the presence of applied stress (load) [14]. Vickers micro hardness gives the appropriate amount of the plastic behavior exhibited by a material and measures its mechanical strength [15].

Recently micro hardness tests have been conducted on both pure and deuterated KHP crystals [16]. Sivakumar et al. observed the impact of glycine on the structural, optical, and dielectric behavior of KHP crystals. Also, they discussed the mechanical studies of pure and Fe^{3+} ion-doped KHP crystals with lower concentrations [17, 18]. In our earlier article [19, 20], we reported the structure, spectroscopic, dielectric, and developmental characteristics of both un-doped and Fe^{3+}-doped KHP crystals. A crystal's chemical forces oppose dislocation motions because they involve atomic displacement. This resistance reflects the crystal's inherent hardness. The crystal structure and molecular makeup of the material are primarily responsible for the attributes of hardness. Therefore, hardness investigations on the crystalline materials were conducted in order to comprehend the plasticity of the crystal [21]. We have made hard measurements on the cleavage plane (010) of undoped and Fe^{3+} doped KHP single crystals with higher concentrations and the results are discussed and compared in detail.

2. Experimental

Potassium Hydrogen Phthalate (KHP) crystals were produced using an aqueous solution of KHP created using the solubility values that had been reported (12.5g/100ml at 30°C) [22]. As a solvent, 18.2 MΩ.cm resistivity deionized water was used to prepare a saturated KHP solution. As a dopant, varied quantities of ferric ions (Fe^{3+}) in the form of $FeCl_3$ were utilized, say, 0.2 mol%, and 0.3 mol%. The saturated aqueous solution of unadulterated and Fe^{3+} doped KHP was agitated over a period of 10 hours resulting in a clear, homogeneous solution. At ambient temperature, the solution's pH was kept constant at 3.98. The resulting statured solution was filtered using a syringe filter with a hole size of 0.45μm to get a high purity form. After 25 days in the petridish solution, the translucent bulk-sized crystals of pure and Fe^{3+} doped KHP were collected.

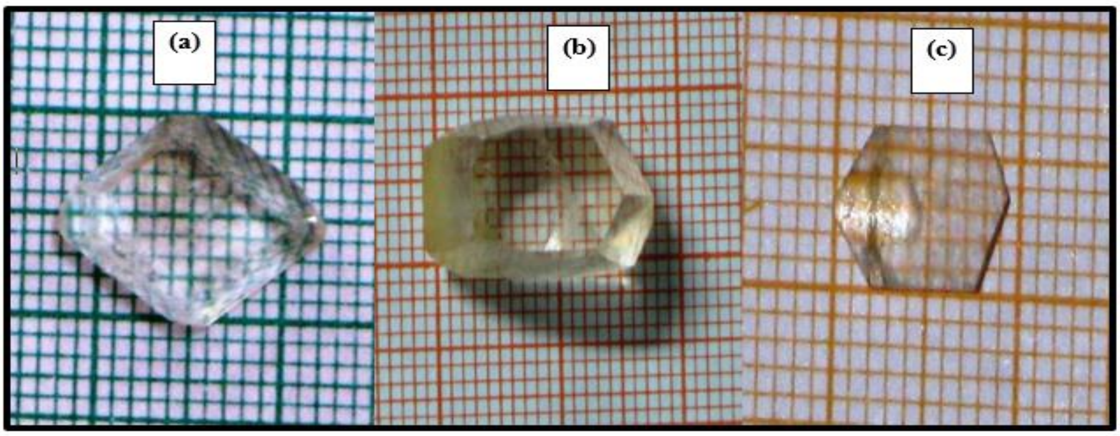


Fig. 1 As grown crystal of (a) pure KHP, (b) 0.2 mol% and (c) 0.3 mol% of $FeCl_3$ doped KHP crystals

Fig. 1, show the photographs of pure and Fe^{3+} doped KHP crystals. The crystals in pure and varying doping concentrations of ferric (Fe^{3+}) ion are known as KHP, 2FKHP (0.2 mol% of $FeCl_3$) and 3FKHP (0.2 mol% of $FeCl_3$) respectively. To lessen the secondary growth that might occur on the surface of the harvested grown crystals, they were briefly submerged in n-hexane.

3. Results and Discussions

3.1. Vickers micro hardness test

Micro hardness analysis of pure and doped KHP single crystals has been tested utilizing a Leitz-Wetzlar Vickers micro hardness tester with a diamond square indenter to investigate the mechanical traits of materials. At normal temperatures, micro hardness tests were performed on flawlessly cut and polished crystals. Hardness tests were conducted on all the undoped and doped title crystals using loads ranging from 10 to 100g and a fixed indentation for duration of fifteen seconds was performed. By gentle application of loads, indentation is made on the surface of the test sample. The trials were run 2-3 times for each and every load. The (Hv) value was derived using the average indentation impression for each load. These investigations are essential to avert the surface impacts [23].

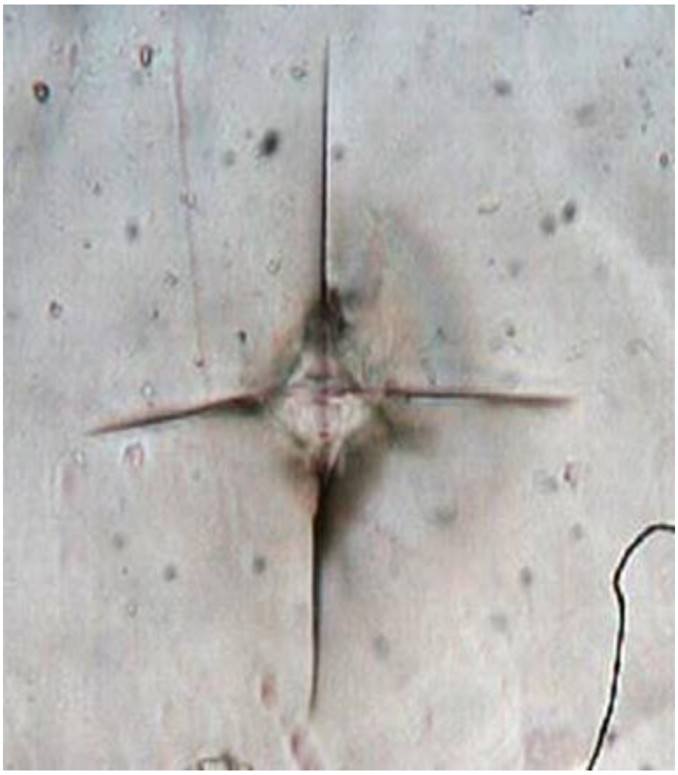
The crystals' Vickers micro hardness value was determined by the following equation:

$H_V = 1.8544\ P/d^2\ kg/mm^2$ (1)

Where p is the applied load in kg and d is the diagonal length of the indentation in mm.

A snapshot of an indentation made on a pure KHP crystal's (010) plane with a 50g weight is shown in Fig. 2. The Vickers hardness number (Hv) vs load (p) is plotted in Fig. 3. Dislocation movement of the material affects the materials' strength and hardness. It is evident from the graph that the initial hardness of both un doped and doped KHP crystals will rise with increasing load.

Fig. 2 Diamond Indentation on (010) plane of un doped KHP crystal for a load of 50g



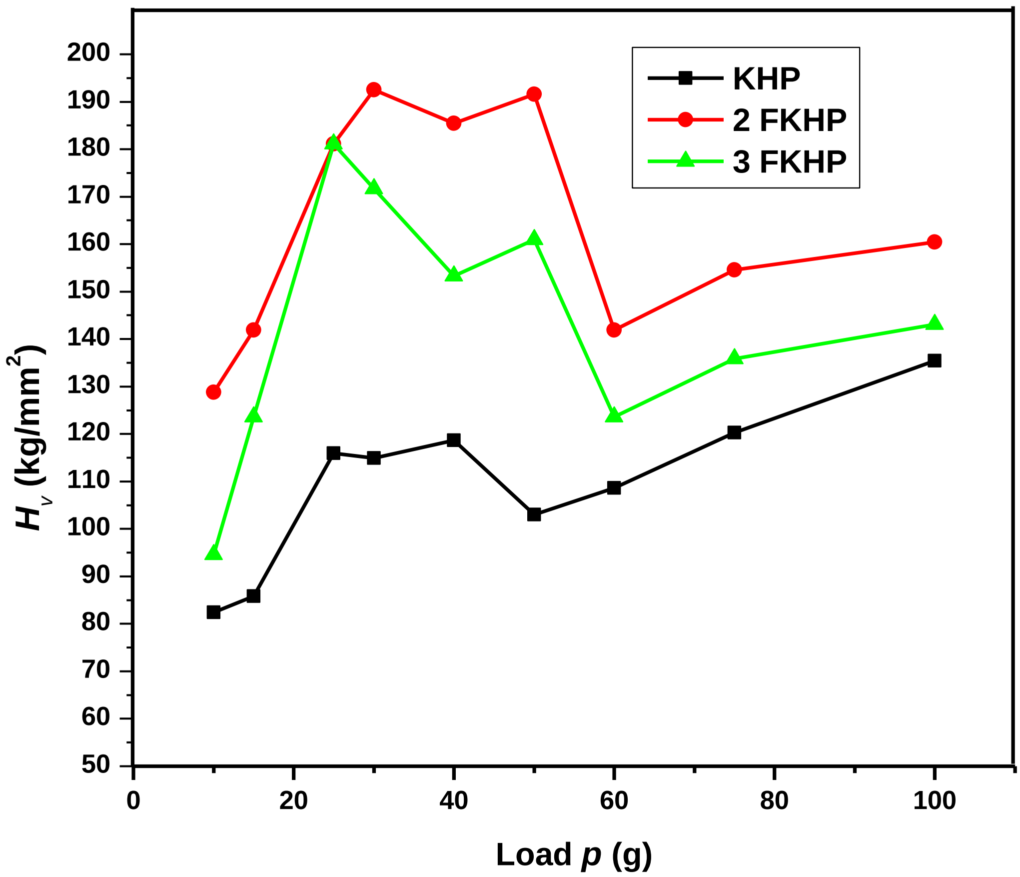


Fig. 3 (Hv) versus (p) for un doped and Fe^{3+} doped KHP crystals

According to Meyer's index, at the beginning, (Hv) value rises with the load owing to the ongoing rise of dislocation interactions that result in anomaly of crystal planes. For all of the pure and doped KHP crystals, the (Hv) value declines with rising load at about 30 g. The work softening process, which is initiated by the slipping of screw dislocations causes the further drop in material hardness with a climb in load introduced [24]. However, the depth of indenter impression penetration rises for applied loads greater than 60 g. As a result, a linear relation is seen between the hardness and the stresses for all un doped and doped KHP crystals. And, this is found to impact both the inner and outer layers. There were no cracks visible prior to reaching the 100 g load. However, if the load is greater than 100 these crystals may break. This can be the result of internal strains that were released as a result of the applied load. The primary factor in a material's hardness is said to be the large stress, necessary to initiate uniform dislocation within the narrow zone of indentation [25]. Therefore, a higher hardness value of un doped and doped KHP crystals reveals the need for larger stress is needed to generate dislocations, to ensure a high crystalline quality [26].

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

Load	**KHP**		**2FKHP**		**3FKHP**	
(*p*)	***Hv***	C_{11}	***Hv***	C_{11}	***Hv***	C_{11}
x 10^{-3} kg	kg/mm^2	x10^{14} Pa	kg/mm^2	x10^{14} Pa	kg/mm^2	x 10^{14} Pa
10	82.417	6.9863	128.777	15.2558	94.612	8.8945

15	85.851	7.5037	141.918	18.0834	123.626	14.2040
25	115.900	12.6870	181.093	27.7042	181.093	27.7042
30	114.942	12.5041	192.498	30.8291	171.703	25.2394
40	118.681	13.2246	185.440	28.8782	153.256	20.6869
50	103.022	10.3238	191.570	30.5695	160.972	22.5438
60	108.656	11.3321	141.918	18.0834	123.626	14.2040
75	120.311	13.5441	154.533	20.9895	135.820	16.7456
100	135.456	16.6672	160.415	22.4075	143.086	18.3447

Table 1 displays the computed Vickers hardness number (Hv) values for both pure and doped KHP crystals. From the table 1, it can be seen that raising the concentration of dopant has enhanced the hardness. The 0.2 mol% of Fe^{3+} ion doped KHP crystal reveals improved hardness which could be due to the result of the Fe^{3+} ions forming a solid connection with the phthalate group. Therefore, it can be inferred from the graph (Fig. 3) that the addition of the dopant Fe^{3+} ion can increase the hardness of pure KHP crystals. These crystals have more potential for use in optical device applications due to the dopant's improvement in hardness [27].

3.2 Work hardening Co-efficient (n) and Minimum load indentation (W)

The relation between size of indentation mark made on a surface and its corresponding value of load is given by Meyer's law,

$$P = k_1 d^n \qquad (2)$$

Where, p-pressure; d-indentation diameter; r-resistance of the material for the initial indentation and n- Meyer's index or hardening co-efficient.

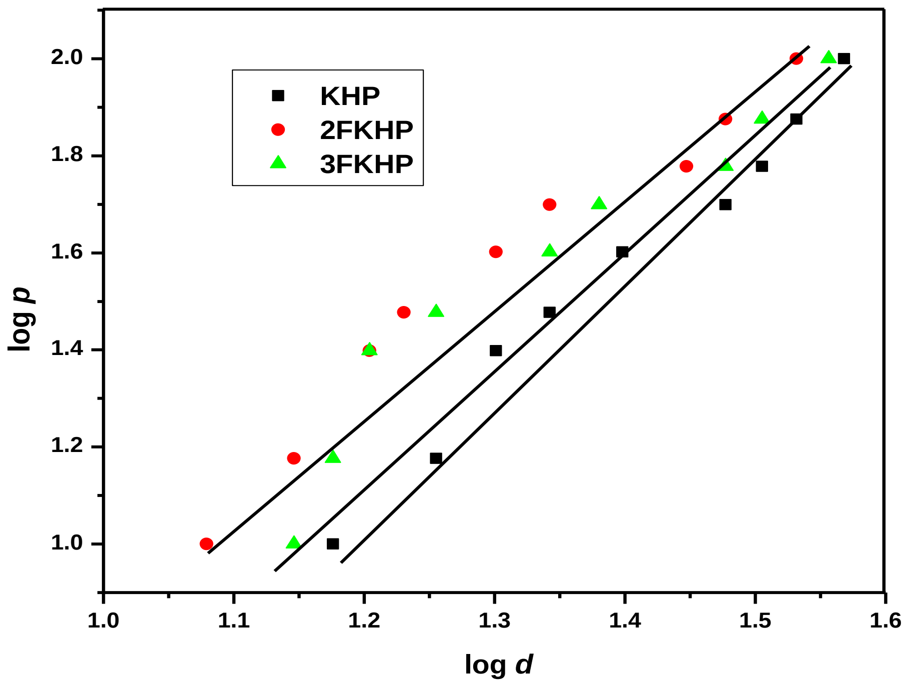


Fig. 4 Plots of log *p* vs. log *d* for doped KHP crystals

For both pure and Fe^{3+} doped KHP crystals, the plot of log d against log p yields straight lines, as shown in Fig. 4. The slope of every straight line determines the coefficient value (n). The plot of p vs. d^n can be used to determine the value of the materials constant (k_1). Straight lines will emerge from the graph, as seen in Fig. 5. Each straight line's slope determines the value of the materials constant (k1).

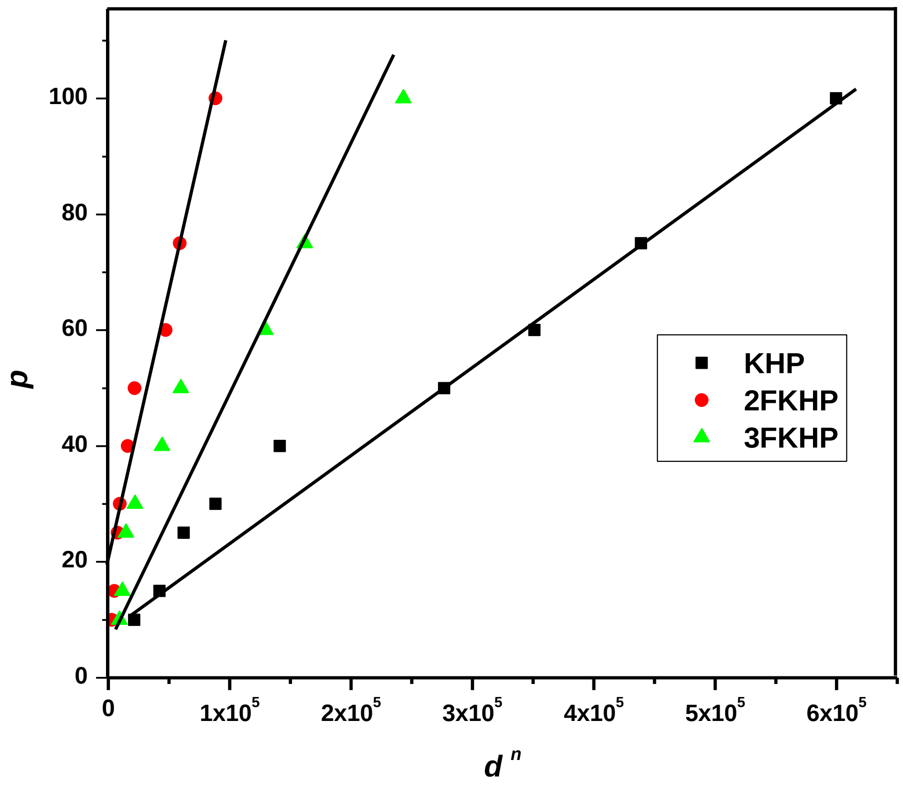


Fig. 5 Plots of p vs. d^n for pure and Fe^{3+} doped KHP crystals

Hanneman [28] and Onitsch [29] stated that the value of n ranges between 1 and 1.6 for moderately hard materials and is more than 1.6 for the soft materials based on their in-depth investigations on a variety of materials. As a result, the work hardening co-efficient (n) value implies that all the un doped and doped KHP crystals come under soft materials. It was suggested by Hays and Kendall that there is a minimum test load (W) required to cause plastic deformation below which only elastic deformation happens [30].

Load dependence of hardness can be explained by Hays-Kendall law [31] and is given by,

$$p = W + A_1 d^2 \qquad (3)$$

Here, W is the minimal applied stress necessary to start plastic deformation, and A_1 is the constant that varies with load. The values of W and A_1 can be determined by plotting the results of p vs. d^2 in a straight line, as illustrated in Fig. 6.

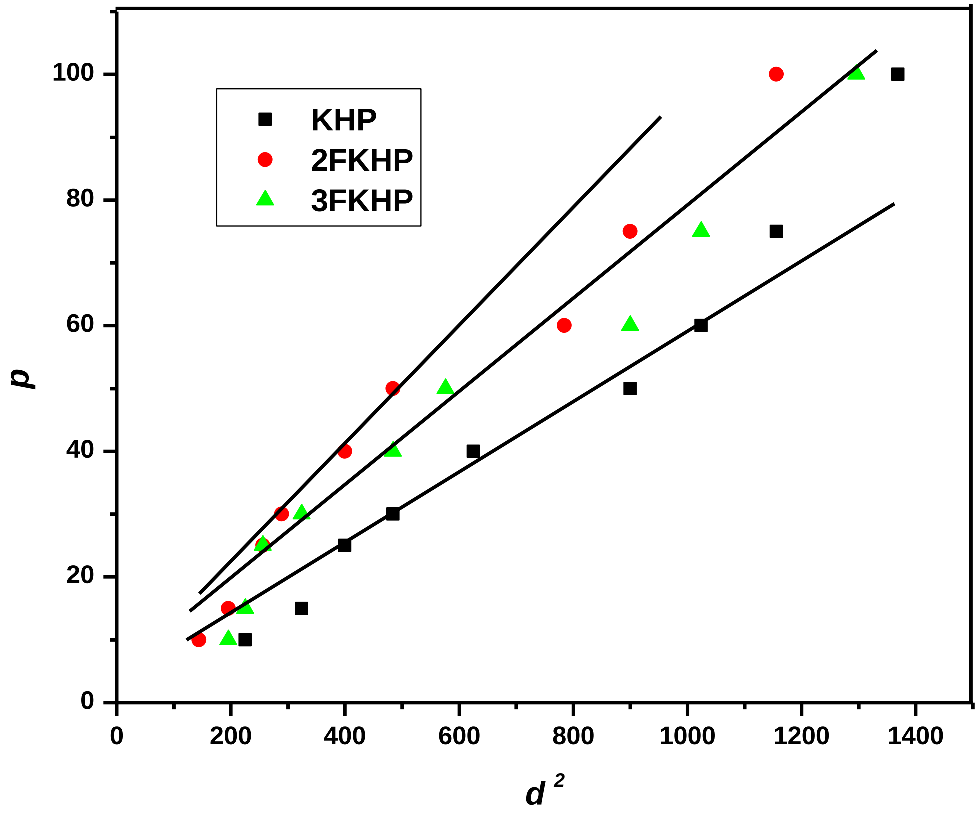


Fig. 6 Plots of p *vs.* d^2 for pure and Fe^{3+} doped KHP crystals

Here, W is the minimal stress necessary to start plastic deformation, and A_1 is the constant that varies with load. The values of W and A_1 may be found by drawing a straight line between the p vs. d^2, as illustrated in Fig. 6. From each straight line, the Values W and A_1 are determined by the intercept and slope respectively along the load axis.

3.3. Elastic stiffness constant (C11)

Wooster's empirical relation was used to compute the elastic stiffness constant (C11) for both the un doped and Fe^{3+} doped KHP crystals. [32],

$$C11 = (Hv)^{7/4} \quad (4)$$

Both un doped and doped KHP crystals' stiffness constant values for multiple loads have been computed. The hardness indicators such as n, k_1,W and A_1 are displayed 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^2)
KHP	3.68	18.7057	1.965	70.9
2FKHP	3.23	6.2293	3.401	90.1
3FKHP	3.46	11.1112	6.272	62.5

It is evident from Table 1 that a dopant concentration increases the elastic stiffness constant (C_{11}) of un doped KHP crystal. The interaction between adjacent ions is indicated by the elastic stiffness constant (C_{11}). Results confirmed that the dopant Fe^{3+} ions strengthen the pure KHP crystals. Also, from the

Table 2, it is noted that the dopant Fe^{3+} ion reduces the work hardening co-efficient (n) which moderately enhances the hardness of un doped KHP crystal.

4. Conclusions

By using a slow evaporation approach, KHP crystals both un doped and doped with Fe^{3+} were produced. On the (010) plane of pure and doped KHP crystals, the Vickers micro hardness (Hv) was measured for different values of stress. It was shown that the key factor influencing hardness is the applied loads. According to the Meyer's index (n), both doped and pure KHP crystals fall under the category of soft materials. The least load indentation (W) needed to initiate plastic behavior on the crystal surfaces was calculated using the concept put out by Hays and Kendall. As the dopant concentration rises, W value grows. For both pure and doped KHP crystals, the hardness indicators such as materials constant (k_1) and load dependent constant (A1) have also been discovered. The doped KHP crystals have exceptionally high values for (C_{11}). It is evident that the ionic interaction becomes extremely stronger due to doping. Therefore, the enhancement of hardness through an increase of dopant concentration in the KHP crystal leads to the fabrication of many optical devices.

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